INVESTIGATION OF INSECTICIDE LEACHING FROM POTTED NURSERY STOCK AND AQUATIC HEALTH BENEFITS OF BIORETENTION CELLS RECEIVING NURSERY RUNOFF

By

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Abstract: Tree nurseries and greenhouses within the USDA red imported fire ant (RIFA) quarantine zone are required to incorporate insecticides into their potting media to prevent artificial spread of RIFA. Bifenthrin and fipronil are two common insecticides that are incorporated into potting media. During irrigation and stormwater events, there is potential for insecticides to leach from nursery pots, resulting in contamination of nearby surface waters. In this study, occurrences of insecticides in simulated nursery runoff were compared for two irrigation strategies and two types of containers in single pot leaching and field runoff simulations. In addition, toxicity of pot leachate to the aquatic invertebrate, Hyallela azteca, was measured, and removal efficiencies of insecticides from bioretention cell media were evaluated. Overhead irrigation resulted in significantly higher concentrations than drip irrigation, and Root Maker® pots allowed more leaching as compared to standard slick-wall pots. However, in all tests, the average concentration of bifenthrin during 15 days of leaching in both pot and field simulations was greater than 200 ng/L- more than 100-fold greater than the LC₅₀ for *H. azteca*. Toxicity studies confirmed this level of toxicity. Higher amounts of compost, 20% and 40%, in bioretention cell media resulted in greater percent reduction of both bifenthrin and fipronil. This study determined that management techniques may be able to limit the amount of insecticide that leaches from pots and runs off to receiving water bodies. Specifically, selection of appropriate pot types, irrigation strategies, or filtering runoff through bioretention cells may reduce contamination loads. Thus, further best management strategies such as use of bioretention cells are needed in nursery and greenhouse facilities to prevent surface water runoff from transporting toxic insecticides to nearby water bodies.

Keywords: Bifenthrin, Fipronil, Tree nursery, Runoff, Bioretention cell, Hyallela.

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CHAPTER I

PROJECT INTRODUCTION

Background

Tree nurseries are required by the USDA to incorporate insecticides into their pots to prevent the shipping and transport of red imported fire ants. Consequently, the approved insecticides have shown to leach from the pots, and can have negative consequences for nearby waterbodies that receive runoff from irrigation and stormwater. In 2010, an Oklahoma tree nursery consulted with OSU's stormwater extension specialist, Dr. Jason Vogel, to develop a solution for reducing insecticide loads running off into nearby surface waters. Because of the advantage that bioretention cells can be retrofitted into an existing production, the Oklahoma nursery installed them at nursery runoff outlets to filter their irrigation and stormwater runoff to help reduce insecticides from reaching the adjacent stream. Shortly following installation, monitoring by the Oklahoma Department of Agriculture, Food and Forestry showed non-detects of bifenthrin in the nearby stream (unpublished data, Oklahoma Department of Agriculture, Food and Forestry, 2011). Following feedback and interest from nurseries, state agencies, and Oklahoma State research extension, ideas were suggested for future work on this project through research and monitoring of bioretention cells as an

insecticide removal tool. As a result, a proposal was submitted and funded for research on using these systems as a part of a best management practice and integrated pest management technique.

Project Design

A funded, 2-year study from the Oklahoma Department of Agriculture's Integrated Pest Management (IPM) program was awarded to OSU's Biosystems and Ag Engineering program to investigate insecticide fate leaving nursery pots and removal efficiency and aquatic benefits of bioretention cells receiving nursery runoff. This project lies under the National Pesticide Program Stewardship program, and pertains to water quality issues in agriculture.

The overall objective of this project was to research management strategies to reduce aquatic health risks associated with insecticide use, especially in potted tree nurseries. The specific goals of the project included:

- Investigation of pot management techniques and leaching of insecticides from potted nursery stock.
- 2. Evaluating the effectiveness and feasibility of using bioretention cells at nurseries as an IPM strategy for insecticide reduction.
- 3. Relaying information to the public and nursery industry to help improve aquatic health by implementing best management practices for insecticide reduction.

The tasks of the project to meet these goals and objective included:

- 1. Investigation of various management options on pesticide leaching and transport in runoff using column studies and irrigation simulations.
- Investigation of removal efficiency of insecticides from storm runoff by a laboratory investigation to compare the effectiveness of various typical and "designer pesticide-targeted" media on insecticide removal by bioretention cells.
- 3. Measurement of toxicity of simulated bioretention cell influent and effluent to *Hyalella azteca*.

Organization of Thesis

The thesis is organized into four chapters in regard to a journal article format. All included information preceding and following the journal article provides a framework for the project. Below are descriptions for chapters II-IV and appendices.

Chapter II: The objective of the background and literature review was to identify and introduce two common insecticides that are used in the nursery and greenhouse industry.

Chapter III: This chapter contains a publication currently under review in the journal of *Environmental Science and Pollution Research* titled "Investigation of Insecticide Leaching from Potted Nursery Stock and Aquatic Health Benefits of Bioretention Cells Receiving Nursery Runoff". Authors included in this publication are G. Graves, J. Vogel, J. Belden, E. Rebek and A. Simpson.

Chapter IV: Lessons learned and suggestions for future work.

Appendices: Appendix (A-E) includes background calculations and data for all experiments performed in this study. Appendix F includes line drawings for each experiment setup.

CHAPTER II

BACKGROUND INFORMATION

The spread of red imported fire ants (RIFA), *Solenopsis invicta*, in the United States has increased rapidly due to transport and shipment of potted nursery stock (Lockley and Collins 1990). Historically, chlorinated insecticides such as DDT and chlordane that were used to control RIFA were banned in the 1970's in the U.S., and organophosphate insecticides were the replacement for agricultural pest control. With recent changes in regulations and agreements with the Environmental Protection Agency due to environmental concern in the 1980's and 1990's, newer generations of insecticides such as bifenthrin and fipronil are now used for RIFA control in nurseries (Calcott 2003). This chapter provides information regarding the environmental fate and mode of action for bifenthrin and fipronil.

Bifenthrin

Bifenthrin {(2-methyl-3-phenylphenyl) methyl (1*S*, 3S)-3-[(*Z*)-2-chloro-3,3,3trifluoroprop-1-enyl] - 2,2-dimethylcyclopropane-1-carboxylate} is a third-generation synthetic pyrethroid insecticide developed and produced by the FMC Corp. (Figure 1). Common trade names in industry include Talstar®, Brigade®, and Ortho® Home Defense Max[™]. Bifenthrin is one of the pyrethroids that are currently sold to Certified Pesticide Applicators for uses such as RIFA control (Fecko 1999). Bifenthrin is considered a restricted use pesticide because of its high toxicity to aquatic species. Bifenthrin is in the class of pyrethroids and is often characterized by its ability to immobilize insect communities by causing nerve system damage (Miller 1985). The insecticide interferes with nerve cell endings and can effectively decrease neurotransmission causing paralysis (Salgado et al. 1983). Aquatic organisms are affected by bifenthrin because it can hinder ATPase enzyme production. ATPase enzyme production breaks down when pyrethroids are introduced and the organism is unable to maintain the ionic gradient between the cell walls leading to the aquatic organism's death (Siegfried 1993).

Environmental Fate of Bifenthrin

Bifenthrin is stable in aqueous and photolysis and only has one degradation product; 4'-hydroxy bifenthrin. Bifenthrin is known to strongly adsorb to soils and sediments because of its high K_{oc} . In almost all cases, bifenthrin exhibits a half-life greater than 100 days (Table 2-1). Half-lives in soil often depend on soil type, and has shown a longer half-life in soils with higher percentages of organic matter. In water, bifenthrin has a low solubility due to its high octanol-water coefficient and is considered stable. The aqueous photolysis half-life was shown to be greater than 250 days (Fecko, 1999).

Physical Properties									
Molecular weight	422.9								
Water solubility (at 25°C)	0.1mg/L								
Vapor pressure (at 25°C) mm/Hg	1.81x10 ⁻⁷								
Henry's constant (pH 7, 25°C)	7.20x10 ⁻³ atm m ³ /mol								
Hydrolysis half-life (in natural water, at pH 6.7 and 25°C)	Stable								
Octanol-water coefficient (Kow)	1.0×10^{6}								
Anaerobic half-life	97-156 days								
Aerobic half-life	65-125 days								
Field dissipation half-life	122 to 345 days								
Specific gravity (at 25°C)	1.212 g/ml								
Bio-concentration factor (whole body, bluegill sunfish)	6000x								
Soil adsorption coefficient (Koc)	$1.31 - 3.02 \times 10^5$								
Photolysis	276-416 days								

Table 2-1. Physical properties of bifenthrin. Directly from (Fecko 1999)

Fipronil

Fipronil {5-amino-1-[2, 6-dichloro-4-(trifluromethyl) phenyl]-4-

[(trifluromethyl)sulfinyl]-1H-pyrazole} is a broad-spectrum, phenylpyrazole insecticide that is manufactured by the BASF chemical company. Originally, fipronil was discovered and developed by Rhône-Poulenc Agro in 1987, and placed under the market in 1993. Common trade names for fipronil in the nursery and agriculture industry include Termidor®, Taurus®, Chipco®, and Quali-Pro®. Fipronil is also used in many other applications such as flea and tick, termite, mole cricket and corn pest control. Fipronil targets the GABA receptor of insects and blocks the chloride channels of neurons (Connelly 2001). Demonstrated effects include over-excitation of the central nervous system resulting in convulsions and paralysis of the organism (Gunasekara and Troung 2007).

Environmental Fate of Fipronil

Fipronil dissipation includes four main degradation products: fipronil-sulfide (reduction), fipronil-desulfinyl (oxidation), fipronil-sulfone (biotic, oxidation), and fipronil-amide (biotic, hydrolosis). Fipronil's half-life is highly dependent on soil type or environment. Studies have shown fipronil has moderate mobility within soil with a K_{oc} range of 427-1248 (mean of 825) and moderate water solubility (Rhone-Poulenc Ag Company; Ying and Kookana 2001) (Table 2). Fipronil's degredates are shown to have soil sorption coefficients greater than two to three times of fipronil and low water solubility (Bobe et al 1998). Fipronil is moderately water solubility with a range of 1.9-2.4 mg/L depending on pH, and degrades quickly in water when exposed to UV light with an expected half-life of 6-8 hours (Gunasekara and Troung 2007) (Table 2-2).

Table 2-2. Physical and chemical properties of fipronil. Directly from (Gunasekara and
Troung 2007).

