DEVELOPMENT AND EVALUATION OF SELECTED LOW IMPACT DEVELOPMENT PRACTICES FOR RUNOFF MANAGEMENT AT THE NURSERY AND WATERSHED SCALES

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Abstract: Agricultural and urban runoff can threaten water resources. Land disturbances related to urbanization and agriculture can change hydrologic characteristics such as volume of runoff and peak flow. In addition, activities related to urbanization and agriculture can increase pollutants such as pesticides and nutrients present in runoff. The goal of this research was to evaluate and develop selected low impact development practices for management of runoff in two different settings, plant nurseries and urban areas. The specific objectives were: (1) Evaluate pesticide, nutrient, and sediment removal performance of two different types of constructed wetlands (one subsurface-flow and one free-surface) at two nurseries in Oklahoma; (2) Examine the effects of saturation conditions and irrigation patterns on pesticide removal using a lab-scale column study; and, (3) Develop a simple tool that enables practitioners with limited technical expertise to quickly and easily determine optimal combinations of LID practices that optimizes runoff reduction and cost. The pollutant removal performance evaluation of the two constructed wetlands demonstrated that both systems effectively reduced nutrients in runoff, but pesticide reduction was variable. The subsurface-flow constructed wetland significantly reduced most of the commonly seen pesticides however, pesticide removal was variable in the free-surface constructed wetland and no pesticide compound exhibited mass reduction that was statistically significant. While the lab-scale column study was exploratory in nature, results indicated higher pesticide removal under certain hydrologic patterns. There was a general trend indicating that holding water within the column system for a longer time increased removal efficiency. There was no indication that saturation conditions (fully saturated vs variably saturated) impacted pesticide removal. Finally, the optimization procedure addressed a need for developers and smaller municipalities that want to implement low impact development practices to reduce runoff while minimizing cost. The procedure used available software that did not require significant expertise in programming or hydrology, Microsoft Excel and the EPA Stormwater Calculator. Users could determine combinations that met different hydrologic or cost goals by modifying the objective function and/or constraints. Overall, meeting each research objective contributed to the overarching goal of reducing the impact of agricultural and urban runoff on water resources.

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FOREWORD

The work presented in this dissertation evaluates and develops tools to address runoff issues in the settings of nursery and greenhouse production and urban areas. The objectives of the dissertation were:

1. Evaluate pesticide, nutrient, and sediment removal performance of a two different types of constructed wetlands at two nurseries in Oklahoma.
2. Use lab-scale column studies to examine the effects of saturation conditions and irrigation patterns on pesticide removal.
3. Develop a simple tool that enables practitioners with limited technical expertise to quickly and easily determine optimal combinations of LID type and amount that concurrently minimize cost and maximize volume reduction.

The dissertation was organized in the modified three-paper format. Chapter one is a review of available literature related to pesticide and nutrient transport and fate and constructed wetlands. Both pesticide transport and fate and constructed wetlands are broad topics, so general detail is given for each overall topic and increased detail is given for aspects related specifically to this project. Chapter two details the purpose, methods, and results and conclusions of the field studies used to meet the overall objectives. Two types of constructed wetlands were built at two different nurseries in Oklahoma and were monitored to evaluate pesticide and nutrient removal. Chapter three explains the purpose, methods, and results and conclusions of the lab-scale column experiments used to meet the overall project objectives. Results from the column study investigated the effects of saturation conditions and irrigation management on pesticide removal in a porous media. Chapters two and three will be submitted to Journal of Environmental Quality for publication. Chapter four deals with the development of a tool to determine combinations of types of low impact development that optimize runoff reduction and cost. Chapter four will be submitted for publication in Journal of Water Resources Planning and Management. Chapter five outlines conclusions drawn from the field and lab studies and makes recommendations for future work. A comparison is drawn between runoff in nursery settings and urban areas and the challenges faced in each along with recommendations for practitioners.

CHAPTER I

REVIEW OF LITERATURE

Runoff from urban and agricultural sources is a threat to water resources through increased pollutant loading and altered hydrologic cycle. This review of literature provides background and context for how this dissertation addressed issues related to urban and agricultural runoff. The first two subsections (1.1 through 1.2.3.4) addresses topics related to the first two papers. Topics include pesticide and nutrient fate and transport as well as risks these pollutants pose to water resources in the first subsection. The second subsection includes background on constructed wetlands, also addressed in the first two papers. Background and context for the third paper is addressed in the third subsection (1.3) and includes information about modeling of low impact development for volume reduction and cost optimization.

1.1 Pesticide Risk to Aquatic Resources

The characteristics of pesticide transport and fate have been studied for many years (Jury et al., 1983, Elabd et al., 1986, van Genuchten and Wagenet, 1989). Although understanding can lead to better management practices, knowledge of how a contaminant moves does not in and of itself reduce its environmental impact. In both urban and agricultural watersheds, stormwater runoff can be a vector for pesticide transport to rivers and lakes. Residential lawns have been identified as a significant source of pesticides; for example, fipronil was present in California waterways at levels that are toxic to aquatic macroinvertebrates (Gan et al., 2012). Sediment in urban streams in Denton, Texas, has been shown to contain many current-use pesticides (Hintzen et al., 2009). In that study, bifenthrin was detected in 94% of the sediment samples and bifenthrin concentrations exceeded the published LC_{50} value for *H. azteca* in almost 50% of the collected samples.

A study of pesticide concentrations in urban streams across eight US states found insecticides and herbicides present in all streams with insecticide concentrations often exceeding the standard for aquatic life (Hoffman et al., 2000). In addition, a German study found pesticides at toxic levels in streams collecting agricultural runoff even at sites that had buffer areas along the stream (Bereswill et al., 2013). Pesticides vary in toxicity to aquatic communities, so the mere presence of a pesticide in a water body does not necessarily indicate a high threat. Aquatic organisms that have similar receptors as a pesticide’s target organism are typically most at risk, however, it is difficult to understand the full effect a pesticide has on an ecosystem (Van Wijngaarden et al., 2005). Even if pesticide exposure does not have an immediate lethal effect, it can result in behavioral changes that affect long-term population viability. While certain pesticides may only affect one or two species of aquatic organisms, these effects may be felt throughout the food chain, decreasing species richness (Relyea, 2005).

1.1.1 Pesticide Transport and Fate

The physiochemical characteristics of each pesticide play a part in determining its transport and fate. In agricultural runoff or within a constructed wetland, pesticides will either be in solution or bound to sediment. The pesticide soil/ solution distribution coefficient (K_d) is commonly used to predict sorption of a pesticide to soil (Weber et al., 2004). K_d is a ratio of pesticide sorbed to pesticide in solution. Values are determined using batch equilibrium experiments where the concentration in solution is measured over time and K_d is determined when the concentration reaches an equilibrium (USEPA, 2008). Most pesticides preferentially sorb to organic content or clay particles, so soil characteristics in addition to pesticide chemical characteristics also affect pesticide transport (Weber et al., 2004). Since organic content affects sorption, K_{oc} value is used to account for organic content present in the soil (Equation 1.1).

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{Equation 1.1}$$

In this equation, K_{oc} is the soil organic carbon/water partitioning coefficient, f_{oc} is the fraction of organic carbon in the soil and K_d is the soil/solution distribution coefficient. While organic matter has generally been presumed to be the dominant sorption source for pesticides, Sheng et al. (2001) found expandable soil clays to retain certain pesticides as effectively as organic matter. Organic matter contains both polar and non-polar functional groups able to complex a range of compounds. Water solubility, the degree to which a compound dissolves in water, is another chemical characteristic that affects pesticide transport and fate in the environment. Since water is a polar molecule, polar compounds are generally more likely to dissolve in water while non-polar compounds are generally less likely to dissolve in water. Correspondingly, compounds that have a low water solubility are generally more likely to sorb to particles. For example, bifenthrin is a non-polar compound and has a water solubility of 0.1 mg/L and a K_{oc} that ranges from

1.31×10^5 to 3.02×10^5, or a relatively low water solubility and relatively high K_{oc} (Fecko, 1999). Carbaryl is made up of two benzene rings and an attached methyl group so exhibits properties of polar chemical structure. It has a relatively high water solubility of 110 mg/L and a relatively low K_{oc}, around 160 to 450 (USDA ARS, 2016). These properties affect the transport and fate of chemical compounds.

1.1.2 Pesticide Degradation

In the soil environment, pesticide degradation primarily occurs by chemical or biological transformation. Microbial degradation is a primary pathway for degradation of most pesticides, however, in some situations abiotic transformation is equally important. Often, it is a combination of both chemical and biological factors that influence the degradation of pesticides in water and soil environments. Temperature and moisture affect both microbial activity and abiotic transformation, which affects rate of pesticide degradation. During abiotic transformation of pesticides in the soil environment, processes such as hydrolysis and reduction oxidation reactions can occur simultaneously. Each process can be affected differently by temperature and soil moisture thus making it difficult to predict the effects of these factors (Wolfe and Macalady, 1992). Temperature effects are important to consider since soil temperature will vary spatially (over depth and area) and temporally (diurnal and seasonal). The effect of soil moisture has implications on persistence in ground water and controlled drainage situations as well as the effectiveness of pesticide transformation in treatment structures such as constructed wetlands and bioretention.

1.1.3 Effects of Soil Moisture and Temperature on Pesticide Transformation

In general, soil moisture can affect degradation directly (chemical processes) and indirectly through effects to microbial activity. Nair and Schnoor (1994) postulated that microbial activity was hindered at very low and very high soil water contents. Their reasoning was that some soil moisture is necessary for microbial activity, but saturation may result in a lack of oxygen necessary for some microbial communities. DeLaune et al. (1997) validated this conclusion showing that complete atrazine degradation in aerobic conditions was accomplished after 14 days while atrazine persisted in anaerobic conditions after 99 days. However, some studies found atrazine degradation is equal or even enhanced in saturated, anaerobic conditions as compared to unsaturated, aerobic conditions (Seybold et al., 2001, Chung et al., 1995, Ro and Chung, 1995). Veeh et al. (1996) found that 2,4-D degradation rates decreased when soil temperature decreased from 24°C to 10°C. Although this study did not measure soil moisture, the authors indicated that there would likely be interaction between soil moisture, temperature, and microbial degradation. Alletto et al. (2006) examined effects of two different water contents and two different temperatures and found that microbial mineralization of isoproturon was minimal when water content was reduced to 50% of the soil's water holding capacity (WHC). In all cases, half-life increased when temperature went from 22°C to 10°C and when water content was reduced from 90% WHC to 50% WHC. It was concluded that soil water content had the greater effect due to its influence on microbial activity, however was more of a limiting factor than an expediting factor. This limiting factor is seen again in situations where half-life is highest at very low or very high temperatures or soil moisture conditions (Shymko et al., 2011). Pesticide persistence predictions on a large scale, such as in a management model, can be off by orders of magnitude if temperature is unaccounted for (Wu and Nofziger, 1999). Due to this error, equations have been developed to adjust pesticide degradation estimations based on temperature and soil moisture.

1.1.3.1 Degradation Rate Adjustments for Temperature and Soil Moisture

It is well established that soil moisture and temperature affect degradation of pesticides in soils and to accurately predict degradation, models must account for these effects. Pesticide degradation is commonly predicted using first order kinetics (Equation 1),

$$C(t) = C_0 e^{-kt}, \qquad \text{Equation 1}$$

where C(t) is concentration over time, C_0 is the initial concentration, k is a rate constant, and t is time (Jebellie et al., 1999). To account for the effects of temperature, typically the rate constant is adjusted. Three methods are used to account for the effect of temperature on pesticide degradation: the Arrhenius equation, equations based on the Q_{10} coefficient, and the O'Neill equation (Beulke et al., 2005, Soulas and Lagacherie, 2001). The Arrhenius equation is most widely used (Alletto et al., 2006, Cupples et al., 2000, Gan et al., 1999, Wu and Nofziger, 1999) and includes the "pesticide activation energy" (Equation 2),

$$lnK = -(E_a/RT) + lnA \qquad \text{Equation 2}$$

where K is the degradation rate constant, E_a is the pesticide activation energy, R is the universal gas constant, T is temperature, and A is an empirical constant.

The pesticide activation energy is determined experimentally for specific pesticides and system characteristics by regression of known terms taken in a controlled setting and has been determined for around 150 different herbicides (Soulas and Lagacherie, 2001). Activation energy can be affected by catalysts within the soil matrix which can introduce error into pesticide degradation and transport prediction. Wu and Nofziger (1999) found that only a 5% difference in activation energy would lead to a 38% error in pesticide transport prediction. As with other parameters, activation energy must be considered in context.

The Q_{10} coefficient is based on the principle that microbial activity increases every 10°C but is most accurate at temperatures from 5°C to 30°C (Beulke et al., 2005, Soulas and Lagacherie, 2001). Equations based on the Q_{10} coefficient again serve to calibrate the rate constant used in Equation 1. Q_{10} is determined by using data collected in a controlled setting. Results of Q_{10} based equations are similar in shape to the Arrhenius equation. The O'Neill equation was used the least in the reviewed papers, but the rationale behind the O'Neill equation was alluded to in several results and discussion sections. The principle behind the O'Neill equation is since degradation is microbial, it will follow a bell curve with optimal degradation at middle temperatures and diminishing degradation at higher and lower temperatures (Beulke et al., 2005, Soulas and Lagacherie, 2001).

The effect of soil moisture is most often estimated by an empirical equation that directly relates half-life and soil moisture content (Gan et al., 1999, Walker and Zimdahl, 1981) (Equation 3),

$$H = AM^{-B} \qquad \text{Equation 3}$$

where H is the pesticide half-life, M is moisture content, and A and B are constants. Beulke et al. (2005) includes both soil moisture content and temperature into an equation that adjusts the degradation rate constant.

Equations have been developed to account for the effects of temperature and soil moisture on pesticide degradation, however, they are pesticide specific and must be used in context. Adjustment equations greatly increase prediction accuracy, however, they must be used within the prescribed range of conditions. Degradation is complex and depends on soil conditions and chemical characteristics.

1.1.3.2 Nutrient Risk to Aquatic Resources

Nitrogen and phosphorus have long been identified as a risk to aquatic resources (Turner and Rabalais, 1991, Sims et al., 1998, Carpenter et al., 1998). Since nitrogen and phosphorus are limiting nutrients for algae, aquatic ecosystems experience rapid algal growth when these nutrients are introduced (Schindler, 1977). In general, freshwater environments are phosphorus limited and marine environments are nitrogen limited. Increased algal growth can be detrimental to and permanently alter aquatic ecosystems (Anderson et al., 2002, Smith 2003).

1.1.4 Transport and Fate of Nutrients in Aquatic Ecosystems

Nitrogen and phosphorus have different mechanisms that determine their transport and fate in the environment. The transformation of nitrogen in soil and aquatic environments is dependent on microbial activity, pH, and the amount of oxygen present. Nitrate is the most common form of nitrogen and is highly mobile. Denitrification is performed under low oxygen conditions by bacteria that transform nitrite and nitrate into gaseous species of nitrogen. Nitrogen is able to be transformed multiple times as it is transported through soil and aquatic environments and exists as solid, soluble, and gaseous phases. In addition, different phases and conditions make it more or less likely to be transformed leading to short transformation cycles up to transformation cycles that react on a scale of hundreds of years (Follett and Delgado 2002).

Environmental phosphorus exists primarily in the particulate phase (bound to a solid particle) instead of the soluble phase. Ortho-phosphate (PO_4^{3-}) is an anion and readily binds with cations. Ortho-phosphate is also the most likely species to be bioavailable to planktonic algae and bacteria (Boström et al., 1988). While ortho-phosphate is of particular concern in runoff because of its bioavailability, the phosphorus cycle in an aquatic environment is dynamic and particulate phosphorus can be converted to bioavailable phosphorus over time (Correll, 1998). Similarly, in soils the transformation of phosphorus is dynamic and particulate phosphorus should not be considered removed from the system (Smeck, 1985).

1.2 The Use of Constructed Wetlands to Remove Pesticides and Nutrients from Agricultural Runoff

There are two general design distinctions of constructed wetlands: free surface (also called free water surface or surface flow) and subsurface flow. Subsurface flow constructed wetlands (SFCWs) were originally used to provide secondary treatment to municipal wastewater and are still commonly used for that purpose. Since their introduction to water treatment, the SFCW concept has been applied in other settings including agriculture and container nurseries. SFCWs are designed to be predominantly saturated (to 0.1 m to 0.2 m below the surface) but not have ponded water for extended periods of time. Many studies exist on the performance and design of submerged flow constructed wetlands (Rousseau et al., 2004, Chazarenc et al., 2003), however, these primarily treat municipal wastewater and few attempt to characterize pesticide reduction. Free surface constructed wetlands differ in design from subsurface-flow constructed wetlands but share a similar history. Free surface constructed wetlands (FSCW) are designed to have ponded water. Some designs recommend having different water depths throughout the wetland to provide multiple habitats and thus promote biodiversity. FSCWs that are designed purely for treatment purposes may still have different water depths throughout to provide different treatment mechanisms.

The first research performed on engineered wetlands with plants to treat wastewater occurred in the 1950s (Vymazal 2011). Research of constructed wetland design and performance continued in the 1960s and 1970s by Spangler et al. (1976), Fetter et al. (1976), and others. As Vymazal (2011) indicates, research and adoption continued to grow globally but were still used mostly for municipal wastewater treatment through the late 1980s. However, during the 1980s, constructed wetlands expanded in scope to treat wastewater from different sources including agricultural runoff (Hammer 1992, Rodgers and Dunn 1992).

Research has been performed regarding pesticide removal by constructed wetlands from different sources of wastewater or runoff including agricultural runoff (Kohler et al., 2004, Blankenburg et al., 2006, Budd et al., 2009, Maillard et al., 2011, Agudelo et al., 2012). Only a few studies have been performed that look at pesticide removal by constructed wetlands specifically in nursery runoff. While contaminants of concern may be similar between nursery and other agriculture runoff, hydrology and hydraulic loading differs significantly due to frequent irrigation events. Irrigation creates daily runoff and above-ground pots lead to prolonged pollutant loading. In a review of pesticide removal by constructed wetland from agricultural runoff, Vymazal and Březinová (2015) identified only three studies that specifically used container nurseries (George et al., 2003, Runes et al., 2003, Stearman et al., 2003). Of the 47 studies identified by Vymazal and Březinová (2015), nine were mesocosm studies, six were microcosm or lab studies and only six used agricultural runoff. Removal rates between these studies varied.

George et al. (2003) and Stearman et al. (2003) both monitored the same 14 subsurface-flow constructed wetland cells that received runoff from a 465 m^2 container nursery plot. Simazine and metolachlor were applied prior to the pots being placed on the plot. The studies looked at effects of plant presence (bulrush), hydraulic loading, media depth and aspect ratio. Overall, hydraulic loading rate (and thus mass loading rate) and plant presence showed a statistically significant relationship to pesticide removal but media depth and aspect ratio did not. Mass removal rates for simazine ranged from 51% (high hydraulic loading and no plants) to 96% (low hydraulic loading and plants). For metolachlor, mass removal rates ranged from 34% (high hydraulic loading and no plants) to 96% (low hydraulic loading and plants present). Herbicide was applied once, before irrigation began, but then the pots were irrigated every 24 hours unless a rain event occurred. Samples were taken every 24 hours for the first 10 days and then every 48 to 72 hours until pesticide concentrations reached pre-application levels.

Runes et al. (2003) monitored atrazine removal of a surface flow constructed wetland receiving irrigation runoff from a 2.4 hectare container nursery plot. This study used five surface flow (free surface) constructed wetland cells arranged in series. While each cell was planted with a variety of wetland species, the predominant species was typha latipholia (cattail). Experiments were conducted over a 7-day period. Atrazine was added to inflow entering the first cell from irrigation runoff of the first irrigation event. During atrazine addition, samples were collected every hour and then every two hours after day five and every three hours for the remainder of the seven days. Irrigation intensity and frequency changed between events and experiments, so load reduction was analyzed against hydraulic loading rates. The study concluded that removal rates were only affected by intensity, duration, and frequency of runoff when these factors were high. Through the first five experiments, runoff characteristics varied, but treatment was not significantly affected. However, in the sixth experiment, “treatment was compromised” and runoff characteristics were higher than in the previous five experiments. Runes et al. (2003) identified sorption as the primary removal mechanism for atrazine.

