

Abstract

JOHN, CHRISTOPHER. Determining Pesticide Dislodgeable Foliar Residues and Their Persistence Following Application to Tall Fescue Lawn Turf. (Under the direction of Dr. Richard J. Cooper).

Dislodgeable foliar residues (DFR) can be a primary route for human exposure following pesticide application to turfgrass areas. Consequently, a significant portion of applied pesticide may be available for human exposure via dislodgeable residues. In this study, DFR were determined over a 15-day-period following application of the broadleaf weed herbicide carfentrazone (Ethyl alpha, 2-Dichloro-3-{2-chloro-4-fluoro-5-{4-(difluoromethyl)-4, 5-dihydro-3-methyl-5-oxo-1H-1, 2, 4-triazol-1-yl}-4-fluorobenzenepropanoate), the pre-emergent herbicide prodiamine (5-dipropylamino- α,α,α -trifluoro-4,6-dinitro-*o*-toluidine or 2,6-dinitro- N^1,N^1 -dipropyl-4-trifluoromethyl-*m*-phenylenediamine) and the insecticide bifenthrin (2-methylbiphenyl-3-ylmethyl (1*RS*,3*RS*)-3-[(*Z*)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropanecarboxylate) to a mature stand of 'Confederate' Tall Fescue (*Festuca arundinacea* Schreb). Dislodgeable foliar residues were determined by wiping treated turfgrass with a distilled-water-dampened cheesecloth and analyzing samples using gas chromatography/ mass spectrometry (GC/MS). Less than 20% of the total applied carfentrazone was dislodged with 14% of DFR occurring immediately after application and a total of 6% for the remainder of the 15-day study. Prodiamine DFR averaged 80% over the 11-day study with dislodgeable residue levels ranging from a maximum of 17% of the total applied chemical 8 hours after treatment to a low of 4% 11 days after treatment. Approximately 35% of the total applied bifenthrin was available to be dislodged over 15-day study with 34% DFR loss occurring immediately after

application and a total of 1% for the remainder of the sampling periods. If pesticides are allowed to dry on the leaf surface, shortly after application carfentrazone, prodiamine and bifenthrin pose minimal risk to human health via dermal exposure when applied at the labeled rate.

Determining Pesticide Dislodgeable Foliar Residues and Their Persistence Following Application to Tall Fescue Lawn Turf

by
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Dedication

I would like to dedicate this thesis to my parents, Vaughn and Joan John, for their continued support throughout my college education. Their financial and emotional support has allowed me to focus my efforts on my education, inside and outside of the classroom, and I owe all of my success to them. I would like to thank my sister, Lauren, for what I have learned from her as well as her encouragement and support. She has taught me that life is about having fun and to have faith in that where you are is where you're supposed to be. Thanks to my friends and girlfriend, Todd Love, Kevin Foley, Allyson Harris and Starr Benson, for giving me someone to talk to and providing me guidance when times were tough. This thesis, and my college education, is dedicated to all of them.

Thanks for everything!

Biography

Christopher Vaughn John was born on 7 April 1982 to Vaughn and Joan John, and has a younger sister, Lauren, that was born 16 months later on 15 August 1983. He grew up in Winston-Salem, North Carolina before graduating from West Forsyth High School. Upon Graduation he attended North Carolina State University in the fall where he started work on a Bachelor of Science Degree in Crop Science with a concentration in turfgrass management which he received in December 2004.

At that point, Mr. Christopher John decided to stay in school and pursue a Master of Science Degree in the same curriculum. He began his thesis study under the direction of Dr. Richard Cooper, Dr. Damian Shea, and Dr. Charles Peacock.

Over the span of his college education, Mr. John spent his summers working in the turfgrass industry. He spent the summer of 2001 at Highland Creek Golf Club in Charlotte, North Carolina. He then switched directions and spent the summer of 2002 with Niebur Golf Course Construction and Renovation constructing Three Crowns Golf Club in Casper, Wyoming. He spent the summer of 2003 at Galloway National Golf Club in Atlantic City, New Jersey. That same summer he traveled along side United States Golf Association Green Section consulting agronomists Christopher Hartwiger and Patrick O'Brien as they visited golf courses in the Southeast Region.

Mr. John currently resides in Raleigh, North Carolina until completion of his college education after which he is on to wherever life takes him.

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I would also like to recognize the help and guidance of Peter Lazaro and other members of the N.C. State Pesticide Lab. My time here would have been much more difficult without their help and friendship.

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Literature Review

Persistence of pesticide residues on foliar surfaces and in the soil profile have been an important concern since the early 1980's when researchers including Crutchfield et al. (1980), Jacques and Harvey (1979) and Pritchard and Stobbe (1980) evaluated the persistence and distribution of pesticides applied to field and row crops on several different soil types. Crutchfield et al. (1980) in Texas demonstrated that pesticides such as prodiamine (5-dipropylamino- α,α,α -trifluoro-4,6-dinitro-*o*-toluidine or 2,6-dinitro-*N*¹,*N*¹-dipropyl-4-trifluoromethyl-*m*-phenylenediamine) and fluridone (1-methyl-3-phenyl-5-(α,α,α -trifluoro-*m*-tolyl)-4-pyridone) have the ability to persist in the soil to prevent germination of pigweed (*Amaranthus retroflexus* L.) for more than 36 months after application.

Jacques and Harvey (1979) evaluated dinitroaniline herbicide application to oats (*Avena sativa* L.) and found that trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) remained detectable until the last sampling date 346 days after treatment (DAT) in Wisconsin. They also demonstrated that the dinitroaniline herbicides had limited movement through the soil profile, accumulating in the top 7.5 cm due to their low water solubility and high absorption to the soil. Pritchard and Stobbe (1980) reported that trifluralin and profluralin (*N*-cyclopropylmethyl- α,α,α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine) applied to sorghum (*Sorghum sudanense* L.) had 26% and 25% of the total amount applied still detectable in the soil 50 weeks after application. Jacques and Harvey (1979) also reported that pesticide persistence was dependent upon soil organic matter content and soil type. Increased organic matter content and soil types with higher clay

content bound pesticides more than sandy soils with low organic matter. These reports demonstrate that applied pesticides can persist in the environment long after application with possible adverse implications for non-target organisms.

In addition to research showing that pesticides can persist in the environment long after their application a new research focus emerged evaluating the amount of dislodgeable foliar residues (DFR) that might be available for dermal absorption shortly after application. Thompson et al. (1984) were among the first to evaluate DFR following pesticide application to turfgrass. They reported on the commonly used herbicide 2, 4- D (2, 4-dichlorophenoxy acetic acid) applied to a Kentucky bluegrass (*Poa pratensis* L.) lawn in Ontario, Canada. Their research demonstrated that even though pesticides may persist in the soil for a very long time, DFR declined rapidly and within 7 days after treatment (DAT) residue levels of 2, 4- D had dissipated to only 0.02% of the amount initially applied. This amount is significantly smaller than residues found in the soil profile indicating that minimal amounts of applied pesticides were available for dermal exposure through foliar contact.

Goh et al. (1986) were among the first researchers to recommend safe re-entry intervals following the application of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and dichlorvos (2,2-dichlorovinyl dimethyl phosphate) applied to tall fescue (*Festuca arundinacea* Schreb). Foliar residues were evaluated under both the recommended conditions of 3.79 L dichloronTM in 613.24 L of water applied to 508 m² of lawn and a possible worse-case situation (using half the recommended amount of water with no irrigation after spraying). DichloronTM contains 3% chlorpyrifos and 2.6% dichlorvos as the active ingredients. Foliar residues of dichlorvos under

recommended conditions followed by 12.7 cm of irrigation never exceeded the estimated safe residue level of $0.06 \mu\text{g cm}^{-2}$. In the worst case scenario, Goh et al. (1986) reported that it took 14 h for dichlorvos residues to dissipate below the estimated safe reentry level. No residues of dichlorvos for either treatment were detected 48 HAT. Foliar residues resulting from application of chlorpyrifos in 613.24 L ha^{-1} of water followed by 12.7 cm of irrigation never exceeded the estimated safe residue level of $0.5 \mu\text{g cm}^{-2}$. Under worst case scenario conditions it took 6 h for residue levels of chlorpyrifos to dissipate below the estimated safe reentry level. Post-application irrigation was found to be a more influential factor in reducing the amount of DFR than application volume. Both studies show that when residues are allowed to dry on the leaf surface they typically decline to safe levels shortly after application.

Sears et al. (1987) reported on the DFR of diazinon (O,O-diethyl 0-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate), chlorpyrifos and isofenphos (O-ethyl O-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate) following application to Kentucky bluegrass maintained at 3 cm in Ontario, Canada. Dislodgeable residue levels for diazinon just after application were 1.44% of applied diazinon or 5.65 mg m^{-2} . Levels steadily dissipated to 0.09% (0.34 mg m^{-2}), 0.03% (0.11 mg m^{-2}), 0.01% (0.05 mg m^{-2}), 0.01% (0.04 mg m^{-2}) and $<0.01\%$ (0.01 mg m^{-2}) of the total amount of diazinon applied 1, 2, 5, 7 and 14 DAT, respectively. Residue levels for chlorpyrifos just after application were 2.34% of the applied chlorpyrifos or 4.56 mg m^{-2} . Levels steadily declined to 0.1% (0.19 mg m^{-2}), 0.09% (0.17 mg m^{-2}), 0.01% (0.03 mg m^{-2}), 0.01% (0.02 mg m^{-2}) and $<0.01\%$ ($<0.01 \text{ mg m}^{-2}$) of the total amount of chlorpyrifos applied 1, 2, 5, 7 and 14 DAT, respectively. Residue levels for isofenphos just after application were 2.41% of the

applied isofenphos or 4.7 mg m^{-2} . Residues levels steadily dissipated to 0.25% (0.48 mg m^{-2}), 0.18% (0.34 mg m^{-2}), 0.04% (0.07 mg m^{-2}), 0.02% (0.03 mg m^{-2}) and $<0.01\%$ ($<0.01 \text{ mg m}^{-2}$) of the total amount of isofenphos applied 1, 2, 5, 7 and 14 DAT, respectively. Results showed that all three insecticides had maximum DFR just after application and dislodgeable residues dissipated to 0.25% or less of the total amount applied by 1 DAT.

In field experiments where 4.5 kg ha^{-1} of diazinon was applied in either liquid or granular formulations, about 20 times more diazinon was dislodged from the liquid formulation immediately after application than from granular (Sears et al., 1987). At 1 DAT, the percentage of applied diazinon dislodged was equal for both formulations, signifying that after sufficient re-entry time liquid formulations pose the same risk as granular formulations. To evaluate the influence of sunlight on dislodgeable residues, plots were exposed to either full sun or partial sun using a shade cloth. Surprisingly sunlight had no influence on the decline of DFR or residues within the plant. Rainfall and mowing were also evaluated for their influence on dislodgeable residue dissipation. Rainfall 8 HAT significantly reduced DFR by 40% compared to plots receiving no rainfall. One DAT, foliar residues did not differ significantly from DFR of plots that received rainfall. Mowing had no influence on DFR levels during any sampling period.

Zweig et al. (1985), using DFR data, developed relationships between foliar residues and dermal exposure in an attempt to define the amount of residue that could be transferred and absorbed through the skin. Their focus was to determine the amount of residue that could be dislodged after foliar applications and to further determine if this amount of DFR might have human toxicity implications.

As technology developed to measure minute pesticide residue levels as well as what levels caused human toxicological implications, research focused on improving product efficacy by evaluating various application methods. Western and Woodley (1987) evaluated the influence of droplet size and application volume on pesticide efficacy when applied to Italian ryegrass (*Lolium multiflorum* Lam.) and found that without access to a range of formulations it is impossible to adjust application volume without altering the chemical dose and changing a formulations surfactant concentration. Using an atomization system with and without electrostatic charge to apply diclofop-methyl (methyl 2-[4-(2,4-dichlorophenoxy) phenoxy]propanoate), quantities of spray deposits were measured on whole shoots to determine total deposition and it's relation to herbicidal effect. Results showed that with decreased application volume and the addition of an electrostatic charge, total deposition was increased however herbicidal effect was poor. In conclusion, they believed that the distribution of spray deposits between different parts of the treated plant or the pattern of deposition over the plant surface is more critical than total deposition on herbicidal effect.

While some researchers sought improved product performance through new application methods, others evaluated the commonly used pesticides to determine residue persistence and distribution. Hurto and Prinster (1993) evaluated the dislodgeable foliar residues of chlorpyrifos, DCPA (dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid), diazinon, isofenphos and pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylylidine) following application to a Kentucky bluegrass lawn in Delaware, Ohio. Foliar residues as a percent of the target application rate ranged from a high of 10.7% for isophenfos to a low of 0.6% for chlorpyrifos 2 HAT. Pesticide applications that received

no post-application irrigation showed DFR levels which dissipated rapidly to less than 10% of the target application rate 1 DAT and to less than 5% for isophenfos and 2% for chlorpyrifos when measured 3 and 7 DAT. At 14 DAT, pesticide levels declined to < 1% of the target application rate. Post-application irrigation of 13mm significantly reduced DFR levels of both pendimethalin and DCPA during all sampling periods through 7 DAT, while differences in isofenphos foliar residue levels were significantly reduced only through 3 DAT. Post-application irrigation following diazinon and chlorpyrifos application did not significantly reduce residue levels at any time during the study. This shows that not all pesticide DFR can be reduced using post-application irrigation.

Cooper et al. (1990) reported on the DFR of pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) following application to Kentucky bluegrass maintained at 5.1 cm. In this study, DFR within the canopy were thought to be the primary residue reservoir responsible for volatile residues with time. Rainfall during the study was thought to aid in the redistribution of residues from the foliage to deeper into the canopy where they were less available to be dislodged or volatilized. Cooper et al. also described residue dissipation as having a diphasic curve in which phase 1 consist of a rapid decline in residues shortly after application and phase 2 exhibited a steady decline until the pesticide was no longer detectable.

Reports of diphasic dissipation of dislodgeable residues have also been reported by Whitmyre et al. (2004). Their work using diphasic kinetics helped to establish safe re-entry intervals for agricultural workers applying endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzadioxathiepin 3-oxide). Their research showed that first order kinetics may overestimate DFR and post-application worker

exposure during the critical period (2-4 HAT) when entry to the fields is most likely to occur. Use of biphasic kinetics in place of first order kinetics will result in higher R^2 values for the regression curves describing the dissipation of foliar residues. The use of biphasic kinetics allows for more accurate estimations of DFR and aids in establishing correct re-entry intervals following pesticide application.

Murphy et al. (1996a) reported on the DFR resulting from MCP (2-Methyl-4-chlorophenoxy propanoic acid) and triadimefon (1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone) application to creeping bentgrass (*Agrostis stolonifera* L.) determined by using the Theoretical Profile Shape Method. Triadimefon dislodgeable residues were greatest 3 HAT accounting for 1.5% of the target application rate. Over time, dislodgeable residues decreased to 1.0, 0.6, 0.06 and 0.01% of the applied chemical available 1, 2, 5, and 15 DAT, respectively. Dislodgeable residues of MCP dissipated rapidly so that only 0.1% of applied chemical was available 3 HAT. Dislodgeable residues declined to 0.08% on day 2 and were nondetectable by day 5.

