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Influence of Atrazine Formulation and Irrigation Incorporation of Off-site Transport in a Centipedegrass Home Lawn

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INFLUENCE OF ATRAZINE FORMULATION AND IRRIGATION INCORPORATION OF OFF-SITE TRANSPORT IN A CENTIPEDEGRASS HOME LAWN

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Atrazine, one of the most widely used herbicides in the United States, is commonly applied to southern lawn grasses to reduce weed encroachment. According to the EPA, atrazine is also one of the most frequently identified herbicidal compounds in surface and ground waters. Given the increased management intensity of home lawns in Louisiana, coupled with urban sprawl and high rainfall has led to a higher potential for movement of atrazine into surface waters during runoff events. Experiments were conducted at the LSU AgCenter Burden Botanic Gardens on centipedegrass (*Eremochloa ophiuroides*) at a 5% slope to evaluate the effect of atrazine formulation and post application management on atrazine movement. Atrazine was applied as a granular or liquid and either incorporated with 1.25 cm of irrigation or not incorporated. Four days post-atrazine application, treatment combinations were subjected to rainfall simulation at 5.5 cm hr^{-1} for 30 min of surface runoff. All herbicides exhibited the highest loss at 4 DAT followed by declines in losses with subsequent surface runoff events. In both experimental runs, granular atrazine resulted in lower total atrazine runoff losses compared to liquid applied atrazine. However, in the second experimental run irrigation reduced liquid applied atrazine 36% from unincorporated liquid applied atrazine. When simazine was compared to atrazine following the same application parameters, simazine resulted in >90% total reduction in herbicide losses compared to atrazine. Based on this research atrazine losses from surface runoff can be mediated through application of granular applications, irrigation when liquid atrazine is applied, or selection of simazine for area prone to frequent surface runoff.

CHAPTER 1: REVIEW OF LITERATURE

Centipedegrass

Centipedegrass (*Eremochloa ophiuroides* [Munro] Hack.), a warm-season turfgrass, was introduced into the United States by Frank Meyer from Southern China in 1916 (Hanna, 1995). Since that time, centipedegrass has been primarily adopted for use in lawns, parks, and low maintenance areas throughout the Southeastern United States from Eastern Virginia to Southern Texas. Growth of centipedegrass further north is limited by its poor cold tolerance compared to cool-season turfgrasses such as Kentucky bluegrass (*Poa pratensis* L.) and tall fescue (*Festuca arundinacea* Schreb.) or warm-season turfgrass species including zoysiagrass (*Zoysia* sps.) and bermudagrass (*Cynodon dactylon* L. Pers.).

Centipedegrass can be characterized as a warm-season, perennial turfgrass that has a coarse leaf texture with rounded leaf tips. Leaves can vary in color from green to yellow-green and are arranged in an alternating pattern from nodes of a stolon (Hanna and Burton, 1978; Hanna and Liu, 2003). Centipedegrass' stoloniferious growth allows prostrate growth albeit at a slower rate of growth compared to many other warm-season turfgrass species such as St. Augustinegrass (*Stenotaphrum secundatum* [Walt] Kuntze.) (Busey and Myers, 1979). Rooting typically occurs in the upper 15 cm of soil.

Centipedegrass can be propagated from seed or vegetatively as sod, sprigs, or plugs. However, sod and seed are the primary methods of establishment. If seed is sown, centipedgras germination occurs with 14 to 21 days under suitable conditions with full ground coverage attained within 18 to 24 weeks depending on cultivar, fertility, and irrigation management. Vegetative establishment from sod occurs within 28 days while establishment from sprigs and plugs, depending on cultivar, spacing, and cultural management, can provide full ground coverage within 14 to 16 weeks.

Centipedegrass is adapted to warm subtropical climates with >40 inches of rainfall yr^{-1} and acid soils (pH 5) (Hanna and Burton, 1978). Centipedegrass can grow on fine or coarse textured soils depending on soil fertility and pH. Centipedegrass has moderate shade tolerance but limited cold and salt tolerances relative to other warm-season turfgrasses. Although, centipedegrass is believed to not have a true dormant state (Duble, 2015), growth rate will decrease as temperatures decreases; with purpling of the leaves evident during cool periods. When centipedegrass is again subjected to suitable temperatures, centipedegrass will resume growth.

Centipiedegrass is often referred to as ‘lazy man’s grass’ or ‘poor man’s grass’ as a result of its slow growth and low maintenance requirements. Management of centipedegrass involves judicious applications of no more than 100 kg N ha^{-1} once established. Excessive N applications have been shown to retard prostrate growth (Duble, 2015). In more alkaline soils or under higher P applications, Fe deficiencies can occur (Hanna and Liu, 2003). Mowing heights should be between 2 and 3 inches with mowing frequency depending on rate of leaf expansion and growth to remove no more than 1/3 of the leaf blades. Supplemental irrigation may be necessary during extended dry periods depending on cultivar grown.

Centipedegrass is susceptible to several diseases and insects such as large patch (*Rhizoctonia solani* [J.G. Kuhn]) and fall armyworms (*Spodoptera frugiperda* [J.E. Smith]). However, chemicals are available for treatment. Unlike St. Augustinegrass, another warm-season turfgrass used for similar applications, centipedegrass has gramicides available for perennial and annual warm-season grass control in addition to herbicides targeting broadleaf control.

Atrazine history, characterization, and use

Atrazine [6-chloro-N-ethyl-N-(1-methylethyl)-1.3.5-triazine-2,4-diamine], a triazine-based herbicide, is one of the most widely applied herbicides at >34 million kg to agricultural and horticultural crops, forests, and right-of-way areas in the United States (EPA, 2006). Atrazine was first created Geigy, Ltd. in 1956 before being registered with the United States Government in 1958 for wide-scale use. The introduction of atrazine to the agricultural sector represents one of the first broad spectrum herbicides developed that allowed farmers to efficiently and effectively control numerous broadleaf weed species (Syngenta, 2015; EPA, 2006).