By looking at published performance studies, some pesticide reduction trends emerge. It is understood that pesticide reduction occurs through sorption, sedimentation, and microbial breakdown. Studies indicate that soil organic matter and retention time affect pesticide removal, however many fundamental and applied questions still remain. Rodgers and Dunn (1992) undertook an extensive research effort to answer several foundational questions about pesticide removal by constructed wetlands. The research context of that project was areas where floodplain wetlands had been replaced by row crops. One study used a simulated runoff event on five of these wetland cells determined necessary wetland length for atrazine mitigation (Moore et al, 2000). These recommendations were made based on observed concentration reductions over time and distance. This study was performed in the context of introducing constructed wetlands as buffers between row cropping fields and receiving waters. Locke et al. (2011) found some reduction in concentration of atrazine and fluometuron in a free water surface constructed wetland. A simulated runoff event was used in this study and no runoff was received after the event. Concentrations were measured over time and maximum concentrations decreased between 58% and 89% for atrazine and fluometuron in two different cells. Sherrard et al. (2004) found rapid and high rates of removal for chlorpyrifos and chlorothalonil in constructed wetland mesocosms, but used one pulse of simulated stormwater runoff. These three studies used one simulated storm event with no additional inputs and measured concentrations over time. While the knowledge gained from these studies indicates the potential for pesticide removal by constructed wetlands, they were not dynamic with multiple event inflows and outflows. To better understand field performance, typical field hydrologic and hydraulic conditions must be considered.

1.2.1 Treatment Mechanisms of Constructed Wetlands

In both subsurface flow constructed wetlands and free surface constructed wetlands, contaminant removal mechanisms are physical, chemical, and biological in nature. Although removal mechanisms are known, since multiple processes occur simultaneously and interact with each other, CWs continue to be regarded as somewhat of a black box with regard to effectiveness of contaminant removal (Garcia et al, 2010). Removal mechanisms also differ depending on what contaminant is being considered. Since this project focuses primarily on pesticides and secondarily on nutrients in nursery runoff, the removal mechanisms for these contaminants will be considered. Pollutant removal can be separated into two end-points, capture and transformation. Imfeld et al. (2009)

characterizes these endpoints as “non-destructive” and “destructive”. Capture refers to the removal of the pollutant from the runoff that has entered the system and is governed by physical or chemical processes: settling, physical capture, and sorption. Note that some pollutants can be temporarily removed from the water column via sorption and settling for example, but can be reentrained and present in the system effluent. Under uniform ideal flow conditions, settling and physical capture are straight forward to predict, however under field conditions a combination of preferential flow and dead zones often exists making prediction more difficult. Transformation refers to the breakdown or change of the particular contaminant via a chemical or biological process. Transformation is typically more difficult to predict since it is affected by many factors including pH, temperature, microbial community, presence of oxygen, and redox potential.

1.2.2 Pesticide Removal

Pesticides cover a large range of physiochemical characteristics. The chemical makeup of the pesticide itself has a significant effect on how effectively it can be removed. The primary removal mechanism for hydrophobic pesticides is adsorption to soil particles, often clay particles or organic matter (Cheng 1990). When a pesticide is sorbed to a soil particle, its removal is often governed by physical mechanisms: settling and physical trapping. It should be noted that if a pesticide is sorbed to a clay particle it is still subject to movement even in a porous media (McDowell-Boyer et al 1986). Physical removal of particles is determined by particle size, flow velocity, porosity, and tortuosity. Even in seemingly straight-forward situations such as steady, constant surface flow, inconsistencies exist in velocities and consequently hydraulic retention time within a wetland (Chazarenc et al 2003). Since a SFCW forces flow through a porous media, fluid contact with soil particles is enhanced. Sorption to all particles is not equal. Many pyrethroids (including bifenthrin) have a high affinity to sorb to particles, and preferentially sorb to clay particles and to partially decayed plant material (Budd et al., 2011). Thus, systems that effectively reduce total suspended solids don’t necessarily reduce pesticide loading since clay particles are difficult to remove solely through settling.

It is generally agreed that wetland plants, or macrophytes, play a role in increasing effectiveness of pesticide removal in constructed wetlands. Vegetation plays multiple roles in constructed wetland function. Physically, vegetation modifies hydraulic characteristics, causes trapping, mixing, reduces resuspension and can aid in hyporheic exchange. Plants also aid in the formation of microbial communities through the transfer of oxygen to root zones. Plants can take up and accumulate pesticides. There is still disagreement as to how significant each pathway is in overall removal and degradation mechanisms, but it is generally agreed that wetland vegetation plays a part in effective pesticide removal by constructed wetlands.

1.2.3 Constructed Wetland Design

Since little was known about effects of different design components on effect of pollutant removal, early design of constructed wetlands was not consistent (Reed and Brown 1992). Some key design considerations are retention time, length to width ratio, planting type, and media type. Much of the design guidance has been made for municipal wastewater and considers pollutants such as biochemical oxygen demand (BOD), total suspended solids (TSS), pathogens, nitrogen, and phosphorus. This design guidance is pertinent to constructed wetlands in agricultural settings and similar considerations are made. Also, much of the design guidance is derived from established practice while rigorous comparison of design characteristics is ongoing.

1.2.3.1 Retention time

Retention time (also called residence time or hydraulic residence time) has a significant effect on pollutant removal. Retention time affects the capacity of the constructed wetland to settle out sediment as well as affect the contact time that pollutants have with mineral and organic matter. Retention time is one of the controlling factors for treatment efficiency (Garcia et al., 2005). Theoretical retention time is affected by flow rate and wetland dimensions in that flow rate divided by cross sectional area equals velocity and velocity multiplied by hydraulic length equals retention time. Actual retention time is reduced by preferential flow paths from erosion and channeling (Budd et al., 2009). Published retention times vary from 1 hour to almost 3 weeks (O’Geen et al., 2010). Budd et al., (2009) found that pyrethroids were significantly reduced (64%-94%) with a retention time of 18 hours. While retention time affects pollutant removal, O’Geen et al., (2010) recommends maximizing retention time as much as possible but indicates that statistical comparison between studies is difficult due to inconsistencies in reporting. In practice, retention time may be limited by land available and flow rate.

1.2.3.2 Length to width ratio

Length to width ratio (also called aspect ratio) affects hydraulic retention time because it can influence mixing and flow distribution. Theoretically, an equal hydraulic retention time could be achieved with many different length to width ratios since both length and width are accounted for in theoretical hydraulic retention time. In practice, as width increases, it is more difficult to evenly distribute inflow leading to increased short circuiting (Reed and Brown 1992, Vymazal 2011). While length to width ratio is less significant that other design considerations (Garcia et al., 2005), increased length to width ratio does increase retention time (Garcia et al., 2004). If length to width ratio is low, care must be taken to ensure even distribution of inflow.

1.2.3.3 Media

Media composition and dimension are important design considerations. Media type can include sand, gravel, organic matter, soil, and different amendments to target specific pollutants. Media affects a range of physical, chemical and biological performance characteristics of the constructed wetland including infiltration rate, long-term performance related to clogging, trapping efficiency, and sorption capacity. In addition, since most chemical reactions occur on the surface of particles, particle surface area to volume ratio is important. In a comparison with different sizes of gravel, smaller sized gravel showed higher pollutant removals (Garcia et al., 2005). Media type plays a significant role particularly with pollutants that are removed primarily through sorption processes such as phosphorus (Brix et al., 2001).

1.2.3.4 Constructed Wetland Vegetation

Plants are agreed to aid in pollutant removal in constructed wetlands although the extent of their role is uncertain (Stottmeister et al., 2003, Brisson and Chazarenc, 2008). Plants or macrophytes affect physical and biochemical conditions above and below the media surface. Physically, plants help stabilize the surface preventing erosion and the development of preferential flow paths (Budd et al., 2009) and helps prevent clogging on the media surface (Brix, 1994). Biochemically, plants aid in microbial community establishment and growth by providing surface area and oxygen transfer from the surface to the subsurface (Brix, 1994, Stottmeister et al., 2004, Brisson and Chazarenc, 2009). Plants can also play a role in pollutant removal through uptake (Brix, 1994, Tanner, 1996, Stottmeister et al., 2004, Liu et al., 2007, Gottschall et al., 2007) however effects of plant diversity and type are still being investigated.

1.3 Modeling Tools for Optimizing Low Impact Development

Optimization of type, size, and placement of LID has been researched and applied in various settings. The majority of these projects use models that require a certain level of expertise to operate. The United States Environmental Protection Agency (USEPA) has developed multiple modeling applications to aid in stormwater management design and LID BMP implementation including the Storm Water Management Model (SWMM), System for Urban Stormwater Treatment and Analysis Integration (SUSTAIN), and Opti-Tool for Stormwater and Nutrient Management. SWMM is one of the most popular models used for urban stormwater runoff (Tobio et al., 2015, Jayasooriya and Ng, 2014, Joksimovic and Alam, 2014, Krebs et al., 2012, Jia et al., 2012). A common modeling application is to compare pollutant reduction or volume reduction for different scenarios. Joksimovic and Alam (2014) used SWMM to model 18 different combinations of LID for runoff-volume reduction and then determined cost per m^3 of volume reduction. Zhang et al. (2013) also combined SWMM and a genetic algorithm to determine optimal amount and location of pervious pavement, green roof, and bioretention. The model optimized for cost and volume reduction and included a requirement that designs must also be beneath a certain peak flow threshold. The model optimization resulted in 37 designs that formed a pareto curve of near optimal solutions. While these are very useful comparison of different LID combinations for cost and volume reduction, the application of these methods may not be attainable by some practitioners since the methods used require an advanced level of expertise.

Another modeling platform used to design and optimize stormwater runoff management is SUSTAIN. SUSTAIN optimizes cost, volume reduction, and pollutant reduction by varying LID type, size, and location. SUSTAIN uses SWMM, ArcGIS (Geographical Information System), and sediment transport processes in the Hydrologic Simulation Program – Fortran (HSPF). ArcGIS (Esri, Redlands, California) incorporates layers such as soil type, slope, and land use into the design process. HSPF (US Geological Survey, Reston, VA) is used to model sediment transport and sediment loading for the design. Lee et al. (2012) used SUSTAIN to determine two groups of cost-effective solutions for annual flow volume reduction and annual TSS load reduction. Two LID types, porous pavement and bioretention, were modeled. Certain design parameters for bioretention and porous pavement were held constant: width, ponding depth, soil media depth, and gravel layer depth for bioretention and width, pavement depth, and gravel layer depth for porous pavement. Porous pavement was applied to sidewalks and bioretention to right of way areas. Finally, length of sidewalk or right of way was varied to determine optimal design. Chen et al. (2014) used SUSTAIN to determine pollutant reduction in a large watershed in Taiwan by incorporating four combinations of bioretention ponds, pervious pavement, and grass swales. Since cost data was not available for Taiwan, this design was not optimized for cost.

The Stormwater Management Optimization Tool (Opti-Tool) is a simpler spreadsheet-based tool that enables users to determine combinations of LID that meet pollutant and volume reduction goals while minimizing cost (USEPA, 2014). The tool uses external algorithms from SUSTAIN and is calibrated for EPA Region 1, the north eastern United States. While the tool can be used in areas outside of EPA Region 1, it is recommended for other areas to use SWMM to determine runoff from each hydrologic response unit. The tool produces a pareto curve between pollutant removal and cost that shows all possible results.

While stormwater management design and optimization techniques and tools exist, these tools require an advanced level of expertise and computing resources. SWMM and SUSTAIN are free for download, but SUSTAIN works on an ArcGIS platform which is not free. Opti-Tool is available to anyone with Microsoft Excel and was built with auser-friendly spreadsheet based interface. While Opti-Tool can be used throughout the US, if the watershed is outside EPA Region 1, users must determine local runoff values using SWMM. Advances have been made for urban planners to design and implement LID in a cost-effective manner, but smaller organizations or municipalities lack the expertise or financial resources to utilize available tools.

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CHAPTER II

EVALUATING PESTICIDE AND NUTRIENT REMOVAL FROM NURSERY AND GREENHOUSE RUNOFF USING CONSTRUCTED WETLANDS

Abstract: Pesticides and nutrients in nursery runoff pose a potential threat to aquatic ecosystems. Constructed wetlands possess mechanisms for contaminant removal, however limited research has been performed regarding the effectiveness of pesticide removal by constructed wetlands from nursery runoff. This study monitored a subsurface-flow constructed wetland (SFCW) and a free-surface constructed wetland (FSCW) at two different nurseries. Samples were analyzed for nutrients and 16 current-use pesticides. The SFCW demonstrated statistically significant reduction for the majority of commonly seen pesticides and nutrients. The FSCW exhibited statistically significant reduction for non-pesticide analytes. However, perhaps partially due to a limited sample size, the FSCW did not demonstrate significant reduction for any of the pesticide analytes. Overall, the study documented that the constructed wetlands analyzed were an effective management tool for nursery and greenhouse runoff, however pesticide removal performance was variable.

2.1 Introduction

Pesticides and nutrients present in nursery runoff pose a potential threat to water resources. The combination of frequent irrigation, absence of vegetation, and application of a variety of pesticides and fertilizers creates a scenario conducive to pesticide and nutrient loading in receiving water bodies (Briggs et al., 1998). Pesticide concentrations in pot leachate can be toxic to aquatic organisms (Graves et al., 2014). Wilson et al., 2010 found that 29% of chlorothalonil application in a nursery setting was deposited on the ground surface instead of in pots which led to concentrations up to 500 μg/L in runoff, a level that is toxic to aquatic microorganisms (for example 96-hour LC_{50} for adult grass shrimp was 150 μgL^{-1} according to Key et al., 2003). Nutrients contribute to algal blooms and are an on-going challenge in both agricultural and urban runoff (Anderson et al., 2002, Smith, 2003). Constructed wetlands are a potential tool to remove pesticides and nutrients from runoff, reducing the threat to aquatic ecosystems. This study was undertaken to provide evidence for constructed wetland performance for pesticide and nutrient removal from nursery runoff. During this study, two constructed wetlands, one free-surface constructed wetland (FSCW) and one subsurface-flow constructed wetland (SFCW) were built and subsequently monitored.

The greenhouse and nursery industry has a significant economic impact in Oklahoma and throughout the United States. In the early 2010s, the green industry employed over 2 million individuals in the US (Hodges et al., 2015). In addition, the industry had $136 billion of direct economic output in the US (Hodges et al., 2015). Nurseries can have a negative environmental impact as well. To reduce economic losses due to weed contamination as well as insect and disease pressure, the use of pesticide is commonplace at nurseries throughout the US. Weed management in a container nursery often involves removing as much vegetation from the landscape as possible since foreign vegetation can introduce unwanted weeds into containers, hindering plant growth and making pots less marketable (Case et al., 2005). Although nurseries use mechanical methods such as hand-weeding, herbicides are still used and are present in runoff. Nurseries are using integrated pest management (IPM) methods to control insects with reduced pesticide application. In these cases, pesticide use is decreased but often not completely eliminated (Hodges et al., 2008). Container nurseries are also required to take actions to prevent the movement of invasive insect species and noxious weeds (Newman, 2014). For example, to limit the spread of red invasive fire ants (RIFA), nurseries within the RIFA quarantine zone (much of the Southern US, including parts of Oklahoma) are required to incorporate insecticide into any container media being transported outside the quarantine zone. Insecticide is then potentially present in runoff at the destination nursery even if that nursery only minimally applies pesticide.

The reduction of pesticide loading from nursery runoff can be accomplished through a number of methods and sometimes a combination of these methods is needed (Newman, 2014):

1. Reduction of amount applied (hand-weeding, precision application, integrated pest management)
2. Reduction of concentration in runoff (improved timing of application and irrigation, reduced irrigation intensity and volume)

3. Reduced volume of runoff leaving site (more efficient irrigation methods such as drip irrigation, water reuse, disconnected impervious surfaces)
4. Treatment of runoff (constructed wetlands, vegetated filter strips, riparian buffer areas)

Even sustainably minded nurseries may have pesticide present in their runoff and so treatment of runoff is an important tool for sustainable nursery operation. Constructed wetlands are engineered systems with characteristics that are likely to provide effective treatment of nursery runoff.

There are two general design distinctions of constructed wetlands: free-surface (also called free water surface or surface flow) and subsurface-flow. Both subsurface-flow constructed wetlands (SFCWs) and free surface constructed wetlands (FSCWs) have been shown to improve water quality of runoff from different sources. Subsurface-flow constructed wetlands (SFCWs) are designed to be predominantly saturated (to 0.1 m to 0.2 m below the surface) but not have ponded water for extended periods of time. Free-surface constructed wetlands (FSCWs) differ in design from SFCWs but share a similar history. Free surface constructed wetlands (FSCW) are designed to have ponded water. The first research performed on constructed wetlands with plants to treat wastewater occurred in the early 1950s by Kathë Seidel in Germany (Vymazal, 2011). Research of constructed wetland design and performance continued in the 1960s and 1970s by Spangler et al. (1976), Fetter et al. (1976), and others. As Vymazal (2011) indicates, research and adoption continued to grow globally but constructed wetlands were still used mostly for municipal wastewater treatment through the late 1980s. However, during the 1980s, constructed wetlands expanded in scope to treat wastewater from different sources including agriculture (Hammer, 1992, Rodgers and Dunn, 1992). Research has been performed on pesticide and nutrient removal by constructed wetlands from different sources of wastewater or runoff including agricultural runoff (Kohler et al., 2004, Blankenburg et al., 2006, Budd et al., 2009, Maillard et al., 2011, Agudelo et al., 2012). While contaminants of concern may be similar between nursery and other agriculture runoff, hydrology and hydraulic loading differs significantly due to frequent irrigation events. Also, pot leachate presents potential for continued loading of pesticides and nutrients every irrigation and storm event (Graves et al., 2014). In a review of pesticide removal by constructed wetlands from agricultural runoff, Vymazal and Březinová (2015) identified only three that specifically used container nurseries (George et al., 2003, Runes et al., 2003, Stearman et al., 2003). Of the 47 constructed wetland studies identified by Vymazal and Březinová (2015), nine were mesocosm studies, six were microcosm or lab studies and only six used agricultural runoff. Removal rates between these studies varied. Another review (Li et al., 2014) indicated that similar mechanisms of sorption and microbial degradation were involved in removal of other organic compounds such as pharmaceuticals in wastewater. Ávila et al., 2015 indicated that multiple processes, photodegradation, sorption, aerobic and anaerobic biodegradation, contributed to the removal of organic compounds in wastewater. While these studies are not specific to removal of pesticides in nursery runoff, it is apparent that similar mechanisms contribute to removal of organic compounds in multiple settings and likely that constructed wetlands can be effective in multiple settings. These experiments indicated that constructed wetlands have the capacity to reduce pollutants in agricultural runoff but there is a great need for further field demonstrations on nurseries.

Constructed wetlands have characteristics enabling them to effectively capture and transform pesticides. Pesticide removal is influenced by multiple factors: physical, chemical, and biological. Removal processes within constructed wetlands include physical trapping within the soil matrix, sorption to soil particles, uptake by vegetation, chemical transformation, microbial degradation, and photolysis (breakdown by exposure to light). The effectiveness of removal depends on chemical characteristics of individual pesticides as well as the hydrologic and soil properties of the wetland system.

Constructed wetlands are a potential tool for nurseries to reduce pesticide concentrations present in runoff. This study demonstrated performance for pesticides, nutrients, and total suspended solids removal by a subsurface-flow and a free surface constructed wetland installed at two different nurseries in Oklahoma. While it was not a direct comparison of the two different design types, this study provides guidance for nurseries that are faced with both regulatory and economic pressure to incorporate pesticides into their operations and regulations to eliminate pesticide in runoff.

2.2 Objectives

Performance of constructed wetlands in other settings has shown them to be a potential tool for nurseries to reduce pesticide loading in runoff however, more documentation of in-field performance is needed. The overall objectives for this project are:

1. Determine hydrologic performance and removal efficiency for selected pesticides, nutrients, and total suspended solids (TSS) of a SFCW receiving greenhouse irrigation and stormwater runoff.
2. Determine hydrologic performance and removal efficiency for selected pesticides, nutrients, and total suspended solids (TSS) of a FSCW receiving nursery irrigation and stormwater runoff.

2.3 Methods

Two constructed wetlands were built and monitored to determine their effectiveness in reducing pesticides from nursery and greenhouse runoff. Each system was completed in the fall of 2015 and monitored May through November of 2016. Each constructed wetland was at a different type of nursery (wholesale vs retail) and was a different design (FSCW vs SFCW) (Table 2.1).

Table 2.1 - Characteristics of the two field sites used in the study.