Table 1. Physical-chemical propert	ies of fipronil. All parameters are	at 25°C unless specified.
Chemical Abstract Service registry	number (CAS #) ¹	120068-37-3
Molecular weight (g/mol) ¹	473.2	
	Water (mg/L; $pH = 5$)	1.90
Solubility 1	Water (mg/L; $pH = 9$)	2.40
	Hexane (mg/L)	28.0
	Toluene (mg/L)	3000
Melting point (°C) ¹		200-201
Density (g/mL 20°C) ¹		1.48-1.63
Vapor pressure (mPa; calculated) ⁶		3.7×10^{-4}
Henry's constant (m3-atm/mol; exp	erimental) ²	6.60 x 10 ⁻⁶
Henry's constant (m3-atm/mol; cal	culated) ⁶	$8.50 \ge 10^{-10}$
Octanol-water partition coefficient	$(\text{Log } K_{\text{ow}})^6$	3.50
Organic carbon normalized partition	825	
Aqueous photolysis (days; pH = 5)	0.33	
	pH = 5.5	>100
	pH = 7.0	>100
Hydrolysis half-life (days) ⁴	pH = 9.0	32.08
	pH = 10	4.75
	pH = 11	0.45 (11 hours)
	pH = 12	0.1 (2.4 hours)
Aerobic soil half-life (days) 5		188
Anaerobic soil half-life (days) ²	Dry flowable formulation	19.3-22.2
	Granular formation	18.3
Anaerobic water half-life (days) 1	Dry flowable formulation	0.92-2.83
	Granular formation	5.20

CHAPTER III

INVESTIGATION OF INSECTICIDE LEACHING FROM POTTED NURSERY STOCK AND AQUATIC HEALTH BENEFITS OF BIORETENTION CELLS RECEIVING NURSERY RUNOFF

Introduction

Pesticide use has become a great concern because it poses a significant threat as non-point source pollution. Pyrethroids and other insecticides are used often in agricultural and nursery industries where there is potential for runoff into nearby water sources (Gan 2006; Mangiafico et al. 2009). For example, due to artificial distribution and rapid spread of red imported fire ants (RIFA), *Solenopsis invicta*, the United States Department of Agriculture's Animal and Plant Health Inspection Service (APHIS) created regulations to incorporate an approved insecticide into insect management practices for nurseries under quarantine (Lockley and Collins 1990). Bifenthrin and fipronil are two commonly used insecticides in nurseries for control of RIFA and typically are incorporated into potting media (USDA 2007). With heavy irrigation and storm events on largely impervious surfaces at nursery sites, there is high potential for leaching and runoff of insecticides from planter pots (Kabashima et al. 2003).

Research on sources and impacts of these insecticides are well documented (Budd et al. 2007, Bennett et al. 2005, Gan 2005), but there is limited information on their environmental fate in nursery containers and best management practices for controlling runoff. Recent studies have shown that pyrethroids and fipronil are highly toxic to aquatic invertebrates (Amweg 2006; Gan 2012; Weston 2005; Yang et al. 2006). Many nursery operations employ best management practices such as retention basins, flood control channels, and natural channels to control and manage runoff, but erosion and overflow of these nursery landscapes lead to sources of runoff (Lao et al. 2008). Therefore, it is critical to identify management strategies that reduce damage from insecticides to aquatic ecosystems.

Bennett et al. (2005) and Budd et al. (2009) showed that vegetated waterways and constructed wetlands greatly reduce the amount of insecticides leaving nursery and agriculture sites. Conversely, to the authors' knowledge no research has been completed on the mitigation of nursery runoff through bioretention cells. Bioretention cells are used typically as stormwater management devices, and have shown to be an effective physical and biological filter for removing suspended solids, nutrients, and pathogens (Hsieh and Davis 2005). Bifenthrin ($K_{oc}=1.3 \times 10^5$) and fipronil metabolites ($K_{oc}=1300-1600$) attach to suspended sediments and organic matter (Gan 2005; Lin et al. 2009; Yang et al. 2006). Fipronil, conversely, has a lower sorption potential ($K_{oc}=825$) and higher water solubility, but still has shown to have limited mobility in soil and sediment (Ying and Kookana 2006). Hence, since bioretention cells are comprised of high percentages of organic matter, they may provide a new best management strategy for removal of insecticides from nursery and agricultural effluent.

The objectives of this study were to evaluate the fate of bifenthrin and fipronil in a controlled nursery application, compare and contrast irrigation strategies and production techniques in nurseries, determine aquatic health impacts of nursery runoff through toxicity tests, and investigate the insecticide removal efficiency of bioretention media receiving runoff. Specifically, we performed column media leaching tests, pot leaching simulations, field runoff simulations, leachate toxicity tests on *Hyallela azteza*, and bioretention cell media column tests to meet these objectives.

Methods and Materials

Method design includes the setups for the four main objectives: potting media column tests, pot leaching simulations, nursery runoff simulations, acute toxicity tests, and bioretention cell media studies. In addition, this section contains potting media preparation techniques, sample collection procedures, and sample and data analysis for all studies. Drawings for all experimental setups can be found in Appendix F.

Potting Media Preparation

Potting media were pre-formulated and uniformly mixed on site at an Oklahoma tree nursery and donated for this project in 11.4-L Root Maker® pots (Root Maker Products Company, Huntsville, AL) and standard slick-wall pots. Media consisted of 90% pine bark chips and 10% peat by volume. Dolomitic limestone was incorporated at 3.6 kg/m³ into the media. Commercial grade Talstar® G granules (FMC Corp., Philadelphia, PA) (0.2% bifenthrin by weight) were incorporated into the media with a commercial mixer at a rate of 15 ppm at the Oklahoma nursery facility. Over 'n Out® fipronil granules (Garden Tech, Palatine, IL) (0.0143% fipronil by weight) were

uniformly incorporated into the potting media by hand mixing at a rate of 1 ppm. Incorporation rates of bifenthrin and fipronil were based on the dry bulk density of the media (0.26 g/cm³) and were calculated using the method described in the Imported Fire Ant (IFA) Manual (USDA 2007). Because only one insecticide is typically incorporated in nursery pots, 1 ppm of fipronil was incorporated into the media, which is lower than the recommended rate minimum of 10 ppm as stated in the IFA manual (USDA 2007). The lower rate allowed measurement of fipronil leaching potential, yet did not influence toxicity measurements of bifenthrin.

Potting Media Column Tests

Column studies were performed on the media for leachability of insecticides using a 30.5-cm long, 7.6-cm diameter, stainless steel pipe capped with a size 8 wire screen and a 12.7-cm diameter stainless steel funnel located at the bottom for catchment. The column was lightly packed with 20.3 cm of insecticide-inoculated media. A 2.5-cm constant head of water was applied to the column to allow gravimetric flow and ensure complete contact of water to media throughout the column. A 1-L amber bottle was placed under the setup to collect the leachate. This procedure was replicated with three columns and 100 pore volumes of water were added. Leachate samples were collected at 1, 2, 3, 5, 10, 30, and 100 pore volumes. One pore volume was determined as 600 mL based on the porosity (66%) of the pine bark potting media.

Pot Leaching Simulations

Pesticide concentrations for single pot types and irrigation strategies were measured and compared for degree of insecticide leaching from the pots over a 15-day period. We evaluated Root Maker® pots and conventional slick-wall pots with two different irrigation regimes, overhead and drip irrigation. The overhead irrigation system consisted of a Gilmour® 7-pattern spray nozzle (Gilmour, Peoria, IL) set on the shower spray setting and attached to a ring stand at a height of 1 m. A Raindrip® micro-spray irrigation kit (Rainbird Corporation, Azusa, CA) was used for drip irrigation. The overhead irrigation rate was 265 L/h and the drip irrigation rate was 22.7 L/h. The average pH of irrigation water was 7.9 with a hardness of 200 mg/L. Pots were placed in stainless steel 0.95-L bowls with a pre-drilled 6.35 mm hole, and 24.6-L glass carboys were positioned beneath them for leachate catchment. We collected the first two pore volumes of leachate from the pots (20.8 L). Two pore volumes were calculated from the porosity (66%) of the media in an 11.4-L pot and were determined to be 15.1 L. All pots were irrigated daily, leachate was collected on days 1, 2, 3, 5, 10, and 15, and three replications were performed for each pot and irrigation type.

Nursery Runoff Simulations

Typically, nurseries store above-ground pots directly on top of landscape cloth with underlying, compacted soil. To simulate and evaluate runoff in a nursery setting, three replications of small-scale runoff simulations were performed, and irrigation and pot types were compared. For this study, plastic bins measuring 91 cm x 61 cm x 15 cm set at a 5% slope were filled with Renfrow clay soil that was tightly compacted and covered with landscape fabric. The bins had a stainless steel tray measuring 61 cm x 15 cm x 9 cm attached at the end with a 6.35 mm hole drilled in the bottom for drainage into a glass carboy. Each bin was arranged with four pots of the same type in an offset row. The overhead irrigation system was comprised of a rainfall pressure nozzle set at a height

of 2 m, and the drip irrigation was a Raindrip® micro-spray irrigation system. The overhead irrigation rate applied to each of the four pots was 56.8 L/h and the drip irrigation rate for each pot was 7.6 L/h. A first-flush of 18.9 L of runoff water was collected for each pot and irrigation type bin.

Sample Collection

All samples for the pot leaching and field simulations were collected in 24.6-L glass carboys. Subsamples were split from the collected leachate for insecticide and water-quality analysis. To ensure a representative sample was analyzed, all carboys were lightly swirled and shaken before splitting samples. Collected samples were split from each carboy sample into 1-L amber glass bottles for analysis, and water-quality samples were split from carboy samples into 300-mL high-grade plastic bottles. Samples were stored in a refrigerator at 4° C for no more than 72 hours.

Acute Toxicity Tests

To determine the toxicity of leachate from two pot types (Root Maker® and standard), we performed static acute survival tests on the benthic amphipod, *Hyalella azteca*, following US Environmental Protection Agency methods (USEPA 2000). Amphipods were cultured within the laboratory according to standardized protocols (USEPA 2000). Organisms used in the tests were selected from a mixed-age culture using two sieves. A #40 sieve was used to filter for appropriately sized organisms, while a #60 sieve retained the desired amphipods. All sieved amphipods were housed separately for 4 days prior to use and fed 24 hours before each test.

For each pot-leachate sample tested, a dilution curve (each step listed) was made using dechlorinated and charcoal-filtered tap water and stainless-steel measuring spoons resulting in final volumes of 340-600 mL contained in 800-mL stainless steel containers. Each experimental unit (stainless steel container) contained ten amphipods and at each dilution there were three replicates. Stainless steel containers and measurement devices were used to reduce the loss of bifenthrin to container surfaces. Each test contained two controls: dechlorinated water and straight leachate acquired from untreated pots. Temperature remained at 23 °C (\pm 1 °C) with a light cycle 16:8 hours (light:dark). Upon completion of the test, organisms that could not actively evade a probe were considered dead.