Atrazine is a synthetic herbicide with no natural sources. Atrazine is produced as a white crystal from the constituents cyanuric acid chloride, ethylamine, isopropylamine, and tetrachloromethane. Atrazine has a specific gravity of 1.187 g cm^3, melting point of 173-175 C, Koc of 100 and 5.6 g ml^{-1} on sandy loam and silty clay, respectively, and has a water solubility of 33 mg L-1 at 25 C. Volatility is not considered a main pathway for loss under most applications.

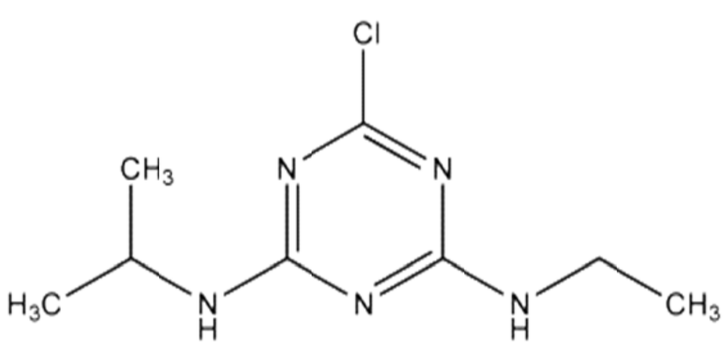

Figure 1. Chemical structure of atrazine.

Atrazine is classified as a triazine herbicide. Atrazine can be characterized as having limited leaf absorption with root absortion as the primary method of plant uptake. Atrazine accumulates at meristems where electron transport processes in photosystem II are disrupted. Areas generally can be replanted within 1 year post atrazine application (Herbicide Handbook, 2014).

Currently, atrazine is registered for application in field or sweet corn (*Zea mays* L.), sorghum (*Sorghum bicolor* L.), wheat (*Triticum sps.* L.), guava (*Psidium guajava* L.), macadamia nuts (*Macadamia integrifolia* Maiden & Betche), pasture species, summer fallow application, forestry or woodland species, conifers, woody ornamental species, Christmas tree production, and turfgrass applications related to sod, sportsfields, and residential lawns. The predominant application of atrazine occurs on corn at approximately 29,801 metric tons per year, or 86% of all atrazine applied. Other crops that are major users of atrazine are sorghum at 10% and sugarcane at 3% (USDA, 1994).

Atrazine is commonly applied in southern warm-season turfgrass lawns because it effectively controls numerous broadleaf weed species at an economical cost. Atrazine is labeled for use in centipedegrass, zoysiagrass, St. Augustinegrass and dormant bermudagrass. Atrazine is also available as part of a granular fertilizer combination known as a 'weed & feed'. Application for winter weed management as preemergent and early postemergent control is recommended in late autumn with reapplication in spring (Herbicide Handbook, 2014).

Simazine history, characterization, and use

In 1956, simazine [3,5 diethyl 1-chloro (or-6-chloro-N,N'-diethyl)] was created and tested for herbicidal activity by Geigy, Ltd (Heri, W. et al., 2008). In fact, the discovery of simazine led to examination of similar triazine compounds for selective pest control. In 1957 and

1958, simazine gained approval for use in the United States in industry and agriculture (Herbicide Handbook, 2014). In the agricultural sector, simazine provided preemergent weed control of broadleaf and annual grassy weeds before being applications declined with the introduction of atrazine.

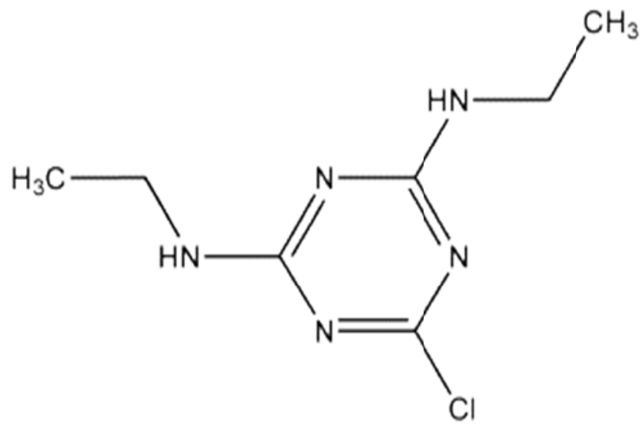

Figure 2. Chemical structure of simazine.

Simazine is a synthetic triazine herbicide with no natural sources. Simazine is a white powder with a specific gravity of 1.302 g cm^3, melting point of 225-227 C, Koc of 138 g ml^{-1}, and a water solubility of 3.5 mg L^{-1} at 25 C declining to 5 mg L^{-1} 20 C (Herbicide Handbook, 2014). Volatility is not considered a main pathway for loss under most applications.

Simazine is almost solely absorbed by a plant's root system with limited leaf uptake. Once absorbed, simazine moves into leaves and meristem tissues where photosystem II is disrupted in susceptible plants (Herbicide Handbook, 2014). Simazine is a soil-applied preemergence as follows: strawberries (*Fragaria sps.* L.), almonds (*Prunus dulcis* [Mill.] D.A. Webb.), nectarines (*Prunus persica* L.), apples (*Malus domestica* Borkh.), avocadoes (*Persea Americana* Mill.), blueberries (*Vaccinium cyanococcus* L.), cranberries (*Vaccinium oxycoccos* L.), established Christmas trees, fiberts, shelterbelts, sour cherries (*Prunus cerasus* L.), walnuts (*Juglans regia* L.), peaches (*Prunus persica* L.), plums (*Prunus* L.), sweet cherries (*Prunus* *avium* (L.) L.), lemons (*Citrus x limon* (L.) Burm.f.), oranges (*Citrus x sinensis* (L.) Osbeck.), grapefruit (*Citrus x paradise* Macfad.), grapes (*Vitis vinifera* L.), and early preplant in corn. Simazine is currently sold under the trade names: Aquazine, Cekusima, Framed, Princep, Gesatop, simtrol, simadex, tatazina.