Nishioka et al. (1996) determined the amount of 2, 4-D dislodgeable residues transported into a home 4 h after application at 26.7 mg m^{-2} and detected on carpet surfaces in the home. Their research showed that DFR were 0.1-0.2% of the applied chemical and of that 0.3% was transferred by regular foot traffic onto the carpet surface inside of the home. Residue levels on carpet surfaces were reduced by 25% when subjects walked across entryway mats prior to entering the home. Residues tracked into the home and found on carpet surfaces could persist in the home for up to 1 year increasing the chance for human implications through chronic exposure.

Williams et al. (2003) reported on the DFR of chlorpyrifos applied to perennial

ryegrass (*Lolium perenne* L.) grass maintained at 1.6 cm in Riverside, CA. Using the California roller method, which employed a 1000 cm² cotton roller and 30-lbs of lead shot rolled across the treated turf, chlorpyrifos residues 1 DAT were 0.064 µg cm⁻². Two and four DAT residue levels dissipated to 0.027 and 0.012 µg cm⁻², respectively.

Additional research has focused on determining human hazard implications from exposure to pesticide residues. Clark et al. (2000) evaluated the hazards and management of volatile and dislodgeable residues following application of pendimethalin, isazofos, diazinon and isofenphos to turfgrass and found that reduced thatch levels and post-application irrigation can reduce residue levels for some pesticides. The use of post-application irrigation allows the residues to be redistributed from the leaf surface and penetrate into the soil profile. However, there is speculation that irrigation might enhance transformation of parent compounds to more toxic secondary metabolites for some compounds. Murphy et al. (1996a) found this to occur with trichlorfon (dimethyl (*RS*)-2,2,2-trichloro-1-hydroxyethylphosphonate) converting to DDVP. Also the use of post-application irrigation might increase runoff risk as demonstrated by Evans et al. (1998) in their work using post-application irrigation increasing the amount of diazinon removed from the target site when applied to tall fescue. Their research applied 6.4 and 12.7 mm of irrigation immediately following application and then simulated a heavy rainfall (64 mm h⁻¹) 2 HAT. Runoff concentration of diazinon was greater for irrigated plots when compared to non irrigated plots indicating post-application irrigation increased diazinon losses when heavy rainfall occurs soon after application.

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**Dissipation of Foliar Carfentrazone Residues Following Application to a Tall
Fescue Lawn and Implications for Human Exposure**

Abstract

Dislodgeable foliar residues (DFR) can be a primary route for human exposure following pesticide application to turfgrass areas. Consequently, a significant portion of applied pesticide may be available for human exposure via dislodgeable residues. In this study, DFR were determined over a 15-day-period following 20 October 2005 application of the broadleaf weed herbicide carfentrazone (Ethyl alpha, 2-Dichloro-3-{2-chloro-4-fluoro-5-{4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl}-4-fluorobenzenepropanoate) to a mature stand of ‘Confederate’ Tall Fescue (*Festuca arundinacea* Schreb). Dislodgeable foliar residues were determined by wiping treated turfgrass with a distilled-water-dampened cheesecloth and analyzing samples using gas chromatography/ mass spectrometry (GC/MS). Less than 20% of the total applied carfentrazone (18,000 ng dm⁻²) was dislodged with 13.8% of DFR occurring immediately after application. Dislodgeable residue as determined 1, 4, and 8 hours after treatment (HAT) contributed an additional 5.5% to the total applied carfentrazone dislodged from the foliar surface. One day after treatment (DAT), dislodgeable residue levels had declined to below 1% of the total applied carfentrazone. By day 3, carfentrazone DFR were nondetectable.

Carfentrazone residue levels resulted in a maximum estimated hazard quotients < 1 for the entire study, indicating that potential human toxicological effects associated with maximum field residue levels are unlikely. This work indicates that carfentrazone poses minimal risk to human health via dermal exposure when applied at the labeled rate.

Introduction

Pesticide use on residential lawns has increased as homeowner awareness of weed and insect problems have grown, largely as a result of the rapid expansion of the lawncare industry in the United States (Hurto and Prinster, 1993). When pesticides are applied to residential lawns the potential exists for exposure by people using the treated area (Williams et al., 2003). While pesticide exposure concerns often focus on contamination of groundwater or surface runoff, Zaterian et al. (2000) have identified dermal exposure as the primary route of exposure for chemicals typically used in home lawn pest control. Inhalation is also a potential exposure route but one of much lower magnitude due to the low volatility of most commercial pesticides and ample air circulation on areas where these pesticides are used (Plog and Quinlan, 2001). Increased attention has focused on the evaluation of DFR for pesticides as a means to gauge potential human exposure from contact with treated turf.

Thompson et al. (1984) reported on the dislodgeable foliar residues of 2, 4-D (2,4-dichlorophenoxy acetic acid) applied to a Kentucky bluegrass (*Poa pratensis* L.) lawn in Ontario Canada. DFR declined rapidly following application with dislodgeable residue levels of only 1.0 and 0.02% of the target application rate as determined 3 and 7 DAT.

Murphy et al. (1996b) reported on the dislodgeable foliar residues of MCPP (2-(2-Methyl-4-chlorophenoxy propanoic acid) and triadimefon (1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone) applied to creeping bentgrass (*Agrostis stolonifera* L.). Triadimefon dislodgeable residues were greatest 3 HAT accounting for 1.5% of the target application rate. Over time, dislodgeable residues decreased to 1.0, 0.6, 0.06 and 0.01% of the applied chemical available 1, 2, 5, and 15 DAT, respectively. Dislodgeable residues of MCPP dissipated rapidly so that only 0.1% of applied chemical was available 3 HAT. Dislodgeable residues declined to 0.08% on day 2 and were nondetectable by day 5.

Hurto and Prinster (1993) reported on the dislodgeable foliar residues of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate), DCPA (dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid), diazinon (O,O-diethyl O-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate), isofenphos (O-ethyl O-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate) and pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) applied to Kentucky bluegrass lawn turf maintained at a height of 7.6 cm in Delaware, Ohio. Dislodgeable foliar residues as a percent of the target application rate ranged from a high of 10.7% for isofenphos to a low of 0.6% for chlorpyrifos 2 HAT. From their research with pesticides that received no post-application irrigation, dislodgeable pesticide levels on foliage naturally dissipated rapidly to less than 10% of the target application rate 1 DAT and to less than 5 and 2% at 3 and 7 DAT. By 14 DAT pesticide levels fell below 1% of the target application rate. Post-application irrigation resulted in significant differences in DFR levels of pendimethalin and DCPA at all sampling periods through 7 DAT, while differences in

isofenphos residue levels were significantly different through 3 DAT. Post-application irrigation for diazinon and chlorpyrifos did not show any significant differences at any sampling period through out the study.

Previous research has focused on residue losses from older commonly used herbicides such as MCPP, pendimethalin and 2, 4-D. With advancements in pesticide chemistry new active ingredients have been developed to provide turfgrass professionals with improved pesticides. This study evaluated DFR following application of the broadleaf weed herbicide carfentrazone to a tall fescue lawn using equipment and techniques commonly used by lawncare professionals.

MATERIALS AND METHODS

Experimental Site

A field experiment was conducted from 20 Oct. 2005 – 4 Nov. 2005 at the North Carolina State University Turfgrass Field Laboratory located in Raleigh, NC.

‘Confederate’ tall fescue mowed with a rotary mower at 7.6 cm was used for the study.

Turfgrass quality and density were typical of a well maintained residential lawn. The experimental area consisted of six carfentrazone-treated strips (1.5 x 6.0 m) where each strip constituted one replication. Plots were not mown during the experiment and no irrigation or precipitation occurred throughout the study. Weather data recorded during the study is reported in Table 1.

Pesticide Application

Application of carfentrazone (Speed Zone® Southern, (0.67% a.i.) Pbi/ Gordon Corp., Kansas City, MO) was made to plots at 08:00-08:45 using a Lesco/ Chemlawn® spray gun equipped with a standard 810 L ha⁻¹ nozzle at a pressure of 137 kPa.

Carfentrazone was applied at the labeled rate of 0.04 kg a.i. ha⁻¹ in 810 L of water. The Lesco/ Chemlawn® Gun was mounted 114 cm above the ground on a rolling spray boom. To treat the area the gun was swept parallel to the ground with the nozzle pointing downward toward the turf as the applicator moved forward. The effective spray width was 1.5 m and the applicator positioned the gun 2 m away from the edge of the plot.

Cheesecloth squares measuring 20 x 20 cm were placed in the center of each turf plot to collect initial spray deposition (ng carfentrazone dm⁻²). These deposition samples were collected, wrapped in aluminum foil and immediately placed in plastic storage bags. Samples were stored in a freezer at -8° C until analysis.

Dislodgeable Foliar Residue Collection

Dislodgeable foliar residues were measured using a method similar to that described by Thompson et al. (1984) which is thought to provide a good estimate of unbound dislodgeable residues (Cowell et al., 1993). A 20 x 20 cm piece of distilled-water-dampened cheesecloth (Fisher Scientific, Springfield NJ) was used to wipe a 9.3 dm² area of herbicide treated turfgrass two times east → west, two times west → east, two times north → south and two times south → north to ensure that the entire area was uniformly wiped. Residue samples were wrapped in aluminum foil and placed in a plastic bag. Samples were stored at -8° C until analysis. Each sampled area was marked with orange paint to avoid resampling that area during future sampling. Samples were collected immediately after application and 1, 4, and 8 HAT on the day of application. Additional samples were collected at noon 1, 2, 3, 5, 7, 11, and 15 DAT.

Residue Analysis

Cheesecloth residue wipes were extracted by placing each wipe into a 300 ml glass jar with 150 ml of dichloromethane and shaking (Lab-Line Instruments Inc., Melrose Park, IL) for one h at 300 rpm on an orbital shaker. Extraction solvent was then evaporated to approximately 20 ml using a Büchi Rotavapor® (Büchi, Zurich, Switzerland) at 40° C. The solvent was further evaporated to approximately 3 ml using the Meyer analytical nitrogen-evaporator (Organomation Associates Inc., Berlin, MA) under a steady stream of nitrogen at 40° C. Extracts were then filtered using a UNIPREP® .45 µm PTFE membrane syringeless filter device (Whatman®, Middlesex, England) and transferred to 30 ml Pyrex test tubes for further evaporation of solvent using nitrogen-evaporation. All sample extracts were analyzed using an Agilent 6890 gas chromatograph(GC) equipped with electronic pressure control connected to a 5973n mass selective detector (MSD). Extracts were injected in pulsed split less mode and separated on a Restek 30-m x 0.25-mm Rtx-5 (0.25-µm film thickness) MS with Integra-Guard column. The pressure was ramped to 30 psi before injections with a 1-min hold time. The pressure was then dropped to a constant flow of 1 ml/min for the duration of the run. The temperature program was as follows, Carfentrazone: initial temperature 150 °C for 1.0 min, 12.5 °C/min to 310 °C, hold for 5 min, the injector was set at 250 °C and the detector was set at 300 °C. The MSD was operated in the selective ion monitoring mode. Analytes were quantified using the internal standard method.

Exposure and Hazard Quotient Determinations

An estimated dermal exposure dose (D_d) for a 70 kg adult taking part in leisure activity for 4 h on his home lawn was estimated for each sampling period using Eq [1] (Murphy et al., 1996a).

Eq [1].
$$D_d = S \times P / 70 \text{ kg} \times 1000 \mu\text{g mg}^{-1}$$

Where: D_d = Estimated dermal exposure dose ($\mu\text{g kg}^{-1}$).

S (calculated dermal exposure, mg) = DFR (obtained on cheesecloth wipes) $\times 5 \times 10^3 \text{ cm}^2 \text{ h}^{-1}$ (dermal transfer coefficient, Zweig et al., 1985) $\times h$ (exposure period in hours)

P = dermal permeability (0.1, USEPA default value, 1989)

Hazard quotients (HQ) were estimated using Eq [2] (Murphy et al., 1996a).

Eq [2].
$$\text{HQ} = D_d / \text{Rfd}$$

Where: HQ = Estimated potential human hazard

D_d = Estimated daily dermal exposure dose

Rfd = NOAEL/ uncertainty factor

Acute reference dose (Rfd) was determined by dividing the daily dose shown to cause no observable effects (NOAEL) on laboratory animals by an uncertainty factor. An uncertainty factor of 100 is commonly used; 10x to account for intraspecies differences and 10x to account for interspecies differences (USEPA, 2001). Hazard quotients ≤ 1 indicate that dislodgeable residues are present at concentrations below those expected to cause adverse effects to humans. A hazard quotient > 1 does not indicate that residue concentration will necessarily cause adverse effects but does indicate a higher potential risk of causing adverse effects to humans. Calculations of hazard quotients in this study

use the maximum DFR determined in the field and estimate a worst case scenario.

RESULTS AND DISCUSSION

Dislodgeable Foliar Residues

Dislodgeable foliar residues following application of carfentrazone to tall fescue turf are shown in Figure 1. Total applied carfentrazone collected on the spray deposition samples was 18,000 ng dm⁻². Carfentrazone DFR were greatest immediately following application during the initial wiping within 30 seconds of application and averaged 2,500 ng dm⁻² (14%) of the total amount applied. At 1 HAT, when the herbicide solution had dried on the leaf surface, dislodgeable residues had dissipated to 525 ng dm⁻² or 3% of the total amount applied. By 4 and 8 HAT dislodgeable residues had dissipated to 250 ng dm⁻² (2%) and 200 ng dm⁻² (1%) respectively, of the total amount applied. Twenty-four HAT dislodgeable residues were hardly detectable; however, 25 ng dm⁻² (0.1%) of the total amount applied was detected. Forty-eight HAT 3 ng dm⁻² (0.01%) of the total amount applied was dislodged from the leaf surface. By seventy-two HAT no dislodgeable residues were detected.

Over the entire 15 day study, DFR totaled 20% of the total amount applied. Approximately, 14% DFR were detected immediately after application with only 6% of the total application rate available to be dislodged after the herbicide had dried on the leaf surface one HAT. Dissipation of carfentrazone DFR occurred in two phases in first-order kinetics (Table 8). Residue half-life ($T_{1/2}$) values in the first phase were 6.9 HAT and 346 for the second phase.

The dissipation of dislodgeable residues from carfentrazone-treated turf declined in a pattern similar to that described for 2, 4-D (Thompson et al., 1984), MCPP and

triadimefon (Murphy et al., 1996b). Total DFR through out the entire study were higher for carfentrazone when compared to 2, 4-D and MCPP, however, our reports include residue levels immediately after application while others do not. Research data demonstrates that carfentrazone has little potential for DFR shortly after application.