In addition to leachate tests, we conducted toxicity tests with bifenthrin and fipronil to establish expected toxicity based on concentration in laboratory water. Each test was performed using the same organisms, conditions, and experimental units as described for leachate studies. Concentrations tested for bifenthrin ranged from 0.75-24 ng/L, while concentrations for fipronil ranged from 75-1200 ng/L. Ranges were based on established LC_{50} values for similar amphipods.

Bioretention Media Column Studies

Four different homogenized mixtures of bioretention media were evaluated for removal efficiency of insecticides in column studies. The mixtures included the following ratios of sieved sand to peat compost by volume: 100/0, 90/10, 80/20, and 60/40. A 25.4cm long, 7.6-cm diameter, stainless steel pipe was capped with a size 24 wire screen and a 12.7-cm diameter stainless steel funnel located at the bottom for catchment. Each of the

mixtures was added to a height of 15.2 cm in the column. Three replications of pot leaching runs were performed to obtain 60 pore volumes of leachate for each of the column tests. Pore volumes were determined by the average porosities of the media: 35% for 100/0, 36% for 90/10, 37% for 80/20, and 42% for 60/40. From these calculations, one average pore volume was calculated as 263 mL for sample collection. A peristaltic pump was used to deliver a 2.54-cm constant head of leachate water to the top of the column media. To account for low flow rates through the bioretention cell media, we constructed a constant head overflow by drilling a hole at 15.2-cm on the side of the column and using 0.64-cm plastic tubing to divert the influent back into the carboy. Samples of 525 mL (two pore volumes) were collected for pore volumes 1-2, 3-4, 10-11, 29-30, and 59-60 with 1-L amber glass bottles, and an additional 500 mL influent sample was collected from the peristaltic pump.

Sample Analysis

All solvents were purchased from Sigma Aldrich (St. Louis, MO, USA) and were reagent grade. Analytical standards for bifenthrin and fipronil were of high purity (>98%), and were purchased from AccuStandard (New Haven, CT, USA). Following collection, 20 g of NaCl was added to all water samples, and samples were extracted using Agilent® Technologies 1000 mg C18 solid phase extraction cartridges. Each amber sample bottle was rinsed and shaken vigorously with 20-30 mL of ethyl acetate to remove residual insecticides from the sides of the glassware. The C18 cartridge was eluted with 9 mL of ethyl acetate and added to the solvent rinse, and 3-4 g of anhydrous sodium sulfate was added to the vial. Final extracts were evaporated to 1 mL with nitrogen and 40⁰ C heat and analyzed using an Agilent 6850 Gas Chromatograph coupled with a 5975C

Mass Spectrometer (Agilent, Palo Alto, CA USA) using electron ionization and selective ion monitoring (3- ion SIM) (bifenthrin: 181, 165, 166 and fipronil: 367, 369, and 213). Calibration standards for bifenthrin and fipronil were prepared at 30, 100, 300, and 1000 μ g/L. Internal calibration was performed using Chrysene D12.

We conducted full quality control including use of a surrogate spike in all samples, conducting method blanks, laboratory spikes, and sample duplicates at a rate of 5% of samples. Mean recoveries in blank spikes were 96% (SD=11) for bifenthrin and 103% (SD=6) for fipronil. Sample duplicate means were within ±15% of original samples. The mean recovery of dibutyl chlorendate surrogate spike was 84% for all samples (SD=13).

Water-quality samples were taken to evaluate and compare additional parameters that may influence leachability of insecticides. Turbidity readings were taken using a Hach® 2100Q (Hach Company, Loveland, CO) handheld turbidity meter, and pH and specific conductivity were recorded using a Vernier® Lab Quest multi-probe (Vernier Company, Beaverton, OR). Quality control for turbidity was ensured by replicating each reading 5 times, and pH and specific conductivity readings were duplicated at a rate of 5%.

Data Analysis

Minitab® 16 (Minitab Inc., State College, PA) software was used to perform a two-factor ANOVA with a general linear model to compare pot types and irrigation strategies for differences among treatment groups (α =0.05). If differences existed, posthoc tests such as Tukey's multiple comparisons were used to assess variances. In

addition, a regression analysis was performed on column media tests to identify if trends existed between turbidity and insecticide concentrations. Toxicity to pot leachate was quantified using the median lethal concentration (LC_{50}). We calculated LC_{50} values for each test using Probit Analysis (Society of Environmental Toxicology and Chemistry: *Hazard Assessment Tools v1.0*). For leachate samples, the LC_{50} , reported as a dilution, was multiplied by measured sample concentration to obtain the leachate LC_{50} .

Results and Discussion

Column Leaching

Both bifenthrin and fipronil exhibited a reduction in concentration over 100 pore volumes. A log-log regression ($R^2=0.99$, $R^2=1$) of mean bifenthrin levels and fipronil concentrations ($R^2=0.62$) were shown over time throughout the column runs (Figure 3-1). Turbidity (Nephelometric Turbidity Units (NTU)) showed a strong correlation with column leachate bifenthrin concentrations ($R^2=0.85$, p=0.001) (Figure 3-2). Fipronil was variable throughout the entire sampling period. The highest concentrations of fipronil were pore volumes 1-3, and the levels declined gradually with the lowest concentration at 100 pore volumes (Figure 3-1). A weak correlation was shown ($R^2=.28$, p=0.29) between leachate fipronil concentrations and turbidity (Figure 3-2).

Bifenthrin and fipronil showed a higher release at the beginning of the runs due to leaching of the most available fractions of pesticide and potentially release of pesticides adsorbed to free particulate that was pushed from the column with the initial flush of water. Since both bifenthrin and fipronil were incorporated as granular formulations, release and dissolution from the formulation are additionally important to consider in regard to leaching potential. Bifenthrin exhibited a rapid ($y=451x^{-1.21}$) and slow fraction ($y=54.1x^{-0.27}$) relationships as pore volumes were added, indicating that bifenthrin may release from formulation at different rates. (Figure 3-1).

A strong correlation between bifenthrin concentrations and turbidity may indicate that bifenthrin is dependent on particulates or organic materials for transport through the water. Past studies have shown that pyrethroids strongly adsorb to suspended solids and sediments in runoff (Gan et al. 2005). Our results indicate that bifenthrin may demonstrate adsorption and desorption depending on available particles and organic matter moving through the column. The variations in fipronil concentrations may be due to moderate water solubility of the fipronil formulation and minute changes in hydrologic flow patterns (Gunasekara and Troung 2007). Furthermore, the spikes of fipronil as pore volumes were added could be in part due to the design of the slow-release granular formulation. In summary, bifenthrin and fipronil may adsorb and desorb moving through the column depending on binding sites available and disperse into solution depending on granular formulation properties.



Figure 3-1. Log-log plot of mean (± standard error) bifenthrin and fipronil concentrations versus 1-100 pore volumes. *Note: Initial pot concentrations were 15 ppm bifenthrin and 1 ppm fipronil*



Figure 3-2. Bifenthrin and fipronil concentrations from three replications comparing column leachate versus median turbidity. Concentrations and turbidity readings shown are results from pore volume leachate. *Note: Initial pot concentrations were 15 ppm bifenthrin and 1 ppm fipronil.*

Pot Leaching

Specific conductivity was recorded for all leachate samples. The specific conductivity was variable with no consistent trend throughout the experiment with a range of 513-1142 μ S/cm, with a median of 794 μ S/cm. Additionally, pH was consistent throughout all the samples with a range of 7.5 to 8.3 and median pH of 8.0. No insecticides were detected for control blanks.

The concentrations of bifenthrin decreased over time (p=0.018), and significant (p<0.05) concentrations remained after 15 days of irrigation (Figure 3-3a). Bifenthrin concentrations were significantly different for pot type (p=0.039) and irrigation type (p<0.001) for all days. In general, bifenthrin concentrations in Root Maker® pots with overhead irrigation leachate demonstrated highest leaching potential, and were 21% higher than leachate concentrations in slick-wall with overhead irrigation (Figure 3-4a). Bifenthrin concentrations were lowest with standard slick-wall pots with drip irrigation, or 28% lower than Root Maker® pots with drip irrigation (Figure 3-4a). A strong correlation (R^2 =0.84, y = 49.7x + 210) was shown between turbidity levels and bifenthrin concentrations for the Root Maker® pots with overhead irrigation. Overall, turbidity readings were less than 10 NTU for all days sampled. Weak or no correlations (R^2 <0.30) were shown between bifenthrin concentration and turbidity for any of the remaining pot and irrigation types.

Fipronil leachate concentrations were variable, with no significant trend indicated over the leaching period (p=0.052) (Figure 3-3b). However, there was a decreasing trend in fipronil concentrations when numerically comparing day 1, day 5, and day 15 levels.

Additionally, no significant differences were shown for pot type (p=0.31) and irrigation type (p=0.24). Overall, Root Maker® pots with overhead irrigation resulted in the highest fipronil concentrations, and were 19% higher than slick-wall pots with overhead irrigation (Figure 3-4b). The other three (Root maker®/drip, slick-wall/overhead, slick-wall/drip) pot and irrigation types resulted in similar means ($\pm 5\%$) of fipronil leachate levels (Figure 3-4b). Decreasing trends for turbidity and fipronil leachate concentrations were not indicated during the experiment.



Figure 3. Mean (± standard error) (a) bifenthrin concentrations and (b) fipronil concentrations in pot leachate from two different pot (Standard and Root Maker®) and irrigation types (Overhead and Drip) over 15 days. *Note: bifenthrin incorporation in the pots initially before runs was 15 ppm bifenthrin and 1 ppm fipronil.*



Figure 3-4. Comparision of pot (Standard and Root Maker®) and irrigation type (Overhead and Drip) versus (a) 15 day mean (± standard error) bifenthrin concentrations and (b) fipronil concentrations in pot leachate.

Field Simulation Leaching

Water quality readings for pH and specific conductivity were recorded for all samples, with no trends or relationships with insecticide leachate concentrations indicated. pH was uniform with a range of 7.7-8.2 and median of 7.8. Specific conductivity was variable with a range of 495-2560 μ S/cm and a median of 1260 μ S/cm. Insecticides of interest were not detected in control blanks.

Bifenthrin levels remained constant, with no significant decrease in levels over time (p=0.989). Significant differences between irrigation (p<0.001) and pot type (p<0.001) were shown. Root Maker® and slick-wall pots with overhead irrigation showed highest overall bifenthrin levels by 48% and 49% compared to Root Maker® and slick-wall pots with drip irrigation, respectively (Figure 3-5a). Root Maker® pots with overhead irrigations resulted in the highest runoff bifenthrin concentrations, and were 29% higher than standard slick-wall pots with overhead irrigation (Figure 3-6a). No or weak correlations were determined between turbidity measurements and bifenthrin concentrations (\mathbb{R}^2 <0.30).