Simazine is applied in southern warm-season turfgrasses especially to control broadleaf weeds and annual grasses such as annual bluegrass (*Poa annua* L.) in autumn or early winter. Over time weed species such as annual bluegrass have demonstrated increased levels of resistance after numerous years of application (Hutto, K.C. et al., 2004).

Turfgrasses effects on surface runoff

Turfgrasses have been reported within the literature to reduce surface runoff occurrence and severity as well as limit affect offsite transport of fertilizers and chemicals (Burwell et al., 2011; Butler et al., 2006, 2007; Gross et al., 1990, 1991; Krenitsky et al. 1998; Kussow 2008; Linde and Watschke, 1997). Higher ground coverages and density have been correlated to extending the duration until surface runoff is initiated, decreasing runoff volumes, and reducing sediment losses. For example in research conducted by Easton and Petrovic (2008) they indicated higher maintained turfgrass areas reduced runoff volume two times that of low maintenance turfgrass areas.

Other studies have research the effects of cultural practices on surface runoff because turfgrasses that are managed often result in higher turfgrass canopy cover (Turgeon, 2008). In research conducted by Gross et al. (1991) higher density tall fescue reduce erosion from 225 kg ha^{-1} for an established tall fescue to 15 kg ha^{-1} for fallow soil after a 30-min rainfall event. However, the use of fertilizers to accelerate turf density may not significantly increase reduce erosion sufficiently to offset increases in fertilizer losses (Burwell et al., 2011; Butler, 2006 and

2007). Even in dense turfgrasses, the majority of water soluble compounds are lost during the initial rainfall event to produce runoff application (Easton and Petrovic, 2004; Gaudreau et al., 2002; Kelling and Peterson, 1975; Rector et al. 2003a, 2003b). Therefore, factors that can reduce initial losses during the first runoff event would potential have a greater impact on total losses.

As oversight and regulations increase from federal agencies (Rosen and Horgan, 2005; Throssell et al., 2009) as well as increased concerns by local populations further research is needed concerning the transport of fertilizers and pesticides during surface runoff from grassed areas (Haith, 2001; Haith and Rossi, 2003; Hong and Smith, 1997; Kauffman III and Watschke, 2007; Kramer et al., 2009; Lee et al., 2000; Moss et al., 2005; Smith and Bridges, 1996; Steinke et al., 2009; Vincelli, 2004) in order to devise better best management practices to reduce chemical movement

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CHAPTER 2: INFLUENCE OF ATRAZINE FORMULATION AND IRRIGATION INCORPORATION OF OFF-SITE TRANSPORT IN A CENTIPEDEGRASS HOME LAWN

Introduction

The triazine herbicide atrazine [6-chloro-N-ethyl-N-(1-methylethyl)-1.3.5-triazine-2,4-diamine] is commonly applied to control broadleaf weeds and some grassy weed species in centipedegrass, St. Augustinegrass, and dormant bermudagrass in the southern United States (Cox et al. 2003; Rector et al., 2003; Hixson et al., 2009; Caron et al., 2010). However, the Environmental Protection Agency has routinely identified atrazine as a potential pollutant to surface and ground waters (Giroux, 2002). Numerous published research studies have reported triazine herbicide losses in various agricultural commodities (Hixson et al., 2009; Caron et al., 2010; Rector et al., 2003a 2003b; Glenn and Angle 1987; Gaynor et al. 2001; Selim, 2003; Wauchope, 1978; Edwards, 1972; Liu and O'Connell, 2002; Glotfelty et al. 1983) with typical surface runoff losses of 15.9% and 3.5% for atrazine (Wauchope, 1978) and simazine (Edwards, 1972), respectively. The potential risk of triazine herbicides movement into surface and ground waters has led the EPA to enact several restrictions over time including varying application rates and increasing buffer widths in order to prevent water body concentrations occurring above 3 $\mu g\ L^{-1}$ for atrazine and 4 $\mu g\ L^{-1}$ for simazine [3,5 diethyl 1-chloro (or-6-chloro-N,N'-diethyl)] (USEPA, 2006a and 2006b).

Management of turfgrass, one of the largest horticultural crops in the United States (Kramer et al., 2009), could have an increasingly significant impact on potential triazine herbicide losses in urban areas due to continued urban development and increased consumer demand for aesthetically pleasing landscapes that require greater inputs (Haith and Rossi, 2003;

Kaufmann II and Watschke, 2007; Kramer et al., 2009). The majority of research evaluating atrazine losses have been conducted in agricultural commodities. Research concerning movement of chemicals from surface runoff in turfed areas has primarily focused on nutrients, cultural practices, and to a lesser extent pesticides (Haith, 2001; Haith and Rossi, 2003; Hong and Smith, 1997; Kauffman III and Watschke, 2007; Kramer et al., 2009; Lee et al., 2000; Moss et al., 2006; Smith and Bridges, 1996; Steinke et al., 2009; Vincelli, 2004).

In agronomic studies evaluating pesticide losses during surface runoff factors such as formulation, tillage, and irrigation have been shown to effect surface runoff loses. For example, in an orchard Liu and O'Connell (2002) reported increasing irrigation incorporation of 0 to 0.5, 1.25, and 1.75 cm correlated to decreased simazine runoff losses. Wauchope (1987) demonstrated atrazine applied in an emulsion, wettable powder, dispersible liquid, and disperable granule formulation affected surface runoff losses differently with dispersible granule and wettable powder formulations resulting in the highest losses of 9 to 12%. These studies along with several other agronomic studies examining herbicide runoff losses indicate simple management strategies could reduce the potential for atrazine transport in surface runoff in turfgrasses.

To date, effects of atrazine formulation and irrigation management as potential management strategies to curb atrazine losses during surface runoff from centipedegrass have not been fully investigated. Therefore, the objectives of this research were to evaluate the effect atrazine formulation and irrigation incorporation have on atrazine losses during surface runoff from centipedegrass maintained as a home lawn as well as examine the effect herbicide solubility, atrazine versus simazine, has on potential herbicide losses.