Type of Nursery	Type of Constructed Wetland	Drainage Area	Forebay Volume (m^2/ft^2)	Treatment Area (m^2/ft^2)	Total Area of System (m^2/ft^2)	System Area/ Drainage Area	Media Type	Ponding Depth	Underdrain
Retail	Subsurface-flow	Total - 0.7 ha, greenhouse - 0.5 ha, open-air planting - 0.2 ha	4.5/160	89/960	92/990	1.3%	Bottom 0.46 m river rock, Top 1.2 m construction sand	0.15 m	Dual pipes, 0.076 m diameter
Wholesale	Free-surface	Total - 6 ha, all open-air planting	45/1,600	280/3,000	480/5,150	0.80%	0.76 m of sand and compost mixture	0.15 m to 0.20 m	None

2.3.1 Site Descriptions

2.3.1.1 Subsurface-flow Constructed Wetland Treating Runoff at a Retail Nursery

A SFCW was constructed at a retail nursery in Oklahoma City, OK in September 2015. The area draining to the SFCW contained perennial ornamentals such as crepe myrtle (Lagerstromeemia spp.) and switchgrass (Panicum virgatum), evergreen shrubs and trees such as cypress (Cupressus spp.) and spruce (Picea spp.), and deciduous trees such as maple (Acer spp.) and redwood (Metasequoia spp.). The drainage area consisted of greenhouses (0.5 hectares) and open-air planting areas (0.2 hectares) for a total contributing area of 0.7 hectares. The SFCW was 0.3% as large as the contributing drainage area. As built, the subsurface-flow constructed wetland consisted of a sediment forebay that approximately 1.5 m (5.0 ft) wide, 1.5 m (5.0 ft) long and 1.8 m (6.0 ft) deep (Figure 2.1). The forebay was separated from the treatment cell by a poured concrete wall containing 9 poly vinyl chloride pipes (5.1 cm/2.0 in diameter) connecting the forebay to the treatment cell. The cell was 8.8 m (29 ft) long and 1.5 m (5.0 ft) wide. The bottom 0.46 m (1.5 ft) of the cell was made up of river rock and the top 1.2 m (4.0 ft) is concrete sand. The river rock and sand layers were separated by 4 oz needle-punched geotextile fabric. Runoff entered the system via overland flow from the open-air planting area and a culvert from the greenhouse area. Two underdrain pipes ran through the middle of the gravel layer. The underdrains were connected to a standpipe and a 180° bend at an elevation 15 cm (6.0 inches) lower than the media surface. This prevented water from leaving the treatment cell media through the underdrains unless the water level was higher than the elbow elevation. After leaving the cell, the underdrains emptied into a stormsewer catchment.

The approximate theoretical storage volume of the SFCW was calculated. Storage components included forebay, ponding, and media. The porosity of the sand was not measured directly, but unconsolidated sand with normal packing has a porosity between 0.39 and 0.41 (Corey, 1994). The total theoretical storage volume was approximately 15,000 L which included 4,200 L (forebay), 2,000 L (ponding), and 8,800 L media.

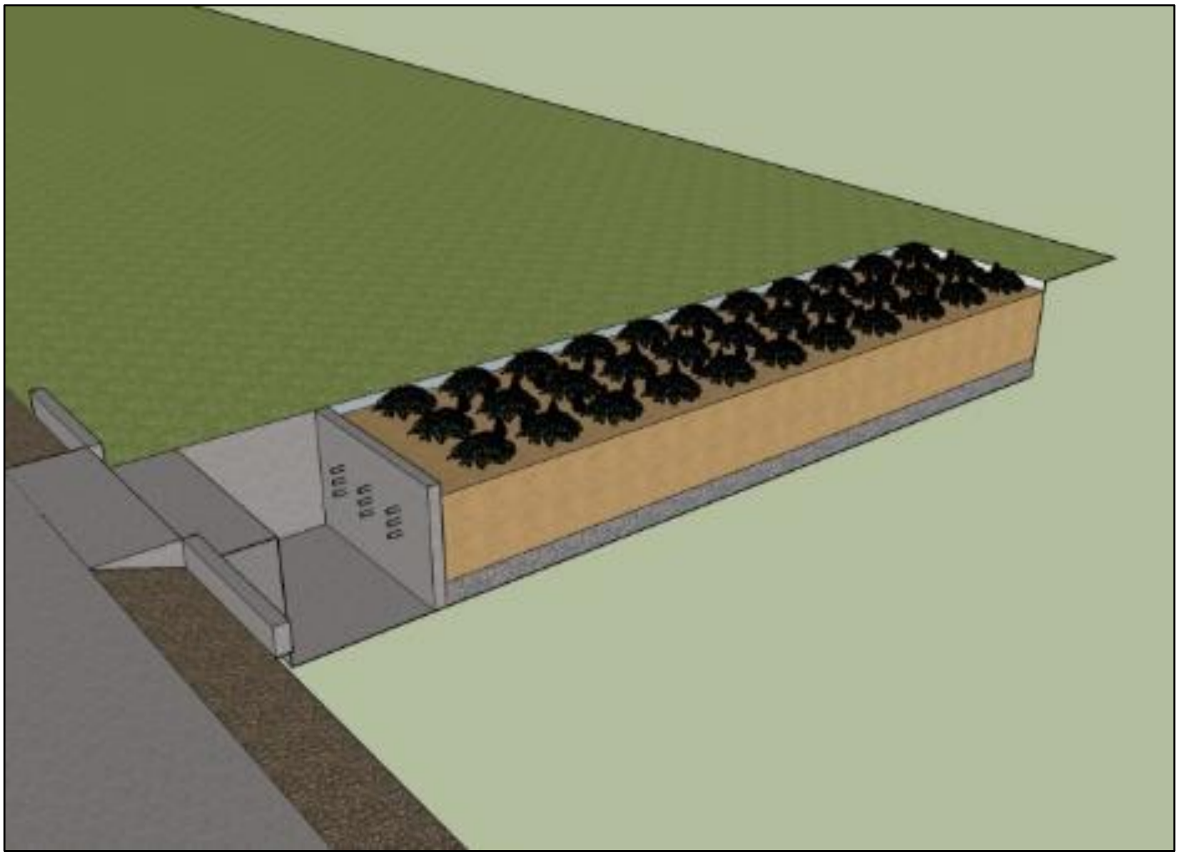

Figure 2.1 - Conceptual drawing of subsurface-flow constructed wetland showing sediment forebay and treatment cell separated by a poured concrete wall.

2.3.1.2 Free-Surface Constructed Wetland Treating Runoff at a Wholesale Nursery

A FSCW was constructed at a wholesale nursery located in northeastern Oklahoma near Hulbert, OK and the Fort Gibson Reservoir. The nursery landscape was made up of compacted cobble. The nursery used overhead irrigation to water all containers. Plants in the area draining to the FSCW consisted of fruits such as peach (Prunus persica), blueberry (Cyanococcus spp.), and grape (Vitis vinifera), and groundcovers such as lily turf (Liriope spp.) and winter creeper (Euonymus spp.). Overhead irrigation in container production settings can result in low capture efficiencies (amount of water that is retained in the container/total amount applied) (Beeson and Knox, 1991). This leads to high volumes of runoff even during dry weather. To minimize the volume of water leaving the site, the nursery captures and stores some runoff in retention ponds. The constructed wetland was designed with these hydrologic characteristics in mind: frequent irrigation, large runoff volumes, and high erosion potential. While typical FSCWs cover large areas, treatment area was reduced and only a portion of runoff was treated to minimize land taken out of production. During the study, the nursery declared bankruptcy and ended operations at this location limiting the number of events that were sampled.

The drainage area to the system was 6 hectares. The constructed wetland system had three components: a diversion channel, sediment forebay, and treatment cells. Runoff was routed into the diversion channel by a low wooden dam across the existing channel. The dam was low enough to provide permanent flow diversion for irrigation flow but did not force the entirety of storm flows into the diversion channel overwhelming the wetland system. The inflow to the FSCW system was regulated by a sluice gate that could be raised and lowered to control flow rate. Runoff flowed through the diversion channel and then entered a sediment forebay. Runoff flowed in parallel into the treatment cells after passing through the sediment forebay. The wetland was designed with six separate cells in parallel with different amounts of compost and either with plants or without plants (Figure 2.2). The cell contents starting from the upstream end of the wetland are listed in

Table 2.2. The cell order was determined at random.

Figure 2.2 - Cells with different media mixes and that either contained plants or did not contain plants.

Table 2.2 - Each of the six cells of the free-surface constructed wetland had a different combination of sand:compost ratio and either had plants or did not have plants.

Cell	Compost Content	Sand Content	Plants Present
1	0%	100%	No Plants
2	12.5%	87.5%	No Plants
3	0%	100%	Plants
4	12.5%	87.5%	Plants
5	25%	75%	No Plants
6	25%	75%	Plants

2.3.2. Hydrologic Monitoring

2.3.2.1. Subsurface-flow Constructed Wetland

Inflow, outflow, water level (forebay and treatment cell), and rainfall were continually monitored to determine hydrologic performance. To ensure that all runoff was quantified, runoff was prevented from entering the treatment cell or the forebay via overland flow. A wooden barrier was installed along the sides of the cell and sealed with silicon sealant. Inflow entered the forebay through a 0.15 m (0.5 ft) H-flume (Figure 3.3). To quantify overflow, a 0.12 m (0.4 ft) HS-flume was installed as the outlet of the treatment cell. This type of flume was chosen to measure low flows that occur during irrigation events, the predominant type of event treated by the SFCW. During large storm events, water ponded in the entire area around the SFCW, so these large events were not able to be accurately quantified. To quantify outflow through the underdrain system, a Palmer-Bowlus flume was installed on one of the underdrain pipes. The second underdrain pipe was plugged for the duration of the experiment. A stilling well was attached to each flume and water level was measured using an ISCO 720 Submerged Flow Probe.

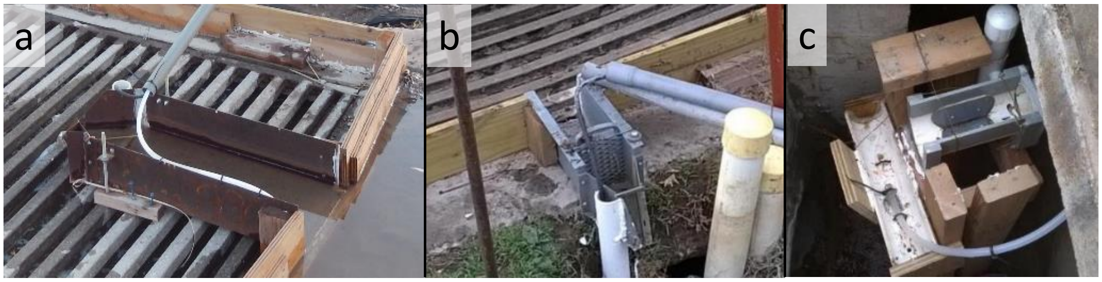

Figure 2.3 - Flumes used for flow measurement for the subsurface-flow constructed wetland. a - H-flume measuring inflow. b - HS-flume measuring overflow. c – Palmer-Bowlus flume measuring underdrain.

2.3.2.2 Free Surface Constructed Wetland

For the FSCW, inflow and outflow were measured for all events using ISCO 720 Flow Modules or ISCO Bubbler Modules and H-flumes. The outlet of each cell had three 15 cm (0.5 ft) H-flumes fabricated in the Oklahoma State University Biosystems and Agricultural Engineering machine shop from sheet metal (Figure 2.4). All other outlet openings were sealed using plywood and silicon. A custom calibration was performed for each H-flume to determine a stage-discharge relationship for each flume (Appendix A). The calibration was needed to account for variation in fabrication and installation. To calibrate each flume, mass flow rate was measured by filling a bucket for a set amount of time and then taking the weight of the bucket. Flow in the main drainage channel that was not diverted into the FSCW system was measured using a 46 cm (1.5 ft) H-flume. Hydrologic data collection began in May 2016 and continued through November 2016.

A rhodamine WT tracer study was performed in September, 2015. This was performed prior to the installation of the sluice gate in the inlet channel and flumes. Flow rate was measured using a 45° v-notch weir and an ISCO 720 Flow Module. A slug of rhodamine dye was injected immediately downstream of the sharp-crested weir. Samples were taken immediately downstream of each cell inlet and immediately downstream of each cell outlet for a total of 12 sampling locations. Water samples were taken at all sampling points prior to dye injection to establish background fluorescence. Water samples were taken every five minutes until the rising and falling limb of the concentration curve were accounted for and then the sampling frequency was increased to ten minutes. Sampling continued until concentrations were within 15% of background levels and change in concentration was 15% or less. Fluorescence was measured in the field using a Trilogy Fluorometer (Turner Designs, Sunnyvale, California) immediately after samples were taken. Retention time was calculated as time to peak. Theoretical retention time was calculated as flow rate divided by volume. Hydraulic efficiency was calculated as actual retention time divided by theoretical retention time.

Figure 2.4 - Flumes used for flow measurement for the free-surface constructed wetland. a - H-flume measuring inflow. b - H-flume measuring flow in the main channel. c – Configuration of 3 H-flumes measuring outflow.

2.3.3 Water Quality Sampling Collection Methods

2.3.3.1. Subsurface-flow Constructed Wetland

For the SFCW, water samples were collected using ISCO refrigerated autosamplers with Teflon-lined tubing. Samples were composited into glass carboys to minimize sorption of pesticides onto the sampling container. Both irrigation and storm samples were flow weighted over the duration of each event. Inflow and overflow samples were collected through an intake tube located within the flume (Figure 2.3). Underdrain samples were taken from a sampling trough directly downstream of the Palmer-Bowlus flume. A covering was placed over the underdrain outlet pipes so inflow from the street grate would not affect the water level or water quality samples. Sampling began in May 2016 and continued through December 2016.

2.3.3.2. Free Surface Constructed Wetland

For the FSCW, ISCO refrigerated autosamplers were used to collect samples. Glass sample containers and Teflon-lined tubing were used to minimize sorption of pesticides onto sampling equipment. Samples were taken on a flow-weighted basis over the full event and composited into a single container. The sampling point for both inflow and outflow samples were in the flume throat. Outflow samples were taken from the middle flume of each cell.

2.3.4. Water Quality Sample Analysis

For both sites, samples were retrieved within 24 hours of the runoff event and transported to Stillwater, Oklahoma in coolers with cold packs or ice. Field blanks were taken at a rate of 5% of all samples for quality assurance and quality control. Field blanks were performed by taking reverse osmosis (RO) water to the field site during a sampling event, pouring the (RO) sample into a glass carboy and then retrieving and returning the blank sample with the water samples. Field blank samples were then analyzed according to the same procedure as the water samples. Field blank samples had concentrations less than 10% of sample concentrations, a common standard consistent with Ohio EPA, 2013. Samples were separated upon return into subsamples consisting of 30 ml for ortho phosphate and nitrate analysis, 30 ml for total nutrient analysis, 1 L for pesticide analysis, 1 L for TSS analysis, and additional sample was saved as backup. Orthophosphate-P and nitrate-N samples were filtered using a 0.45 µm polytetrafluoroethylene (PTFE) filter from Scientific Strategies (Oklahoma City, Oklahoma) and refrigerated until analysis. Nutrient samples were analyzed at the Soil, Water and Forage Analytical Laboratory (SWFAL) at Oklahoma State University according to Lachat Method 10-115-01-1-A for orthophosphate-P and Lachat Method 12-107-04-1-B for nitrate-N. These samples were also analyzed for pH and electrical conductivity (EC). Total nitrogen and total phosphorus samples were digested before being analyzed at SWFAL. The digestion was based on the methods described in Ebina et al. (1983) and Gross and Boyd (1998). Each sample was combined at a 1:1 ratio with an oxidizing agent (combine 20.0g of potassium persulfate ($K_2(SO_4)_2$) and 3.0g of sodium hydroxide (NaOH) and brought to a total volume of 1L with deionized water and then autoclaved at 120°C for 30 minutes.

Pesticide analysis was performed at Oklahoma State University. Samples analyzed for pesticides were extracted within 72 hours of collection onto Agilent Technologies 50 mg C8 solid-phase extraction cartridges. One liter of sample was passed through the extraction cartridge if enough sample was available. To reduce rapid clogging by excess sediment in the samples, a filter made from glass wool and kimwipe in a clean SPE cartridge with no resin was implemented in series prior to the C8 cartridge. Cartridges and filters were then frozen until analyzed. The C8 cartridges were then eluted with 9 ml of ethyl acetate. The filters were removed from the cartridge housing and placed in a clean glass vial. Ethyl acetate was added to the vial and agitated on a shaker table for one hour before the elution solution was transferred using quantitative transfer (rinsed three times with ethyl acetate) to a test tube. To dry the solvent, 3-4 g of anhydrous sodium sulfate was added. Finally, the sample was analyzed using an Agilent 6850 Gas Chromatograph coupled with a 5975C Mass Spectrometer.

The samples were analyzed for pesticides listed in Table 2.3. These pesticides were selected because they are often applied on large-scale container nurseries. The pesticides were also selected to represent a range of mobile and immobile compounds.

Table 2.3 - Pesticides analyzed for in water samples at all sampling points during study, ordered from largest to smallest K_{oc} (K_{oc} is the soil organic carbon-water partitioning coefficient)

							OPP Aquatic Life Benchmarks (µg/L)[5]			
Compound	Type	Water Solubility (mg/L)	K_{oc}	Field Dissipation Half-Life (days)	Anaerobic Half-Life (days)	Aerobic Half-Life (days)	Fish Acute	Fish Chronic	Invertebrates Acute	Invertebrates Chronic
Acephate[1]	Insecticide	818,000	2	2 to 10	-	3	416,000	5760	550	150
Bifenthrin[1]	Insecticide	0.1	237,000	7 to 62	-	65 to 125	0.075	0.04	0.8	0.0013
Carbaryl[1]	Insecticide	110	288	4 to 22	46	17	110	6	0.85	0.5
Chlorothalonil[1]	Fungicide	0.6	4,000 to 4,800	2 to 90	-	-	5.25	3	1.8	0.6
Chlorpyrifos[1]	Insecticide	1.18	13,400	4 to 139	-	12 to 120	0.9	0.57	0.05	0.04
Dimethenamid[4]	Herbicide	1,200	105-396	-	-	-	-	-	-	-
Fipronil[2]	Insecticide	1.9	825	-	-	-	41.5	6.6	0.11	0.011
Indaziflam[3]	Herbicide	2.8	426	-	-	-	-	-	-	-
Isoxaben[1]	Herbicide	1.42	1,400	90 to 120	-	-	>500	400	>650	690
Myclobutanil[1]	Fungicide	142	500	61 to 71	-	-	1200	980	5500	-
Oryzalin[1]	Herbicide	2.5	600	20 to 128	-	-	1440	220	750	358
Oxadiazon[1]	Herbicide	0.7	3,345	30 to 180	180	180	600	33	1090	33
Oxyfluorfen[1]	Herbicide	0.1	100,000	30 to 40	554 to 603	291 to 296	100	1.3	750	13
Pendimethalin[1]	Herbicide	0.275	17,200	8 to 480	60	1,300	69	6.3	140	15.5
Propiconazole[1]	Fungicide	100	648	109 to 123	>84	43 to 70	425	95	650	260
Trifluralin[1]	Herbicide	0.32	7,200	15 to 139	-	116 to 189	20.5	1.14	280	2.4

1 - USDA ARS, 2017
2 - Gunasekara and Troung, 2007
3 - Bayer, 2016
4 - Gillespie et al., 2011
5 – US EPA, 2017

2.3.5 Mass Reduction Calculation and Statistical Methods

Mass and concentration reduction were calculated for all events that had samples from all sampling points. Concentration reduction was calculated using samples from the inlet and underdrain. Mass reduction was determined using concentration and volume from the inlet, overflow, and underdrain. Flow-weighted mean concentration for each event at each sampling point was multiplied by event volume at each sampling point to determine pesticide event mass for each event at each sampling point. Average mass reduction was determined for all events that had samples from all sample points that had flow.

Mass reduction of each constituent was determined using Equation 2.1.

$$Mass\ reduction = \frac{\sum(C_i \times V_i)_{influent} - (\sum(C_i \times V_i)_{underdrain} + \sum(C_i \times V_i)_{overflow})}{\sum(C_i \times V_i)_{influent}} \qquad \text{Equation 2.1}$$

Where, C_i is event concentration of the composite event sample and V_i is the event volume. The subscript of influent refer to inflow samples, underdrain refers to underdrain samples, and overflow refers to overflow samples. This analysis was performed for all constituents (if enough sample volume was available) for each event. For samples that were below reporting limits (pesticides below 10 ng/L, nitrate-N, ortho-phosphate-P, total nitrogen, and total phosphorus below 0.01 mg/L) concentrations were set at one-half of the reporting limit for that sample to determine overall system mass removal.