With sufficient drying time under moderate temperatures and low humidity, dislodgeable residues are expected to be below the EPA's pesticide tolerance level of $1000 \text{ mg kg}^{-1} \text{ d}^{-1}$ which is reported to produce no toxicological effects based on a 21 day dermal exposure assessment (USEPA, 2000).

Dislodgeable residues from carfentrazone-treated turfgrass resulted in estimated hazard quotients (HQ) below 1 during the entire 15 day study (Table 2). Maximum HQ occurred immediately after application (0 HAT) and had an estimated value of 1.8×10^{-5} . These HQ values are significantly lower than those of triadimefon, MCPP, trichlorfon and isazofos reported by Murphy et al. (1996a/b). These differences might be a result of the different mechanisms of pesticidal action associated with the various materials. Chemicals which attack sites that are similar to human cellular physiology will have larger HQ than those chemicals that only affect sites specific to fungus or plant cellular physiology. Thus, insecticides generally exhibit HQ's higher than those for herbicides and fungicides. In this particular study, carfentrazone inhibits the enzyme protoporphyrinogen oxidase in the chlorophyll biosynthetic pathway specific to plants and algae (Lee et al. 2003).

Post-application irrigation is effective in reducing dislodgeable residues; however, post-application irrigation is not appropriate for all pesticides. The use of post-application irrigation or rainfall may transport the pesticide residues deeper into the turf canopy

where the pesticide is available to bind to thatch and soil (Cooper et al., 1995). The use of adjuvants and thatch management with organophosphorous and carbamate insecticides do not appear to be practical means to minimize residues once applied to turfgrass (Clark et al. 2000). Further research is warranted to determine the affects of irrigation, adjuvants and thatch management on carfentrazone dislodgeable residues.

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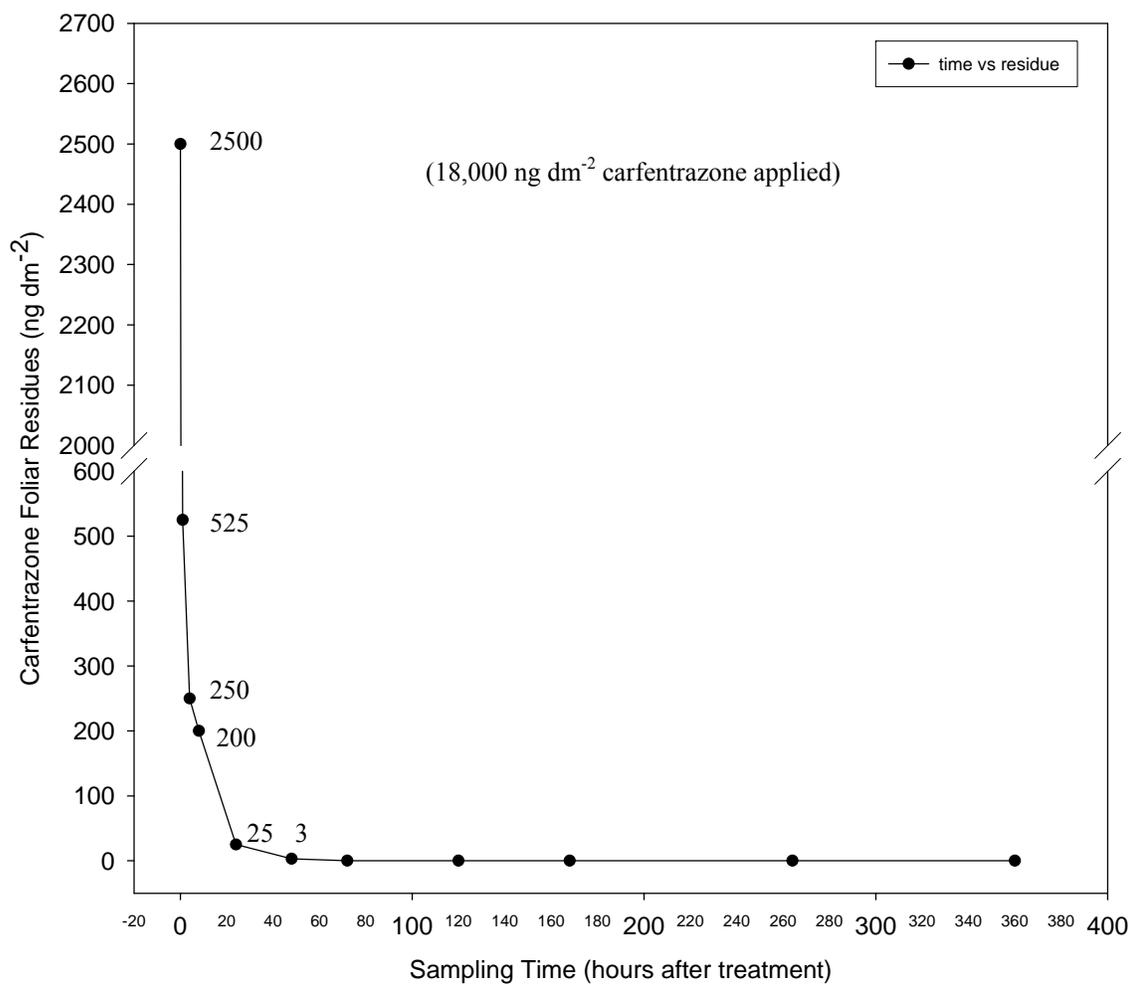


Figure 1. Dissipation of carfentrazone dislodgeable foliar residues from a tall fescue lawn over a 15-day period following 20 Oct. 2005 application.

Table 1. Mean air temperature, wind speed, and relative humidity during the 15-day experimental period following carfentrazone application on 20 Oct. 2005*

Day	Time Period (h after treatment)	Average Air Temp ° C	Average Wind Speed m/s	Relative Humidity %
1	0	23.6	2.9	71
1	0-1	24.6	3.0	68
1	1-4	27.8	6.0	56
1	4-8	27.4	5.7	52
1	20-24	19.2	1.6	89
2	24-48	20.6	9.8	82
3	48-72	17.2	9.2	79
5	96-120	12.7	7.6	62
7	144-168	14.4	5.1	67
11	240-264	21.6	3.2	68
15	336-360	21.2	5.9	74

* Weather station located at the Lake Wheeler Turfgrass Field Lab, Raleigh, NC within 457 m of experimental plots

Table 2. Estimated dermal exposure dose (D_d), calculated dermal exposure (S) and dermal hazard quotients (HQ) estimated for exposure to carfentrazone dislodgeable foliar residue (DFR) following application to a tall fescue lawn in 810 L ha⁻¹.

Estimated Dermal Exposure Dose (D_d)*	Calculated Dermal Exposure (S)	DFR	Hours after Treatment	Hazard Quotient (HQ)§	Reference Dose (Rfd)**
$\mu\text{g kg}^{-1}$	mg	ng carfentrazone dm ⁻²		(x 10 ⁻⁶)	$\text{mg kg}^{-1} \text{d}^{-1}$
71	50	2500	0	18	4000
15	11	525	1	4	4000
7	5	250	4	2	4000
6	4	200	8	1	4000
0.8	1	20	24	0.2	4000
0.08	0.06	3	48	0.02	4000

* Estimated dermal exposure using model of Zweig et al. (1985)

** Rfd = NOAEL(No Observable Adverse Effect Level) / UF (Uncertainty Factor)

§ HQ = D_d / Rfd

**Influence of Application Volume, Post-Application Irrigation and Mowing
Height on the Persistence and Distribution of Prodiamine Residues Following
Application to a Tall Fescue Lawn**

Abstract

Persistence of dislodgeable foliar residues (DFR) and soil residues following pesticide application are an important concern because of their implications for human exposure. This study was designed to determine the effect of application volume, post-application irrigation and mowing height on the persistence and distribution of foliar and soil residues from a commonly used pre-emergent herbicide. Foliar and soil residue levels were determined over an 11-day period following 10 April 2006 application of the pre-emergent herbicide prodiamine (5-dipropylamino- α,α,α -trifluoro-4,6-dinitro-*o*-toluidine or 2,6-dinitro- N^1,N^1 -dipropyl-4-trifluoromethyl-*m*-phenylenediamine) to a mature stand of 'Confederate' Tall Fescue (*Festuca arundinacea* Schreb). Increasing application volume from 810 to 1,236 L ha⁻¹ reduced DFR by an average of 3.8% over the entire study with significantly lower residue levels 3 hours after treatment (HAT), and 5, 7, and 11 days after treatment (DAT). Increased application volume resulted in an average of 46% less prodiamine soil residues with significantly lower residue levels 1, 3, and 11 DAT. Clippings removed from plots treated with an application volume of 810 and 1,236 L ha⁻¹ resulted in approximately 13% reduction in the amount of applied prodiamine lost from the treated surface. Post-application irrigation reduced DFR by an average of 10% for the entire study with significantly lower residue levels at all sampling periods except 3 DAT. Post-application irrigation reduced soil residue

levels 1 DAT but then increased residue levels 3, 7, and 11 DAT by an average of 37% when compared to plots that did not receive post-application irrigation. Soil residues were not significantly different during any sampling period throughout the experiment. Clippings removed from plots that received post-application irrigation exhibited a 12% reduction in the amount of applied prodiamine lost from the treated plots. Increased mowing height did not significantly affect DFR throughout the entire study. Increased mowing height resulted in an average of 28% higher prodiamine levels in soil for all sampling periods except 3 DAT; however, they were not statistically different during any sampling period. Prodiamine residue levels resulted in a maximum estimated hazard quotient of 1.18×10^{-3} for study, indicating no potential human toxicological effects from maximum field residue levels.

Introduction

The period during which a pesticide remains biologically active is important in determining its effectiveness, but also in determining its implications for human exposure. As residue persistence increases, the possibility of increased human exposure, movement outside the intended zone of activity and injury to nontarget plants and animals also increases. Ideally a pesticide should persist long enough to control the target pest then degrade into harmless byproducts before it is time to reapply or plant a succeeding crop (Jacques and Harvey, 1979). Because people typically use turf areas following pesticide application, increased attention has been given to reducing the persistence of pesticides used in turfgrass management.

Jacques and Harvey (1979) reported on the persistence of dinitroaniline herbicides

in soil following application to an agricultural field in Wisconsin. Samples were taken from depths of 0 - 7.5 cm and 7.5 - 15 cm. Results indicated that dinitroaniline herbicides accumulated in the top 7.5 cm due to their low water solubility and high absorption to the soil. Dinitramine (N1,N1-diethyl-2,6-dinitro-4-trifluoromethyl-m-phenylenediamine) dissipated more rapidly than any other dinitroaniline herbicide applied but remained detectable 89 DAT. Residues of fluchloralin (*N*-(2-chloroethyl)-2,6-dinitro-*N*-propyl-4-(trifluoromethyl)aniline), isopropalin (4-isopropyl-2,6-dinitro-*N,N*-dipropylaniline), oryzalin (3,5-dinitro-*N*4,*N*4-dipropylsulfanilamide), profluralin (*N*-cyclopropylmethyl- α,α,α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine), and trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) remained detectable until the final sampling date 346 DAT.

Crutchfield et al. (1980) reported on the efficacy of prodiamine and fluridone (1-methyl-3-phenyl-5-(α,α,α -trifluoro-*m*-tolyl)-4-pyridone) applied to a cotton field in Texas. Results were determined by the percent of pre-emergent pigweed (*Amaranthus retroflexus* L.) control in the field. Prodiamine produced 98, 97, 57 and 42% pigweed control 2, 12, 24 and 36 months after application, respectively. Fluridone provided 99, 100, 71 and 38% pigweed control 2, 12, 24 and 36 months after application, respectively. This research indicates that pre-emergent herbicides have the ability to persist and provide pre-emergence control of weed seed in the soil for up to 36 months.

Pritchard and Stobbe (1980) reported on the persistence and phytotoxicity of dinitroaniline herbicides in Manitoba Canada soils. Trifluralin, profluralin, fluchloralin and dinitramine were applied to a sandy loam, clay loam and a clay soil for persistence evaluation. Results indicated that herbicide persistence was dependent on organic matter

and soil type. Fifty weeks after application, percent of applied herbicide remaining for trifluralin, profluralin, fluchloralin and dinitramine applied to a clay soil were 26, 25, 20, and 17% of the initial application, respectively. Researchers found that these residue levels under certain cropping conditions have the ability to cause plant injury.

Thompson et al. (1984) reported on dislodgeable foliar residues of 2, 4-D (2,4-dichlorophenoxy acetic acid) following application to a Kentucky bluegrass (*Poa pratensis* L.) lawn in Ontario Canada. Dislodgeable foliar residues declined rapidly following application with dislodgeable residue levels of only 1.0 and 0.02% of the target application rate as determined 3 and 7 DAT.

Murphy et al. (1996b) reported on dislodgeable foliar residues of MCPP (2-(2-Methyl-4-chlorophenoxy propanoic acid) and triadimefon (1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone) applied to creeping bentgrass (*Agrostis stolonifera* L.). Triadimefon dislodgeable residues were greatest 3 HAT accounting for 1.5% of the target application rate. Over time, dislodgeable residues decreased to 1.0, 0.6, 0.06 and 0.01% of the applied chemical available 1, 2, 5, and 15 DAT, respectively. Dislodgeable residues of MCPP dissipated rapidly so that only 0.1% of applied chemical was available 3 HAT. Dislodgeable residues declined to 0.08% on day 2 and were nondetectable by day 5.

Hurto and Prinster (1993) evaluated the dislodgeable foliar residues of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate), DCPA (dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid), diazinon (O,O-diethyl O-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate), isofenphos (O-ethyl O-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate) and pendimethalin (N-(1-

ethylpropyl)-2,6-dinitro-3,4-xylidine) following application to a Kentucky bluegrass lawn turf maintained at a height of 7.6 cm in Delaware, Ohio. Dislodgeable foliar residues as a percent of the target application rate ranged from a high of 10.7% for isophenfos to a low of 0.6% for chlorpyrifos 2 HAT. From their research with pesticides that received no post-application irrigation, dislodgeable pesticide levels on foliage naturally dissipated rapidly to less than 10% of the target application rate 1 DAT and to less than 5% for isophenfos and 2% for chlorpyrifos at 3 and 7 DAT. By 14 DAT, pesticide levels fell below 1% of the target application rate. Post-application irrigation of 13 mm significantly reduced DFR levels of pendimethalin and DCPA during all sampling periods through 7 DAT, while differences in isophenfos foliar residue levels were significantly reduced through 3 DAT. Post-application irrigation for diazinon and chlorpyrifos did not significantly reduce residue levels during any sampling period through out the study.