Materials and Methods

Centipedegrass Establishment and Maintenance

Experiments were conducted in 2014 at the Louisiana State University Agricultural Center Burden Botanical Gardens in Baton Rouge, La. Trays with dimensions of 6.1 m x 1.8 m x 0.4 m were constructed from steel (2.5 cm) with orifices located in the bottom of the tray to allow drainage. Trays were filled with a silty loam with 18.4% sand, 62.1% silt, and 19.2% clay. Soil tests were collected and analyzed by the Louisiana State University Agricultural Center Soil Testing and Plant Analysis Laboratory prior to each experiment and resulted in soil pH 6.3 and 52 kg P ha^{-1} and 192 kg K ha^{-1}.

Soil was lightly compacted in trays using a hand tamp with an area of 232 cm^2 in 10 cm lifts to reduce voids. Once trays were filled with soil, each tray was divided into eight experimental units measuring 0.76 x 1.83 m using wood inserts to the depth of the tray. Inserts were not only used to prevent lateral surface water movement but also lateral subsurface water movement between experimental units. Trays were set at a 5% slope.

Centipedegrass (*Eremochloa ophiuroides Munro)* sod was planted and allowed to establish for 30 d. During the establishment period an ammonium sulfate fertilizer was applied at 25 kg N ha^{-1} 21 days after installation with no additional fertilizers or pesticides applied. Centipedegrass was irrigated at 10 cm d^{-1} the first 14 days after establishment followed by irrigation applied as needed to allow proper centipedgrass growth. Centipedegrass was maintained at a height of 6.25 cm weekly with clippings returned to the centipedegrass sward.

Rainfall Simulation Setup

The protocols for rainfall simulations adhered to the USDA National P Research protocols (USDA, 2008). The rainfall simulator was fitted with 3 spray nozzles with a spray angle of 104^{O} (Spraying Systems Co. Fulljet ½HH SS 50WSQ) that delivered 5.5 cm hr^{-1} to an entire tray. At the downslope of each tray at the end of each experimental unit, stainless steel was mounted to direct surface runoff water into 40 L plastic containers for collection during simulated rainfall events. Water for all rainfall simulations and irrigation events was from a municipal source and filtered to prevent nozzle malfunctions. The rainfall system was evaluated several times prior to initiating surface runoff experiments to ensure even rainfall application. Simulated rainfall was applied at 4 d post pesticide application and again at 14 and 42 d post pesticide application in the first experimental run and 4, 14, and 28 d post pesticide application in the second experimental run.

Pesticide Application

Atrazine was applied at the manufacturers' labelled rates of 2.24 kg ai ha^{-1} in a granular or liquid formulation 4 d before the initial rainfall simulation event. The liquid atrazine formulation treatments were applied using a CO_2 pressurized backpack sprayer calibrated to deliver 280 L ha^{-1} and equipped with 8002 XR TeeJet®flat-fan nozzles (Spraying Systems Co. Wheaton, IL). Granular atrazine formulation treatments were applied by hand using shaker jars to allow for even distribution across the centipedegrass sward. Half of the atrazine formulation treatments were not incorporated with irrigation while the remaining treatments were incorporated with irrigation at 1.25 cm. The irrigation depth applied did not result in surface runoff prior to the initial rainfall simulation. Untreated experimental units served as controls. In the second run of the experiment, a simazine treatment was added. Simazine was applied at the manufacturer's labelled rate of 2.24 kg ai ha^{-1} following the parameters adhered for liquid atrazine. However, no granular simazine formulation was available and no simazine was incorporated using irrigation.

Measurements pre and post-rainfall simulation

Prior to rainfall simulation events soil moisture ($m^3 m^{-3}$) content was recorded for each experimental unit utilizing a portable TH_2O probe (Dynamax Inc., Houston, Tx). Other measurements included canopy coverage, grass height, and quality ratings were recorded prior to each rainfall simulation event to measure any discrepancies in vegetation between experimental units.

Once surface runoff was initiated, rainfall was allowed for a 30 min period per experimental unit. Experimental units that resulted in surface runoff occurring more quickly were covered with visqueen plastic once 30 min of runoff occurred to allow equal runoff times between experimental units. Water samples were collected 30 min for each experimental run with the addition of sampling times of 7.5, 15, 22.5 and 30 min post runoff initiation 4 DAT during the second experimental run. One liter samples were collected in glass containers and stored at 4 C until pesticide analysis was completed.

Herbicide extraction

Atrazine was extracted and quantified using the Louisiana State University AgCenter W.A. Callegari Water laboratory facilities in Baton Rouge, La. Herbicide analysis in water was performed according EPA method 3510C. Samples of 100 mL had 18 g of sodium chloride dissolved to maintain a 50% salt-saturation. Once the sodium chloride was fully dissolved, 5 mLs of hexane and 1 mL of Surrogate Spike mix was added to the sample. The sample was inserted into the extractor at a speed of 4800 – 5200 rpm for 5 minutes to perform the liquid-

liquid separation. After settlng 5 minutes the hexane solution was collected and the process repeated for two addition times. The hexane sample was concentrated to 0.1 mL under N_2 at 203 mL/min at room temperature (22 C).

Simazine herbicide was extracted and quantified using the Louisiana Department of Agriculture and Forestry Chemistry Department's laboratory facilities in Baton Rouge, La. Herbicide analysis in water was performed according to EPA method 525 for the determination of simazine. Samples were centrifuged with an Algera-6 table-top centrifuge (Beckman Coulter Inc., Brea, Ca) at 3500 rpm for 15 min. Liquid-liquid partitioning was performed using 500 mL of sample with 75 mL methylene chloride. Liquid-liquid partitioning was completed twice and the methylene chloride solution was poured through sodium sulfate to remove any additional water before being placed in a 50°C water bath for concentration. The sample was dissolved in 10 mL hexane for analysis.