For fipronil, no significant decrease (p=0.46) was shown for fipronil levels over the sampling period. Significant differences were not shown when comparing pot types (p=0.067) and when comparing irrigation types (p=0.60). Numerical analysis showed no significant increase or decrease from day 1 to day 15 leachate regardless of pot or irrigation type (Figure 3-5b). Highest levels of fipronil were shown in Root Maker® with overhead and drip irrigation (Figure 3-6b). Fipronil concentrations were 7% greater in Root Maker® pots compared with slick-wall pots with overhead irrigation, and 19% greater on average in the Root Maker® with drip irrigation as compared to standard pots

with drip irrigation (Figure 3-6b). No correlation was shown ($R^2 < 0.07$) for fipronil leachate levels versus turbidity. It should be noted that for the entire run, median turbidity levels were higher on day 1 than day 15 for all runs, indicating higher sediment loadings.



Figure 3-5. Mean (± standard error) (a) bifenthrin concentrations and (b) fipronil concentrations in field simulation leachate from two different pot (Standard and Root Maker®) and irrigation types (Overhead and Drip) over 15 days. Note: *bifenthrin incorporation in the pots initially before runs was 15 ppm bifenthrin and 1 ppm fipronil.*



Figure 3-6. Comparision of pot (Standard and Root Maker®) and irrigation type (Overhead and Drip) versus (a) 15 day mean (± standard error) bifenthrin concentrations and (b) fipronil concentrations in field simulation leachate.

Factors Influencing Insecticide Runoff

Overall, bifenthrin levels remained constant over the 15-day period in the runoff simulations, possibly due to the fact that higher loads of sediments from the clay soil bins

were transported by the leachate. Gan (2006) expressed that suspended and dissolved solids adsorb a substantial amount of insecticides in surface water runoff from agricultural sites. Our results support this relationship that binding to the clay soil leveled off the amount of bifenthrin that is transported off site in surface runoff. In addition, the compost may serve as a dissolved organic carbon (DOC) source. Delgado (2010) found that DOC from gardening and agricultural amendments such as compost, peat, and mulches increased the potential for pyrethroids to leave in surface runoff in a solution phase. These relationships correlate to the highest concentrations of bifenthrin released from Root Maker® pots, which have additional vent holes on the sides to encourage root growth, and therefore, the potential to leach higher amounts of sediment and organic matter. Results from the pot leaching experiments show a high spike of bifenthrin during the first few days and a significant decrease over 15 days. Although significant decreases of bifenthrin throughout the run were shown, highest concentrations remained in leachate from Root Maker® pots with drip and overhead irrigation. Drip irrigation showed an average marginal increase from day 1 to day 5 before the concentrations remained steady throughout the runs.

Bifenthrin and fipronil levels in the runoff simulations from four pots were similar to the concentrations leaching from a single pot. Dilution from additional water running off the clay surface during overhead irrigation may have lowered the concentrations in the "first flush" that was captured. Drip irrigation water had less energy and more retention time through the media and across the clay bin. The runoff simulations were considered worst-case scenarios because of short overland flow, heavy irrigation, and capturing the first pore volumes leaving the pots. Although high concentrations were

shown in both the pot leaching and runoff simulations, mean mass removal from each pot during leaching experiments over a 15-day period was 0.09% and 0.12% for bifenthrin and fipronil, respectively. These results indicate that high levels of insecticide leaching could continue for a substantial amount of time.

Fipronil levels were variable throughout all of the experiments. Increased water solubility and lower soil organic carbon-water partitioning coefficient of fipronil $(K_{oc}=825)$ reduces the ability for this insecticide to be transported by soil particles (Gunasekara and Troung 2007). In essence, fipronil leaving the system was likely to be in a dissolved phase, or from granules leaving the pots. Fipronil concentrations were similar in both the drip and overhead irrigation strategies in both pot and field simulations (p>0.24), indicating that altering production practices may not be beneficial to limiting leaching potential of fipronil. No correlations were shown with turbidity, demonstrating that fipronil is leaving as a dissolved phase or volatilizing from the granules.

Acute Toxicity Tests

Control mortality was <10% for all tests. Results from the bifenthrin and fipronilspiked laboratory water demonstrated the mean expected LC_{50} values as 1.5 ng/L and 322 ng/L, respectively. Since overhead irrigation strategies produced the highest levels of insecticides and sediment loads in runoff, the expected worst-case scenario, acute toxicity tests were only performed on two combinations: Root Maker® pots with overhead irrigation and standard slick-wall pots with overhead irrigation. Bifenthrin was determined as the driver for toxicity within these experiments. Although fipronil concentrations in leachate averaged 300 ng/L, near the expected LC_{50} , bifenthrin concentrations were always 100x the expected LC_{50} value. Thus, following dilution for

bifenthrin, fipronil concentrations were negligible. Based on the dilution required to reduce toxicity to 50% lethality and the measured sample concentration, LC_{50} measurements can be made for each sample diluted. Pot leaching results showed a mean LC_{50} of 2.02 ng/L, and the runoff simulation mean was 1.21 ng/L. Resulting LC_{50} 's in the pot leaching and field simulations were all within a factor of two of the expected LC_{50} for bifenthrin, except for replicate 2 in the pot leaching. In both the pot leaching and runoff simulations, mean LC_{50} values decreased overall through days 1, 5, and 15 (Table 3). V

Table 3-3. Leachate concentrations of Root Maker® with overhead irrigation (RMOH) and standard slick-wall pots with overhead irrigation (SWOH) with resulting LC_{50} based on dilutions of leachate. Two replications were performed for each pot and irrigation type combination; (a) represents pot leaching toxicity data and (b) represents runoff simulations toxicity data. Dilution is the dilution required to reduce the leachate effect to only cause 50% mortality. LC_{50} was calculated by dividing leachate concentration by dilution. Note: dashes in (a) represent sample lost during processing; no data available.

RMOH	Leachate	Conc. (ng/L)	Dilu	ition	LC ₅₀	(ng/L)	swoн	Leachate	Conc. (ng/L)	Dilu	tion	LC ₅₀ (ng/L)
Day	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Day	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1	391.07	425.91	-	65.6	-	6.49	1	351.11	312.49	-	91.7	-	3.41
5	353.68	368.66	137	302.1	2.58	1.22	5	174.72	262.16	186.6	216.9	0.94	1.21
15	276.67	395.24	370.4	219.3	0.75	1.80	15	285.23	277.18	561.8	215	0.51	1.29

а

RMOH	Leachate	Conc. (ng/L)	Dilu	ition	LC ₅₀	(ng/L)	swoн	Leachate	e Conc. (ng/L)	Dilu	ition	LC ₅₀	(ng/L)
Day	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Day	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
1	683.2	509.0	383.1	216.9	1.78	2.35	1	296.7	219.5	243.3	199.2	1.22	1.10
5	524.9	471.3	311.5	389.1	1.69	0.77	5	328.1	292.9	327.9	197.6	1.00	1.48
15	613.6	402.3	625	479.6	0.98	0.84	15	470.6	319.5	671.1	561.8	0.70	0.57
b													

The higher mean LC_{50} in the runoff simulations suggests that additional suspended sediments may play a role in toxicity; either through bifenthrin adsorbed to suspended particles or increased sediment load reducing water quality. Mean turbidity readings on day 1 compared to the remaining 14 days averaged 53% and 27% higher for pot leaching and field simulations, respectively. Results from Weston et al. (2009) suggested that suspended sediments were likely to reduce bifenthrin bioavailability, and estimated expected LC_{50} 's in runoff as 5-20 ng/L. Our data indicate that bifenthrin is bioavailable within the pot leachate and resulting toxicity was similar to predictions based on initial water concentration tests. Results indicated that sediment may play a factor as LC_{50} values were lower at the beginning of runs when there was greater potential for a flush of sediment and organic matter from the pots and bins. Although, it is possible that tannins from sediment loads or pine bark increased mortality. Yang et al. (2006) revealed that up to 50% of bifenthrin was in a dissolved phase in surface-water runoff. In comparison, our results demonstrate that even with a substantial amount of sediments (>90 NTU), much of the bifenthrin was bioavailable and toxic to *H. azteca*.

Environmental Implications

The threat of nursery and greenhouse site runoff with leachate similar to these experiments creates a significant problem for many aquatic organisms. Concentrations of bifenthrin in the pot and runoff simulations regularly exceeded 200 ng/L, which is more than 100 times greater than the LC₅₀ for *H. azteca*. Additionally, studies have shown that insecticides from stormwater and urban runoff accumulate in streambed sediments (Gan 2005, 2006, 2012; Hintzen et al. 2009; Weston et al. 2009). The aqueous photolysis half-life of bifenthrin ranges from 276-416 days and aquatic sediments for up to 16 months, indicating that accumulation of insecticide running off into streams is likely (Fecko 1999). Results from toxicity tests indicate that, on average, pot leachate will need to be diluted 200-300x before concentrations are no longer at the LC₅₀ for *H. azteca*. Additional factors such as a longer overland flow over sediments, vegetation, and manmade surfaces may reduce the impact of these insecticides before entering a stream (Gan

2012; Jiang et al. 2010; Bennett et al. 2005). In contrast, the high volume of leachate and runoff leaving a site during a storm or irrigation event significantly increases the possibility of toxic leachate reaching nearby surface waters and accumulating in stream bottom sediments.

Bioretention Cell Media Insecticide Removal

Column experiments allowed for investigation of removal efficiency of bifenthrin and fipronil from potting media leachate using bioretention cell media comprised of various combinations of sorted sand and compost. Results indicate that higher amounts of compost significantly improve removal of both insecticides from leachate. Mean reductions show 82% and 83% reduction (SD=7) of bifenthrin in columns with 80% sand/20% compost and 60% sand/40% compost, respectively (Figure 3-7a). Concentrations of bifenthrin leaving the columns were still 4-75x above the LC₅₀ for *H. azteca*, however, depending on the initial influent concentrations (pot leaching LC₅₀=2.02 ng/L). Strong reductions (mean of 72%, SD=20) of fipronil were only shown in the 60/40 blend. Other bioretention cell media mixtures were highly variable for removal of fipronil, and mean reductions were less than 50%. The 100% sand and the 90/10 mixture resulted in a decrease of removal of bifenthrin and fipronil over time (Figure 3-7a and 3-7b). Additionally, a downward trend was shown for mean reduction of fipronil versus pore volumes (Figure 3-7b).



Figure 3-7. Represents mean (\pm standard error) percent reduction of (a) bifenthrin and (b) fipronil concentrations through four bioretention cell media compositions: sand(%)/compost(%) by volume (100/0, 90/10, 80/20, 60/40) for 60 pore volumes.