Previous research has focused on the residue levels of MCPP, pendimethalin, 2, 4-D and other commonly used pesticides. With advancements in modern technology and chemical research, new active ingredients have been developed to provide turfgrass professionals with a variety of pesticides. This study evaluated DFR and soil residues following application of the pre-emergent herbicide prodiamine to a tall fescue lawn using equipment and techniques commonly used by lawncare professionals. The influence of application spray volume, turfgrass mowing height, and post-application irrigation on residue levels were determined.

MATERIALS AND METHODS

Experimental Site

A field experiment was conducted from 10 - 12 April 2006 at the North Carolina State University Turfgrass Field Laboratory located in Raleigh, NC. 'Confederate' Tall Fescue maintained with a rotary mower at 7.6 cm was used for the study. Turf quality and density was typical of a well-maintained residential lawn. The experimental area consisted of 3 randomized split strip replications with eight plots each (Figure 2). Treatments included 810 or 1,236 L ha⁻¹ application spray volumes, 7.6 or 12.7 cm mowing heights and 0.6 cm irrigated or non- irrigated plots. Plots were not mown during the experiment and no precipitation occurred during the data collection. Weather data recorded for the entire study is reported in Table 3.

Pesticide Application

Application of proflaminate (Barricade® 65 WG, Syngenta Crop Protection Inc., Greensboro, NC) was made to plots at 11:30-13:30 h using standard equipment and techniques employed by lawncare professionals. A Lesco/ Chemlawn Gun and 810 L ha⁻¹ nozzle (Lesco, Inc., Rocky River, OH) at 137 kPa was held at waist height and angled down toward the turf during application. To treat the area the gun was swept parallel to the ground as the applicator moved forward. The effective spray width was 1.5 m and the applicator positioned the gun 2 m from the edge of the plot. Proflaminate was applied at the labeled rate of 793 g a.i. per ha⁻¹.

Cheesecloth squares measuring 20 x 20 cm were placed in the center of each turf plot to collect initial spray deposition (ng prodiamine dm⁻²). The deposition samples were collected and placed in amber glass containers for storage. Samples were stored in a freezer at -8° C until analysis.

Dislodgeable Foliar Residue Collection and Analysis

Dislodgeable foliar residues were measured using a method similar to that described by Thompson et al. (1984) which is thought to provide a good estimate of unbound dislodgeable residues (Cowell et al., 1993). A 20 x 20 cm piece of distilled water dampened cheesecloth (Fisher Scientific, Springfield NJ) was used to wipe a 9.3 dm² area of herbicide treated turfgrass two times east → west, two times west → east, two times north → south and two times south → north to ensure that the entire area was uniformly wiped. Residue samples were placed in an amber glass container and stored in a freezer at -8° C until analysis. Each sampled area was marked with orange paint to avoid resampling that area during future sampling. Samples were taken three and eight HAT and at noon 2, 3, 5, 7, and 11 DAT.

Cheesecloth residue wipes were extracted by placing 50 ml of dichloromethane into sample jars and shaking for one h at 300 rpm on an orbital shaker (Lab-Line Instruments Inc., Melrose Park, IL). The extraction solvent was then evaporated to approximately 5 ml using a TurboVap® nitrogen evaporator (Caliper Life Sciences, Hopkinton, MA) at 40° C. The solvent was further reduced in volume to approximately 3 ml using a Meyer analytical nitrogen evaporator (Organomation Associates Inc., Berlin, MA) under a steady stream of nitrogen at 40° C. Extracts were then filtered using a UNIPREP® 0.45 µm PTFE membrane syringeless filter (Whatman®, Middlesex,

England) device and transferred to 30 ml Pyrex test tubes for further evaporation of solvent using nitrogen-evaporation. All sample extracts were analyzed using an Agilent 6890 gas chromatograph(GC) equipped with electronic pressure control connected to a 5973n mass selective detector (MSD). Extracts were injected in pulsed splitless mode and separated on a Restek 30-m x 0.25-mm Rtx-5 (0.25- μ m film thickness) MS with Integra-Guard column. The pressure was ramped to 30 psi before injections with a 1-min hold time. The pressure was then dropped to a constant flow of 1 mL/min for the duration of the run. The temperature program was as follows, Prodiame: initial temperature 100 °C for 1.0 min, 25 °C/min to 300 °C, hold for 6 min, the injector was set at 250 °C and the detector was set at 300 °C. The MSD was operated in the selective ion monitoring mode. Analytes were quantified using the internal standard method.

Soil Sample Collection and Analysis

Soil samples were collected to a depth of 7.6 cm using a 2.5 cm diameter soil probe. Samples were obtained from three random locations inside each plot and combined into a composite sample after thatch was removed from the core. Each soil sample was placed in an amber glass jar and stored frozen until analysis.

In preparation for extraction, samples were freeze dried using a Virtis bench top freeze drier (Virtis, Gardiner, NY) for 24 hours. Ten grams of the freeze dried sample was extracted to determine prodiamine residue levels. Ten gram soil samples placed in 100 ml Teflon sampling jars were extracted by adding 50 ml of dichloromethane and shaking (Lab-Line Instruments Inc., Melrose Park, IL) for 24 h at 300 rpm on an orbital shaker. Samples were centrifuged for 30 minutes at 550 g or until sediment had settled. Extraction solvent was decanted using a funnel lined with 0.45 μ m filter paper into two

30 ml Pyrex test tubes. The extraction solvent was evaporated under nitrogen gas at 40° C using the turbo-evaporator. The extraction solvent was then further evaporated to approximately 5 ml using a TurboVap® nitrogen evaporator (Caliper Life Sciences, Hopkinton, MA) at 40° C. Samples were further reduced and analyzed using the analytical method described previously for the cheesecloth residue wipes.

Foliar Sample Collection and Analysis

Seventy-two hours after prodiamine application grass clippings were collected for pesticide residues analysis. A 0.6 x 0.6 m strip of treated turfgrass was collected from selected plots at noon using a reel mower set at 7.6 cm cutting height equipped with a bagger attachment. Unmowed plots had reached a height of 12.7 cm at the time of sampling. Samples were placed in amber glass containers and were freeze dried for 24 h before extraction.

Five grams of freeze dried leaf tissue were extracted by placing each sample into 100 ml glass sampling jars containing 50 ml of dichloromethane and shaking (Lab-Line Instruments Inc., Melrose Park, IL) for one h at 300 rpm on an orbital shaker. Samples were further reduced and analyzed using the analytical method described previously for the cheesecloth residue wipes.

Exposure and Hazard Quotient Determinations

Estimated average dermal exposure doses (D_d) for a 70-kg-adult taking part in daily leisure activity on his home lawn for 4 h was estimated using Eq [1] (Murphy et al., 1996a).

Eq [1].
$$D_d = S \times P / 70 \text{ kg} \times 1000 \mu\text{g mg}^{-1}$$

Where: D_d = Estimated dermal exposure dose ($\mu\text{g kg}^{-1}$).

S (calculated dermal exposure, mg) = DFR (obtained on cheesecloth wipes) x $5 \times 10^3 \text{ cm}^2 \text{ h}^{-1}$ (dermal transfer coefficient, Zweig et al., [1985]) x h (exposure period in hours)

P = dermal permeability (0.1, USEPA default value, 1989)

Hazard quotients (HQ) were estimated using Eq [2] (Murphy et al., 1996a).

Eq [2].
$$HQ = D_d / Rfd$$

Where: HQ = Estimated potential human hazard

D_d = Estimated daily dermal exposure dose

Rfd = NOAEL/ uncertainty factor

Acute reference dose (Rfd) was determined by dividing the daily dose level shown to cause no observable adverse effects (NOAEL) in laboratory rats period by an uncertainty factor. An uncertainty factor of 100 is commonly used; 10x to account for intraspecies differences and 10x to account for interspecies differences (USEPA, 2001). Hazard quotients ≤ 1 indicate that dislodgeable residues are present at concentrations below those expected to cause any adverse effect in humans. A hazard quotient > 1 does not indicate that residue concentration will necessarily cause adverse effects but does indicate a higher potential risk of causing adverse effects in humans. Calculations of hazard quotients in this study use the maximum DFR determined in the field and estimate a worst case scenario.

Statistical Analysis

All data regarding foliar residues and soil residues were subjected to an Analysis of Variance (ANOVA) using the Statistical Analysis System (SAS Inst. Inc., 2001). Data were subjected to mean separation using the Waller-Duncan k-ratio t-test (k-ratio=100) when the ANOVA F-test indicated that treatment effects were significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

Dislodgeable Foliar Residues

The influence of application volume on DFR following application of prodiamine is reported in Figure 3. Prodiamine residues collected immediately after application for an application volume of 810 L ha⁻¹ totaled 465,400 ng prodiamine dm⁻². Dislodgeable residue levels 3 HAT averaged 69,000 ng dm⁻² (15%) of the total amount applied. At 8 HAT, DFR collected totaled 82,600 ng dm⁻² (17%) of the total amount applied. Residue samples taken at 8 HAT were obtained shortly after sunset when dew and gutation on the leaf tissue may have rehydrated foliar residues and made them available to be dislodged. Two DAT, dislodgeable residues began to steadily dissipate and were 76,000 ng dm⁻² (16%) of the total amount applied. By 3, 5, and 7 DAT dislodgeable residue levels had declined to 49,900 ng dm⁻² (10%), 53,500 ng dm⁻² (11%) and 33,600 ng dm⁻² (7%) of the total amount applied, respectively. At 11 DAT, dislodgeable residues had dissipated to 17,500 ng dm⁻² (4%) of the total amount applied. When prodiamine was applied at the higher 1,236 L ha⁻¹ application volume, DFR throughout the entire study were less than the 810 L ha⁻¹ application volume. Dislodgeable foliar residues were significantly lower when measured 3 HAT and 5, 7 and 11 DAT. Decreased dislodgeable residues associated with the higher 1,236 L ha⁻¹ application volume may be due to the increased canopy penetration achieved through the higher application volume. Knoche (1994) reported that droplets with a diameter of less than 67µm often do not reach their intended target due to air turbulence, while those with a diameter greater than 400 µm shatter on impact and are not retained on the leaf surface. Droplets between 100 and 400 µm are often chosen to give good retention of the droplets on the target surface (Knoche, 1994). The Chemlawn

spray gun produces a volume median density of droplet sizes between 250 - 350 μm which would be ideal for applying pesticides.

The influence of post-application irrigation on DFR following application of prodiamine are shown in Figure 4. When turf received 0.6 cm of post-application irrigation following prodiamine application, DFR were reduced throughout the entire study. Residue levels three HAT for turf that received post-application irrigation were 25,400 ng dm^{-2} (5%) of the total amount applied. Eight HAT and two DAT residue levels measured 28,800 ng dm^{-2} (6%) and 30,100 ng dm^{-2} (6%), respectively, of the total amount applied. At 3, 5, 7 and 11 DAT residues levels were 24,300 ng dm^{-2} (5%), 14,700 ng dm^{-2} (3%), 14,900 ng dm^{-2} (3%) and 6,100 ng dm^{-2} (1%), respectively, of the total amount applied. Dislodgeable foliar residues obtained from plots that received post-application irrigation showed significantly lower DFR three and eight HAT, and 2, 5, and 11 DAT. The delay in reaching maximum residue levels following prodiamine application and the reduction in DFR after post-application irrigation is consistent with the findings of Clark et al. (2000) and their work with isazofos residues. Clark et al. (2000) theorized that post-application irrigation allowed the residues to be redistributed from the leaf surface and penetrate into the soil profile. However, there are reports that irrigation might enhance the transformation of parent compounds to more toxic secondary metabolites, as with the case from Murphy et al. (1996a) in their work with trichlorfon converting to DDVP. Also the use of post-application irrigation could increase the risk of runoff as seen by Evans et al. (1998) in their work with post-application irrigation which increased the amount of diazinon removed from tall fescue.

The influence of mowing height on DFR following application of prodiamine are reported in Figure 5. Three HAT, DFR were 49,500 ng dm⁻² (11%) of the total amount applied. At 8 HAT residue levels increased and were 76,800 ng dm⁻² (17%) of the total amount applied. Two DAT, residue levels were steadily declining and were 62,100 ng dm⁻² (13%) of the total amount applied. At 3, 5, 7, and 11 DAT residue levels were 39,600 ng dm⁻² (9%), 39,600 ng dm⁻² (8%), 28,200 ng dm⁻² (6%) and 15,000 ng dm⁻² (3%) of the total amount applied, respectively. Throughout the entire study there was not a significant difference in the amount of prodiamine DFR, as influenced by mowing at 7.6 cm vs. 12.7 cm. Increasing the amount of foliar tissue present via increased mowing height did not have an impact on the amount of DFR available for human exposure.

Dissipation patterns of prodiamine DFR occurred in 1 phase and followed first-order kinetics (Table 9). Residue half-life ($T_{1/2}$) values were 126 and 93 HAT for 810 and 1236 L ha⁻¹, respectively. Residue half-life values were 106 and 121 HAT for non-irrigated and 0.6 cm irrigated plots, respectively. Residue half-life values for 7.6 and 12.6 mowing heights were 101 and 121 HAT, respectively. This research indicates that prodiamine can have a residue half-life between 101 and 126 HAT allowing it to persist for long periods of time after application.

Soil Residues

The influence of application volume on soil prodiamine levels following application are reported in Table 4. Increasing application volume from 810 L ha⁻¹ to 1,236 L ha⁻¹ significantly reduced soil residues as determined 1, 3 and 11 DAT. Soil residue levels at 7 DAT for the 1,236 L ha⁻¹ application volume also appeared lower,

however, the results were not statistically different. Knoche (1994), while evaluating droplet size and application volume on several different monocots and dicots, reported that when higher application volumes are used there is a dilution in the chemical dose resulting in decreased product performance. Thus, increasing application volume may not necessarily increase the amount of chemical reaching the soil surface. Increased application volume may increase herbicide performance as long as the chemical dose and droplet size affecting canopy penetration are kept constant (Knoche, 1994).

The influence of post-application irrigation on soil residues following application of proflaminate is reported in Table 4. When post-application irrigation was applied to treated turfgrass, soil residue levels at 1 DAT showed a trend toward lower soil residues for irrigated plots when compared to non-irrigated plots. Three DAT, soil residues for irrigated plots appeared slightly higher but differences were minimal. At 7 and 11 DAT, soil residue levels for irrigated plots showed a trend that averaged twice as large when compared to non-irrigated plots, however, there was not a statistical difference during any sampling period in the amount of proflaminate soil residues. Post-application irrigation showed limited ability to increase residue penetration into the soil profile 1 DAT.

The influence of mowing height on proflaminate soil residue levels following application is shown in Table 4. Soil residue levels at the 12.7 cm mowing height showed a trend toward higher soil residue levels compared to the recommended mowing height of 7.6 cm for the entire study except 3 DAT when residue levels appeared slightly lower. Even though apparent trends developed throughout the study there was not a statistical difference during any sampling period. Higher soil residue levels at the 12.7 cm mowing height might be a result of increased foliar tissue creating a more suitable microclimate

for the persistence of prodiamine residues. Bailey (2003) developed a model for the persistence of isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) used on various cropping conditions based on previous weather data and laboratory degradation research. They observed that minor differences in soil temperature or moisture content impacted the degradation and accumulation of pesticides in the soil. In theory, with an increased turf canopy there is potential for greater soil moisture and decreased soil temperatures elevating the possibility of greater soil residue levels.