<u>Herbicide analysis</u>

Samples were analyzed with a Hewlett-Packard (HP) 6890 GC (Agilent Technologies Inc. Santa Clara, CA) equipped with an autoinjector, split-splitless front inlet, and a single RTX-35SIL MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness). The autoinjector delivered 2.0µL sample injections. The HP 6890 GC was equipped with an Agilent 5975 C mass selective detector (MSD). Column oven temperatures were as follows: initial 120ºC for 2 min, ramp at 30ºC min^{-1} to 340 ºC and held for 3 min for a total run time of 12.33 min. The carrier gas was ultra-high pure helium with an inlet pressure of 17.55 psi, 20.0 psi pulse pressure and initial injector temperature of 250 ºC.

Statistical Analysis

Herbicide treatments were arranged in a complete randomized design with three replications. Data including canopy coverage, density, and quality ratings were analyzed according to the Analysis of Variance (ANOVA; $\alpha=0.05$) following the general linear method in the statistical software SAS (SAS Institute, 2000). Data for total herbicide losses are reported as a mass of applied herbicide per active ingredient. Post-hoc testing was performed on means per date and cumulative means for atrazine and simazine using Fisher's protected least significant difference (LSD; $\alpha = 0.05$). Atrazine and simazine data recorded over time were regressed against time. Data for measurements were pooled when interaction terms had a p-value ≥ 0.20.

Results

Centipedegrass Swards

Centipedegrass subjected to rainfall simulations for each experimental run had similar canopy coverage, height, and visual quality ratings at each rainfall simulation performed (table 1). These measurements were recorded to ensure similar centipedegrass conditions across experimental units per rainfall simulation as well as document changes in centipedegrass across rainfall simulations dates. In general centipedegrass canopy coverage ranged between 92 and 95% with heights of 3.8 to 7 cm across each experimental run. The only differences in centipedegrass occurred at the final rainfall simulation 42 DAT for the first experimental run concerning overall visual quality.

Controls exhibited the lowest rating of 6.7 compared to quality ratings of 7 or 8 for the remaining centipedegrass treated with herbicide. Controls in this experiment were used to confirm no pesticide was present in surface runoff waters from untreated centipedegrass.

Rainfall Simulations

Prior to each rainfall simulation, soil moisture was recorded (table 2). In the first experimental run, differences in soil moisture occurred at the first rainfall simulation 4 DAT. Centipedegrass with treatments of irrigation incorporated atrazine resulted in higher soil moistures of 0.339 and 0.336 compared to corresponding centipedegrass with unincorporated atrazine at soil moistures of 0.248. However, the differences in soil moisture did not result in faster runoff occurring from treatments receiving herbicide incorporation through irrigation compared to unincorporated treatments as noted with the lack of significance among duration needed to initiate surface runoff 4 DAT. No further differences in soil moisture or duration until surface runoff was observed at each subsequent rainfall simulation event among treatments for the first or second experimental runs.

Pesticide losses from surface runoff events

Atrazine losses after 30-min of surface runoff, regardless of formulation and irrigation incorporation, resulted in high initial losses across each experimental run during the first rainfall simulation 4 DAT (figures 1 and 2). Atrazine losses declined from initial losses 4 DAT when subjected to subsequent rainfall simulations at 14, 28, or 42 DAT. For example, in the first experimental run atrazine losses were highest for the liquid formulation of atrazine at 38.8 mg 4 DAT compared to 0.3 and 0.2 mg at 18 and 42 DAT; while in the second experimental run liquid formulation of atrazine not subjected to irrigation incorporation exhibited a similar pattern with losses of 49.6, 3.0, and 0.2 mg at 4, 14, and 28 DAT, respectively.

Table 1. Percent coverage, canpoy height, and quality of centipedegrass prior to rainfall simulations capturing pesticide losses from surface runoff experiment 1 and 2 in 2014.

Experiment 1											
			% Coverage			Height			Quality		
			-----------------%-----------------			-----------------cm----------------					
Pesticide	Formulation	Irrigation	4 DAT**	14 DAT	42 DAT	4 DAT	14 DAT	42 DAT	4 DAT	14 DAT	42 DAT
Control		No	93	92	93	7.0	5.7	5.2	7.5	7.3	6.7c*
Atrazine	Granular	Yes	93	93	95	6.0	6.5	6.2	7.8	7.0	7.3b
Atrazine	Granular	No	93	95	92	6.0	5.0	5.2	7.7	8.0	7.0cb
Atrazine	Liquid	Yes	93	93	93	6.7	5.3	5.8	7.7	7.0	7.0cb
Atrazine	Liquid	No	95	92	93	6.7	5.5	5.5	7.7	7.7	8.0a
			NS	NS	NS	NS	NS	NS	NS	NS	

Experiment 2											
			% Coverage			Height			Quality		
			-----------------%-----------------			-----------------cm----------------					
Pesticide	Formulation	Irrigation	4 DAT	14 DAT	28 DAT	4 DAT	14 DAT	28 DAT	4 DAT	14 DAT	28 DAT
Control		No	95	95	93	6.7	5.8	6.1	8.0	7.0	7.0
Atrazine	Granular	Yes	95	90	90	5.0	5.8	6.0	7.0	6.7	7.3
Atrazine	Granular	No	95	95	93	3.8	4.5	4.8	6.7	7.3	7.0
Atrazine	Liquid	Yes	95	92	92	6.0	6.0	6.7	6.7	7.0	7.7
Atrazine	Liquid	No	92	92	92	5.5	5.3	6.2	6.3	7.0	6.7
Simazine	Liquid	No	93	95	93	6.5	6.3	6.2	6.7	8.0	7.0
			NS	NS	NS	NS	NS	NS	NS	NS	NS

*Means within a column followed by the same letter are not significantly different (P<0.05, LSD); NS - Not Significant.