The levels of insecticide in these column studies represent a worst-case scenario and dilution from rainwater and adsorption of insecticides to large particles may reduce the initial loadings entering the bioretention cell. Higher removals shown in the first two pore volumes may correlate to the media not being fully saturated, and therefore, higher retention time within the media. The fact that fipronil is moderately water soluble $(K_{oc}=825)$ and less likely to adsorb to organic matter may explain why removal efficiency became lower as more pore volumes of leachate were added. Levels of bifenthrin showed similar trends in the 100% and 90% sand. Due to the higher hydraulic conductivity of these two mixtures, leachate water moved through the column at a rate that may have reduced the potential for adsorbance of bifenthrin to sand particles. However, results showed that the 90/10 composition had reduced bifenthrin reduction and was significantly different (p < 0.001). We think this may be due to the fact that the mean influent used during these runs was 56% higher than the other column test means overall. Influent was variable because leachate was taken from pots and concentrations depended on the specific pot that was leached for each column test. This conclusion may suggest

that fluxes in concentrations may play a role in removal efficiencies with lower amounts of organic matter or compost.

One consideration of these column tests is the depth of media may play a large role in insecticide reduction. Increasing the retention time through the bioretention cell may significantly improve the removal efficiency of these insecticides. Flow rates of leachate through the column were faster in the 100% sand (11 cm/min) compared to 60% sand/40% compost (5 cm/min), and may be indicative of removal efficiency of insecticides as the leachate has a longer contact time. Reduction of flow and sediment trapping and incorporation of vegetation has shown good efficiency in reducing pyrethroids (Bennett et al. 2005; Kabashima 2004). Furthermore, one recent study indicated that increased bioretention cell media depth vastly improves load reduction of nutrients, pathogens, and suspended solids (Brown et al. 2010). Bioretention cells typically contain 12-24 inches of sand/compost media, in addition to 3-6 inches of organic matter at the surface. Therefore, from our results and known adsorbent properties of the insecticides, removal efficiencies of bifenthrin and fipronil should increase with media depth.

Conclusions

Insecticide leaching potential from potted nursery stock at tree nurseries and greenhouse productions was investigated, along with a preliminary evaluation of the feasibility of bioretention cells for reducing insecticide concentrations in runoff. This project identified that insecticides such as bifenthrin and fipronil have a high potential to leach from nursery containers and affect water quality in nearby water bodies. In addition, bifenthrin was shown to be bioavailable and toxic to *H. azteca*, regardless of

sediment influences. Given that a small fraction of bifenthrin was leached from the pots, leaching could be a significant toxicity problem long-term. Root Maker® pots with overhead irrigation produced the highest levels of insecticides leaving the pots. Use of drip irrigation with standard slick-wall pots may limit the leaching potential of insecticides, specifically, bifenthrin. Overall, bioretention cell media resulted in strong removal efficiencies for bifenthrin and for fipronil if enough organic matter is present in the system. Media with at least 20% compost by volume was shown to have the highest removal potential. As previous studies and this one indicate, introducing best management practices such as bioretention cells or vegetated swales can greatly reduce the amounts of insecticides leaving in runoff from agricultural sites.

Considering that the nursery industry has thousands of operations that sell nursery stock containers within the RIFA quarantine zone, insecticides such as bifenthrin and fipronil have the potential to create immense problems for aquatic environments if best management practices are not applied. The importance of implementing new remediation strategies in continuation with existing management practices such as using smaller quantities of water and insecticides is critical for optimal effectiveness of insecticide reduction. Additional studies in the future that could enhance best management practices include field monitoring of previously installed bioretention cells at a tree nursery or greenhouse facility, and a full-scale performance study of introducing pot leachate directly into a bioretention cell.

CHAPTER IV

LESSONS LEARNED

This chapter provides reflection of the project, areas to improve the project, and ideas for future research. In addition, concepts were evaluated for how the results and conclusions of this research can be used in other applications outside of the nursery and greenhouse industry.

Areas to Improve the Project

Overall, the project provided an in-depth analysis of the transport and fate of two insecticides from potted nursery stock, and determined if these insecticides can potentially be removed from the runoff water through bioretention cell media. This section provides an overview of some areas that could be improved for future work.

Typically, only one insecticide is added to a potting media, but we wanted to investigate the fate of two common insecticides leaving the pots. The pots that were donated from the nursery were inoculated with 15 ppm bifenthrin. We added fipronil at a rate of 1 ppm because of economic reasons, and due to the fact that it was added as additional insecticide beyond the grant. I would recommend adding the same application of insecticide in a study such as this one due to the fact of comparison of one insecticide to the other. For our purpose, the results were beneficial because during the toxicity tests we discovered that adding fipronil at a lower level allowed us to investigate toxicity of bifenthrin without any other influences.

The bioretention cell media column tests provided introductory information about insecticide removal efficiency. Therefore, more research in the future should focus on scaling the project setup into similar dimensions as what is commonly installed at a bioretention cell site. A larger setup such as a box with 12-24 inch depth might have given us an ideal comparison to a bioretention cell in the field. Additionally, if time had allowed, sediment samples taken from the column media may have provided a sense of where the insecticides partitioned on the media.

Ideas for Future Research

This research represents a foundation of work that can possibly develop into a series of new projects that advance insecticide and pollutant management in the nursery industry, agriculture, and urban landscapes. For example, evolving this project into a field monitoring or larger-scale study would be beneficial to investigate systems that are similar to what is applied in the field. Other possible areas of research include research with previously or newly installed bioretention cells at nurseries or greenhouses, modeling, and investigating removal potential of other pesticides (herbicides, fungicides).

The first idea included spiking a bioretention cell during a number of years (or different aged BRC's) with pot leachate and collecting effluent from the outlet. This would be a very large, multi-year study, but might provide insight of how a complete system handles this leachate. In addition, lab column studies and transport/fate modeling could correspond with the field studies. Another possibility is collection of sediment

cores from previously installed bioretention cells in areas that are suspected for insecticide use, and analyze for insecticide retention.

Modeling would include the transport and fate of insecticides leaving the pots and carried by surface runoff to nearby surface waters. Models would account for insecticide application rates, insecticide physical/chemical properties, turbidity, runoff velocity and volume, and composition of land (vegetated, concrete, compacted clay). In addition, models could also include the introduction of bioretention cells and vegetated channels for percent reduction under the same hydrological and physical conditions. Lastly, given that strong correlations were shown for turbidity and bifenthrin, studies including determining a relationship between turbidity and nursery insecticides might serve as a predictor for insecticide loads in runoff water.

Finally, investigating nutrient implications from increased compost load to adsorb pesticides might be beneficial to determine optimal insecticide removal efficiency and lowest nutrient leaching. Additionally, research on similar systems such as flow-through wetlands, constructed wetlands and vegetated filter strips for pesticide removal might provide information on alternatives for areas where nutrient management is critical, and/or bioretention cells may not serve as an ideal management strategy

Project Outlook

This project emphasizes use of bioretention cells for removal of pesticides from nurseries and greenhouses, but the use of bioretention cells as a best management practice for pesticides could be expanded into many different areas beyond the nursery industry. Applications of this research could be extended into residential and urban settings where

there is potential for large amounts of pesticides applied to lawns and landscapes to leave in runoff. In addition, other crops such as grapes, vegetables, and ornamentals often require insecticides or herbicides use, and therefore, become a likely non-point pollution source.

The long-term outcome of this project and future projects should provide quality information to industries and state and federal agencies with regard of how to manage surface runoff from potential pesticide hotspots. Overall, this research identified the need for new and improved technology to limit toxic pesticides from entering nearby waterbodies and a potential remediation technology. Alternative solutions such as use of organic farming, or other integrated pest management strategies should first be considered when developing a project, although, this is often not possible and a pesticide is the best option for ensuring healthy crops. Therefore, best management practices should be considered in any instance to limit the aquatic risks associated with pesticide usage.

REFERENCES

- Amweg, Erin, Donald Weston, Jing You, et al (2006). Pyrethroid Insecticides and Sediment Toxicity in Urban Creeks from California and Tennessee. *Environ. Sci. Technol.* 40: 1700-1706.
- Calcott, A. M. 2003. Imported fire ant: quarantine treatments for nursery stock and other regulated articles. Program aid no.1735. U.S. Dept. of Agr. Animal Plant Health Inspection Serv.
- Connelly, Pete. (2001). Environmental Fate of Fipronil. California Environmental Protection Agency. Department of Pesticide Regulation.
- Bennett, Erin, Matthew Moore, Charles Cooper, et al (2005). Vegetated Agricultural Drainage Ditches for the Mitigation of Pyrethroid-Associated Runoff. *Environmental Toxicology and Chemistry*. 24.9: 2121-2127.
- Bobe, A., Meallier, P., Cooper, J-F, Coste, C. M. 1998b. Kinetics and mechanisms of abiotic degradation of fipronil (hydrolysis and photolysis). J. Agric. Food Chem. 46: 2834-2839.
- Brown, R. A., & Hunt III, W. F. (2010). Impacts of media depth on effluent water quality and hydrologic performance of undersized bioretention cells. *Journal of Irrigation* and Drainage Engineering, 137(3), 132-143.
- Budd, R, S. Bondarenko, D. Haver, et al (2007). Occurrence and Bioavailability of Pyrethroids in a Mixed Land Use Watershed. *Journal of Environmental Quality*. 36: 1006-1012.
- Budd, R., O'Geen, A., Goh, K. S., Bondarenko, S., & Gan, J. (2009). Efficacy of constructed wetlands in pesticide removal from tailwaters in the Central Valley, California. *Environmental Science & Technology*, 43(8), 2925-2930.
- Delgado-Moreno, L., Wu, L., & Gan, J. (2010). Effect of dissolved organic carbon on sorption of pyrethroids to sediments. *Environmental Science & Technology*, 44(22), 8473-8478.