Concentration descriptive statistics for all pesticide compounds were calculated using methods described in Helsel (2005) and Helsel (2012). If samples below reporting limits comprised 75% or greater of the analyzed samples, then only the number of samples above reporting limits was reported. If 50%-75% of samples had concentrations below reporting limits, then robust regression on order statistics (ROS) was performed. If fewer than 50% of samples had concentrations below reporting limits, then the Kaplan-Meier method was used. Outflow concentration for the FSCW was calculated as a flow-weighted concentration (Equation 2.2).

$$Cfw_i = \frac{C_i \times V_i}{V_T} \qquad \text{Equation 2.2}$$

Where Cfw_i is the flow-weighted concentration for an individual cell, C_i is the event concentration of an individual cell, V_i is the event volume for an individual cell, and V_T is the total outflow volume for that event.

All statistical tests were performed using Minitab 17® (State College, PA). To determine statistical significance of concentration and mass reduction, either a paired t-test for normally distributed differences or Wilcoxon signed rank test for non-normally distributed differences was used. Normality of differences was tested using the Anderson Darling test.

It was expected that percent mass reduction would vary among pesticides depending on Koc. Linear regression analysis was performed between Koc and percent mass reduction. Additional linear regression analyses were performed to determine if percent volume reduction was correlated to inflow volume, antecedent dry period (ADP), or Julian day. If the distribution of residuals was not normal, then variables were transformed using a log normal or natural log transformation to achieve normality. If distributions of residuals were still non-normal, then no further transformations were performed.

2.4 Results

2.4.1 Subsurface-flow Constructed Wetland

2.4.1.1. Volume Reduction

Inflow and outflow were measured from May, 2016 through November, 2016 to determine overall hydrologic performance of the SFCW. A total of 159 events were used to estimate volume reduction through the system. These included irrigation, storm, and combined events and ranged in inflow size from 276 L (small irrigation event of 3.3 mm in 8 minutes) to 29,700 L (storm event of 17.8 mm in 139 minutes) with an average of 4,400 L (Table 2.4). Five storm events were likely larger than the largest recorded event, however these had inlet depths that were greater than 15 cm (6 inches), the height of the inlet h-flume (flow rate of 590 L/min), and were not used in calculations. Results from an Anderson Darling test indicated that the flow data did not follow a normal distribution, therefore statistical significance was tested using the Wilcoxon signed rank test. For the 159 events used to calculate volume reduction, the average reduction was 79% and was statistically significant with a p-value of < 0.001.

To determine which statistical test to use to determine significance between inflow and outflow, the Anderson-Darling test was used to test normality.

Table 2.4 - Volume characteristics of 159 runoff events for the subsurface-flow constructed wetland treating runoff from a retail nursery.

Measurement Location	Mean Volume (L)	Standard Deviation (L)	Range (L)
Inflow	4,400	3,900	280 - 30,000
Overflow	410	750	0 - 5,700
Underdrain	510	550	0 - 3,800

Linear regression analysis indicated that event size (inflow volume), time of year (represented by Julian day), and ADP (hours since cessation of inflow from previous event) were not correlated to volume reduction (R^2 = 0.051, 0.001, and 0.001 for event size, day of year, and ADP, respectively).

2.4.1.2. Water Quality

A total of 21 total events were sampled at the subsurface-flow constructed wetland, 11 paired pesticide samples were used for statistical analysis irrigation events at the subsurface-flow constructed wetland. Descriptive statistics for non-pesticide analytes are detailed in Table 2.5.

Table 2.5 - Concentration characteristics of the inlet, overflow, and underdrain of the subsurface-flow constructed wetland treating runoff from a retail nursery of non-pesticide analytes.

	Inflow			Overflow			Underdrain		
Constituent	Mean	Median	Stnd. Dev.	Mean	Median	Stnd. Dev.	Mean	Median	Stnd. Dev.
Volume (L)	3,930	3,670	2,680	520	540	370	440	340	370
pH	8.1	8.2	0.3	8.3	8.3	0.2	8.2	8.2	0.2
EC (µS/cm)	1,168	1,153	66	1,137	1,155	104	1,100	1,162	143
Total Suspended Solids (mg/L)	11	11	8	3.6	3.3	3	2.7	2.1	2
NO_3-N (mg/L)	0.67	0.59	0.31	0.34	0.37	0.15	0.51	0.51	0.3
PO_4-P (mg/L)	0.090	0.090	0.03	0.083	0.078	0.042	0.091	0.10	0.03
Total Nitrogen (mg/L)	0.80	0.61	0.6	0.57	0.57	0.43	0.46	0.21	0.5
Total Phosphorus (mg/L)	0.091	0.060	0.09	0.080	0.067	0.06	0.065	0.058	0.03

Mass reduction was significant for all non-pesticide water-quality constituents measured (Table 2.6). Mass reduction was calculated as the reduction of mass from the inflow to both the underdrain and overflow. The average volume reduction was 78% for the events used for concentration and mass reduction calculations.

Table 2.6 - Mass reduction of non-pesticide analytes for the subsurface-flow constructed wetland treating runoff from a retail nursery.

Constituent	P-value (Mass Reduction>0)	Number of Paired Samples	Mass Reduction	P-value (Mass Reduction>0 Volume Reduction)
Volume	<0.001	16	78%	-
NO_3-N	< 0.001*	16	86%	0.032*
PO_4-P	< 0.001*	16	79%	>0.99
Total Nitrogen	0.002*	14	85%	0.328
Total Phosphorus	< 0.001*	14	78%	0.851
Total Suspended Solids	0.002*	12	89%	0.050*

* – Statistically significant with 95% confidence

Paired samples were taken for events to directly compare inflow concentrations with underdrain concentrations. There was a statistically significant reduction in concentration at a 95% confidence for eight of the analyzed compounds (Table 2.7).

Table 2.7 - Descriptive statistics for pesticide concentrations in the subsurface-flow constructed wetland treating runoff at retail nursery. All concentrations include both dissolved and particulate components. Only number of samples above the reporting limit is given for compounds with four or fewer samples with concentrations above reporting limits. If there were five samples with concentrations above reporting limits then mean was calculated using regression on order statistics. If six or greater samples had concentrations higher than the reporting limit, then the Kaplan-Meier test was used to determine descriptive statistics for compounds.

	Inflow Concentration (ng/L)				Overflow Concentration (ng/L)				Underdrain Concentration (ng/L)			
Compound	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.
Acephate	2	-	-	-	1	-	-	-	3	-	-	-
Bifenthrin	11	49	37	40	7	23	16	34	7	13	16	13
Carbaryl	8	32	19	51	6	28	11	74	5	68	-	-
Chlorothalonil	1	-	-	-	2	-	-	-	1	-	-	-
Chlorpyrifos	3	-	-	-	0	-	-	-	0	-	-	-
Dimethanamid	5	11	-	-	2	-	-	-	1	-	-	-
Fipronil	3	-	-	-	4	-	-	-	4	-	-	-
Indaziflam	1	-	-	-	1	-	-	-	0			
Isoxaben	8	34	14	49	1	-	-	-	4			
Myclobutanil	11	123	137	69	6	24	20	33	11	61	54	30
Oryzalin	0	-	-	-	0	-	-	-	1	-	-	-
Oxadiazon	11	11	12	12	6	-	-	-	11	10	7	9
Oxyfluorfen	2	-	-	-	1	-	-	-	2	-	-	-
Pendimethalin	8	29	16	34	3	-	-	-	4	-	-	-
Propiconazole	11	79	75	40	6	22	18	27	11	43	40	19
Trifluralin	0	-	-	-	0	-	-	-	0	-	-	-

Pesticide mass was calculated for each sample point (inflow, overflow, and underdrain) for each event. Multiple sampled irrigation events did not result in flow at the overflow sampling point. These events were included for calculations of average mass reductions if they contained samples from the inflow and underdrain sampling points. Since inflow volume for irrigation events was typically lower than inflow volume for storm events, reductions for irrigation events were calculated separately from storm events. Mass reduction was significant at a 95% confidence interval for 10 of the 15 detected compounds (Table 2.8). For four of the five non-significant compounds, there were six or fewer detections. Mass reduction was significantly different from volume reduction for six compounds (Table 2.8). Values in Tables 2.7 and 2.8 were calculated using irrigation events only. There was no correlation between percent mass reduction and log(K_{oc}) (Figure 2.5).

Table 2.8 - Pesticide mass reduction for11 irrigation events in the subsurface-flow constructed wetland treating runoff from a retail nursery . Pesticide analysis included both dissolved and particulate components for each compound.

Compound	P-value (Mass Reduction>0)	Number of Paired Samples	Mass Reduction	P-value (Mass Reduction>Volume Reduction)
Volume	<0.001*	11	78%	-
Acephate	0.423	3	81%	>0.99
Bifenthrin	0.004*	11	92%	0.011*
Carbaryl	0.838	10	91%	0.529
Chlorothalonil	0.009*	9	92%	0.097
Chlorpyrifos	0.036*	6	99%	0.036*
Dimethanamid	0.009*	9	97%	0.009*
Fipronil	0.787	5	-14%	0.584
Indaziflam	0.035*	7	86%	0.142
Isoxaben	0.021*	8	88%	0.022*
Myclobutanil	0.004*	11	92%	0.056
Oryzalin	>0.99	3	79%	>0.99
Oxadiazon	0.004*	11	89%	0.005*
Oxyfluorfen	0.295	6	74%	0.100
Pendimethalin	0.006*	10	79%	0.083
Propiconazole	0.004*	11	88%	0.004*
Trifluralin	No detections in any sample			

* – Statistically significant with 95% confidence

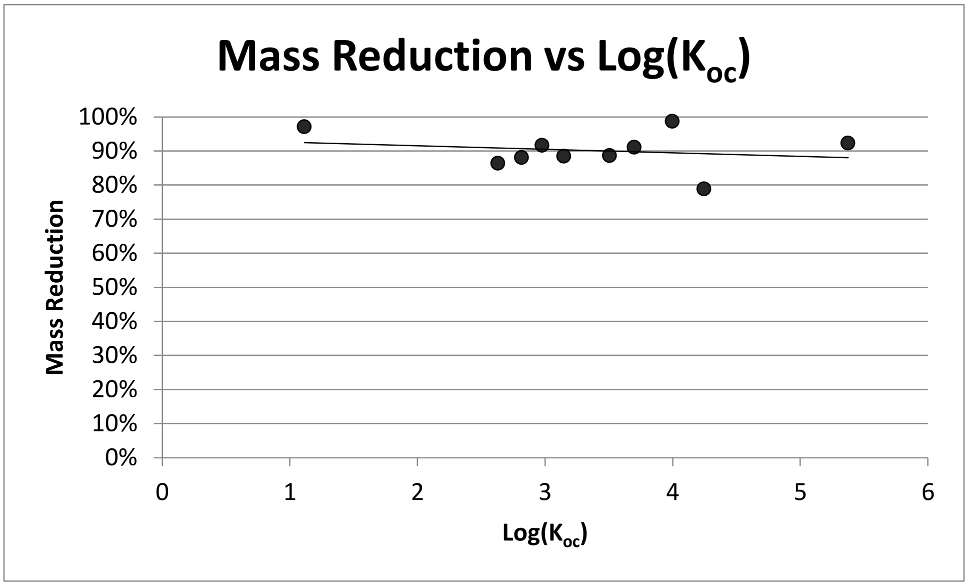

Figure 2.5 - Mass reduction vs log(Koc) for 10 pesticide compounds that had statistically significant concentration reduction in the subsurface-flow constructed wetland treating runoff from a retail nursery. Koc is the soil organic carbon/water partitioning coefficient.

Stormwater events were also sampled and analyzed for nutrients and pesticides (Tables 2.9 and 2.10). A total of five events were sampled however only 3 were analyzed due to either equipment malfunction or inundation of the system by high flow volume.

Table 2.9 - Descriptive statistics for non-pesticide analytes measured in paired stormwater samples for the subsurface-flow constructed wetland.

	Inflow			Overflow			Underdrain		
Analyte	Mean	Median	Stnd. Dev.	Mean	Median	Stnd. Dev.	Mean	Median	Stnd. Dev.
pH	7.8	7.9	0.19	8.0	8.0	0.29	8.1	8.2	0.14
EC (μS/cm)	417	332	211	446	399	97	711	714	69
Total Suspended Solids (mg/L)	143	143	15	138	138	15.4	5.3	5.3	3.0
NO_3-N (mg/L)	0.77	0.73	0.28	0.69	0.70	0.082	0.87	0.71	0.27
PO_4-P (mg/L)	0.057	0.030	0.038	0.054	0.053	0.012	0.090	0.090	0.016
Total Nitrogen (mg/L)	1.1	1.4	0.44	0.75	0.75	0.35	1.1	1.1	1.1
Total Phosphorus (mg/L)	0.093	0.060	0.069	0.055	0.055	0.005	0.055	0.055	0.005

Table 2.10 - Descriptive statistics for pesticide analytes measured in three paired stormwater samples (not irrigation samples) for the subsurface-flow constructed wetland. If there was only one sample with a concentration above the reporting limit, then this is reported. If two samples had concentrations above the reporting limit, then mean was calculated using regression on order statistics. Pesticide analysis included both dissolved and particulate components for each compound.

	Inflow Concentration (ng/L)				Overflow Concentration (ng/L)				Underdrain Concentration (ng/L)			
Compound	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.	Samples Above Reporting Limit	Mean	Median	Stnd. Dev.
Acephate	0	-	-	-	0	-	-	-	0	-	-	-
Bifenthrin	3	34	32	15	2	48	-	-	21	-	-	-
Carbaryl	2	8	-	-	1	-	-	-	1	-	-	-
Chlorothalonil	1	-	-	-	0	-	-	-	0	-	-	-
Chlorpyrifos	1	-	-	-	1	-	-	-	0	-	-	-
Dimethanamid	1	-	-	-	0	-	-	-	0	-	-	-
Fipronil	0	-	-	-	0	-	-	-	1	-	-	-
Indaziflam	0	-	-	-	0	-	-	-	0	-	-	-
Isoxaben	2	15	-	-	1	-	-	-	22	-	-	-
Myclobutanil	3	19	17	7	2	32			3	46	45	37
Oryzalin	0	-	-	-	0	-	-	-	0	-	-	-
Oxadiazon	0	-	-	-	1	-	-	-	2	15	-	-
Oxyfluorfen	1	-	-	-	1	-	-	-	0	-	-	-
Pendimethalin	0	-	-	-	2	40	-	-	2	28	-	-
Propiconazole	3	36	29	5	2	46	-	-	2	52	-	-
Trifluralin	0	-	-	-	0	-	-	-	0	-	-	-

2.4.2 Free Surface Constructed Wetland

2.4.2.1 Water Quantity Results

A tracer study was performed for the FSCW prior to the installation of flow control structures (sluice gate and flumes). The tracer study was performed at a typical flow rate that was higher than the typical flow rate during the monitoring period (750 L min^{-1} and 250 L min^{-1} respectively). Results from the tracer study are given in Table 2.11.

Table 2.11 - Results from tracer study for free surface constructed wetland.

	Time to Peak (minutes)		Hydraulic Efficiency	
Cell	To Cell Inlet	Cell Inlet to Outlet	To Cell Inlet	Cell Inlet to Outlet
1	30	20	53%	20%
2	30	15	47%	19%
3	30	25	42%	50%
4	35	30	45%	41%
5	35	30	41%	36%
6	40	60	43%	47%

The FSCW was continuously monitored for inflow rate and outflow rate from June 2017 through November 2017. The FSCW system treated approximately half of the total runoff at this nursery outfall for the measured events (Table 2.12). Inflow was slightly higher than outflow of the system, indicating that there some infiltration or leakage between events. On average, outflow continued for 6.3 hours after inflow had stopped or decreased to a negligible amount. In many cases, a small amount of inflow continued for an extended period of time.

Table 2.12 - Summary of descriptive statistics of volume for inflow, outflow, and bypass of the free-surface constructed wetland treating runoff from a wholesale nursery.

Measurement Location	Mean Volume (L)	Percent of Total Runoff	Standard Deviation (L)	Range (L)
Inflow	76,000	52%	23,000	27,000-110,000
Bypass	73,000	48%	41,300	19,200-145,400
Outflow	70,000	-	27,000	22,000-122,000

2.4.2.2 Water Quality Results

Concentration descriptive statistics and mass reduction were calculated for inflow and outflow of the FSCW for five events (Table 2.13). A total of seven events were sampled at the free-surface constructed wetland however five paired samples were used for calculations in the free-surface constructed wetland.

For non-pesticide analytes, since the differences were normally distributed according to the Anderson Darling test, samples were analyzed using a paired t-test. The null hypothesis was that inflow-outflow was greater than zero. Values were significant if the p-value was less than 0.05. Even with a small sample size, four of the five non-pesticide contaminants had statistically significant concentration mass reduction (Table 2.14). The exception to this was total nitrogen which did not have statistically significant reduction.

Table 2.13 – Descriptive characteristics of concentration of non-pesticide analytes at a free-surface constructed wetland treating runoff at a wholesale nursery.

	Inflow Concentration			Outflow Concentration		
Analyte	Mean	Median	Stnd. Dev.	Mean	Median	Stnd. Dev.
pH	7.6	7.5	0.32	5.1	7.5	3.4
EC (μS/cm)	300	290	14	200	290	130
Total Suspended Solids (mg/L)	60	54	33	49	55	12
NO_3-N (mg/L)	0.80	0.65	0.48	0.64	0.65	0.13
PO_4-P (mg/L)	0.27	0.25	0.066	0.20	0.25	0.09
Total Nitrogen (mg/L)	1.8	1.5	0.97	1.4	1.5	0.33
Total Phosphorus (mg/L)	0.32	0.24	0.13	0.23	0.24	0.08

Table 2.14 – Mass reduction of non-pesticide analytes by a free-surface constructed wetland treating runoff at a wholesale nursery.

Analyte	**P-value (N)**	**Number of Paired Samples**	**Mass Reduction**
NO_3-N	0.005*	5	47%
PO_4-P	0.002*	5	47%
Total Nitrogen	0.13	5	17%
Total Phosphorus	0.013*	5	46%
Total Suspended Solids	0.023*	5	78%

* – Statistically significant with 95% confidence

Concentration descriptive statistics were calculated for pesticides for all analyzed samples (Table 2.15). All pesticide compounds except trifluralin were detected in at least two of the five sampled events. Mass reduction was calculated for inflow and outflow of the FSCW for five events (Table 2.16).

Table 2.15 – Concentration characteristics of pesticides in the free-surface constructed wetland treating runoff from a wholesale nursery. Only number of detections above the reporting limit is given for compounds with 2 or fewer detections. Mean for compounds with three detections was calculated using robust regression on order statistics (ROS). Median and standard deviation could not be calculated if there were greater than two non-detects. The Kaplan-Meier test was used for compounds with one non-detect. Reporting limits were 10 ng L^{-1}.

	Inflow Concentration (ng/L)				Outflow Concentration (ng/L)			
Compound	Number of Samples with Concentrations above Reporting Limits	Mean	Median	Stnd. Dev.	Number of Samples with Concentrations above Reporting Limits	Mean	Median	Stnd. Dev.
Acephate	2	-	-	-	2	-	-	-
Bifenthrin	5	14	14	7	5	10	10	4
Carbaryl	5	64	16	97	2	-	-	-
Chlorothalonil	2	-	-	-	4	450	960	3
Chlorpyrifos	5	350	160	330	5	210	240	140
Dimethanamid	5	220	250	180	5	160	200	95
Fipronil	1	-	-	-	2	-	-	-
Indaziflam	5	230	280	140	5	160	190	110
Isoxaben	3	41	-	-	4	27	32	11
Myclobutanil	5	950	410	880	5	560	650	380
Oryzalin	2	-	-	-	2	-	-	-
Oxadiazon	5	3,400	180	6,100	5	2,400	1,800	2,500
Oxyfluorfen	1	-	-	-	2	-	-	-
Pendimethalin	4	370	65	630	4	310	560	43
Propiconazole	5	650	430	560	5	410	490	250
Trifluralin	0	-	-	-	0	-	-	-

Table 2.16 - Mass reduction for compounds in the free-surface constructed wetland treating runoff from a wholesale nursery.