**Days After Treament.

As a result of higher atrazine losses 4 DAT than subsequent rainfall simulations, atrazine losses at 4 DAT accounted for >82% of total atrazine losses over the experimental periods. The only exception occurred with the granular formulation of atrazine that was not incorporated in the second experimental run that had atrazine losses at 4 DAT account for 56% and 92% after

Table 2. Soil moisture and time until runoff initiation of centipedegrass subjected to rainfall simulations to capture pesticide losses from surface in 2014.

Experiment 1								
			Soil Moisture			Time to Runoff		
			$m^3\ m^{-3}$			----------------min----------------		
Pesticide	Formulation	Irrigation	4 DAT**	14 DAT	42 DAT	4 DAT	14 DAT	42 DAT
Control		No	0.255b*	0.278	0.331	11.0	13.0	10.0
Atrazine	Granular	Yes	0.339a	0.327	0.344	6.3	16.3	8.0
Atrazine	Granular	No	0.248b	0.279	0.243	7.7	7.0	3.3
Atrazine	Liquid	Yes	0.336a	0.314	0.337	8.0	17.0	4.7
Atrazine	Liquid	No	0.298ab	0.296	0.259	7.3	14.0	4.0
				NS	NS	NS	NS	NS
Experiment 2								
			Soil Moisture			Time to Runoff		
			$m^3\ m^{-3}$			----------------min----------------		
Pesticide	Formulation	Irrigation	4 DAT	14 DAT	28 DAT	4 DAT	14 DAT	28 DAT
Control		No	0.223	0.237	0.203	8.0	4.0	4.0
Atrazine	Granular	Yes	0.187	0.246	0.310	14.5	3.7	2.7
Atrazine	Granular	No	0.215	0.217	0.227	16.3	4.0	2.7
Atrazine	Liquid	Yes	0.243	0.286	0.281	17.0	3.7	2.0
Atrazine	Liquid	No	0.205	0.238	0.249	20.0	5.0	3.7
Simazine	Liquid	No	0.216	0.227	0.217	20.0	4.0	3.3
			NS	NS	NS	NS	NS	NS

*Means within a column followed by the same letter are not significantly different (P<0.05, LSD); NS - Not Significant.

**Days After Treament.

the second rainfall simulation 14 DAT. The most consistent factor to affect atrazine losses in each experimental run was formulation. The granular formulation of atrazine resulted in a 67% reduction in atrazine losses from 39.2 to 12.8 mg compared to atrazine applied as a liquid formulation in the first experimental run. A similar pattern was also determined in the second experimental run with losses of atrazine of 33.1, 49.6, 2.8, and 5.2 mg for the liquid formulation of atrazine incorporate and unincorporated and granular atrazine incorporate and unincorporated, respectively. The granular formulation of atrazine regardless of incorporation provided the least amount of transport during surface runoff compared to all liquid atrazine applications. Although incorporation with irrigation of atrazine applied as liquid reduced losses from 49.6 to 33.1 mg during the second experimental run. Reductions in granular atrazine from irrigation incorporation were not evident in either experimental run.

Table 3. Effects of formulation on atrazine losses from surface runoff of centipedegrass at 4, 14 and 42 days after initial treatment in the first experimant in 2014.

Experiment 1				
		4 DAT**	14 DAT	42 DAT
Atrazine	Granular	12.3 b*	0.3	0.2
Atrazine	Liquid	38.8 a	0.3	0.1
			NS	NS

*Means within a column followed by the same letter are not significantly different (P<0.05, LSD); NS - Not Significant.

**Days After Treament.

Table 4. Effects of formulation on atrazine losses with and with out irrigation from surface runoff of centipedegrass at 4, 14 and 28 days after initial treatment in the second experiment in 2014.

Experiment 2					
		Irrigation	4 DAT	14 DAT	28 DAT
Atrazine	Liquid	No	49.6 a	3	0.2
Atrazine	Liquid	Yes	33.1 b	0.4	0.2
Atrazine	Granular	No	5.2 c	3.3	0.7
Atrazine	Granular	Yes	2.8 c	0.4	0.2
				NS	NS

*Means within a column followed by the same letter are not significantly different (P<0.05, LSD); NS - Not Significant.

**Days After Treament.

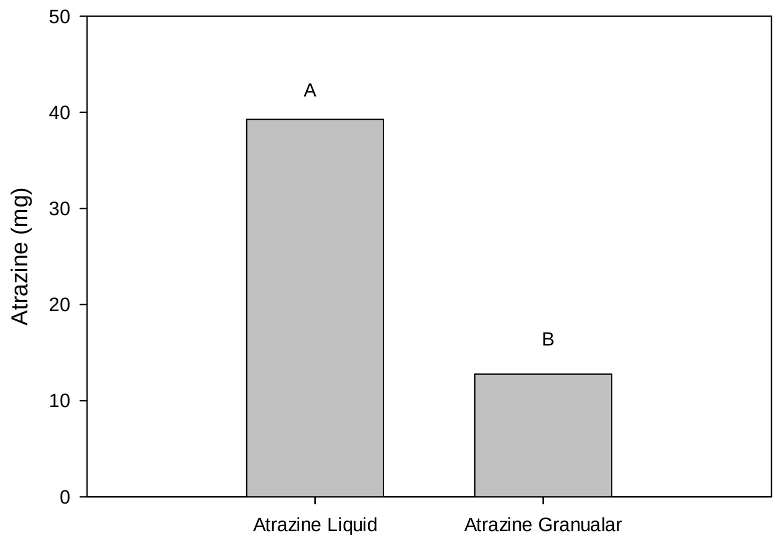

Figure 3. Total surface runoff losses of two formulations of atrazine from centipedegrass during three rainfall simulations 4, 14, and 42 days after treatment in experiment one.