- Gan, J., Bondarenko, S., Oki, L., Haver, D., & Li, J. X. (2012). Occurrence of fipronil and its biologically active derivatives in urban residential runoff. Environmental science & technology, 46(3), 1489-1495.
- Gan, Jay (2006). Pyrethroid insecticides in nursery runoff: Transport and impact on aquatic invertebrates. UC Water Resources Center Technical Completion Report: No. WRC Project W-968.
- Gan, J, S.J Lee, P Liu, et al (2005). Distribution and Persistence of Pyrethroids in Runoff Sediments. *Journal of Environmental Quality*. 34: 836-841.
- Gunasekara, A. S., & Troung, T. (2007). Environmental fate of fipronil. *Environmental Monitoring Branch*.
- Fecko, Andrew (1999). "Environmental Fate of Bifenthrin." Department of Pesticide Regulation: Environmental Monitoring and Pest Management Branch. 1-8.
- Hintzen, E. P., Lydy, M. J., & Belden, J. B. (2009). Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas. *Environmental Pollution*, 157(1), 110-116.
- Hsieh, C. H., & Davis, A. P. (2005). Evaluation and optimization of bioretention media for treatment of urban storm water runoff. *Journal of Environmental Engineering*, 131(11), 1521-1531.
- Jiang, W., Gan, J., & Haver, D. (2010). Sorption and desorption of pyrethroid insecticide permethrin on concrete. *Environmental Science & Technology*, 45(2), 602-607.
- Kabashima, J. N., Lee, S. J., Haver, D. L., Goh, K. S., Wu, L. S., & Gan, J. (2004). Pesticide runoff and mitigation at a commercial nursery site. InACS Symposium series (Vol. 863, pp. 213-230). Washington, DC; American Chemical Society; 1999.
- Lao, W. J., Arye, G., Ernst, F., Xu, Y. P., Bondarenko, S., Haver, D., & Gan, J. (2008). Reduction of pyrethroid runoff from a commercial nursery. *Synthetic Pyrethroids:* Occurrence and Behavior in Aquatic Environments, 991, 426-445.
- Lin, K., Haver, D., Oki, L., & Gan, J. (2009). Persistence and sorption of fipronil degradates in urban stream sediments. *Environmental Toxicology and Chemistry*, 28(7), 1462-1468.
- Lockley, T.C., and H.L. Collins (1990). Imported fire ant quarantine in the United States of America: past, present and future. J. Miss. Acad. Sci. 35: 2326.

- Mangiafico, Salvatore, Julie Newman, Donald Merhaut, et al (2009). Nutrients and Pesticides in Stormwater Runoff and Soil Water in Production Nurseries and Citrus and Avocado Groves in California. *HorTechnology*. 19: 360-367.
- Miller, T.A. and V.L. Salgado. 1985. The mode of action of pyrethroids on insects, in *The Pyrethroid Insecticides*. Leahy, J.P., Ed., Taylor & Francis, London. 43-97.
- Rhône-Poulenc Ag Company. 1998. Application for Registration. Volume No. 52062-071. Vol 1. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA
- Salgado V.L., S.N. Irving and T.A. Miller. 1983. The importance of nerve terminal depolarization in pyrethroid poisoning of insects. *Pesticide Biochemical Physiology*. 20: 169-182.
- Siegfried, B.D. 1993. Comparative toxicity of pyrethroid insecticides to terrestrial and aquatic insects. *Environmental Toxicology and Chemistry*. 12:1683-1689.
- Weston, D. P., Holmes, R. W., & Lydy, M. J. (2009). Residential runoff as a source of pyrethroid pesticides to urban creeks. *Environmental Pollution*,157(1), 287-294.
- Weston, D.P., R.W. Holmes, and J. You (2005). Aquatic Toxicity Due to Residential Use of Pyrethroid Insecticides. *Environ. Sci. Technol.*. 39: 9778-9784.
- Yang, Weichun, Jianying Gan, and Wesley Hunter (2006). Effect of Suspended solids on Bioavailability of Pyrethroid Insecticides. *Environmental Toxicology and Chemistry*. 25.6. 1585-1591.
- Ying, G. G., & Kookana, R. S. (2006). Persistence and movement of fipronil termiticide with under-slab and trenching treatments. *Environmental Toxicology and Chemistry*, 25(8), 2045-2050.
- Ying, G-G., Kookana, R. 2002. Laboratory and field studies on the degradation of fipronil in a soil. Aust. J. Soil Res. 40: 1095-1102.
- USEPA (2000). Methods for Measuring the Toxicity and Bioaccumulation of Sedimentassociated Contaminants with Freshwater Invertebrates. EPA/600/R-99/064, second ed. Office of Science and Technology, Washington, DC.
- USDA (2007). Imported Fire Ant 2007: Quarantine Treatments for Nursery Stock and Other Regulated Articles. Program Aid No. 1904. Animal and Plant Health Inspection Service.

APPENDICES

APPENDIX A

Bulk Density of Potting Media								
	Tin 1	Tin 2	Tin 3					
volume of tin (cm ³)	180	180	180					
mass of soil (g)	50.6	43.9	44.8					
dry bulk density (g/cm ³)	0.28	0.24	0.25					
height of tin (cm)	4.9	4.9	4.9					
diameter of tin (cm)	6.9	6.9	6.9					
	Avg bulk density (g/cm ³) 0.26							
	Porosity of	Potting Med	dia					
Reps	Media (mL)	Water (mL)	Volume diff	%Voids				
1	100	100	33	67				
2	100	100	31	69				
3	100	100	35	65				
4	100	100	37	63				
5	100	100	36	64				
			Avg porosity	65.6%				

Pore Volume Analysis for Potting Media									
Pore volume	mL	Column		3-gallon Pot Volume					
1	607	h (cm)	20.3	11350 cm ³					
2	1215	d (cm)	7.62	Media volume in pot*					
3	1822	v (cm ³)	926	3904 cm ³					
5	3037		3-	gallon Pot Pore Volume					
10	6075	1 pore volume	2	pore vols					
30	18224	1.97 gallons		3.96 gallons					
100	60746	* Media volume determined by Pot vol* (1-porosity)							

APPENDIX B

Potting Media Column Test Data

COLUMN LEACHING EXPERIMENT DATA										
Pore Vol	Sample type	Sample ID	Bifenthrin	Fipronil	Median Turb					
			ng	/L	NTU					
1	Sample	A1	571.0	90.5	25.4					
2	Sample	A2	270.9	79.1	9.34					
3	Sample	A3	178.4	88.1	8.83					
5	Sample	A4	8.89	10.5	5.88					
10	Sample	A5	11.6	10.4	3.00					
30	Sample	A6	29.2	64.7	3.69					
100	Sample	A7	19.5	24.1	1.04					
	Blank	A8 (Blank)	6.70	ND	0.82					
1	Sample	A9	261.0	45.1	53.4					
2	Sample	A10	213.6	47.0	14.3					
3	Sample	A11	73.5	47.9	6.92					
5	Sample	A12	54.3	48.0	7.52					
10	Sample	A13	34.7	34.5	3.07					
30	Sample	A14	13.1	47.7	3.40					
100	Sample	A15	10.1	23.2	1.76					
	Blank	A16	ND	ND	0.36					
1	Sample	A17	276.4	37.6	17.5					
2	Sample	A18	135.9	54.7	6.08					
3	Sample	A19	135.9	63.7	3.22					
5	Sample	A20	111.0	66.4	3.32					
10	Sample	A21	36.2	45.6	1.00					
30	Sample	A22	18.7	32.7	0.70					
100	Sample	A23	14.4	21.9	0.45					
	Blank	A24	ND	ND	0.30					

APPENDIX C

Pot Leaching Experiment Data

POT LEACHING SIMULATIONS INSECTICIDE CONCER									ON DAT	ΓΑ	
Day	ID	Bifenthrin	ipronil	Day	ID	Bifenthrin	Fipronil	Day	ID	Bifenthrin	Fipronil
REP 1		(ng/L)	REP 2		(ng/	Ľ)	REP 3 (ng/L)			L)
		RMOH				RMOH				RMOH	
1	B1	1192	270.5	1	B27	391.1	92.1	1	B51	425.9	218.3
2	B5	511.0	519.2	2	B31	518.5	352.0	2	B55	374.7	235.0
3	B9	488.2	449.0	3	B35	278.8	236.1	3	B59	431.4	458.9
5	B13	526.7	440.5	5	B39	353.7	303.0	5	B63	368.7	425.6
10	B18	260.2	329.7	10	B43	123.7	213.8	10	B67	410.0	455.6
15	B22	367.5	306.8	15	B47	276.7	359.1	15	B71	395.2	305.4
									B71-D	347.6	269.6
		SWOH				SWOH				SWOH	
1	B2	536.3	700.6	1	B28	351.1	40.4	1	B52	312.5	99.8
2	B6	498.4	479.5	2	B32	207.3	194.2	2	B56	300.4	150.3
3	B10	776.5	397.1	3	B36	248.9	167.7	3	B60	260.6	284.4
5	B14	774.7	402.3	5	B40	174.7	334.6	5	B64	262.2	238.3
10	B19	255.9	330.1	10	B44	141.6	256.0	10	B68	136.8	194.7
15	B23	301.4	273.0	15	B48	285.2	226.1	15	B72	277.2	126.0
					B40-D	182.0	372.5		B52-D	309.9	96.1
		RMDI				RMDI				RMDI	
1	B3	421.2	355.3	1	B29	161.8	103.6	1	B53	146.1	184.0
2	B/	315.4	513.8	2	B33	182.2	282.5	2	B57	157.4	361.8
3	B11	300.1	319.2	3	B37	211.5	263.7	3	B61	129.8	421.1
5	B15	222.1	222.3	5	B41	243.8	312.3	5	B65	1/9.0	258.5
10	B20	204.6	198.0	10	B45	/4.5	147.3	10	B69	238.1	2/2.3
15	B24	192.8	140.5	15	B49	151.6	191.1	15	B73	252.5	260.9
	B24-D	190.6	134.4								
1	D.4	151 2	111 2	1	020	3WDI	162 F	1	DE4		421.0
1 2	D4 D0	101.Z 245 5	444.2	1 2	D3U	97.0 112.4	214.2		Б04 БЕО	92.7 120 0	431.0 205.1
2	DO D17	205 6	424.7 204 2	2	D34 D20	70.0	172 1	2	B30	120.0	200 6
5	B16	204.8	102.0	5	BJ0	67 Q	22/ 8	5	B66	120 7	270.0
10	B10 B21	130 8	103.9	10	B46	49 7	255 4	10	B70	184.3	270.0
15	B25	190.0	147 1	15	B50	93.0	173.4	15	B70 B74	178.3	230.0 341 7
15	B17-bl	360 5	386.9	15	000	55.0	125.5	10	074	1/0.5	511.7
		Control	230.5			Control		RMOH= Root Maker/Overhead			
1	G1	107.9	0.5	1	G4	ND	ND	SWOH	= Slick-	wall/Overhe	ead
5	G2	39.6	0.8	5	G5	ND	ND	RMDI=	Root N	laker/ Drip	
15	G3	39.7	0.5	15	G6	ND	ND	SWDI	= Slick-v	vall/Drip	