Compound	Number of Paired Samples	Mass Reduction
Acephate	2	68%
Bifenthrin	5	-48%
Carbaryl	5	68%
Chlorothalonil	3	96%
Chlorpyrifos	5	58%
Dimethanamid	5	25%
Fipronil	2	80%
Indaziflam	5	-2.0%
Isoxaben	4	39%
Myclobutanil	5	-1.5%
Oryzalin	2	1.1%
Oxadiazon	5	21%
Oxyfluorfen	3	5.2%
Pendimethalin	4	12%
Propiconazole	5	-1.0%
Trifluralin	No detections	

2.5 Discussion

The subsurface-flow constructed wetland effectively reduced multiple contaminants in greenhouse runoff. Due to a high capacity to capture and infiltrate runoff, only 21% of all inflow for each event left the SFCW through the overflow or through the underdrain. This led to significant reduction in mass for all non-pesticide contaminants measured except for orthophosphate. With a saturated lower layer, conditions were present for denitrification, so it was expected to see removal of both nitrate and total nitrogen. There was not a significant mass reduction in orthophosphate but there was a significant mass reduction of total phosphorus which indicates that there is minimal sorption of orthophosphate within the system. For pesticide, 10 of the most frequently detected pesticides had significant mass reduction and only one compound that was detected in 10 or more events did not have significant mass reduction. One of the compounds that did not exhibit significant mass reduction was carbaryl which is considered a mobile compound with a K_{oc} of between 205 and 457. This is expected since it is more difficult to sequester mobile compounds out of solution. However, a number of more mobile compounds exhibited mass reduction: dimethenamid, myclobutanil, and propiconazole. Mass reduction indicated no correlation with $\log(K_{oc})$ (Figure 2.3). A study by Graves et al. (2014) indicated significant concentration reductions for both bifenthrin (immobile compound) and fipronil (mobile compound) when sufficient organic content was present (a media of at least 20% compost). While the SFCW did not have any organic carbon source incorporated into the media during construction, since the influent was pot leachate, it likely contained organic content. During the study, a schmutzdecke formed on the top layer of the SFCW treatment cell indicating organic content was present in the cell. Chemical transformation likely had less impact on mass reduction than volume reduction. If volume reduction had been lower, then K_{oc} could have had a larger impact on mass reduction. In this study however, it was likely secondary. Mass reduction was significantly different from volume reduction for six compounds. This indicates that the system is reducing concentration in addition to mass for some compounds. Overall, the SFCW effectively reduced loading of most of the analyzed contaminants into nearby surface waters. Stearman et al. (2003) found removals that ranged from 63% to 90% for metolachlor and simazine by a gravel subsurface flow constructed wetland. These compounds are mobile compounds with a K_{oc} of 200 and 130 respectively. This is comparable to the performance of dimethanimid, an herbicide which has a K_{oc} of 108 and exhibited a mass reduction of 97% by a SFCW in this field study.

For all recorded events (not just sampled events) for the SFCW, volume reduction was 79%. Since mass reduction was a function of both volume and concentration, if mass reduction is equal to volume reduction, then mass reduction was solely due to volume reduction. If mass reduction was higher than volume reduction, then mass reduction was a function of factors other than volume reduction. Mass reduction by the SFCW was higher than volume reduction for six of the 15 detected compounds. The compounds that had higher mass reduction than volume reduction were both mobile and immobile compounds including bifenthrin (92% mass reduction, K_{oc} = 237,000) and indaziflam (86% mass reduction, K_{oc} = 426). Conversely, compounds in the SFCW that had a mass reduction equal to or less than volume reduction had a range of transport properties such as oxyfluorfen (74% mass reduction, K_{oc} = 100,000) and oryzalin (79% mass reduction, K_{oc}=600).

The FSCW did not have significant mass reductions for any pesticide compound. This was likely due to multiple factors. The wholesale nursery went out of business during the study and fewer events were sampled than planned. This reduced sample size reduced power of all statistical analyses. To minimize the area of land taken out of production, the FSCW occupied a footprint that was smaller than typical designs. While the average event volume was less than the theoretical system volume, actual system volume was less than average event volume. The total theoretical storage volume was 155,000 L, however with a hydraulic efficiency of 40%, the actual volume was 62,000 L. This is approximately 20% less than the average event inflow volume. While pesticide mass reductions were not significantly different, there was a significant mass reduction for almost all non-pesticide analytes.

In both systems, many compounds had concentrations near the reporting limits (Tables 2.7 and 2.15). Mass reduction could be affected by consistently low inflow samples and one effluent sample with a disproportionately high concentration. This led to the appearance of pesticide sourcing for some compounds. One example of this was bifenthrin in the FSCW. However, since the mean influent concentration was 14 ng/L, near the reporting limit of 10 ng/L, one effluent sample with a high bifenthrin concentration could lead to a higher effluent mass.

While most of the pesticides were detected above reporting limits multiple times, bifenthrin was the only compound in the retail nursery (treated by the SFCW) runoff with a mean concentration that exceeded an Aquatic Life Benchmark (Tables 2.3 and 2.7). The mean underdrain and overflow concentrations for bifenthrin were below the same Aquatic Life Benchmark. At the wholesale nursery (treated by the FSCW), chlorpyrifos was the only compound with a mean concentration that exceeded the Aquatic Life Benchmark. The effluent mean concentration was lower, but also exceeded the same benchmank.

2.6 Conclusions

The overall goal of this study was to determine if constructed wetlands could be used as a tool for pesticide and nutrient removal and runoff management at nurseries . Two different types of constructed wetlands were implemented at two different types of nursery and monitored for water quality and water quantity parameters. In general, the two systems exhibited significant mass reduction for the non-pesticide contaminants but pesticide mass reduction was variable.

While it is difficult to assign direct monetary value to reducing environmental impact, there are other indirect monetary and other benefits to managing runoff. While nurseries are not regulated as point source discharges, in many cases their runoff is monitored. Runoff with pesticides and nutrients can lead to regulatory action and create an image that the nursery is environmentally negligent. While implementing tools to manage runoff may not eliminate pollutants, it will reduce the pollutant loading from the nursery into receiving bodies of water. Constructed wetlands have advantages and disadvantages as runoff management tools for nursery operations. One advantage is that they are passive systems, systems that do not require energy input. One disadvantage is that for a FSCW to effectively treat a large drainage area, the FSCW needs to occupy a large area. In many cases, this is economically infeasible since it removes land from production. The area of the FSCW in this study was 0.8% as large as its contributing drainage area, and did not exhibit significant mass reduction for any pesticide compound. One of the factors that likely limited performance of the FSCW was the reduced size which led to reduced retention time. The tracer study indicated that the actual storage volume was about 62,000 L, 20% lower than the average inflow volume (76,000 L). In comparison, the SFCW in this study was 1.3% as large as its contributing drainage area and demonstrated significant mass reduction for most of the commonly detected pesticides. However, the theoretical storage volume was 15,000 L and the average inflow volume was 4,400 L. If the SFCW had a hydraulic efficiency of 40%, similar to the FSCW, then the actual storage volume would have been 5,200 which is 27% higher than the average inflow volume. It is likely that the relationship between hydraulic loading rate and system size impacted pollutant removal performance.

One advantage of constructed wetlands is that they can be implemented using equipment that is already owned by nursery operations, skid-steer loader and small backhoe. Also, the materials used in the constructed wetlands in this study were readily available, washed sand, river rock, and compost. The SFCW required approximately $1,500 to $2,000 of materials (sand, river rock, materials delivery, ready-mix concrete, and polyvinyl chloride piping) and approximately 200 man hours. The underdrains were routed to the stormsewer catchment over buried utilities, so excavation was performed by hand instead of using a small backhoe. This extra excavation likely required an additional 10 to 20 man hours. Total cost was between $5,000 and $6,000. It was not possible to determine an accurate cost estimate for the FSCW due to variability in hours worked by the nursery personnel building the constructed wetland.

As nursery operators balance environmental and economic sustainability, constructed wetlands are a viable best management practice for runoff management. While the constructed wetlands in this study did not eliminate all pollutants in the runoff, if sized adequately, they effectively reduced pollutant loading to downstream water bodies for most of the commonly detected analytes. Constructed wetlands can be implemented using equipment, materials, and skills that are already present at or are readily available to nursery operations. Nurseries that implement constructed wetlands demonstrate environmental awareness and a willingness to take steps to reduce their environmental footprint.

Additional research needs to be performed to better understand removal mechanisms within constructed wetland systems. Understanding removal mechanisms can lead to better design guidance and targeting of pollutants through media amendments. Further research is also needed to determine how varying transport properties of different pesticide compounds affect removal performance. These future discoveries can be incorporated into current design recommendations to improve pollutant removal performance. In addition, an in-depth cost-benefit analysis needs to be performed to demonstrate the feasibility of implementation to stakeholders.

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CHAPTER III

A LABORATORY INVESTIGATION ON THE IMPACTS OF SELECTED HYDROLOGIC VARIABLES ON PESTICIDE REMOVAL BY CONSTRUCTED WETLANDS

Abstract: Runoff produced from urban areas such as lawns, landscaping, and nurseries during storm and irrigation events can contain pollutants such as pesticides that pose a threat to receiving water bodies. Constructed wetlands have been used to treat runoff in different settings; however, research is limited regarding the effect of different hydrologic variables on pesticide removal. This study used column experiments with five different pesticide compounds (carbaryl, chlorothalonil, pendimethalin, fipronil, and bifenthrin) to examine how pesticide removal is impacted by saturation (completely saturated or partially saturated), storage between runs, and time between runs (1, 3, or 10 days).Water that was stored in the system between runs had higher removal than water was not stored between runs. Overall, the longest time between runs, 10 days, had the highest removal. There was no difference between saturation treatments. While results from this study may not translate directly to design recommendations, the study demonstrates that different hydrologic variables affect pesticide removal and should be investigated further.

3.1 Introduction

Runoff containing pesticides poses a potential threat to agricultural and urban water bodies. On plant nurseries, pesticide application coupled with frequent irrigation events leads to pesticide loading into nearby water bodies (Briggs et al., 1998). Some pesticides, such as chlorothalonil are aquatically toxic and affect growth and survival of aquatic amphibians (Yu et al., 2013). Pesticide removal by constructed wetlands has been investigated as a possible solution for various sources of runoff. Constructed wetlands were originally developed for wastewater treatment and have been studied extensively for pollutant removal from municipal wastewater (Gersberg et al., 1986, Kemp and George 1997, Vymazal, 2002, Hench et al., 2003, Brix and Arias, 2005, Ghermandi et al., 2007). Later, the use of constructed wetlands was explored for pollutant removal from agricultural runoff (Hammer, 1992, Rodgers and Dunn, 1992, Moore et al., 2000, Poe et al., 2003, Tanner et al., 2005, Blankenburg et al., 2006, Beutel et al., 2009, Gregoire et al., 2009). More recently, the effectiveness of pesticide removal by constructed wetlands has been explored (Rodgers and Dunn 1992, Moore et al., 2000, Moore et al., 2001, Moore et al., 2002, Runes et al., 2004, Stearman et al., 2003, Sherrard et al., 2004, Budd et al., 2009, Budd et al., 2011, Agudelo et al., 2012, Gaullier et al., 2017, Tournebize et al., 2017). The majority of these studies have only looked at pollutant removal under three hydrologic patterns: continuous inflow (wastewater treatment), naturally intermittent flow (runoff from rainfall events), or a one-time flow (simulated runoff event). Irrigation on nurseries produces frequent events during growing seasons (often daily) and less frequent events (multiple days to weeks between runoff events) during dormant seasons. This hydrologic pattern likely affects the performance of constructed wetlands treating this runoff. Untreated effluent is introduced during each event and intermittent cycling causes water levels and saturation conditions to fluctuate.

There are two common designs of constructed wetland, free-surface and subsurface flow. The primary difference in design is the level of saturation. Free-surface constructed wetlands maintain ponded water and subsurface-flow constructed wetlands maintain a layer of saturated media, but the top layer of media is allowed to drain. There has been little direct comparison on any scale of free-surface wetlands and subsurface-flow vegetated wetlands (Vymazal, 2011).

Retention time is often used as a design parameter for constructed wetlands, but does not account for the volume of water retained between events. This volume has an effective retention time that includes both the hydraulic retention time and the time between events. This effective retention time also could have an effect on overall removal and degradation of pesticides by the system.

3.2 Objectives

The following objectives for this study are:

1. Determine the effect of saturation conditions on removal of polar and non-polar current-use pesticides.
2. Determine the effect of antecedent period (time between irrigation) on removal of polar and non-polar current-use pesticides.
3. Determine if removal is affected by increased contact time as a result of storage within the system between runs.

The two different treatment designs in this study examine the effects of two contrasting treatment scenarios: completely saturated throughout and a layer of unsaturated soil and a layer of saturated soil. The two different hydraulic conditions each create a different environment by which pesticides can be removed or transformed. The free water surface wetland is completely saturated, so mostly anaerobic. The submerged flow wetland is a compromise between completely saturated and completely drained. The upper layer of the subsurface-flow constructed wetland is able to drain while the lower layer remains saturated. Multiple layers present a possible treatment train within the same system. A comparison of the two treatment practices with different pesticides under different conditions is needed to guide recommendations for treatment of pesticide runoff in nursery settings.

3.3 Methods

Column experiments were performed to test how pesticide removal was affected by different variables seen in applications of constructed wetlands treating nursery runoff. Pesticide-spiked water was introduced to each column in four separate runs. The outlet elevation was set to either maintain saturation above or below the media surface. Two effluent samples were taken for each run. The first sample was water stored in the column from the previous run and the second sample was water from the current run.

3.3.1 Column Setup

The columns were made of stainless steel tubing and measured 76 mm in diameter and 510 mm in height. The media mixture was packed into the bottom 230 mm allowing for 280 mm of ponding. A mixture of 90% concrete sand and 10% compost by volume comprised the column media. The water level of the saturated columns was set at 76 mm above the media allowing for 200 mm of increased water level during run inflow. The water level of the partially saturated column was set at 150 mm above the bottom of the column forcing the lower 150 mm of media to remain saturated and allowing 76 mm of media to drain between runs (Figure 3.1).

Figure 3.1 - Experimental setup. Saturated column is on left, partially saturated column is on right. Shading approximates media surface.

The column was capped at the bottom by a stainless steel plate welded to the stainless steel tubing. A hole was drilled into the steel plate and a threaded 9.5 mm coupling was welded to the bottom of the plate to allow attachment of tubing to the bottom of the column and to allow access to the bottom of the column if needed. The welds were sealed with silicone to prevent leaking. Tubing was flexible aluminum tubing attached by a flared fitting, nut, and sleeve. Height of tubing outlet was set and remained set for the duration of each experiment.

3.4.2. Experimental Treatments.

The column experiments were designed to test the effects of both irrigation pattern as well as constructed wetland design (Figure 3.2). Treatment variables were saturation level and antecedent dry period (Table 3.1). Free water surface constructed wetlands (FSCW) remain saturated. Typically, this is achieved through setting the outlet elevation higher than the media surface so water remains ponded above the media. Subsurface flow constructed wetlands (SFCW) are designed to remain saturated, but to have the top layer of media be unsaturated. Depending on the design, ponding may be present for some period of time in a subsurface flow constructed wetland, but since the outlet elevation is set lower than the media surface the upper layer of media will drain between runs and does not remain saturated. During the growing season, plants are typically irrigated once per day. However, during late fall, early spring plants are only irrigated once every 2-3 days and are irrigated weekly during the winter months. This essentially lengthens the retention time for water stored in the constructed wetland system between runoff runs. The three antecedent dry period treatments are designed to examine the effects caused by these three different irrigation patterns.

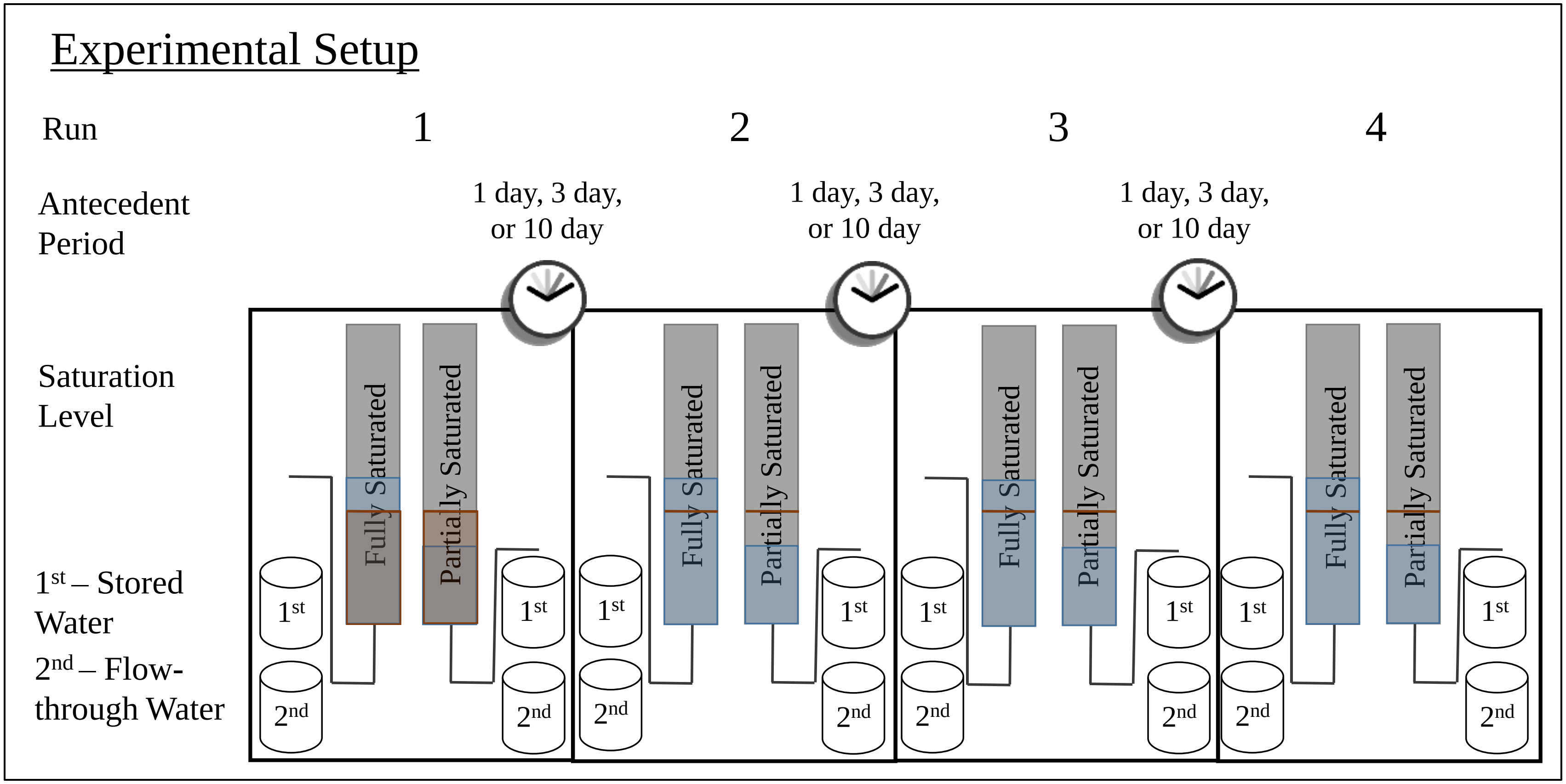

Figure 3.2 - Column study experimental setup.

Table 3.1 - Variables and treatments for lab-scale column study.

Variable	Treatments	Number of Treatments
Saturation level	76 mm above media surface, 76 mm below media surface	2
Antecedent period	1 day, 3 days, 10 days	3
Replications	Triplicate	3
Number of runs per column		4
Outflow samples per run	First (water stored in column from prior event), second (water from current event)	2
Inflow samples per run	One inflow sample was taken for two columns run concurrently	1 (36 total inflow samples are taken)

3.3.3 Packing Procedure and Flow Rate

Flow was set to achieve a rate of three pore volumes in three hours. Higher inflow rates (and thus shorter retention times) are limited by flow rate through the media and low head due to the high outlet elevation. Pore volume is estimated by multiplying media volume by porosity. Column media volume was approximately $1.67 \times 10^6 \text{mm}^3$ (760 mm diameter and 410 mm height) and porosity was measured to be 36% for a 90% sand and 10% compost mixture. From multiple comparisons of weight and volume at a moisture content of 0.1% for sand and 3% for compost, it was determined that this volume ratio is equal to a weight ratio of approximately 94.5% sand and 5.5% compost. To expedite media mixing, the mass ratio of sand and compost were used. The total volume for each run was 1,130 mL (three pore volumes). To achieve a retention time of three hours, a flow rate of 12.5 ml/min was set using a peristaltic pump. This was set using employer supplied relationship between peristaltic pump, tubing size, and flow rate. Flow rate was confirmed by measuring time to fill a set volume. Flow rate was kept consistent throughout all experiments, however there was minor variation (10%) due to wearing of tubing. Tubing was replaced periodically to maintain a consistent flow rate.