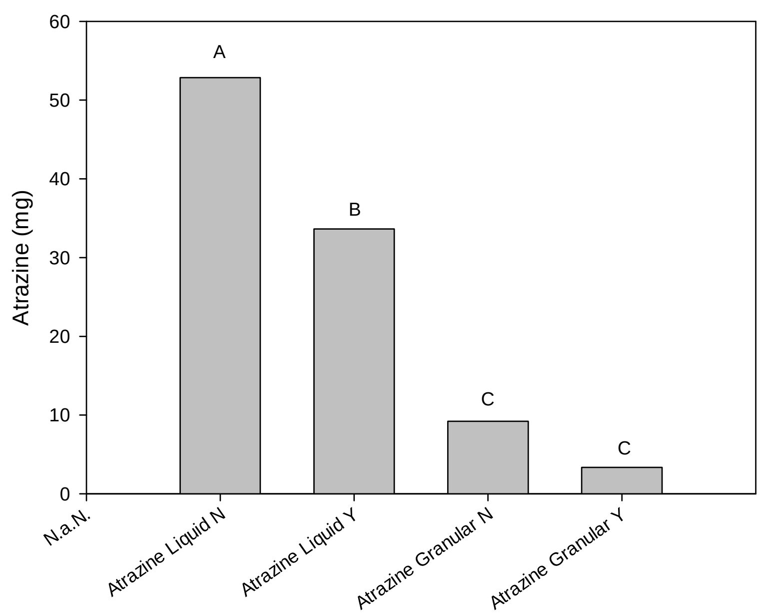

Figure 4. Effect of atrazine formulation and irrigation incorporation on total losses from surface runoff on centipedegrass during three rainfall simulations 4, 14, and 28 days after treatment in experiment two.

Atrazine and Simazine

A comparison of atrazine and simazine applied in liquid formulations following the same application parameters and unincorporated resulted in significantly different losses of 49.6 and 1.4 mg, respectively, at 4 DAT (figure 3). Following a similar pattern of high initial losses followed by a decline in herbicide losses with subsequent rainfall simulations affected both atrazine and simazine total losses over the experimental periods with 52.9 and 1.8 mg, respectively. Analysis of atrazine and simazine losses over the initial 30-min surface runoff event showed a correlation of the highest atrazine losses at the first sampling 7.5 min after surface runoff initiation followed by a linear decline over the remaining 30-min. Simazine losses also declined slightly linearly with differences between initial losses and losses over the 30-min period being less apparent.

Table 5. Comparing liquid formulation of offsite movement of atrazine and simazine during surface runoff.

	4 DAT**	18 DAT	32 DAT
Atrazine	49.62a*	3.05b	0.17b
Simazine	1.37b	0.40b	0.04b

*Means within a column followed by the same letter are not significantly different (P<0.05, LSD)

**Days After Treament.

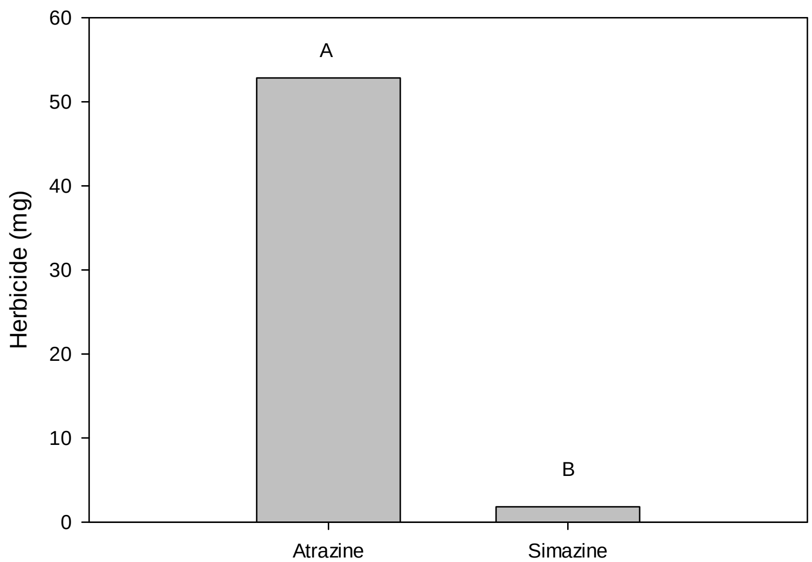

Figure 5. Total surface runoff losses of atrazine and simazine applied as liquid formulations to centipedegrass during three rainfall simulations 4, 14, and 28 days after treatment.

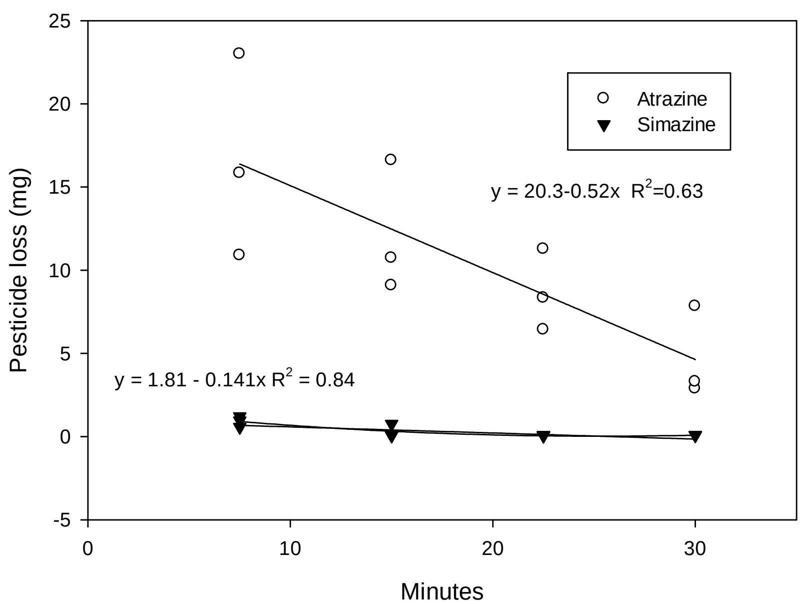

Figure 6. Surface runoff losses of atrazine and simazine applied as liquid formulations to centipedegrass during 30-mins 4 days after treatment.