Clipping Residues

To evaluate the possibility that homeowners may remove a large portion of applied herbicide when lawncare professionals treat turfgrass at higher mowing heights, clippings were removed and collected from plots maintained at 12.7 cm three days after prodiamine application. Three DAT, clippings removed from plots treated with an application volume of 1,236 L ha⁻¹ contained an average of 60,600 ng dm⁻², 13% of the total amount of prodiamine applied. Clippings removed from plots treated with an application volume of 810 L ha⁻¹ contained an average of 61,300 ng dm⁻², a removal of 13% of the total amount of prodiamine applied. Similar loss of applied prodiamine from either 810 L ha⁻¹ or 1,236 L ha⁻¹ application volumes is consistent with the amount of DFR seen three DAT. Results show that increasing application volume will not necessarily result in lower residue loss when clippings are removed from treated areas.

Clippings removed from plots that received post-application irrigation had an average of 59,000 ng dm⁻², which was 12% of the total amount of prodiamine applied. Clippings from plots that receive no post-application irrigation averaged 62,900 ng dm⁻² or 13% of the total amount of prodiamine applied.

The average 13% loss of applied prodiamine removed from clipping samples was significantly higher than the amount of applied chloropyrifos (0.52%), fenamiphos (0.38%) and isofenphos (0.89%) recovered from clipping samples on a bermudagrass putting green (Cisar & Snyder, 1996). Larger amounts of applied prodiamine removed from clipping samples might be a result of the increased amount of leaf tissue available to capture pesticide residues. There is a significantly greater amount of leaf tissue for a tall fescue lawn than a bermudagrass putting green resulting in greater removal of applied pesticides. While removal of large amounts of applied prodiamine on clippings in this study might be expected to reduce the performance and efficacy of the product, this research showed that there was not a decrease in product efficacy when clippings were removed three DAT. Research by Johnson and Carrow (1995) confirmed that rates as much as 33% less than the recommended labeled rate of prodiamine provided greater than 90% control of large crabgrass (*Digitaria sanguinalis* L.) in tall fescue.

Exposure Estimates

Using the estimates of maximum DFR obtained from the comparison of application volumes, maximum prodiamine levels resulted in estimated hazard quotients (HQ) below 1 over the entire 11-day study (Table 5). Maximum HQ values occurred 8 HAT and had an estimated HQ value of 1.18×10^{-3} . This HQ value is significantly lower than trichlorfon (0.4), triadimefon (0.2), MCPP (0.8), and isazofos (14.3) reported by Murphy et al. (1996a/b) and their work establishing HQ from pesticide dislodgeable residues applied to turfgrass. Differences might be associated with the different mechanisms of pesticidal action. Chemicals which attack sites that are similar to human cellular physiology typically have larger HQ's than those

chemicals that only affect sites specific to fungus or plant cellular physiology.

Prodiamine is a mitotic poison meaning that it inhibits cell division by preventing the formation of tubulin which allows the plant to complete mitosis. Similarities in cell division between plants and animals allow this product to have a slightly higher mammalian toxicity (Lee et al., 2001)

Although spraying is still the most common method of pesticide delivery other techniques including granular application or wiping techniques are in many instances more precise and efficient in achieving optimum pesticide deposits (Hislop, 1987). Knowledge about the biology of the pest, weed or disease will allow us to be more specific with our intent but rarely can we aim for this with any degree of exclusivity. The use of increased application volume and post-application irrigation to improve product efficacy have proved impractical due to high application costs, low work rates, potential losses through drift and runoff and possible transformation of parent compounds to more toxic secondary metabolites (Murphy et al., 1996a). Future research on improving product efficacy and reducing human implications might be directed toward reducing/ increasing spray droplet size, drop velocity and pesticide formulation which can have a dramatic affect on product efficacy within and outside the intended target area of the pest (Hislop, 1987).

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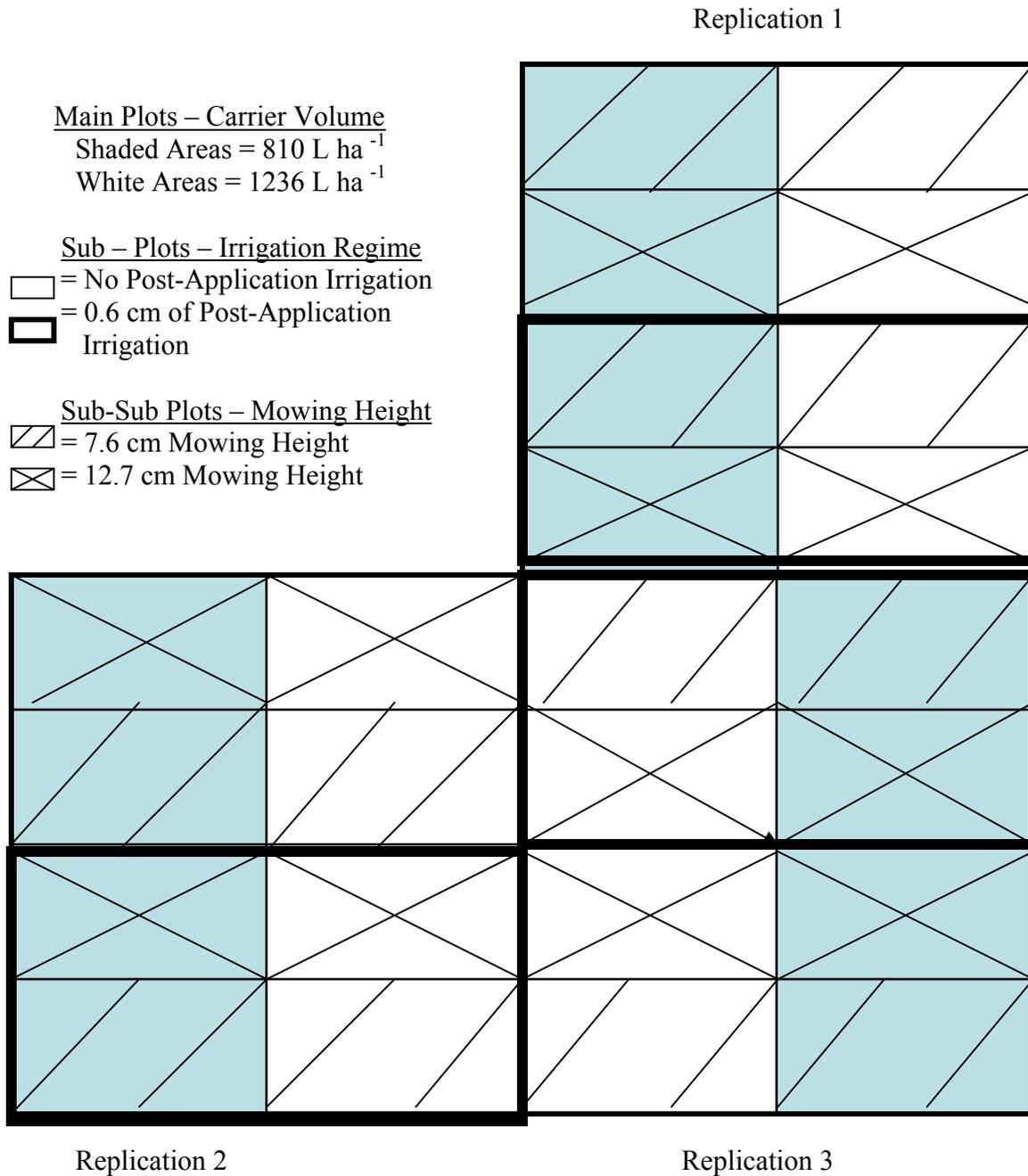
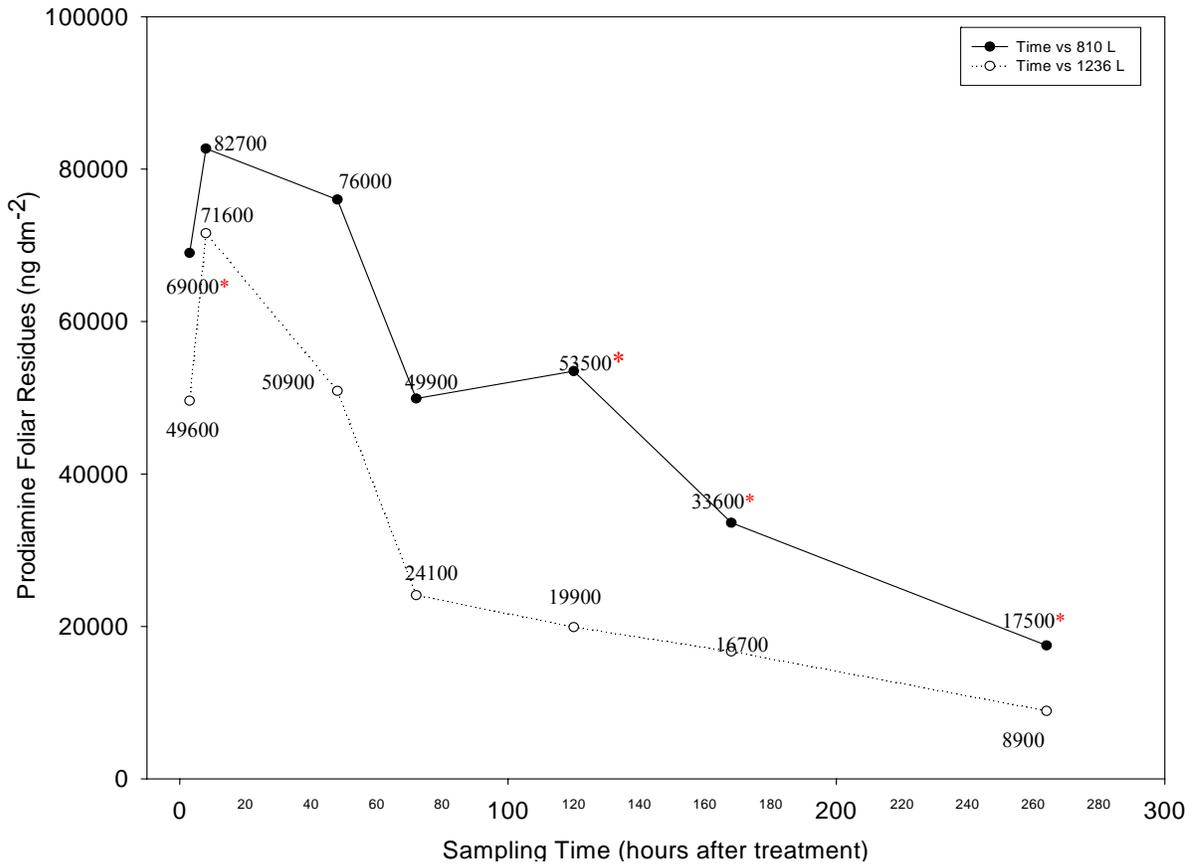
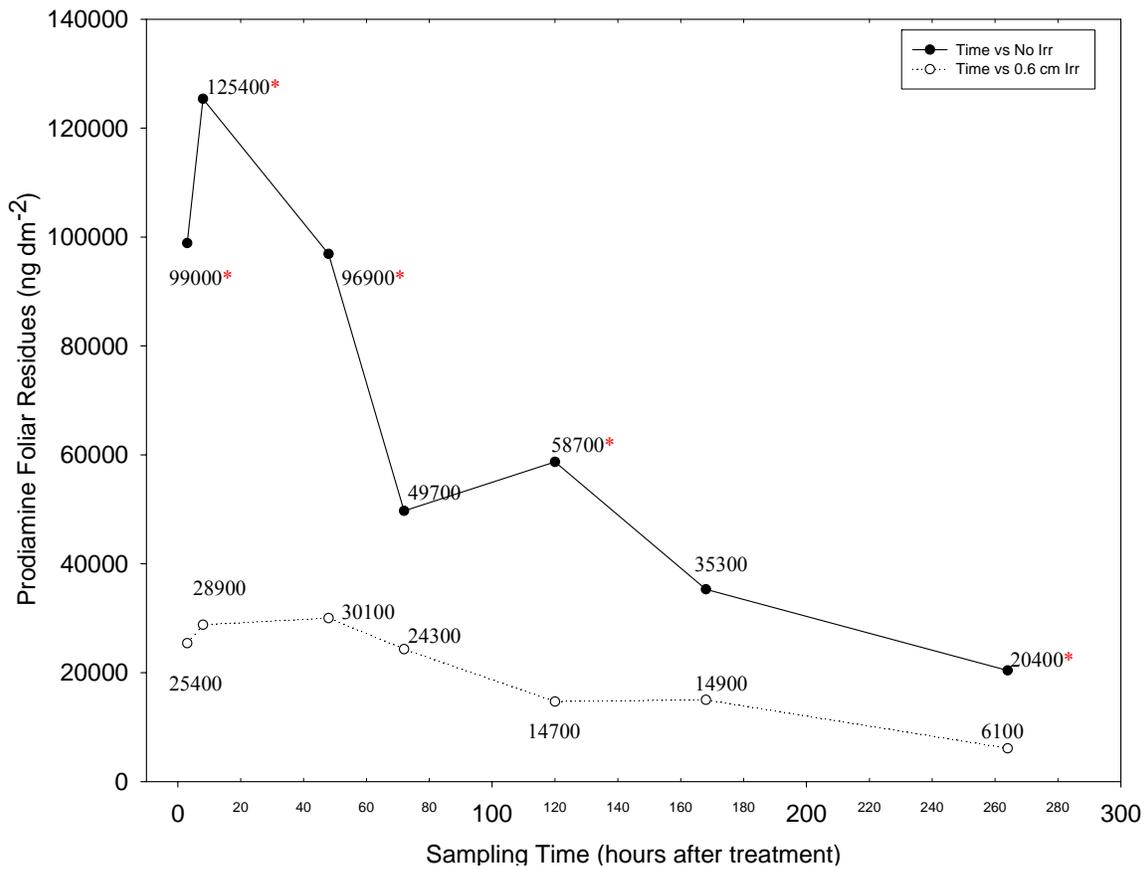


Figure 2. Plot Design for the influence of application volume, post-application irrigation and height of cut on the persistence of prodiamine residues following application to a tall fescue lawn.