Sand and compost were sieved through a 3.35mm opening screen to remove any large particles that would affect packing and flow uniformity. To prevent fine particles from migrating into and clogging the aluminum tubing, two layers of clean geotextile were placed at the bottom of the column prior to adding media. Geotextile is commonly placed between layers of media in bioretention cells for the same purpose, to prevent clogging of pore space due to the migration of fine particles (Davis, 2008). Sand and compost were weighed separately and then thoroughly mixed by hand. The media mixture was added to the column in lifts of 10 cm and then uniformly packed using a metal rod.

3.3.4 Simulated Runoff

A significant source of contaminants in nursery runoff is pot leachate (Colangelo and Brand, 2001, Wilson et al., 2010, Graves et al., 2014). To represent field conditions, simulated pot leachate was created from a combination of deionized water, pesticides, and growing media using the following steps.

1. Unused growing media composed of aged cedar bark and a small addition of fertilizer and lime was obtained from a wholesale nursery..
2. The potting mix was sieved using a 4.75 mm screen to reduce fine particles present in the pot leachate. Particles that passed through the sieve were removed to prevent clogging of the pump tubing. To further prevent entry of fine particles into the pump tubing, geotextile fabric was fastened over the pump tube inlet using a rubber band.

3. A mass of ~100 g of growing media was combined with three L of deionized water.

4. A pesticide stock solution was made by mixing pesticide formulation with deionized water. A portion of this stock solution was added to the influent water and mixed using a magnetic stir rod throughout the experimental run (Table 3.2).

While consistent mixing and preparation procedures were used for each influent batch, the variability present in the potting mix led to variability in sorption to the potting mix and thus to influent concentrations. To account for this variability in concentration and mass reduction calculations, influent concentration was sampled and analyzed for each run. Pesticides used in the simulated runoff were chosen to represent a range of transport properties. Chosen pesticides were: bifenthrin, carbaryl, chlorothalonil, fipronil, and pendimethalin. These five pesticides have a different likelihood of being found in runoff due to different values for water solubility and K_{oc}.

Table 3.2 - Mass of each pesticides used to make simulated runoff for the column studies.

Active Ingredient	Product	% Active Ingredient
Pendimethalin[1]	Scott's Halts	1.71%
Chlorothalonil[2]	Daconil	29.6%
Fipronil[3]	Taurus	9.10%
Carbaryl[2]	Sevin	22.5%
Bifenthrin[4]	Sniper	25.0%

1 – Scott’s Miracle-Gro Company, Marysville, Ohio
2 – Crop Production Services, Chicago, Illinois
3 – GardenTech, Walpole, Massachuesetts
4 – Control Solutions Incorporated, Pasadena Texas

3.3.5 Sample Collection and Analysis

A total of three pore volumes of influent were added to each column during each experimental run. Two samples were taken per column per experimental run. The first sample taken was water that had been stored from the prior run and the second sample was water from the current run. Because a different amount of water was stored between the fully saturated and partially saturated columns, the first and second samples were different for each treatment. Outflow was captured in 1 L glass amber bottles. To estimate average flow rate, time was recorded when each sample was taken and samples were weighed. Influent samples were collected at the outlet of the peristaltic pump since some sorption may have occurred within the pump tubing. Quality assurance and quality control (QA/QC) was performed using laboratory spikes, method blanks, and sample duplicates. Also, the experiment was run in triplicate to account for variation within treatments. QA/QC was randomly performed for approximately 5% of the samples.

To analyze for pesticides, samples were first extracted using a vacuum manifold and Teflon tubing onto Agilent Technologies 50 mg C18 solid-phase extraction cartridges. Samples were extracted within 48 hours of sampling. Cartridges were frozen until analyzed. The C18 cartridge was then eluted with 1 ml of reagent grade acetone and 10 ml of reagent grade ethyl acetate. To dry the solvent, 3-4g of anhydrous sodium sulfate was added. The samples were evaporated to a final volume of 1 mL using low heat and a gentle nitrogen stream and then transferred to a gas chromatography vial. Finally, the sample was analyzed using an Agilent 6850 Gas Chromatograph (Agilent Technologies, Pala Alto, California). This was equipped with a 15 m x 0.25 mm HP-5 column (Agilent Technologies, Pala Alto, California) and splitless inlet. The oven start temperature was

80°C which was held for one minute and then ramped at 11.0 °C/min to 170°C, then ramped at 8.0 °C/min to 190° C, then ramped at 11.0 °C/min to 255°C, and finally ramped at 20.0 °C/min to 295° C. The column had a flow rate of 1.2 ml/min with an average velocity of 57 cm/sec.

The gas chromatograph was coupled with an Agilent 5975c mass spectrometer inert source instrument (Agilent Technologies, Palo Alto, California) which was used to detect and quantify analytes. Temperature of the sources was 230°C and quadropoles were at 150°C. The ionization source was electron ionization (EI) at 70 eV. Detection and quantitation were based on 3-ion selected ion monitoring (SIM) and two deuterated polyaromatic hydrocarbon compounds, chrysene (target ion = 240.0) and anthracene (target ion = 188.0), were used as internal standards. Samples were analyzed for the five pesticides used in the study with the following target and qualifier ions: chlorothalonil (266.0: 264.0, 229.0), carbaryl (144.0: 115.0, 201.0), pendimethalin (252.0: 281.0, 162.0), fipronil (367.0: 351.0, 420.0), and bifenthrin (181.0: 165.0, 166.0). Analyte concentrations were determined by creating a calibration curve with known concentrations for each compound and matching retention time and ratios of the target and qualifier ions to those found in the samples.

3.3.6 Data and Statistical Analysis

Percent removal was calculated for each effluent sample using the influent concentration from the current run (Equation 3.1).

$$Percent\ Removal = \frac{(C_{in} - C_{out})}{C_{in}} \qquad \text{Equation 3.1}$$

Where C_{in} is the influent concentration for the current run and C_{out} is the effluent concentration of the sample. Percent removal was calculated on a run basis to account for variation of influent concentration. A regression was performed between influent concentration and percent removal.

Each compound was tested for statistical significance individually and then results from all compounds were tested for statistical significance together. A one-way ANOVA was performed to determine if differences existed between replications for each compound. Values for percent removal were then grouped by compound and a general linear model was developed for each compound to determine which variables, two-way interaction, and three-way interactions of variables were significant. Variables tested were: first sample or second sample, fully saturated or partially saturated, antecedent period between runs, run. A general linear model was constructed for each compound to determine significant variables. Each variable was tested for significance (p-value < 0.05 was considered significant). If there were variables that were not significant, then the variable or two-way interaction variable with the highest p-value was removed and the general linear model was reconstructed. This was performed until all variables or interaction variables were significant. These variables were then tested using Tukey’s multiple comparisons to determine differences in means. Because each column was used for multiple runs, column identity was included as a repeated measure. As a repeated measure it is not part of the general linear model or the Tukey’s comparisons, but is included to account for multiple runs using the same column. All statistical analysis was performed in Minitab® 17 (Minitab Inc., State College, PA).

3.4 Results

Quality control was performed using lab spikes, method blanks, and sample duplicates. Mean recoveries were 96% for chlorothalonil (SD=14), 100% for carbaryl (SD=6), 98% for pendimethalin (SD=11%), 96% for fipronil (SD=6%), and 96% for bifenthrin (SD=29%). These are within the standards published for similar compounds in EPA Method 1699 (2007) (recovery range is 50%-120%, maximum SD is 30%). Blank sample concentrations were less than 0.05% of average sample concentration for each compound. Duplicate samples were within ±15%. Experimental replications found no significant difference at a 95% confidence in concentration reduction among the three replications for all compounds except pendimethalin (p-value=0.007, mean/standard deviation = 98%/1.8%, 97%/6.2%, 99%/1.8%). Influent concentrations were analyzed for each run (Table 3.3). Flow rate was set at 6 ml/min by the peristaltic pump. The average effluent flow rate was 5.8 ml/min (median=5.9 ml/min, SD=1.5 ml/min) as measured by recording the time that a sample was taken and weighing the sample.

Table 3.3 - Descriptive statistics for influent concentrations for all samples taken during the column study.

	Influent Concentration (µg/L)				
	Carbaryl	Chlorothalonil	Pendimethalin	Fipronil	Bifenthrin
Mean	650	680	62	270	210
Median	660	550	45	270	150
Standard Deviation	130	270	94	60	160

Results from the Tukey's analysis of the general linear model are shown in Table 3.4. This analysis was performed with all pesticide compounds, Tukey's tests were also performed for individual compounds and are presented separately. Pendimethalin and chlorothalonil had the highest reduction of any of the five pesticide compounds and were not significantly different from each other. Overall, saturation did not significantly affect removal. For three of the compounds, there also was not an effect from antecedent period but there was an effect for two of the compounds. The interaction between antecedent period and run was significant when all pesticide compounds were analyzed together. The 3-day and 10-day antecedent periods did not demonstrate a significant reduction in removal after the first run but the 1-day demonstrated significant reduction in removal from the first run to the third and fourth runs (Figure 3.3). There was a difference between sample for three of the compounds with the first sample have higher removal than the second sample (Figure 3.4). The first sample was the volume of water stored in the column between runs and the second sample was water that flowed through during the same run. While there was a significant difference between antecedent period among the first sample, there was also a significant difference between antecedent period among the second sample (Figure 3.5). The interaction between sample and antecedent period was not significant in the general linear model.

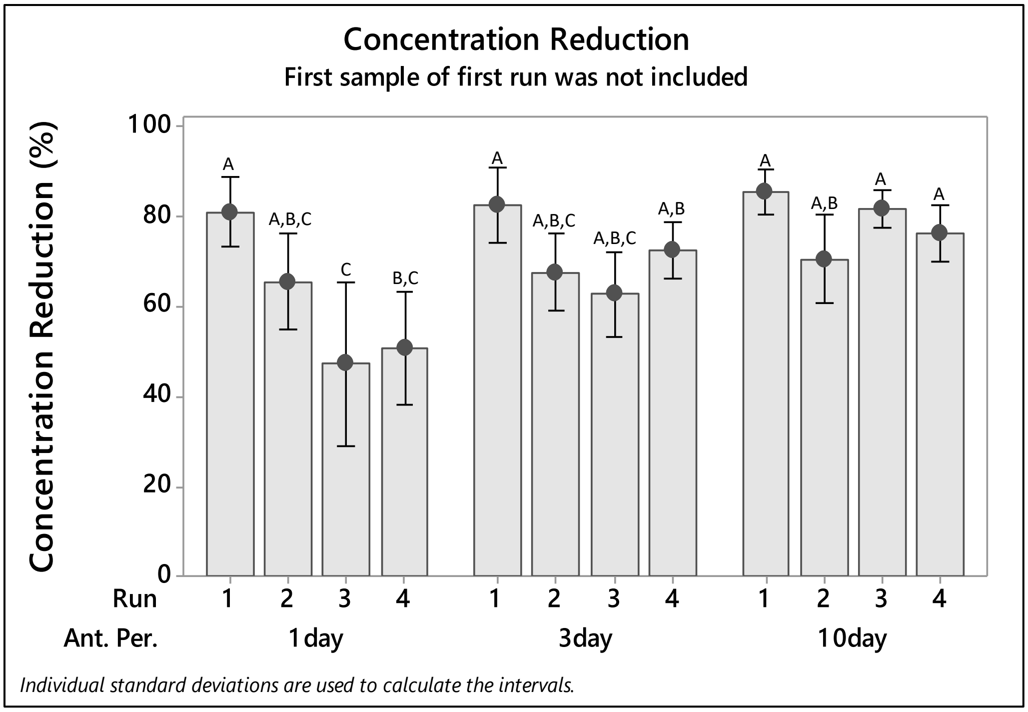

Figure 3.3 – Concentration reduction comparison between the variables of run and antecedent period.

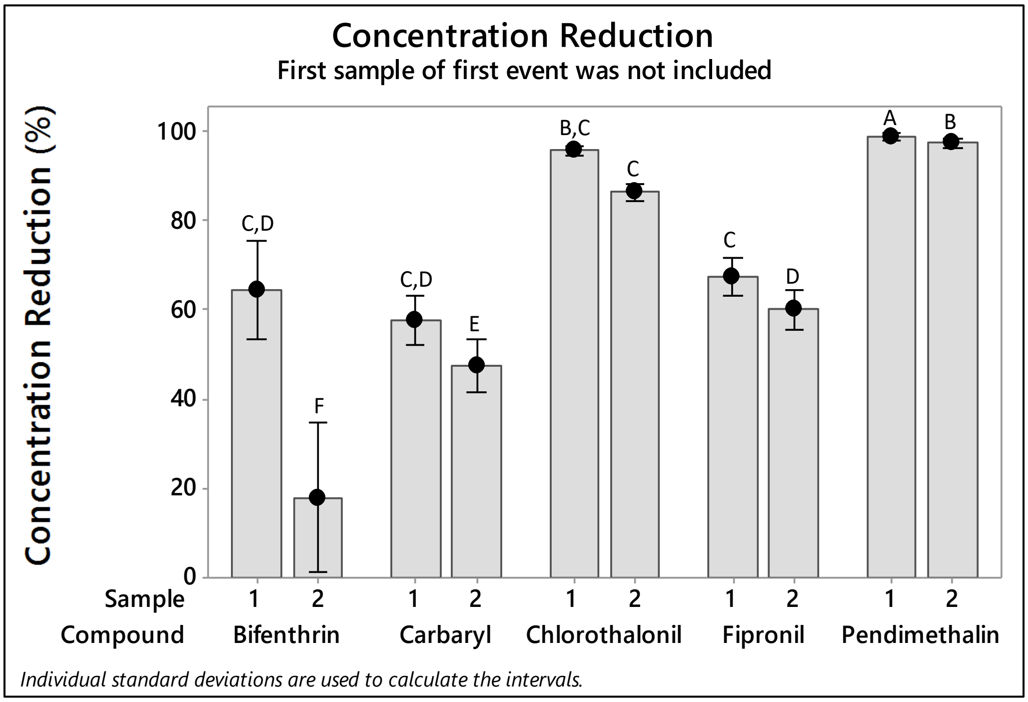

Figure 3.4 – Concentration reduction comparison between compound and sample.

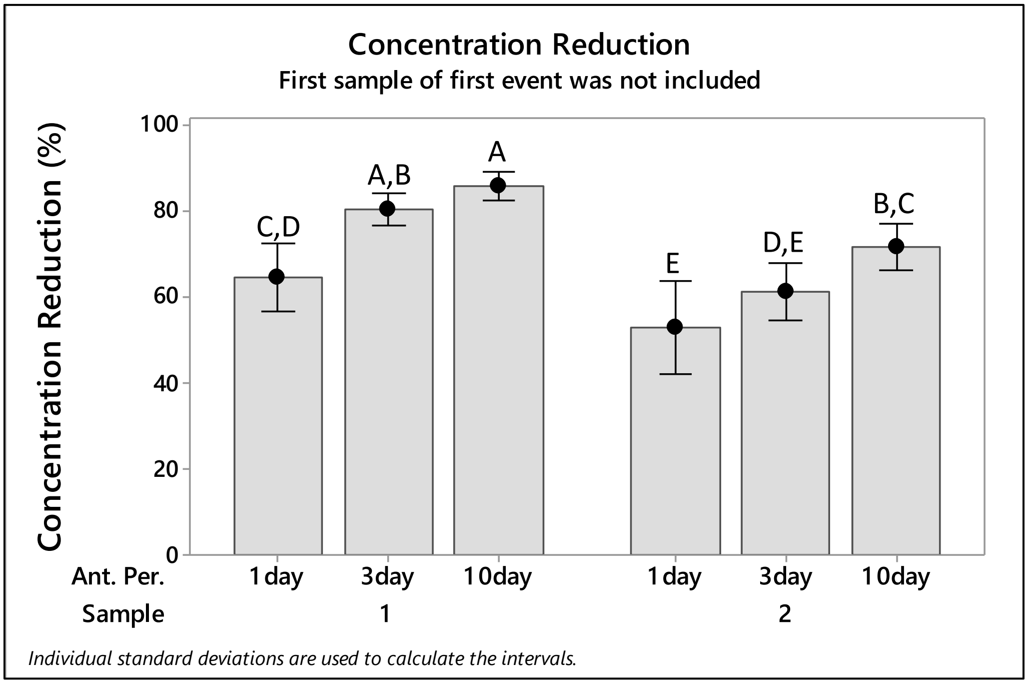

Figure 3.5 – Concentration reduction comparison between antecedent period and sample.

Table 3.4 - Concentration reduction percentages. Values within each variable that do not share a letter are significantly different.

		Concentration Reduction				
Variable	Treatment	Pendimethalin	Chlorothalonil	Fipronil	Carbaryl	Bifenthrin
All Samples	All	98%^{A}	92%^{A}	67%^{B}	47%^{C}	45%^{D}
Saturation	Partial	98%^{E}	91%^{E}	67%^{F}	54%^{G}	51%^{G,H}
	Full	98%^{E}	92%^{E}	68%^{F}	61%^{F,G}	40%^{H}
Antecedent Period	10 days	99%^{I}	94%^{I}	71%^{J}	71%^{J}	67%^{J,K}
	3 days	99%^{I}	89%^{I}	67%^{J,K}	55%^{K,L}	55%^{K,L}
	1 days	99%^{I}	93%^{I}	65%^{J,K}	46%^{L}	11%^{M}
Sample	First	>99%^{N}	97%^{N,O}	74%^{O}	66%^{P,Q}	69%^{P,Q}
	Second	97%^{N,O}	87%^{O}	61%^{Q}	49%^{R}	20%^{S}
Experiment Run	1	>99%^{T}	97%^{T}	92%^{T,U}	79%^{U,V,W}	71%^{V,W,X}
	2	98%^{T}	92%^{T,U}	70%^{W,X}	44%^{Y,Z}	34%^{Z,AA}
	3	98%^{T}	90%^{T,U}	60%^{X,Y}	53%^{Y}	22%^{AA}
	4	98%^{T}	89%^{T,U,V}	48%^{Y,Z}	53%^{X,Y}	51%^{Y,Z}

3.5.1 Pendimethalin

Pendimethalin exhibited very high removals overall, likely due to lower influent concentrations. Due to consistently high removals, fewer differences existed among treatments (Table 3.5). Antecedent period and sample were the only variables that had statistically significant differences and no interactions were significant. The removal of the 1 day and 10 day antecedent periods were significantly higher than the removal for the 3 day antecedent period but were not different from each other. The removal for the first sample was higher than the removal for the second sample.

Table 3.5 - Results from Tukey's test for pesticide concentration reduction for pendimethalin.

Variable	Treatment	Pendimethalin Mean Concentration Reduction
Saturation	Partial	99% ^{A}
	Full	98% ^{A}
Antecedent Period	10 days	99% ^{B}
	3 days	99% ^{C}
	1 days	97% ^{B}
Sample	First	99% ^{D}
	Second	97% ^{E}
Run	1	>99% ^{F}
	2	98% ^{F}
	3	98% ^{F}
	4	98% ^{F}
Antecedent Period*Run	10*4	97% ^{G}
	10*3	98% ^{G}
	10*2	97% ^{G}
	10*1	98% ^{G}
	3*4	99% ^{G}
	3*3	>99% ^{G}
	3*2	>99% ^{G}
	3*1	>99% ^{G}
	1*4	97% ^{G}
	1*3	96% ^{G}
	1*2	97% ^{G}
	1*1	98% ^{G}

3.5.2 Chlorothalonil

Chlorothalonil removal was affected by antecedent period, sample, and run but not by saturation without interaction (Table 3.6). The first sample exhibited higher removal than second sample. Antecedent period exhibited a difference between 3 day and the other two treatments, but 10 day and 1 day were not significantly different. Run played a role with the first run exhibiting the highest removal, second and third exhibiting removals that were not significantly different, and third and fourth exhibiting removals that were not significantly different.

Some interactions between variables were significant. While saturation alone was not significant, its interaction with sample was significant. The first sample exhibited no difference between the saturation treatments, but the second sample exhibited a higher removal for saturated than for unsaturated. The interaction between antecedent period and run was again significant with the first run for the 3 day and 1 day antecedent periods exhibiting higher removal than the other runs of the respective treatments. The 10 day antecedent period did not exhibit significant differences among runs. The interaction between sample and run was significant. The second sample of the first run was not significantly different than the first sample of the second, third, or fourth runs. The second samples of the second, third, and fourth runs were significantly lower than all other samples. Again, no discernable relationships existed for three-way interactions.