Discussion

Offsite transport of atrazine via surface runoff can be mediated through formulation selection and irrigation incorporation. Based on this research, application of atrazine at 2.24 kg ai ha^{-1} in a granular formulation reduced surface runoff losses between 67% and 93% for the experimental periods compared to liquid applications of atrazine applied at the same rate. A similar effect of formulation on atrazine losses during surface runoff has been reported by Wauchope (1987). In a study evaluating the effects of liquid versus granular formulation and irrigation on diazinon surface runoff losses in tall fescue [*Schedonorus arundinaceus* (Schreb.) Dumort.] Evans et al. (1998) attributed decreases in granular losses versus liquid application to differences in active ingredient solubility per formulation. Differences in atrazine solubility between formulations also supports past herbicide efficacy studies that have shown greater weed control with liquid versus granular atrazine formulations (Johnson et al, 1989; Mills and Thurman, 1994; Schreiber et al, 1992). Higher initial solubility of liquid atrazine compared to granular formulations is posited to allow deeper root zone penetration for greater root absorption. This mechanism of atrazine solubility per formulation not only affects herbicide efficacy but most likely governed atrazine losses via surface runoff in this study.

In comparison to the effects of formulation on atrazine losses during surface runoff, incorporation of atrazine through irrigation provided less consistent effects particularly regarding liquid atrazine formulation versus granular atrazine. In each experiment granular atrazine losses were not affected by irrigation incorporation. Only in the second experiment did irrigation incorporation at 1.25 cm reduce atrazine losses 34% when comparing liquid formulation treatments. In a study evaluating another trizaine herbicide, Liu and O'Connell (2002) reported irrigation incorporation reduce simazine surface runoff losses as irrigation depth increased from

0 to 0.5, 1.25, and 1.75 cm in an orchard. They suggested irrigation depth allowed for greater herbicide soil interaction; however penetration of the herbicide into the soil could also move the herbicide beyond the interaction zone of flowing surface waters necessary for offsite transport. In addition, Liu and O'Connell (2002) research suggests increasing the irrigation depth beyond 1.25 cm applied in these experiments may provide more consistent results in terms of reducing losses of all atrazine formulations. For example, increasing the irrigation depth for granular applied atrazine would allow the herbicide to be solubilized for deeper soil penetration and thus reduce losses. Although based on the data from the second experiment irrigation had no significant effect ($p \leq 0.22$) even though granular applied atrazine losses were reduced 63% compared to unincorporated granular applied atrazine. Further study of irrigation depth in turfgrass is warranted to more fully describe the relationship of irrigation on atrazine formulation and losses via surface runoff.

Overall, losses of atrazine from surface runoff for all formulation and irrigation treatment combinations occurred during the first rainfall simulation event 4 DAT at >82% of total atrazine lost during the experimental period. The only exception occurred for centipedegrass treated with unincorporated granular atrazine that resulted in losses of 56% of total atrazine losses. High initial losses with the first runoff event post application followed by declining losses with subsequent runoff events have been extensively reported for various water soluble fertilizers and herbicides in the literature (Rector et al. 2003a). Factors such as the duration until the first surface runoff event, rainfall intensity, application rate, rate of pesticide degradation, and vegetative, soil, and environmental parameters have been shown to alter initial surface runoff losses. However based on the methods employed in this research, reducing early atrazine losses is critical to reducing total atrazine losses. Therefore, enacting strategies that apply granular application and irrigation incorporation provided the greatest reduction in atrazine losses 4 DAT that translated into lower total atrazine losses over the period of observation. Focusing research on the initial surface runoff event post application would not only reduce the period of observation needed for study but provide a more economical approach in evaluating different factors.

A third strategy for reducing atrazine losses was also evaluated. Rather than relying on end users implementing changes to formulation selection or irrigation incorporation, another triazine herbicide, simazine, was selected for comparison. Simazine is commonly applied to control weed species controlled by atrazine (cite), but is characterized as having a water solubility of 3.5 mg L^{-1} and Koc of 130 ml g^{-1} compared to 33 mg L^{-1} and 100 ml g^{-1}, respectively for atrazine. The difference in solubility between atrazine and simazine resulted in a >90% decline in pesticide lost when applied under the same application parameters. Each herbicide exhibited higher losses 4 DAT followed by steep declines as a component of total losses with subsequent surface runoff events. Glenn and Angle (1987) reported similar differences between atrazine and simazine with decreased simazine surface runoff losses compared to atrazine under conventional and no-till fields for agronomic annual crops. Although each herbicide has relatively low Koc values and total solid losses were minimized with high vegetative groundcovers, the 9x reduction in simazine water solubility compared to atrazine greatly affected simazine losses during surface runoff.

A more interesting pattern relating to atrazine and simazine losses in this research occurred during the 30-min surface runoff event 4 DAT. The high initial losses of atrazine at 7.5 minutes post surface runoff initiation indicate atrazine losses for rainfall events less than 30-min would still be significant compared to simazine that illustrated a more static loss pattern over the

30-min time period. This suggests simazine losses are more influenced by surface runoff duration compared to atrazine indicating curbing total runoff volume would have an increased effect on decreasing simazine losses. The effects of formulation and irrigation were not examined in this study due to a limited number of experimental units as well as the lack of available commercial granular formulation of simazine. Further studies regarding simazine movement relating to irrigation incorporation are needed to characterize the relationship to potential reductions of simazine losses via surface runoff.

Based on the findings of this study, strategies can be implemented by consumers and turf managers to decrease the movement of atrazine into surface waters. For example, turf areas that do not have access to irrigation, application of granular formulations resulted in less atrazine offsite movement compared to a liquid formulation. For turf areas with irrigation and not subject to frequent surface runoff, atrazine applied as a liquid and incorporated through irrigation can reduce potential atrazine losses up to 34%. For sloped turf areas subject to frequent surface runoff and located near surface waters, drainage pipes, or canals, application of simazine provides a less water soluble herbicide that can reduce offsite herbicide movement compared to atrazine.

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