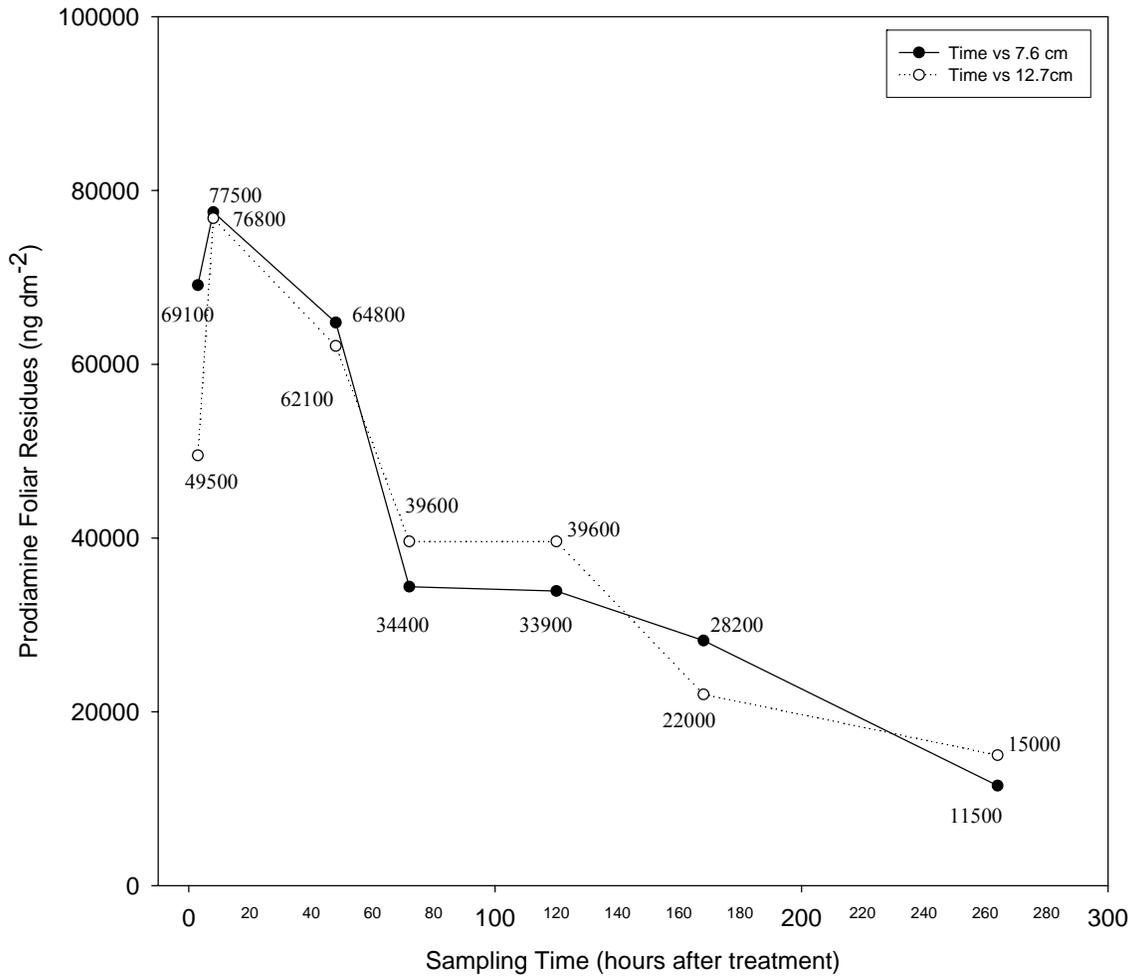
Statistically different residue levels ($P= 0.05$) for a particular sampling time are denoted by an * for that sampling time.

Figure 3. The influence of either 810 L ha⁻¹ or 1236 L ha⁻¹ application volume on dislodgeable foliar residues over an 11-day period following application of prodiamine.



Statistically different residue levels ($P= 0.05$) for a particular sampling time are denoted by an * for that sampling time.

Figure 4. The influence of 0.6 cm post-application irrigation on dislodgeable foliar residues over an 11-day period following application to prodiamine.



Statistically different residue levels ($P= 0.05$) for a particular sampling time are denoted by an * for that sampling time.

Figure 5. The influence of 7.6 and 12.6 cm mowing heights on dislodgeable foliar residues over an 11-day period following application of prodiamine.

Table 3. Mean air temperature, wind speed, and relative humidity during the 11-day experimental period following prodiamine application on 10 April 2006*

Day	Time Period (h after treatment)	Air Temp ° C	Wind Speed m s ⁻¹	Relative Humidity %
1	0-3	14.2	1.3	72
1	3-8	18.3	4.9	32
2	24-48	19.2	6.0	59
3	48-72	19.4	7.2	60
5	96-120	25.3	10.8	44
7	144-168	21.2	4.2	65
11	240-264	24.3	7.8	57

* Weather station located at the Lake Wheeler Turfgrass Field Lab, Raleigh, NC within 457 m of experimental plots

Table 4. The influence of application volume, post-application irrigation and mowing height on soil concentration levels of prodiamine following application.

Days After Treatment	Application Volume (L ha ⁻¹)		Post-Application Irrigation (cm)		Mowing Height (cm)	
	810	1,236	0	0.6	7.6	12.7
	ng Prodiamine/ 10g					
1	450*	275	470	260	225	500
3	600*	295	425	475	560	340
7	490	290	270	515	345	435
11	950*	470	415	1005	685	740

Means followed by a * within each day after treatment are significantly different within comparisons at the 0.05 probability level.

Table 5. Estimated dermal exposure dose (D_d), calculated dermal exposure (S) and dermal hazard quotients (HQ) estimated for exposure to prodiamine dislodgeable foliar residues (DFR) following application to a tall fescue lawn in 810 L ha⁻¹.

Estimated Dermal Exposure Dose (D_d)*	Calculated Dermal Exposure (S)	DFR	Hours after Treatment	HQ§	Rfd**
$\mu\text{g kg}^{-1}$	mg	ng prodiamine dm ⁻²		(x 10 ⁻⁵)	mg kg ⁻¹ d ⁻¹
1972	1380	69000	3	99	2000
2362	1653	82700	8	118	2000
2171	1520	76000	48	109	2000
1425	997	49900	72	71	2000
1528	1070	53500	120	76	2000
959	672	33600	168	48	2000
501	350	17500	264	25	2000

* Estimated dermal exposure using model of Zweig et al. (1985)

** Rfd = NOAEL(No Observable Adverse Effect Level) / UF (Uncertainty Factor)

§ HQ = D_d / Rfd

**Dissipation of Foliar Bifenthrin Residues Following Application to a Tall
Fescue Lawn and Implications for Human Exposure**

Abstract

Dislodgeable foliar residues (DFR) can be a primary route for human exposure following pesticide application to turfgrass areas. Consequently, a significant portion of applied pesticide may be available for human exposure via dislodgeable residues. In this study, DFR were determined over a 15-day-period following 6 October 2006 application of the insecticide bifenthrin (2-methylbiphenyl-3-ylmethyl (1*RS*,3*RS*)-3-[(*Z*)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropanecarboxylate) to a mature stand of ‘Confederate’ Tall Fescue (*Festuca arundinacea* Schreb). Foliar residues were determined by wiping treated turfgrass with a distilled-water-dampened cheesecloth and analyzing samples using gas chromatography/ mass spectrometry (GC/MS). Approximately 35% of the total applied bifenthrin (213,000 ng dm⁻²) was available to be dislodged over 15 days with 34% DFR loss occurring immediately after application. Residue loss measured 3 and 8 hours after treatment (HAT) contributed an additional 0.5% of the total applied bifenthrin dislodged from the foliar surface. Residue levels detected 2, 5, 7, 11 and 15 days after application measured < 1% of the total applied bifenthrin. Bifenthrin DFR detected immediately after application resulted in a maximum estimated hazard quotients of 1.1 x 10⁻³ for the 15-day study. Bifenthrin poses minimal human health risk when applied at the labeled rate.

Introduction

Pesticide use on residential lawns has increased as homeowner awareness of weed and insect problems have grown, largely as a result of the rapid expansion of the lawncare industry in the United States (Hurto and Prinster, 1993). When pesticides are applied to residential lawns the potential exists for exposure by people using the treated area (Williams et al., 2003). While pesticide exposure concerns often focus on contamination of groundwater or surface runoff, Zatarian et al. (2000) have identified dermal exposure as the primary route for chemicals typically used for home lawn pest control. Inhalation is also a potential exposure route but one of much lower magnitude due to the low volatility of most commercial pesticides and ample air circulation on areas where these pesticides are used (Plog and Quinlan, 2001). Increased attention has been focused on evaluation of DFR of applied pesticides as a means to gauge potential human exposure from contact with treated turf.

Thompson et al. (1984) reported on the dislodgeable foliar residues of 2, 4-D (2,4-dichlorophenoxy acetic acid) applied to a Kentucky bluegrass (*Poa pratensis* L.) lawn in Ontario Canada. Dislodgeable foliar residues declined rapidly following application at 2.24 kg ai ha⁻¹ with dislodgeable residue levels of only 1.0 and 0.02% of the target application rate as determined 3 and 7 days after treatment (DAT).

Murphy et al. (1996) determined on the dislodgeable foliar residues of MCPP (2-Methyl-4-chlorophenoxy propanoic acid) and triadimefon (1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazolyl)-2-butanone) following application to fairway-height creeping bentgrass (*Agrostis stolonifera* L.). Triadimefon dislodgeable residues were greatest 3 HAT accounting for 1.5% of the target application rate. Over time,

dislodgeable residues decreased to 1.0, 0.6, 0.06 and 0.01% of the applied chemical available 1, 2, 5, and 15 DAT, respectively. Dislodgeable residues of MCPP dissipated rapidly so that only 0.1% of applied chemical when measured 3 HAT. Dislodgeable residues declined to 0.08% on day 2 and were nondetectable by day 5.

Hurto and Prinster (1993) reported on the dislodgeable foliar residues of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate), DCPA (dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid), diazinon (O,O-diethyl O-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate), isofenphos (O-ethyl O-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate) and pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) applied to Kentucky bluegrass lawn turf maintained at a height of 7.6 cm in Delaware, Ohio. Dislodgeable foliar residues as a percent of the target application rate ranged from a high of 10.7% for isofenphos to a low of 0.6% for chlorpyrifos when determined 2 HAT. From their research with pesticide applications that received no post-application irrigation, dislodgeable pesticide levels on foliage naturally dissipated rapidly to less than 10% of the target application rate 1 day after treatment and to less than 2% by 7 DAT. By 14 DAT, pesticide levels fell below 1% of the target application rate. Post-application irrigation reduced DFR levels of pendimethalin and DCPA significantly during all sampling periods through 7 DAT, while differences in isofenphos residue levels were significantly different only through 3 DAT. Post-application irrigation for diazinon and chlorpyrifos did not show any significant differences at any sampling period through out the study.

Previous research has focused on the residue loss of pre and post-emergent herbicides along with a few of the commonly used fungicides. With the advancements in

modern technology and chemical research, new chemicals are being registered for use in turfgrass management to provide turfgrass professionals with a variety of management tools. The focus of this research was to evaluate the foliar residue levels following application of the insecticide bifenthrin to a tall fescue lawn using equipment and techniques employed by lawncare professionals.

MATERIALS AND METHODS

Experimental Site

A field experiment was conducted from 6 – 19 Oct. 2006 at the North Carolina State University Turfgrass Field Laboratory located in Raleigh, NC. ‘Confederate’ Tall Fescue mowed with a rotary mower at 7.6 cm was used for the study. Turfgrass quality and density were typical of a well maintained residential lawn. The experimental area consisted of ten bifenthrin-treated strips (1.5 x 6.0 m) where each strip constituted one replication. Plots were not mowed and no irrigation or precipitation occurred during the study. Weather data recorded during the entire study is reported in Table 6.

Pesticide Application

Application of bifenthrin (Cross Check Plus®, LESCO Inc., Cleveland, OH) was made to plots at 08:00-08:50 using application equipment and techniques commonly employed by lawncare professionals. The Lesco/ Chemlawn Gun equipped with a 810 L ha⁻¹ nozzle (Lesco, Inc., Rocky River, OH) at 137 kPa was held at waist height and angled down toward the turf during application. To treat the area the gun was swept parallel to the ground as the applicator moved forward. The effective spray width was 1.5 m and the applicator positioned the gun 2 m from the edge of the plot. Bifenthrin was applied at the labeled rate of 0.22 kg a.i. ha⁻¹.

Cheesecloth squares measuring 20 x 20 cm were placed in the center of each turf plot to collect initial spray deposition (ng bifenthrin dm⁻²). The deposition samples were collected and placed in amber glass containers for storage. Samples were stored at in a freezer at -8°C until analysis.

Dislodgeable Foliar Residue Collection

Dislodgeable foliar residues were collected using a method similar to that described by Thompson et al (1984) which is thought to provide a good estimate of unbound dislodgeable residues (Cowell et al., 1993). A 20 x 20 cm piece of distilled-water-dampened cheesecloth (Fisher Scientific, Springfield NJ) was used to wipe a 9.3 dm² area of herbicide treated turfgrass two times east → west, two times west → east, two times north → south and two times south → north to ensure that the entire area was uniformly wiped. Samples were collected immediately after application and 3, and 8 HAT on the day of application. Additional samples were collected at noon 2, 3, 5, 7, 11, and 15 DAT. Residue samples were placed in amber glass containers and stored at -8° C until analysis. Each sampled area was marked with orange paint to avoid resampling of that area during future sampling.

Residue Analysis

Cheesecloth residue wipes were extracted by placing 50ml of dichloromethane into sample jars and shaking for one hr at 300 rpm on an orbital shaker (Lab-Line Instruments Inc., Melrose Park, IL). The extraction solvent was then evaporated to approximately 5ml using a TurboVap® nitrogen evaporator (Caliper Life Sciences, Hopkinton, MA) at 40° C. Solvent was further reduced in volume to approximately 3ml using a Meyer analytical nitrogen evaporator (Organomation Associates Inc., Berlin, MA) under a

steady stream of nitrogen at 40° C. Extracts were then filtered using a UNIPREP® 0.45 µm PTFE membrane syringeless filter (Whatman®, Middlesex, England) device and transferred to 30 ml Pyrex test tubes for further evaporation of solvent using nitrogen-evaporation. All sample extracts were analyzed using an Agilent 6890 gas chromatograph(GC) equipped with electronic pressure control connected to a 5973n mass selective detector (MSD). Extracts were injected in pulsed splitless mode and separated on a Restek 30-m x 0.25-mm Rtx-5 (0.25-µm film thickness) MS with Integra-Guard column. The pressure was ramped to 30 psi before injections with a 1-min hold time. The pressure was then dropped to a constant flow of 1 mL/min for the duration of the run. The temperature program was as follows, Bifenthrin: initial temperature 40 °C for 1.0 min, 25 °C/min to 300 °C, hold for 8 min, the injector was set at 250 °C and the detector was set at 300 °C. The MSD was operated in the selective ion monitoring mode. Analytes were quantified using the internal standard method.

Exposure and Hazard Quotient Determinations

An estimated average dermal exposure dose (D_d) for a 70 kg adult taking part in 4 h of leisure activity on his home lawn was estimated using Eq [1] (Murphy et al., 1996a).