Table 3.6 Results from Tukey's test for pesticide concentration reduction for chlorothalonil.

Variable	Treatment	Chlorothalonil Mean Concentration Reduction
Saturation	Partial	91% ^{A}
	Full	92% ^{A}
Antecedent Period	10 days	93% ^{B}
	3 days	89% ^{C}
	1 days	93% ^{B}
Sample	First	96% ^{E}
	Second	87% ^{F}
Run	1	97% ^{G}
	2	92% ^{H}
	3	90% ^{HI}
	4	88% ^{I}
Antecedent Period*Run	10 day*1	95% ^{JK}
	10 day*2	92% ^{J,K,L}
	10 day*3	94% ^{J,K}
	10 day*4	90% ^{K,L,M}
	3 day*1	98% ^{J}
	3 day*2	88% ^{L,M}
	3 day*3	85% ^{M}
	3 day*4	84% ^{M}
	1 day*1	98% ^{J}
	1 day*2	95% ^{J,K}
	1 day*3	90% ^{K,L,M}
	1 day*4	89% ^{K,L,M}

3.5.3 Fipronil

Fipronil exhibited significantly different removals for antecedent period, sample, and run but not for saturation (Table 3.7). The 10 day antecedent period was not different from the 3 day antecedent period and the 3 day antecedent period was not different from the 1 day antecedent period, but the 1 day and 10 day were different. The first sample (stored water) was different from the second sample (current run water). All runs were significantly different from each other with removal following in order of the first run having highest removal and the fourth run having lowest removal.

Interactions between antecedent period and sample and also antecedent period and run were significant as well. The first sample of the 10 day antecedent period and the 3 day antecedent period were not different but were higher than all other samples. The first sample of the 1 day antecedent period was not significantly different from the second samples for the 1 day and 10 day antecedent periods. Second samples from all antecedent periods were not different.

Table 3.7 - Results from Tukey's test for pesticide concentration reduction for fipronil.

Variable	Treatment	Fipronil Mean Concentration Reduction
Saturation	Partial	68% ^{A}
	Full	69% ^{A}
Antecedent Period	10 days	71% ^{B}
	3 days	63% ^{B}
	1 days	71% ^{B}
Sample	First	75% ^{C}
	Second	62% ^{D}
Run	1	92% ^{E}
	2	70% ^{F}
	3	60% ^{G}
	4	50% ^{H}
Antecedent Period*Run	10*1	90% ^{I,K,L,M,S}
	10*2	70% ^{J,N,O,P,Q,R,T,U}
	10*3	65% ^{N,O,P,Q,R,T,U}
	10*4	58% ^{N,O,P,Q,R,T,U}
	3*1	89% ^{I,J,K,L,N,P}
	3*2	62% ^{M,O,R,S,T}
	3*3	52% ^{O,Q,R,T,U}
	3*4	47% ^{Q,U}
	1*1	97% ^{Q,R}
	1*2	78% ^{K,M,N,O}
	1*3	65% ^{L,P,Q,S,T}
	1*4	45% ^{R,U}

3.5.4 Carbaryl

Carbaryl removal exhibited differences on the greatest number of treatments of any compound (Table 3.8). Carbaryl was the only compound to exhibit a statistically significant difference between saturated and partially saturated with saturated samples having a higher removal. Each treatment among the antecedent period variable was statistically different with 10 day having the highest removal, 3 day having medium removal, and 1 day having the lowest removal. The two samples of the run (stored water vs water from the current run) also exhibited statistically significantly different removals with the sample of the stored water having higher removal than the sample of the water from the current run. Run was significant, but only the first run was significantly different from the other three and the other three were not different from each other.

Some interactions between the variables were also significant. The interaction of the variables of saturation and antecedent period was significant with the saturated 3 day significantly different from the partially saturated 3 day. For both other antecedent periods, saturation was not significantly different. The interaction between antecedent period and run was significant. The first run for the 3 day antecedent period and the 1 day antecedent period were significantly different than the other runs within the respective antecedent periods. Within the 10 day antecedent period however, there was no significant differences among runs. Due to the large number of variations within the interactions no discernable relationships were seen in the three-way interactions.

Table 3.8 - Results from Tukey's test for pesticide concentration reduction for carbaryl.

Variable	Treatment	Carbaryl Mean Concentration Reduction
Saturation	Partial	61% ^{A}
	Full	53% ^{B}
Antecedent Period	10 days	70% ^{C}
	3 days	55% ^{D}
	1 days	46% ^{E}
Sample	First	66% ^{F}
	Second	48% ^{G}
Run	1	78% ^{H}
	2	53% ^{I}
	3	52% ^{I}
	4	46% ^{I}
Antecedent Period*Run	10 day*1	73% ^{J,K}
	10 day*2	63% ^{K,L,M}
	10 day*3	74% ^{J,K}
	10 day*4	70% ^{J,K,L}
	3 day*1	85% ^{J}
	3 day*2	31% ^{O}
	3 day*3	47% ^{L,M,N,O}
	3 day*4	56% ^{K,L,M,N}
	1 day*1	76% ^{J,K}
	1 day*2	43% ^{M,N,O}
	1 day*3	36% ^{N,O}
	1 day*4	29% ^{O}

3.5.5 Bifenthrin

Bifenthrin had the lowest removal of any pesticide compound. Although bifenthrin has a high affinity for soil particles, its transport in the soluble form is increased by dissolved organic carbon (DOC) (Delgado-Moreno et al., 2010). The combination of high influent concentrations and the presence of dissolved organic carbon may have led to reduced removal efficiency. Variables that significantly affected bifenthrin removal were antecedent period, sample, and run but not saturation (Table 3.9). The removals for the 10 day and 3 day antecedent periods were not different from each other but were higher than removal for the 1 day antecedent period. Removal for the first sample (stored water) was higher than removal for the second sample (current run water). The first, second, and fourth runs were not significantly different from each other but the second and fourth runs were significantly different from the third run.

The only significant interaction was between antecedent period and run. All runs for the 3 day antecedent period were not different from one another. The second, third, and fourth runs for the 10 day antecedent period were not significantly different from one another, however the second and third runs were higher than the first run.

Table 3.9 - Results from Tukey's test for pesticide concentration reduction for bifenthrin.

Variable	Treatment	Bifenthrin Mean Concentration Reduction
Saturation	Partial	50% ^{A}
	Full	41% ^{A}
Antecedent Period	10 days	37% ^{B,C}
	3 days	99% ^{B}
	1 days	0% ^{C}
Sample	1	68% ^{D}
	2	23% ^{E}
Run	1	70% ^{F}
	2	34% ^{G}
	3	24% ^{G}
	4	54% ^{F,G}
Antecedent Period*Run	10*1	48% ^{H,I,J,K,L}
	10*2	-9% ^{G,J}
	10*3	50% ^{H,I,J,K,L}
	10*4	61% ^{H,G,I,J}
	3*1	108% ^{H,G}
	3*2	103% ^{H,G}
	3*3	85% ^{H,G,I,J}
	3*4	100% ^{H,G}
	1*1	56% ^{H,G}
	1*2	7% ^{H,G}
	1*3	-63% ^{I,J}
	1*4	2% ^{H,G,I,J}

3.5 Discussion

Pesticide transport and fate varies by compound and environmental condition (Schroll et al., 2006). Variation was apparent in this study as different compounds exhibited higher removals under different conditions. There were also common trends for all or the majority of compounds. Each variable will be discussed individually.

3.6.1 Saturation

The outlet elevation was set at either 15.2 cm (6 inches) or 30.5 cm (12 inches). The media depth was set at 22.9 cm (9 inches), so half of the columns remained saturated with ponded water and half of the columns had only a portion of the media saturated between runs. It was hypothesized that the saturation conditions would lead to differences in pesticide removal. Only one compound, carbaryl, exhibited a statistically significant difference between saturated and partially saturated columns. It is likely that the duration of the experiment influenced the lack of variation between saturation treatments for other compounds because a microbial community was not able to establish in the relatively short duration of the experiment. For example, Zhu et al. (2004) found degradation of fipronil occurred three times more rapidly in a non-sterile soil than in a sterile soil. While the fully saturated columns experienced anaerobic conditions, it is possible that the lower portion of media in the partially saturated columns experienced anaerobic conditions as well. A study by Deul et al. (1985) showed that carbaryl underwent both chemical and biotic transformation in a flooded rice field. Since carbaryl undergoes chemical transformation in addition to biotic transformation, it is possible that saturation affected carbaryl removal due to its ability to be chemically transformed.

3.6.2 Antecedent Period

Antecedent period affected removal for all compounds. In all cases, the 10 day antecedent period had the highest removal, although in most cases it was not significantly different from one of the other treatments. The interaction between antecedent period and sample was not significant meaning that the differences exhibited between antecedent period were consistent for both the first and second samples. Only one compound, carbaryl, exhibited differences among all three antecedent periods. For two compounds, pendimethalin and chlorothalonil, the 1 day antecedent period had higher removal than the 3 day antecedent period. Removal for bifenthrin was higher under the 3 day antecedent period than the 1 day antecedent period. The mixed results indicate that the difference between 1 day between runs and 3 days between runs did not make a significant difference for all compounds. However, 10 days between runs did improve removal for all compounds. The commercial application of this result is that when nursery irrigation runs are less frequent, removal is likely higher. One scenario for a lower run frequency could occur in late fall through early spring when plants still need moisture to prevent desiccation but are not actively growing. Another scenario is a runoff management plan that cycles runoff routing through a different treatment unit for each daily run.

The interaction between antecedent period and run was also significant for multiple compounds. For the majority of the interactions, removals for the 10 day antecedent period did not vary among run, but removal decreased after the first run for the 1 day and 3 day antecedent periods. While this study was different from a typical field installation in that it had high concentrations and was installed for a short period of time, this has possible implications for performance over time. If a constructed wetland receives less frequent runs, then it could potentially maintain performance for a longer period of time.

3.6.3 Sample

Sample (stored sampled or sample of water from current run) exhibited significant differences for every compound. One exception to this was fipronil at a 1 day antecedent period which had no significant difference between the first sample and second sample. This indicates that for fipronil at 1 day, there is no additional removal for water that remained from the previous run vs water from the current run. For all other compounds, the first sample had a higher removal than the second sample. The first sample is the volume of water that remained in the column between runs. The second sample is the volume of water that was not remaining from the previous run but rather flowed through during the run in which it was sampled. The first sample has a higher effective residence time; a residence time that includes travel time from inlet to outlet and also contact time during the antecedent period between runs. There was a significant difference between the first samples for the 10 day and 1 day antecedent periods. There is evidence that the effect for higher removal for the stored water sample is stronger for the longer antecedent period. Studies at both the field- and lab-scale have been performed that attempt to characterize the mechanisms of pesticide removal and transport within saturated or variably saturated systems. Multiple studies found hysteretic effects for pesticide desorption (Mamy and Barriuso, 2007, Agyin-Birikorang et al., 2010, Passeport, et al., 2014). Mamy and Barriuso (2007) also found evidence that time affected retention of pesticides by soils. This supports the results from this study which indicates that the volume of water that is stored within the system between runs experiences higher removal than the volume of water that is not stored between runs.

3.6.4 Run

Previous research indicates that performance will decrease as pesticide is added. Graves et al. (2015) demonstrated a decrease in removal with pore volumes which is similar to run in this study. Chlorothalonil, carbaryl, and fipronil exhibited a similar a trend with run. Pendimethalin demonstrated no difference among runs and the worst run for bifenthrin was the third run. The difference from Graves et al. (2015) is likely due to much higher influent concentrations used in this study for bifenthrin.

3.6 Conclusions

Overall, the removal results from this study indicated positive removal for all five compounds tested. This study was initiated to better understand how pesticide removal is affected by saturation, time between runs and by effective retention time. While completely saturated conditions increased removal for one compound (carbaryl), it did not affect removal for the majority of the compounds tested. Time between runs affected removal with a general result of higher antecedent period resulting in higher removal. The most common trend was higher removal for the volume of water stored between runs than for volume of water that was not stored between runs. While this study was exploratory in nature and may not directly translate to design recommendations for constructed wetlands, variables that show promise in improving pesticide removal should be further investigated.

Wetlands typically go through wetting and drying cycles (van der Valk, 2005). This lab study is representative of the transition period as wetlands go from unsaturated conditions to saturated conditions. During the initial period after a wetland transitions from one hydrologic condition, there would be establishment of microbial communities and chemical conditions associated with that hydrologic condition. While saturation condition was not a significant variable in this scenario, it is possible that it would play a part after the chemical conditions and microbial communities had stabilized after the transition. It is recommended that further research be performed that simulates these stabilized conditions.

As demonstrated in other studies, pesticide removal is sometimes time-dependent and affected by hysteresis (Mamy and Barriuso, 2007, Passeport et al., 2011). This study also demonstrated that pesticide removal was time dependent and possibly experienced hysteretic effects. This has implications for runoff treatment practices that store some volume of water between storm or irrigation events such as constructed wetlands. The volume of water that is stored in the system has a longer contact time, which potentially results in higher pesticide removal. This factor could potentially be utilized to enhance removal efficiency by designing runoff treatment practices to store higher volumes of water for longer periods of time after events. .

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CHAPTER IV

A SIMPLE PROCEDURE FOR OPTIMIZED SELECTION OF LOW IMPACT DEVELOPMENT PRACTICES AND AREA TREATED AT THE WATERSHED SCALE BASED ON USER-DEFINED CRITERIA

Journal: Journal of Water Resources Planning and Management

Abstract: Low impact development (LID) is a stormwater runoff management technology that emphasizes smaller site-scale practices distributed throughout a watershed. Tools for watershed planning with LID are available, but typically require advanced technical expertise to implement. The developed optimization procedure uses simple, readily available software, the EPA Stormwater Calculator and Microsoft Excel, to determine a combination of LID practices that maximizes runoff reduction and minimizes cost. A base model is built in the EPA Stormwater Calculator to determine runoff under existing conditions. Regression equations are built for each LID practice that relate amount of impervious area treated with runoff reduction. These equations are used along with cost per area for each LID practice to determine a combination of LID practices that optimizes runoff reduction and cost. Application of the procedure is illustrated using two case studies in Oklahoma. The spreadsheet model is published online in conjunction with the publication.

4.1 Introduction

Increased impervious area in urban areas leads to high volumes of runoff and peak flows that are detrimental to downstream water bodies (Lee and Heaney, 2003). Peak flows were traditionally managed using stormwater management practices such as detention basins that store runoff and release at a controlled rate (Emerson et al., 2005). Even when these practices successfully reduce peak flow, they do not reduce overall runoff volume and thus change sediment and flow dynamics to receiving streams (Burns et al., 2012). Low impact development (LID) is an alternative philosophy of stormwater management that uses distributed site-scale structures or techniques to reduce peak flows, flow volumes, and pollutants found in stormwater (Vogel et al., 2015). LID emphasizes capture, storage, and infiltration using a suite of tools including: bioretention, downspout disconnection, permeable pavement, rainwater harvesting, and green roofs (Agouridis and McMaine, 2013). Instead of rapid conveyance in concentrated surface-flow channels or a storm sewer, LID slows runoff down, forces it to spread out and infiltrate (Vogel et al., 2015). Multiple low impact development practices can be implemented in a variety of combinations throughout a watershed to reduce runoff volumes.

When planning implementation of LID on a neighborhood scale, LID type and amount is typically designed to achieve a specified runoff reduction such as capturing the first inch of runoff, reducing current runoff volumes by 50%, or capturing a 2-year, 24 hour storm (EPA, 2011). Planning LID should also involve minimizing present and long-term costs. There are many possible combinations of LID type and amount that could result in maximum runoff reduction and minimal cost. An optimal design is difficult to achieve unless an optimization method is employed. Thus, planners need tools to help them decide what the type and number of LID structures to implement in a watershed.

4.2 Background

Optimization of type, size, and placement of LID has been researched and applied in various settings. The majority of these projects use models that require a certain level of expertise to operate. The United States Environmental Protection Agency (USEPA) has developed multiple modeling applications to aid in stormwater management design and LID BMP implementation including the Storm Water Management Model (SWMM) and System for Urban Stormwater Treatment and Analysis Integration (SUSTAIN) (Jayasooriya and Ng, 2014). SWMM is one of the most popular models used for urban stormwater runoff (Jia et al., 2012, Krebs et al., 2012, Joksimovic and Alam, 2014, Tobio et al., 2015,). A common modeling decision application is to compare pollutant reduction or volume reduction for different scenarios. Joksimovic and Alam (2014) used SWMM to model 18 different combinations of LID for runoff-volume reduction and then determined the cost per cubic meter of runoff volume reduction. Zhang et al. (2014) combined SWMM and a genetic algorithm to determine optimal amount and location of pervious pavement, green roof, and bioretention. The model optimized for cost and volume reduction and included a requirement that designs must also be beneath a given peak flow threshold. The model optimization resulted in 37 designs of near optimal solutions. While useful comparisons of different LID combinations for cost and volume reduction, the application of these methods may not be attainable by some practitioners since the methods used require an advanced level of programming and hydrologic expertise. As the implementation of LID increases, there will be greater need for guidance to smaller municipalities and developers.

4.3 Objective

. The objective of this work was to develop a simple tool that uses outputs from the EPA Stormwater Calculator and a spreadsheet built in Microsoft Excel to determine the optimal types and numbers of LID that can be implemented to reduce annual runoff volume and minimize cost (both initial cost of implementation and long-term maintenance costs).

4.4 Methods

4.4.1. EPA Stormwater Calculator

The EPA Stormwater Calculator is a simple tool that incorporates site characteristics and historical rainfall and weather data into Stormwater Management Model (SWMM) to calculate runoff, infiltration, and evapotranspiration for a small watershed. The user can set soil, soil drainage rate, topography, and land cover. Precipitation and evaporation are estimated using historical records from rain gauges and weather stations respectively. It is recommended that the user choose a rain gauge and weather station based on two parameters: proximity to the study watershed and period of record (Rossman, 2014). The calculator analyzes the most recent years on record and the number of years to analyze can be set by the user (Rossman, 2014). The calculator allows up to seven different types of LID practices. downspout disconnection, rain gardens, street planters, permeable pavements, green roofs, and infiltration basins. The design parameters that can be changed differ for each type and include: storage (ponding depth, media depth, cistern size), soil conductivity, and capture ratio (size of LID practice compared to contributing drainage area). It should be noted that the EPA Stormwater Calculator models the watershed by aggregating each LID type and routing a specified percentage of impervious area into each LID type added by the user to the model. Because areas are aggregated, it is not possible to model LID placement or LID position relative to each other.

4.4.2. Optimization Method

There are many combinations of LID type that can reduce stormwater volume in a given watershed. The optimal combination achieves maximum volume reduction at minimum cost.

This optimization method combines relationships between volume reduction and impervious area treated with cost per treated area of each LID type.

4.4.3 Base Model

A base model is built for the watershed of interest in the EPA Stormwater Calculator using existing hydrologic characteristics: soil type, infiltration rate, topography, and slope. Soil type and infiltration rate are intrinsically related but infiltration rate can be input separately from soil type. The selection of soil type is used for estimations of suction head and initial moisture deficit in the Green-Ampt infiltration model used within the calculator. The base model is used to determine runoff depth under existing conditions (no stormwater mitigation) and for predevelopment conditions.. Historical rainfall and weather data is used to simulate annual runoff under the existing conditions. The annual runoff from the base model is the maximum amount of runoff and all implementation of LID will result in a decrease of runoff from this base model depth. The predevelopment runoff depth . is estimated through modifying the impervious area land use to either forest or meadow.

4.4.4 Creating Regression Relationships

The EPA Stormwater Calculator allows a user to set how much impervious area is treated by each LID practice. Each scenario can be rerun to determine how much runoff is produced when different amounts of impervious area are treated by different LID types. A linear relationship exists between the percent impervious area treated and the depth of runoff produced for each LID practice. This relationship is used to combine the amounts and types of LID into different scenarios to determine runoff produced for each scenario. To determine the runoff reduction, precipitation is modeled for scenarios where each singular LID type treats from 0% of the impervious area to 100% of the impervious area. Each scenario produces a runoff depth that corresponds to a different amount of impervious area treated by a singular LID type. These results are then plotted and a linear regression applied to estimate runoff depth versus percent impervious area treated by each LID practice. This enables runoff to be estimated outside of the EPA Stormwater Calculator and allows runoff reduction to be combined with cost estimation to optimize LID practice.