POT LEACHING SIMULATION WATER QUALITY DATA									
Turbidity (NTU)									
	R	ep 1 [#]	Rep 2	Rep 3	Average				
RMOH									
	1	17	7.2	4.3	9.5				
	2	2.7	6.1	2.2	3.7				
av	3	2.7	5.3	2.8	3.6				
Δ	5	2.1	4.2	3.7	3.3				
	10	2.3	*	3.1	2.7				
	15	2.3	5.7	2.4	3.4				
RMDI									
	1	3.5	1.3	1.9	2.2				
	2	2.7	1.5	1.4	1.9				
ay	3	1.6	2.2	2.0	1.9				
Δ	5	1.1	2.2	1.8	1.7				
	10	1.7	*	2.7	2.2				
	15	2.0	1.8	1.9	1.9				
SWOH									
	1	3.4	3.5	4.8	3.9				
	2	3.5	3.2	2.7	3.1				
ay	3	4.3	3.1	2.8	3.4				
Ď	5	2.3	2.1	3.6	2.7				
	10	2.5	*	3.1	2.8				
	15	2.4	2.9	3.6	3.0				
SWDI									
	1	2.1	2.1	1.4	1.9				
	2	1.9	1.8	1.6	1.7				
ay	3	1.7	1.6	2.3	1.8				
õ	5	2.1	3.3	1.6	2.3				
	10	2.4	2.2	2.7	2.4				
	15	2.5	*	2.4	2.4				
* Lost data s	heet								
# Rep 1-3 va	lues are th	ie med	ian from 5	readings					
SWOH=Slick	-wall/Ove	rhead,	SWDI= Slic	k-wall/Dri	ρ				
RMOH =Roo	tmaker/O	verhead	d, RMDI= R	ootmaker/	′Drip				

P	OT LEA	CHING SIMULATIO	ON WATE	RQUALITY	DATA				
pH									
		Rep 1	Rep 2	Rep 3	Average				
RMOH									
		1 * No data	8.6	7.9	8.3				
		2 * No data	8.8	7.4	8.1				
	aγ	3 * No data	8.6	7.1	7.8				
		5 * No data	8.7	6.9	7.8				
		10 * No data	8.6	7.3	7.9				
		15 * No data	8.7	7.3	8.0				
RMDI									
		1 * No data	8.4	8.0	8.2				
		2 * No data	8.8	7.4	8.1				
	ч	3 * No data	8.6	7.5	8.0				
	ä	5 * No data	8.7	7.0	7.9				
		10 * No data	8.8	7.3	8.0				
		15 * No data	8.7	7.3	8.0				
SWOH									
		1 * No data	8.7	7.7	8.2				
		2 * No data	8.9	7.0	8.0				
	ž	3 * No data	8.6	7.1	7.9				
	õ	5 * No data	8.9	6.7	7.8				
		10 * No data	8.7	7.1	7.9				
		15 * No data	8.8	8.1	8.4				
SWDI									
		1 * No data	8.6	8.0	8.3				
		2 * No data	9.1	7.0	8.0				
	≥	3 * No data	8.7	6.6	7.7				
	Da	5 * No data	8.8	6.9	7.9				
		10 * No data	8.9	7.4	8.1				
		15 * No data	7.8	7.2	7.5				
* Star	ted pH	l recordings after		Average	8.0				
	1st ı	replicate		Median	8.0				
SWOH	=Slick-	wall/Overhead, SV	VDI= Slic	k-wall/Drip					
RMOH	=Root	maker/Overhead,	RMDI= R	ootmaker/[Drip				

PO	POT LEACHING SIMULATION WATER QUALITY DATA								
		Specific Condu	ctivity (u	S/cm)					
		Rep 1	Rep 2	Rep 3	Average				
RMOH									
		1 * No data	943	722	833				
		2 * No data	1190	1070	1130				
	a	3 * No data	1020	1060	1040				
C	č	5 * No data	707	1000	854				
		10 * No data	492	536	514				
		15 * No data	868	496	682				
RMDI									
		1 * No data	753	833	793				
		2 * No data	780	1020	900				
į	Y E	3 * No data	717	911	814				
6	Ĕ	5 * No data	725	754	740				
		10 * No data	520	523	522				
		15 * No data	699	511	605				
SWOH									
		1 * No data	689	815	752				
		2 * No data	907	1380	1140				
į	≻ E	3 * No data	922	1310	1120				
6	ä	5 * No data	808	955	882				
		10 * No data	540	513	527				
		15 * No data	790	491	641				
SWDI									
		1 * No data	784	805	795				
		2 * No data	826	1130	978				
į	Y E	3 * No data	750	973	862				
6	Ĕ	5 * No data	687	654	671				
		10 * No data	522	504	513				
		15 * No data	551	521	536				
* St	arted	conductivity		Average	785				
readir	ngs afte	er 1st replicate		Median	794				
SWOH=	Slick-w	all/Overhead, SV	NDI= Slick	<-wall/Drip					
RMOH =	Rootm	aker/Overhead,	RMDI= Ro	otmaker/D	Drip				

APPENDIX D

Runoff Field Simulation Data

	RUNOFF SIMULATIONS INSECTICIDE CONCENTRATION DATA													
Day	ID	Bife	nthrin F	Fipronil	Day ID)	Bifen	thrin	fipronil	Day	ID	Bife	nthrin	fipronil
REP 1	1		ng/L		REP 2			ng/l	L	REP	3		ng/	L
RMOH					RMC	ЭН				RIV	ЮН			
1	C1		666. 7	144.0	1 C2	25		683.2	306.6	1	C49		509.0	410.4
2	C5		539.6	228.8	2 C2	29		147.8	479.7	2	C53		361.5	511.1
3	C9		769.8	259.5	3 C3	33		328.5	399. 7	3	C57		7 38.3	547.3
5	C13		213.1	160.1	5 C3	37		524.9	380.6	5	C61		471.3	613.7
10	C17		534.8	236.6	10 C4	41		397.0	387.5	10	C65		599.9	489.1
15	C21		575.1	286.0	15 C4	45		613.6	292.1	15	C69		402.3	334.3
					69)-D		215.7	396.4		49-D		520.2	401.2
		SW	он				SWO	ЭН				SW	/он	
1	C2		358.0	114.2	1 C2	26		296.7	304.9	1	C50		219.5	29 7 .6
2	C6		235.4	168.9	2 C3	30		308.7	391. 7	2	C54		341.9	408.3
3	C10		343.7	2 7 0.9	3 C3	34		457.3	303.2	3	C58		646.1	421.7
5	C14		558.4	248.4	5 C3	38		328.1	573.2	5	C62		292.9	448.4
10	C18		241.0	192.2	10 C4	42		389.7	475.4	10	C66		361.4	414.6
15	C22		274.2	249.6	15 C4	46		470.6	400.1	15	C70		319.5	302.7
		RN	1DI				RM	DI				RN		
1	C3		130.6	202.9	1 C2	27		425.4	421.1	1	C51		167.5	560.2
2	C7		203.6	244.6	2 C	31		269.8	419.8	2	C55		250.1	513.2
3	C11		317.8	263.1	3 03	35		248.3	524.6	3	C59		272.5	605.8
5	C15		397.7	298.5	5 Ca	39		468.0	461.6	5	C63		290.4	529.1
10	C19		246.5	3/7.4	10 04	43		283.2	351.9	10	C6/		142.5	445.8
15	C23		231.5	317.5	15 C4	4/		220.4	2/9./	15	C/1		138.7	364.8
	С7-D		220.0	299.8	40	J-D		213.4	395.2					
		SIA					SW/					SV		
1	C4	211	150.8	232.0	1 C2	28		78.9	299.7	1	C52		125.6	381.2
2	C8		168.2	195.4	2 C3	32		169.2	311.4	2	C56		129.7	466.7
3	C12		217.8	245.3	3 C3	36		212.3	318.7	3	C60		242.4	492.6
5	C16		205.0	235.5	5 C4	40		178.1	414.5	5	C64		227.3	447.9
10	C20		139.6	122.5	10 C4	44		252.0	298.0	10	C68		189.6	375.3
15	C24		256.5	276.7	15 C4	48		297.7	387.0	15	C72		80.5	301.0
					28	3-D		77.9	290.6					
		Con	trol				Cont	rol				Cor	ntrol	
	F1	ND	1	ND	F3	3	ND		ND		F6	ND		ND
	F2	ND	1	ND	F4	1	ND		ND		F 7	ND		ND
F5 ND ND F8 ND ND					ND									
			RMOH=	Root N	laker/O	ver	head,	SWOF	H= Slick-ν	wall/	Overh	iead,		
	RMDI= Root Maker/Drip, SWDI= Slick-wall/Drip													

	RUNOFF SIMULATION WATER QUALITY DATA									
			Turbio	dity (NTU)						
		F	Rep 1	Rep 2	Rep 3	Average				
RMOH										
		1	59.7	97.8	148	102				
		2	43.4	113	115	90.4				
	ay	3	53.2	85.7	82.9	73.9				
	Δ	5	52.1	74.5	103	76.5				
		10	40.0	110	112	87.2				
		15	49.7	45.7	47.5	47.6				
RMDI										
		1	-	19.7	40.4	30.0				
		2	11.9	7.7	24.8	14.8				
	ay	3	15.3	10.9	14.4	13.5				
	Δ	5	14.3	8.0	8.7	10.3				
		10	18.6	13.2	22.1	17.9				
		15	15.0	5.6	-	10.3				
SWOH										
		1	38.5	135	97.0	90.0				
		2	49.2	106	76.7	77.4				
	ay	3	38.8	96.4	56.9	64.0				
	Ō	5	56.4	60.9	58.3	58.5				
		10	50.6	41.2	72.2	54.7				
		15	46.7	100	-	73.4				
SWDI										
		1	7.2	6.3	14.1	9.2				
		2	9.3	3.7	5.5	6.2				
	ay	3	7.8	13.4	4.5	8.6				
	Õ	5	3.9	10.3	2.8	5.7				
		10	3.1	3.8	6.7	4.6				
		15	6.3	4.3	5.4	5.3				
# Rep	1-3 v	alues are th	ne media	in from 5 re	adings					
SWOF	l=Sli	ck-wall/Ove	rhead, S	WDI= Slick	-wall/Drip					
RMOH	=Rc	otmaker/Ov	verhead,	RMDI= Ro	otmaker/Dri	ip				

	I	RUNOFF SIM	IULATIO	N WATER QU	JALITY DATA				
рН									
		R	lep 1	Rep 2	Rep 3	Average			
RMOH									
		1	8.0	8.0	8.6	8.3			
		2	8.4	8.0	7.5	7.8			
	ay	3	8.3	7.9	7.7	7.8			
	Δ	5	8.3	7.9	7.8	7.8			
		10	8.2	7.9	7.9	7.9			
		15	8.2	7.9	7.8	7.8			
RMDI									
		1	-	7.9	7.6	7.7			
		2	8.3	8.3	7.3	7.8			
	λe	3	8.3	8.1	7.5	7.8			
	õ	5	8.1	7.7	7.5	7.6			
		10	8.1	8.1	7.5	7.8			
		15	8.2	7.8	8.0	7.9			
SWOH									
		1	8.7	7.9	8.0	8.0			
		2	8.5	8.3	7.7	8.0			
	λŧ	3	8.2	8.1	7.9	8.0			
	Õ	5	8.4	8.2	7.1	7.7			
		10	8.0	7.9	7.7	7.8			
		15	8.3	8.2	8.2	8.2			
SWDI									
		1	8.5	7.9	7.5	7.7			
		2	8.3	7.9	7.4	7.7			
	≥	3	8.1	7.7	7.6	7.7			
	Da	5	8.1	8.0	7.5	7.8			
		10	8.1	7.9	7.5	7.7			
		15	8.2	7.8	7.9	7.9			
					Average	7.8			
					Median	7.8			
SWOF	l=Slic	k-wall/Ove	rhead, S	SWDI= Slick	-wall/Drip				
RMOH	=Ro	otmaker/Ov	verhead.	RMDI= Ro	otmaker/Drip	1			