Eq [1].
$$D_d = S \times P / 70 \text{ kg} \times 1000 \text{ } \mu\text{g mg}^{-1}$$

Where: D_d = Estimated dermal exposure dose ($\mu\text{g kg}^{-1}$).

$$S \text{ (calculated dermal exposure, mg)} = \text{DFR (obtained on cheesecloth wipes)} \times 5 \times 10^3 \text{ cm}^2 \text{ h}^{-1} \text{ (dermal transfer coefficient, Zweig et al., [1985])} \times h \text{ (exposure period in hours)}$$

P = dermal permeability (0.1, USEPA default value, 1989)

Hazard quotients (HQ) were estimated using Eq [2] (Murphy et al., 1996a).

Eq [2]. $HQ = D_d / Rfd$

Where: HQ = Estimated potential human hazard

D_d = Estimated daily dermal exposure dose

Rfd = NOAEL/ uncertainty factor

Acute reference dose (Rfd) was determined by dividing the daily dose shown to cause no observable effects (NOAEL) in laboratory animals by an uncertainty factor. An uncertainty factor of 100 is commonly used; 10x to account for intraspecies differences and 10x to account for interspecies differences (USEPA, 2001). Hazard quotients ≤ 1 indicate that dislodgeable residues are present at concentrations below those expected to cause adverse effects to humans. A hazard quotient > 1 does not indicate that residue concentration will necessarily cause adverse effects but does indicate a higher potential risk of causing adverse effects to humans. Calculations of hazard quotients in this study use the maximum DFR determined in the field and estimate a worst case scenario.

RESULTS AND DISCUSSION

Dislodgeable Foliar Residues

Dislodgeable foliar residues following application of bifenthrin total fescue lawn-type turf are shown in Figure 6. Total applied bifenthrin calculated from initial spray deposition samples was 213,000 ng dm⁻². Bifenthrin DFR were greatest immediately following application during the initial wiping within 30 seconds of application.

Dislodgeable residues immediately after treatment averaged 74,000 ng dm⁻² or 35% of the total amount applied. At 3 HAT, when the insecticide solution had dried on the leaf tissue and absorbed into turfgrass canopy, dislodgeable residues had rapidly declined to

750 ng dm⁻² (0.4%) of the total amount applied. By 8 HAT, dislodgeable residues had dissipated to 300 ng dm⁻² (0.1%) of the total amount applied. At 2 and 3 DAT dislodgeable residues continued declining to 240 ng dm⁻² (0.1%) and 160 ng dm⁻² (0.07%), respectively, of the total amount applied. At 5, 7, 11 and 15 DAT dislodgeable residues were still detectable but steadily declining and were 145 ng dm⁻² (0.06%), 85 ng dm⁻² (0.03%), 50 ng dm⁻² (0.02%) and 40 ng dm⁻² (0.01%), respectively, of the total amount applied.

Over the entire 15 day study, DFR totaled 35% of the total amount applied. Thirty-four percent of DFR were detected immediately after application with < 1% of the total application rate available to be dislodged after the insecticide had dried on the leaf surface and absorbed into the turfgrass canopy 3 HAT. Dissipation of bifenthrin occurred in two phases in first-order kinetics (Table 10). Residue half-life (T_{1/2}) values were 0.5 HAT for the first phase and 116 HAT for the second phase.

The availability and persistence of dislodgeable residues of bifenthrin following application declined faster than those of chlorpyrifos, isofenphos and diazinon reported by Hurto and Prister (1993). When compared with chlorpyrifos which showed the least amount of DFR, bifenthrin resulted in less DFR 3 HAT. These results demonstrate that bifenthrin has little potential for DFR shortly after application.

With sufficient drying time under moderate temperatures and low humidity dislodgeable residues can be significantly reduced below the EPA's pesticide tolerance level of 2,000 mg kg⁻¹ d⁻¹ which produces no toxicological effects based on a acute toxicity dermal exposure assessment (USEPA, 2001).

Dislodgeable residues from bifenthrin-treated turfgrass resulted in estimated hazard quotients (HQ) below 1 during the entire 15 day study (Table 7). Maximum HQ occurred immediately after application (0 HAT) and had an estimated value of 11×10^{-4} . These HQ values are significantly lower than the maximum HQ values reported by Murphy et al. (1996a) for the insecticides DDVP (4.6), trichlorfon (0.4), isazofos (14.3). These differences in HQ values are related to the varying mechanisms of pesticidal action. Chemicals which attack sites that are similar to human cellular physiology will have larger HQ's than those chemicals that only affect sites specific to pest cellular physiology. In this evaluation, bifenthrin is considered an axonic poison which works by stimulating nerve cells to produce repetitive discharges and eventually cause paralysis of the central and peripheral nervous system of the insect.

Post-application irrigation is likely to reduce the amount of dislodgeable residues; however, post-application irrigation must be consistent with the placement in the targeted area of the turf/ soil system. Research reported by Murphy et al. (1996) research indicated significantly lower levels of DFR when trichlorfon received post-application irrigation, however, with chlorpyrifos and diazinon (Hurto and Prinster, 1993) post-application showed no significant reduction in the amount of DFR. Post-application irrigation and rainfall have the potential to transport the pesticide deeper into the turf canopy where it can bind to thatch and soil (Cooper et al., 1995). Further research is warranted to determine the affects of irrigation on bifenthrin dislodgeable residues.

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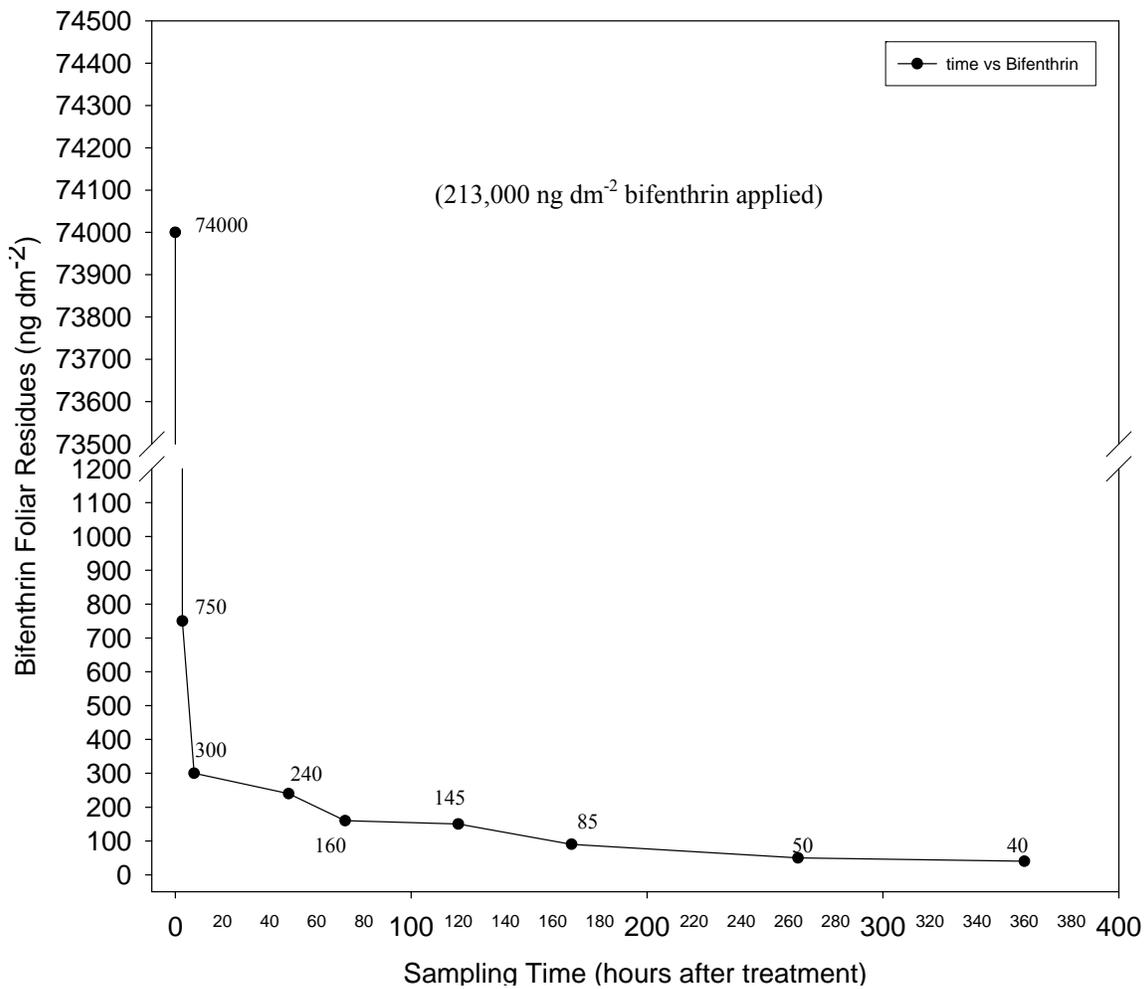


Figure 6. Dissipation of bifenthrin dislodgeable foliar residues from a tall fescue lawn over a 15-day period following 6 Oct. 2006 application.

Table 6. Mean air temperature, wind speed, and relative humidity during the 15-day experimental period following bifenthrin application on 6 Oct. 2006*

Day	Time Period (h after treatment)	Air Temp ° C	Wind Speed m s ⁻¹	Relative Humidity %
1	1-4	27.8	6.0	56
1	4-8	27.4	5.7	52
1	20-24	19.2	1.6	89
2	24-48	20.6	9.8	82
3	48-72	17.2	9.2	79
5	96-120	12.7	7.6	62
7	144-168	14.4	5.1	67
11	240-264	21.6	3.2	68
15	336-360	21.2	5.9	74

* Weather station located at the Lake Wheeler Turfgrass Field Lab, Raleigh, NC within 457 m of experimental plots

Table 7. Estimated dermal exposure dose (D_d), calculated dermal exposure (S) and dermal hazard quotients (HQ) estimated for exposure to bifenthrin dislodgeable foliar residues (DFR) following application to a tall fescue lawn in 810 L ha⁻¹.

Estimated Dermal Exposure Dose (D_d)*	Calculated Dermal Exposure (S)	DFR	Hours after Treatment	Hazard Quotient (HQ)§	Reference Dose (Rfd)**
$\mu\text{g kg}^{-1}$	mg	ng bifenthrin dm ⁻²		($\times 10^{-4}$)	mg kg ⁻¹ d ⁻¹
2114	1480	74000	0	11	2000
21	15	750	3	0.1	2000
9	6	300	8	0.04	2000
7	4.8	240	48	0.03	2000
5	3.2	160	72	0.02	2000
4	2.9	145	120	0.02	2000
2	1.7	85	168	0.01	2000
1	1.0	50	264	0.007	2000
1	0.8	40	360	0.007	2000

* Estimated dermal exposure using model of Zweig et al. (1985)

** Rfd = NOAEL(No Observable Adverse Effect Level) / UF (Uncertainty Factor)

§ HQ = D_d / Rfd

Conclusions

- Approximately 20% of the total applied carfentrazone was dislodged with 13.8% DFR loss occurring 0 HAT after application.
- One day after application, dislodgeable residue levels had declined to below 1% of the total applied carfentrazone.
- Carfentrazone residue levels resulted in estimated hazard quotients < 1 for the entire study, indicating no human toxicological implications.
- Increasing application volume from 810 to 1236 L ha⁻¹ reduced prodiamine DFR by an average of 3.8% for the entire study with significantly lower residue levels 3 HAT, and 5, 7, and 11 DAT.
- Increased application volume resulted in an average of 46% less prodiamine soil residues with significantly lower residue levels 1, 3, and 11 DAT.
- Clippings removed from plots 3 DAT resulted in a $< 1\%$ reduction in the amount of applied prodiamine lost from the treated surface.
- Post-application irrigation reduced prodiamine DFR by an average of 10% for the entire study with significantly lower residue levels at all sampling periods except 3 DAT.
- Post-application irrigation resulted in increased soil residue levels 3, 7, and 11 DAT by an average of 37%.
- Increased mowing height did not result in significantly different prodiamine DFR or soil residues through out the entire study.
- Approximately 35% of the total applied bifenthrin was dislodged over 15 days with 34% DFR loss occurring immediately after application

- Maximum bifenthrin DFR immediately after application resulted in an estimated $HQ > 1$ indicating possible human toxicological implications.
- Eight HAT $< 1\%$ of applied bifenthrin can be dislodged from the leaf surface resulting in estimated HQ values < 1 , indicating no possible human toxicological implications.

Appendix

Table 8. First-order kinetics of carfentrazone dissipation during the 15-day experimental period following application on 20 Oct. 2005.

Phase ^a	Regression equation ^b	T _{1/2} (hours)
First	Y = 7.8 - 0.1 X	7
Second	Y = 1.3 - 0.002 X	346

^a First phase: 0 – 72 HAT; second phase: 72 – 360 HAT

^b Y = ln (DFR); X = hours after treatment

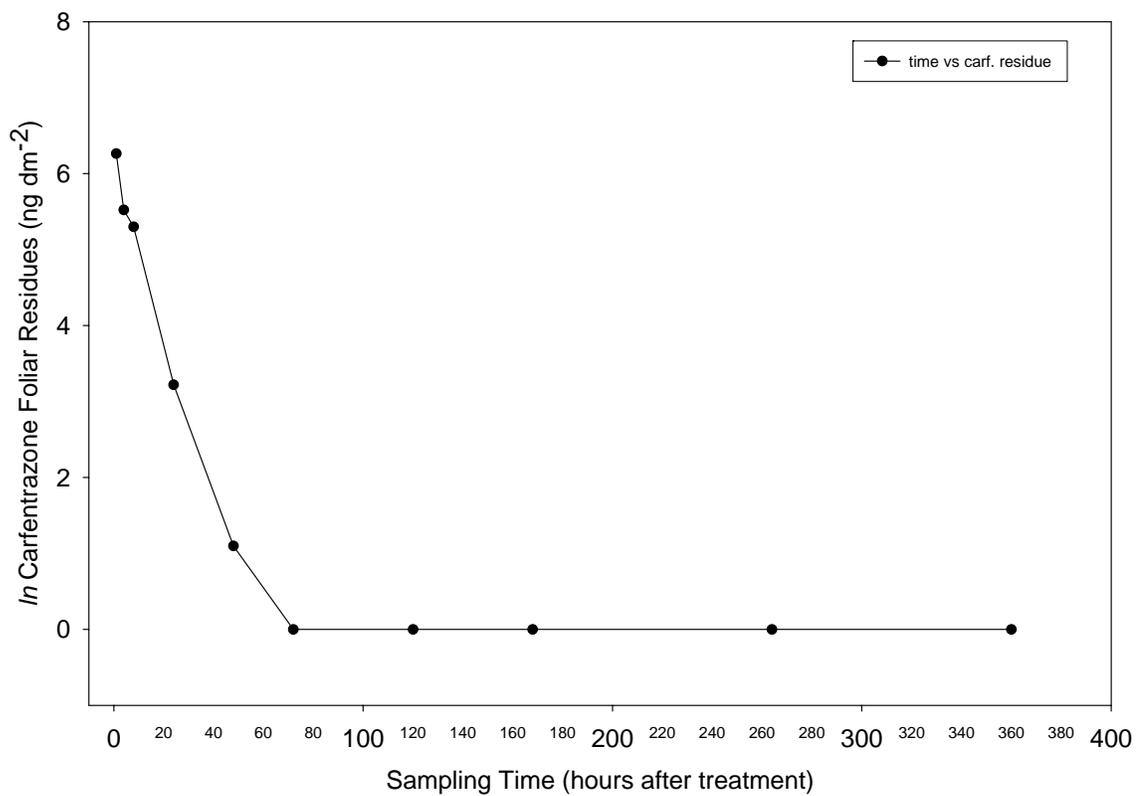


Figure 7. Dissipation of *ln* carfentrazone dislodgeable foliar residues from a tall fescue lawn over a 15-day period following 20 Oct. 2005 application.