		RUNOFF SIM	IULATIO	N WATER QU	JALITY DATA	\
		Spec	ific Conc	luctivity (uS,	/cm)	
L		R	lep 1	Rep 2	Rep 3	Average
RMOH						
		1	880	901	1002	951.5
		2	1089	1432	1546	1489
	ay	3	1233	2411	1630	2021
	Δ	5	1146	2673	2446	2560
		10	761	1106	1656	1381
		15	1022	495	1000	747.5
RMDI						
		1	-	1079	1090	1085
		2	899	1270	1550	1410
	ay	3	997	1200	1270	1235
	ä	5	1120	1416	1340	1378
		10	924	687	1310	999
		15	985	527	1330	929
SWOH						
		1	827	875	866	871
		2	841	1140	1420	1280
	ay	3	1050	1890	1660	1775
	ö	5	1230	763	2280	1522
		10	1120	1190	1560	1375
		15	1010	640	1780	1210
SWDI						
		1	1100	983	943	963
		2	1030	1350	1340	1345
	λe	3	979	1110	1010	1060
	õ	5	1070	1497	1180	1339
l		10	871	642	1120	881
		15	1010	578	1130	906
					Median	1258
					Average	1279
SWOF	l=Slio	ck-wall/Over	rhead, S	WDI= Slick	-wall/Drip	
RMOH	=Ro	otmaker/Ov	verhead,	RMDI= Roo	otmaker/Dri	р

APPENDIX E

Ро	rosity of Bioretention	Cell Media	Volume displace	ment			
% San	d Media (mL)	Water (mL)	Change in V (m	ıl) %	Voids		
100	200	200	13	30	0.35		
90	200	200	127	.5	0.36		
80	200	200	12	26	0.37		
60	200	200	1:	17	0.42		
			Average porosity	porosity 37.4			
	Pore Volume - ba	sed on poros	ity of BRC Media				
Column dim	ensions		Pore Volumes	L			
h (cm)	15.42		1-2	0-500			
d (cm)	7.62		3-5	750-12	50		
v (cm³)	703.21		10-11	2500-3000			
porosity (%)	37.4%		29-30	7250-7	750		
			59-60	14750-	15250		
1 pore volun	ne 263	ml					
			60		15250		
		Est. gallons	of leachate neede	d	4.0		
BRC Colur	nn Leaching Rates	Hydr	Hydraulic conductivity through BRC col				
Time (min) p	er 2 pore vol (500 ml)	K=QL/	Aht Q	(cm^3)			
6 sand	6		L	L (cm)			
6 sand	6.5		A	(cm^2)			
% sand	5.5		h - h	ead (cm)			
sand	7.5						
sand	7						
sand	7	Media	type Avg	. t (min)	K (cm/r		
		1000/		6.0			

Bioretention Cell Media Column Tests

ŀ										
	BRC Column Leaching Rates		Hydraulic conductivity through BRC column							
-	Time (min) per 2 pore vol (500 ml)	K=QL/Aht	Q (cm^3)	500						
100% s	and 6			L (cm)	15.24					
100% s	and 6.5			A (cm^2)	45.6					
100% s	and 5.5			h - head (cm)	2.54					
90% sa	nd 7.5									
90% sa	nd 7									
90% sa	nd 7		Media type	Avg. t (min)	K (cm/min)					
80% sa	nd 8.25		100% sand	6.0	10.96					
80% sa	nd 9		90% sand	7.2	9.18					
80% sa	nd 8		80% sand	8.4	7.82					
60% sa	nd 12		60% sand	14.3	4.59					
60% sa	nd 15									
60% sa	nd 16									

BIORETENTION CELL MEDIA COLUMN TEST INSECTICIDE CONCENTRATION DATA											
Pore vol	ID	Bif	Fip	Pore vol	ID	Bif	Fip	Pore vol	ID	Bif	Fip
	•	(ng	;/L)		•	(ng	;/L)			(ng	/L)
100% Sand			90% Sand/10% Compost				100% Sand				
1-2	D1	10.4	67.4	1-2	D25	76.5	130.1	1-2	D49	34.1	227.2
3-5	D2	7.7	120.9	3-5	D26	106.7	262.9	3-5	D50	30.6	268.2
10-11	D3	15.0	135.4	10-11	D27	115.7	232.1	10-11	D51	28.7	262.2
29-30	D4	27.2	160.1	29-30	D28	123.3	241.6	29-30	D52	24.1	245.4
59-60	D5	54.6	224.1	59-60	D29	149.3	303.0	59-60	D53	26.3	302.0
Influent	D6	132.4	206.2	Influent	D30	231.5	281.1	Influent	D54	132.6	333.6
10	00% S	and		90% Sand/10% Compost				80% Sand/20% Compost			
1-2	D7	70.0	224.3	1-2	D31	76.3	122.3	1-2	D55	7.6	18.1
3-5	D8	47.0	242.7	3-5	D32	81.4	245.2	3-5	D56	11.8	108.4
10-11	D9	42.6	240.8	10-11	D33	115.9	351.5	10-11	D57	11.4	170.2
29-30	D10	54.7	240.8	29-30	D34	168.3	354.2	29-30	D58	11.2	197.7
59-60	D11	58.1	281.2	59-60	D35	157.5	293.0	59-60	D59	9.3	186.4
Influent	D12	185.1	303.2	Influent	D36	335.1	370.2	Influent	D60	74.7	246.0
60% San	d/409	% Com	post	90% Sand/10% Compost				80% Sand/20% Compost			
1-2	D13	16.5	6.0	1-2	D37	32.2	50.4	1-2	D61	12.8	40.6
3-5	D14	21.5	28.0	3-5	D38	47.6	153.4	3-5	D62	14.0	112.2
10-11	D15	22.9	84.8	10-11	D39	69.5	209.8	10-11	D63	21.0	225.4
29-30	D16	22.0	105.4	29-30	D40	67.0	218.1	29-30	D64	18.2	230.2
59-60	D17	20.9	118.6	59-60	D41	62.5	197.4	59-60	D65	25.6	274.3
Influent	D18	189.5	312.2	Influent	D42	153.4	231.9	Influent	D66	94.2	311.8
60% Sand/40% Compost				60% Sand/40% Compost				80% Sand/20% Compost			
1-2	D19	36.6	44.3	1-2	D43	9.6	1.9	1-2	D67	9.8	22.8
3-5	D20	55.5	83.2	3-5	D44	10.4	12.3	3-5	D68	28.0	179.6
10-11	D21	39.5	136.1	10-11	D45	10.7	42.1	10-11	D69	18.7	102.1
29-30	D22	49.0	155.6	29-30	D46	12.5	66.8	29-30	D70	33.0	212.2
59-60	D23	42.4	228.0	59-60	D47	11.4	98.4	59-60	D71	38.7	246.7
Influent	D24	178.1	336.8	Influent	D48	79.7	188.8	Influent	D72	119.8	373.7
								Blnk/800	D73	668.2	836.0

BIORETENTION CELL MEDIA COLUMN TEST PERCENT (%) REDUCTION											
Pore vol	ID	Bif	Fip	Pore vol	ID	Bif	Fip	Pore vol	ID	Bif	Fip
(ng/L)		(ng/L)			(ng/L)						
100% Sand				90% Sand/10% Compost			100% Sand				
1-2	D1	92%	67%	1-2	D25	67%	54%	1-2	D49	74%	32%
3-5	D2	94%	41%	3-5	D26	54%	6%	3-5	D50	77%	20%
10-11	D3	89%	34%	10-11	D27	50%	17%	10-11	D51	78%	21%
29-30	D4	79%	22%	29-30	D28	47%	14%	29-30	D52	82%	26%
59-60	D5	59%	-9%	59-60	D29	36%	-8%	59-60	D53	80%	9%
100% Sand				90% Sand	I /10 %	Com	post	80% Sand/20% Compost			
1-2	D7	62%	26%	1-2	D31	77%	67%	1-2	D55	90%	93%
3-5	D8	75%	20%	3-5	D32	76%	34%	3-5	D56	84%	56%
10-11	D9	77%	21%	10-11	D33	65%	5%	10-11	D57	85%	31%
29-30	D10	70%	21%	29-30	D34	50%	4%	29-30	D58	85%	20%
59-60	D11	69%	7%	59-60	D35	53%	21%	59-60	D59	88%	24%
60% Sand/40% Compost			post	90% Sand	l /10 %	Com	post	80% Sar	nd/209	% Comp	ost
1-2	D13	91%	98%	1-2	D37	79%	78%	1-2	D61	86%	87%
3-5	D14	89%	91%	3-5	D38	69%	34%	3-5	D62	85%	64%
10-11	D15	88%	73%	10-11	D39	55%	10%	10-11	D63	78%	28%
29-30	D16	88%	66%	29-30	D40	56%	6%	29-30	D64	81%	26%
59-60	D17	89%	62%	59-60	D41	59%	15%	59-60	D65	73%	12%
60% Sand/40% Compost				60% Sand/40% Compost			80% Sand/20% Compost				
1-2	D19	79%	87%	1-2	D43	88%	99%	1-2	D67	92%	94%
3-5	D20	69%	75%	3-5	D44	87%	94%	3-5	D68	77%	52%
10-11	D21	78%	60%	10-11	D45	87%	78%	10-11	D69	84%	73%
29-30	D22	73%	54%	29-30	D46	84%	65%	29-30	D70	72%	43%
59-60	D23	76%	32%	59-60	D47	86%	48%	59-60	D71	68%	34%

APPENDIX F





Potting Media Column Leaching Setup



Pot Leaching Setup



Runoff Simulation Setup



Bioretention Cell Media Column Test Setup

VITA

GRANT MATTHEW GRAVES

Candidate for the Degree of

Master of Science

Thesis: INVESTIGATION OF INSECTICIDE LEACHING FROM POTTED NURSERY STOCK AND AQUATIC HEALTH BENEFITS OF BIORETENTION CELLS RECEIVING NURSERY RUNOFF

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