Table 9. First-order kinetics of prodiamine dissipation during the 11-day experimental period following application on 10 Oct. 2006.

Treatment	Application Volume	T _{1/2} (Hours)
810 L ha ⁻¹	Y= 11.3 - 0.0058 X	126
1236 L ha ⁻¹	Y= 10.9 - 0.0074 X	93

Treatment	Post-Application Irrigation	T _{1/2} (Hours)
No Irr	Y= 11.6 - 0.0065 X	106
0.6 cm Irr	Y= 10.4 - 0.0057 X	121

Treatment	Mowing Height	T _{1/2} (Hours)
7.6 cm	Y= 11.2 - 0.0068 X	101
12.6 cm	Y= 11.1 - 0.0057 X	121

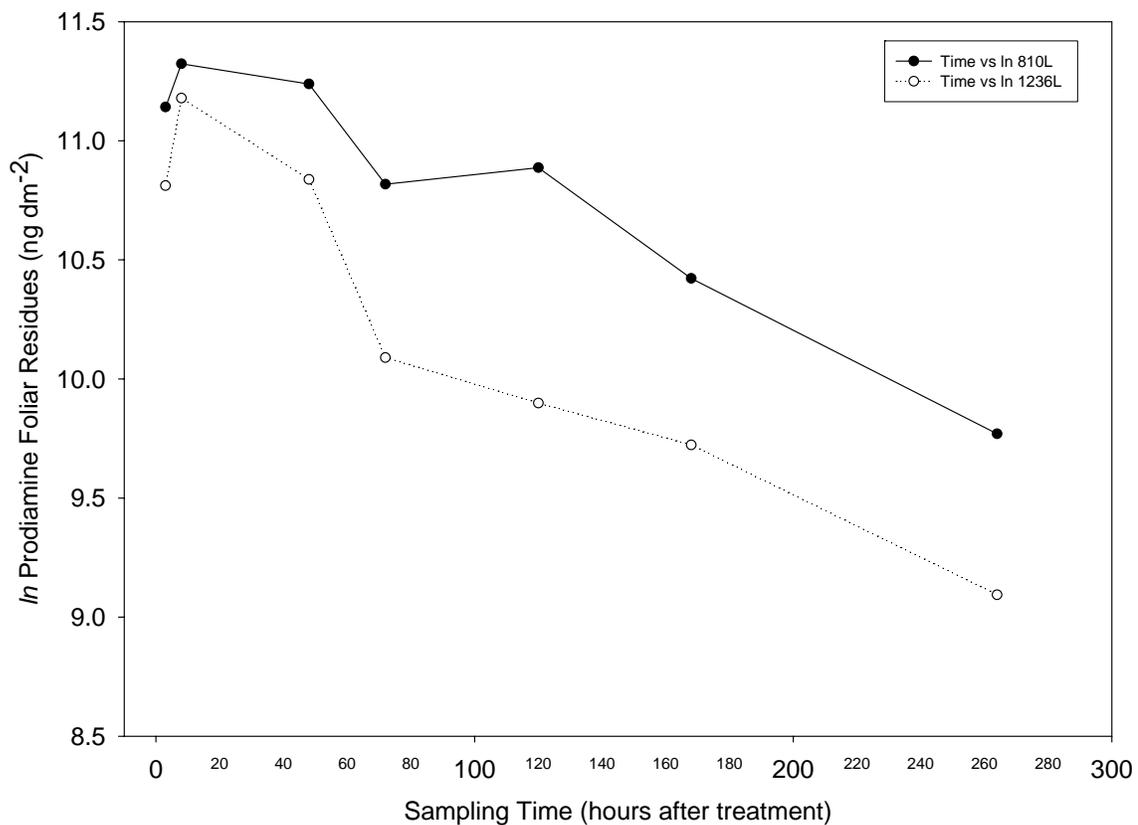


Table 8. The influence of either 810 L ha^{-1} or 1236 L ha^{-1} application volume on \ln dislodgeable foliar residues over an 11-day period following application of prodiamine.

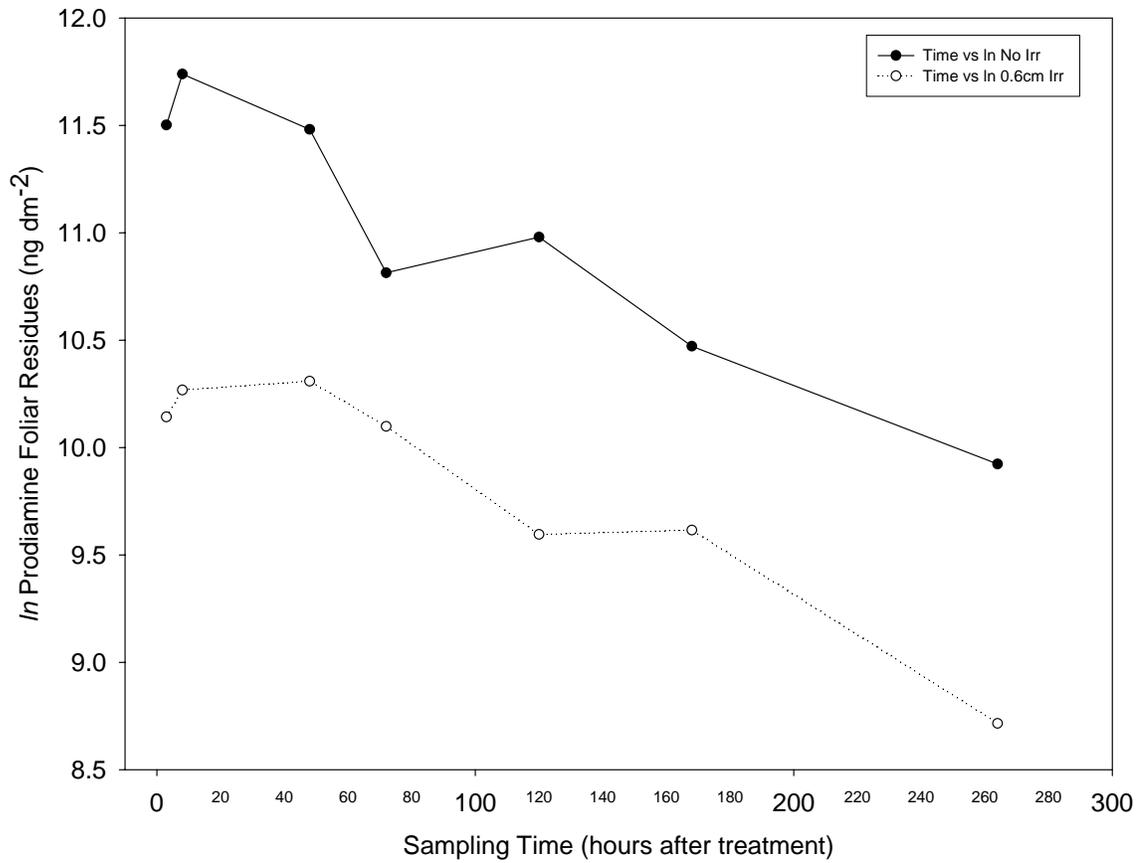


Table 9. The influence of 0.6 cm post-application irrigation on *ln* dislodgeable foliar residues over an 11-day period following application to prodiamine.

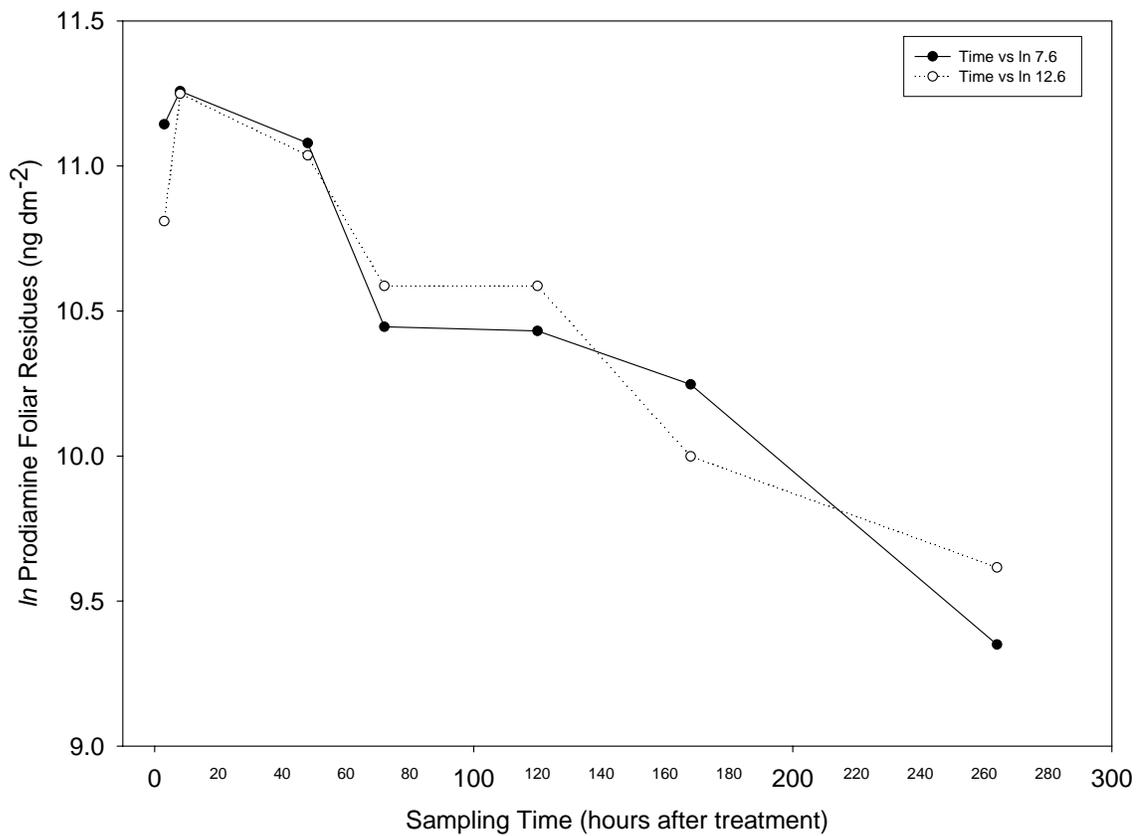


Table 10. The influence of 7.6 and 12.6 cm mowing heights on *ln* dislodgeable foliar residues over an 11-day period following application of prodiamine.

Table 10. First-order kinetics of bifenthrin dissipation during the 15-day experimental period following application on 6 Oct. 2006.

Phase ^a	Regression equation ^b	T _{1/2} (hours)
First	Y= 12.18 - 1.5 X	0.5
Second	Y= 6.4 - 0.005 X	116

^a First phase: 0 – 8 HAT; second phase: 8 – 360 HAT

^b Y = ln (DFR); X = hours after treatment

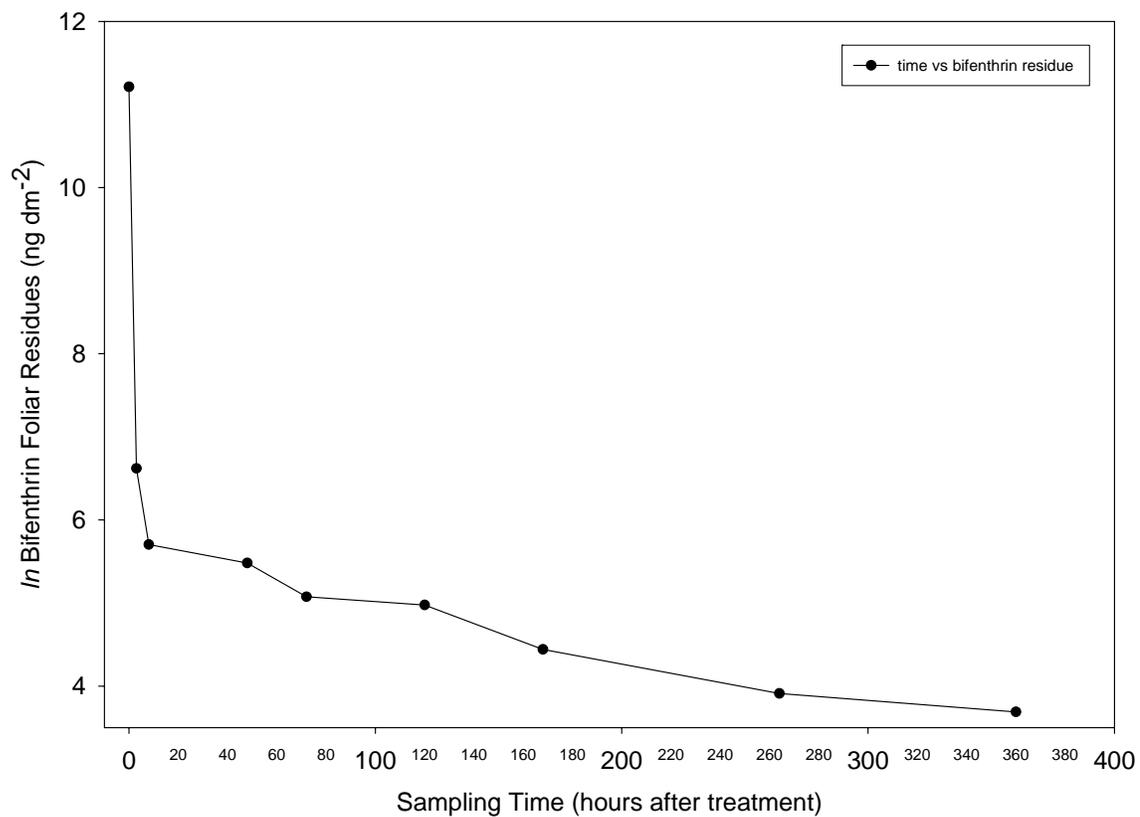


Figure 11. Dissipation of *ln* bifenthrin dislodgeable foliar residues from a tall fescue lawn over a 15-day period following 6 Oct. 2006 application.