4.4.5 Optimization Spreadsheet

4.4.5.1 Runoff Estimation

The maximum depth of runoff produced in the watershed is estimated from the base model. Any addition of LID will decrease the runoff depth. Each regression equation is structured with the y-intercept as the runoff depth of the base model. Total runoff is not the summation of all the regression equations. The regression equations each yield runoff produced for a scenario in which impervious area is treated by a singular LID type. At 0% impervious area treated, each equation yields the depth of the baseline model. Runoff depth for each LID type as calculated by the corresponding regression equation is subtracted from the depth of the baseline model to estimate runoff reduced. The summation of runoff depth reduced is subtracted from the baseline scenario runoff depth to get total runoff under the LID scenario. This depth is then multiplied by the watershed area to determine total runoff volume.

4.4.5.2 Cost Estimation

Cost is an important part of the LID decision making process. Each LID type has an initial capital cost and an ongoing maintenance cost. Costs can be found using online databases such as the Green Values Stormwater database (http://greenvalues.cnt.org/national/cost_detail.php) or the Urban Design Tools Low Impact Development website (http://www.lid-stormwater.net/index.html). There are also publications from organizations like the Water Environment Research Foundation (WERF, 2009). A cost estimation function will be included in an updated version of the EPA Stormwater Calculator to be fully released in Fall, 2017 (Rossman and Berner, 2017). The cost estimation function adjusts cost depending on whether the project is new or re-development, site suitability, and geographical location. The geographical adjustment uses US Bureau of Labor Statistics cost based on the three closest major cities or a user defined adjustment factor. Cost estimates per unit area can be multiplied by the total area of each LID type to determine total cost. Maintenance is a recurring cost subject to inflation and must be converted to present value to compare capital costs and maintenance cost. Present value of the maintenance cost is calculated using a geometric gradient.

$$P = A_1 \left(\frac{N}{1+i} \right) \qquad 6.1$$

where P is present value, A_1 is the first annual maintenance cost, N is the number of years, and i is the annual inflation rate (currently assumed to be 3%). Number of years was assumed to be 20 based on the depreciation rate for land improvements specified by the US Department of Treasury (2016). Number of years can be modified by users within the spreadsheet to reflect local accounting practices or expected design life. Since initial capital cost is already in present value, it can be added to the present value of the maintenance to determine present value total cost.

4.4.5.3 Optimization Results

The regression equations for runoff depth and for cost are added into the optimization spreadsheet. The optimization spreadsheet is flexible and enables the user to achieve different goals through changing the objective function or adding or modifying constraints. One example objective function uses linear scalarization to combine two parameters, runoff ratio and cost per gallon (Figure 4.1). The runoff ratio is the ratio of runoff depth with LID to runoff depth of the predevelopment model. Cost per gallon is the total cost of implementation and maintenance divided by the total volume of runoff reduced.

Other goals can be met through user modification of constraints and the objective function. For example, a city manager may have a set budget for stormwater improvements and wants to achieve the highest volume reduction possible while staying within budget limitations. This can be achieved by adding a constraint that the total initial cost must be less than the budget. Sometimes, a certain type of LID will be included in a project for educational or aesthetic purposes in addition to hydrologic benefit. This can be set by including a constraint that the LID type must occupy at least some minimum area. Many variations of volume reduction and cost objectives can be achieved through addition of constraints.

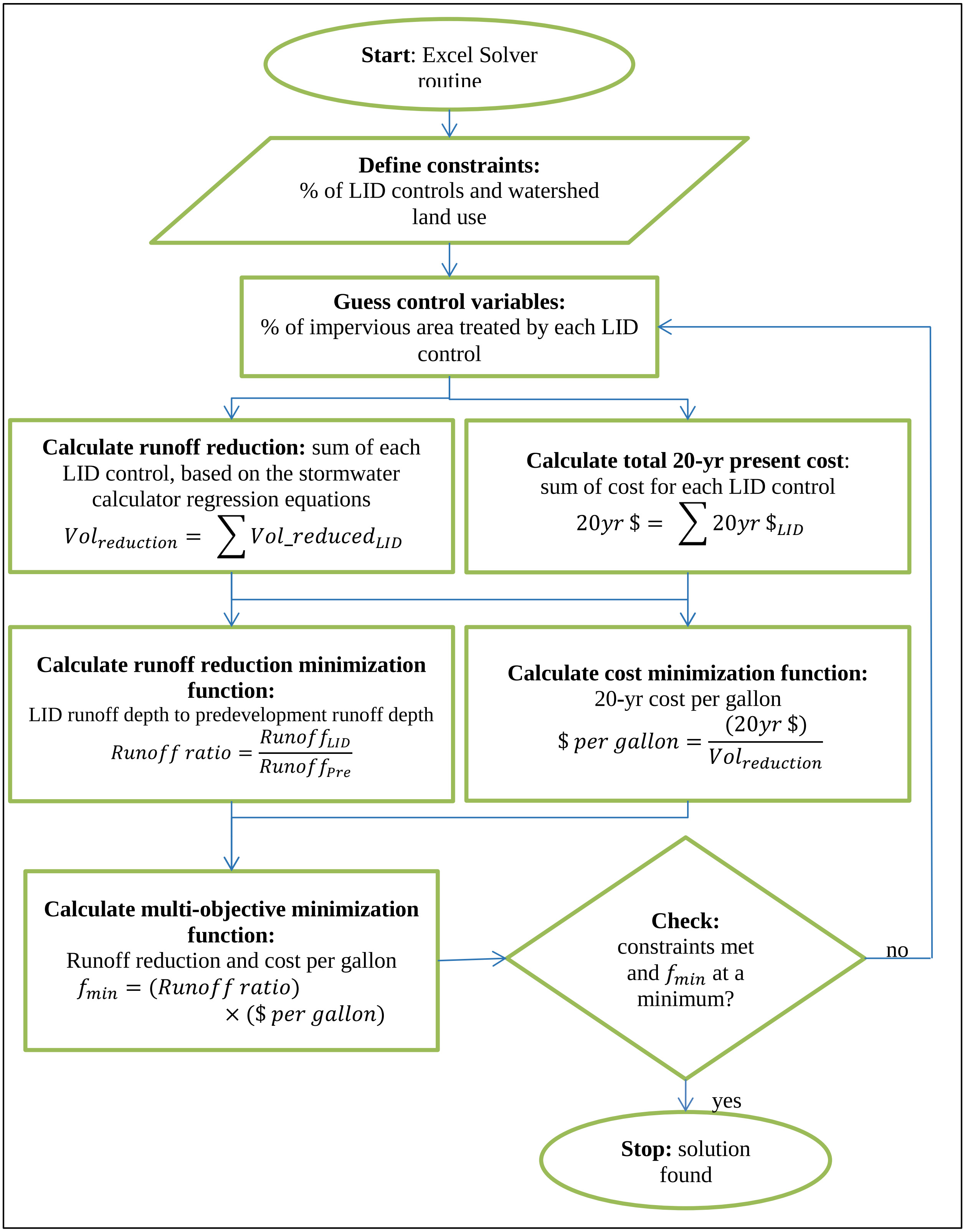


Figure 4.1 - Flow chart of optimization method.

The optimization spreadsheet also includes constraints based on physical limitations. The area that each LID type can occupy and the total area that all LID can occupy in the watershed are constrained by the factors listed in Table 4.1. Different types of LID cannot treat the same area. For example, green roofs and rainwater harvesting are constrained by the available roof area, ie – together they can treat at a maximum, the roof area in the watershed. Similarly, since bioretention and downspout disconnection both occupy green space, these two LID types cannot occupy an area greater than the amount of green space available, but it is assumed that these two LID types can treat any type of impervious area. Finally, all of the LID together cannot treat greater than 100% of the current impervious area. Additional constraints can be added by the user to reflect operational or design goals such as, runoff with LID must be below predevelopment runoff depth or annual maintenance must be within the available budget.

Table 4.1 – Physical and typical operational constraints on LID practices.

Variable	Constraint
Permeable asphalt+Pervious Concrete+Permeable Pavers	Occupy and Treat Less than Pavement Area
Rain Garden+Downspout Disconnection	Occupy Less than Green Space Area
Green Roof+Rainwater Harvesting	Treat Less than Roof Area
All Practices	Treat Less than Impervious Area
Annual Maintenance	Cost Less than Maintenance Budget
LID Runoff Depth	50% Less than Base Model Runoff Depth

4.4.6.1 Microsoft Excel Solver

The Solver function in Microsoft Excel is used to determine an optimal solution using regression equations for runoff reduction and cost. Microsoft Excel Solver uses one of three solving methods: GRG Nonlinear, Simplex LP, or Evolutionary. While the optimization spreadsheet is made up of linear equations and linear constraints, the high number of variables and relatively complex constraints, the Excel Simplex LP and Evolutionary methods will usually not converge to a solution. The iterative, GRG (Generalized Reduced Gradient) Nonlinear (Lasdon et al. 1973) was found effective in this application. It should be noted that while in general non-linear algorithms do not guarantee a global optimum solution, in this application the linear model and constraints ensure convergence to the optimum. The optimization search begins at a point chosen by the user. The program then changes the variable cell values and calculates the difference for the objective cell. Solver uses the difference information to determine which direction to change the variable cells. This is repeated until the change in the objective cell is minimized between iterations. The convergence tolerance was 0.0001.

4.4.7Case Studies

Two case studies are presented to illustrate how the optimization method was used to choose a combination of LID types that maximized runoff reduction while minimizing cost. The first case study is at the State Fair Park, Oklahoma City, Oklahoma and the second is the downtown district of Stillwater, Oklahoma.

4.4.7.1 Case Study I: State Fair Park

Watershed Background. The watershed for Case Study I was urban with high public visibility and high public interaction (Figure 4.2). The annual Oklahoma State Fair was hosted on the site as well as other shows throughout the year. City stormwater managers wanted to implement LID practices for both water quality and water quantity purposes. Impervious area made up 69% of the watershed with parking lots and streets making up 39% of the total impervious area (Table 4.2).

Figure 4.2 - Watershed delineation of State Fair Park in Oklahoma City, OK with land use highlighted.

Building the Base Model. The first step in building the base model was to determine watershed characteristics of soil type, soil drainage rate, topography, and land cover. (Table 4.2). Site characteristics were determined both from the online database accessible in the SWC and prior knowledge of the site (Table 4.3). A precipitation gauge and weather station were chosen based on their proximity to the site and period of record. Both were at the same location (Will Rogers Airport, Oklahoma City, OK) which is approximately 5.3 miles from the site and had 36 years of historical data (1970-2006). After all watershed characteristics were input to the SWC, the baseline model was run and produced 25.1 inches of annual runoff from the average 34 inches of precipitation. The predevelopment runoff depth was determined by changing the land use to 90% meadow and 10% forest. This scenario produced 11.7 inches of annual runoff. Total runoff volume is calculated by multiplying runoff depth by watershed area, 121 acres, which yields 83 million gallons annually for the base model-current conditions base model and 39 million gallons annually for the base model-predevelopment.

Table 4.2 – Land use for Case Study I watershed at the State Fair Park in Oklahoma City, OK.

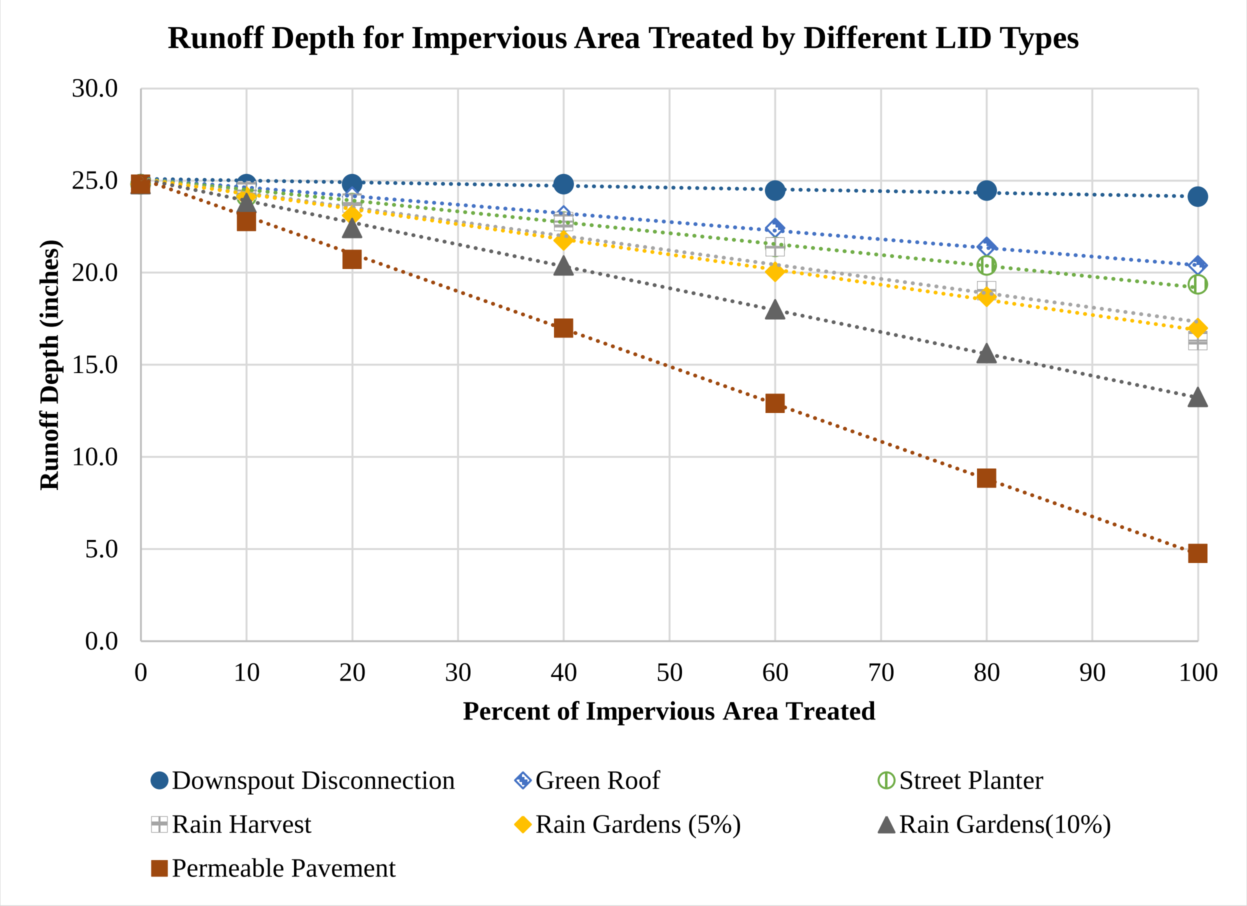
Component	Area (Acre)	% of Total Area	% of Impervious Area	Classification in Stormwater Calculator
Streets/Parking Lots	47	39%	56%	Impervious
Roofs	31	26%	38%	Impervious
Sidewalks/Other	5	5%	7%	Impervious
Total Impervious	83	69%	100%	Impervious
Pervious Area	38	31%	--	Lawn
Total Area	121			

Table 4.3 - Runoff properties that were input to the EPA Stormwater Calculator for the Case Study I watershed at the State Fair Park in Oklahoma City, OK.

Watershed Input Parameters	
Runoff Potential	D - High Runoff Potential
Soil Drainage	0.025 in/hr
Topography	Flat - 2% Slope

Creating Regression Relationships. Regression equations for the various LID practices were developed and input to the optimization spreadsheet. Two designs of rain gardens were included, one that was 5% as large as its contributing drainage area and one that was 10% as large as its contributing drainage area. Regression equations were developed with seven points, when each LID type treated 0%, 10%, 20%, 40%, 60%, 80%, and 100% of the impervious area of the watershed (Figure 4.3). These regression equations were then input to the optimization spreadsheet along with constraints and costs for implementation and maintenance.

Figure 4.3 - Regression equations for LID practices used in the optimization method for the Case Study I watershed at the State Fair Park in Oklahoma City, OK.



Optimization Solution. The optimal solution for the case study was determined by the optimization spreadsheet to be 35.5% of the impervious area treated by rain gardens (with a 10% treatment area to drainage area ratio) and 64.5% by permeable asphalt. This design reduces the runoff volume by 68% which is 69% of the predevelopment runoff depth. Cost per gallon of runoff reduced is $0.15 and total cost was about $8.5 million for around 56 million gallons of runoff reduced (Table 4.4). Other scenarios were also run that included different objectives. The first alternative scenario had an objective to minimize the installation cost per gallon, but still achieve a runoff volume that was 150% the pre-development runoff volume. This scenario led to the selection of downspout disconnection but still required permeable asphalt to achieve sufficient volume reduction (Table 4.4).

Table 4.4 - Different scenarios and the accompanying LID combinations and results. If installation cost is the minimization target, then downspout disconnection is the selected LID type. If there is a volume reduction requirement, then permeable asphalt will also be used to achieve the volume reduction.

Scenario	Primary LID Types Used and Percent of Impervious Area Treated	Percent Volume Reduced	Total Cost/ Volume Reduction ($/1,000gal)	Installation Cost/ Volume Reduction ($/1,000gal)	Total Cost ($)	Total Volume Reduction (gallons)
Original case study - minimize total cost and maximize volume reduction, Runoff volume must be less than 150% of pre-development runoff volume	Permeable Asphalt - 64.5%, Rain Garden - 35.5%	68%	150	37	8,550,000	56,160,000
Minimize Installation Cost/Volume Reduced, Runoff volume must be less than 150% of pre-development runoff volume	Permeable Asphalt - 64.5%, Downspout Disconnection - 35.5%	30%	160	32	402,000	24,940,000
Minimize Installation Cost/Volume Reduced, Runoff volume must be less than 200% of pre-development runoff volume	Permeable Asphalt - 5.3%, Downspout Disconnection - 94.7%	7%	160	22	91,300	5,560,000

4.4.7.2 Case Study II: Commercial District of Downtown Stillwater, OK

Watershed Background. The second case study was performed for the downtown commercial area of Stillwater, Oklahoma (Figure 4.4). The area was also heavily urbanized (97% impervious area) and was one of the main commercial areas of the town. The area was designed and built without subsurface stormwater infrastructure and experienced street flooding during rain events. The primary impetus for LID implementation was runoff volume reduction in order to reduce flooding.

Building the Base Model. Again, the first step was creation of the base model in the SWC in order to determine the runoff depth for the existing condition. The online database did not have coverage for this watershed, so watershed characteristics were based on external knowledge of the site and use of the Web Soil Survey (USDA NRCS). The soil of the site was identified as a Norge-Urban land complex with 1% to 5% slopes. This soil is classified as hydrologic soil group C and a moderately high infiltration rate (0.20 to 0.57 in/hr). These qualities were used to input watershed characteristics to the SWC (Table 4.5). While the soil drainage had higher infiltration rates and only moderately high runoff potential as compared to Case Study I, the watershed had a much higher impervious area (Table 4.6). The location of the precipitation gauge and weather station was 2 miles from the site (Oklahoma State University Research Farm, S. August Drive, Stillwater, OK) and had 36 years of historic data (1970-2006). The base model produces 30.3 inches of annual runoff on 35.5 inches of annual precipitation. The predevelopment scenario assumed 10% forest and 90% meadow and produced only 6.6 inches of average annual runoff. Since the soils have a higher infiltration capacity than Case Study I, the primary driver of runoff is a high amount of impervious area.

Table 4.5 - Runoff properties that were input to the EPA Stormwater Calculator for the Case Study II watershed comprising of the commercial area of downtown Stillwater, OK.

Watershed Input Parameters	
Runoff Potential	C – Moderately High Runoff Potential
Soil Drainage	0.055 in/hr
Topography	Moderate Flat - 5% Slope

Figure 4.4 – Watershed area for Case Study II, the commercial area of downtown Stillwater, OK.

Table 4.6 - Land use for the watershed in Case Study II, commercial area of downtown Stillwater, OK.

Component	Area (Acre)	% of Total Area	% of Impervious Area	Classification in Stormwater Calculator
Streets/Parking Lots	29	58%	61%	Impervious
Roofs	17	34%	35%	Impervious
Sidewalks/Other	2	4%	4%	Impervious
Total Impervious	48	96%	100%	Impervious
Pervious Area	2	4%	--	Lawn
Total Area	50			

Creating Regression Relationships. Regression equations were developed for the LID types used in the optimization spreadsheet. Two designs of rain gardens were included, one that was 5% as large as its contributing drainage area and one that was 10% as large as its contributing drainage area. Regression equations were developed with seven points, when each LID type treated 0%, 10%, 50%, and 100% of the impervious area of the watershed (Figure 4.5). These regression equations were then input to the optimization spreadsheet along with constraints and costs for implementation and maintenance. Downspout disconnection was not included as a possible practice because of the lack of potential connection between roofs and green space.

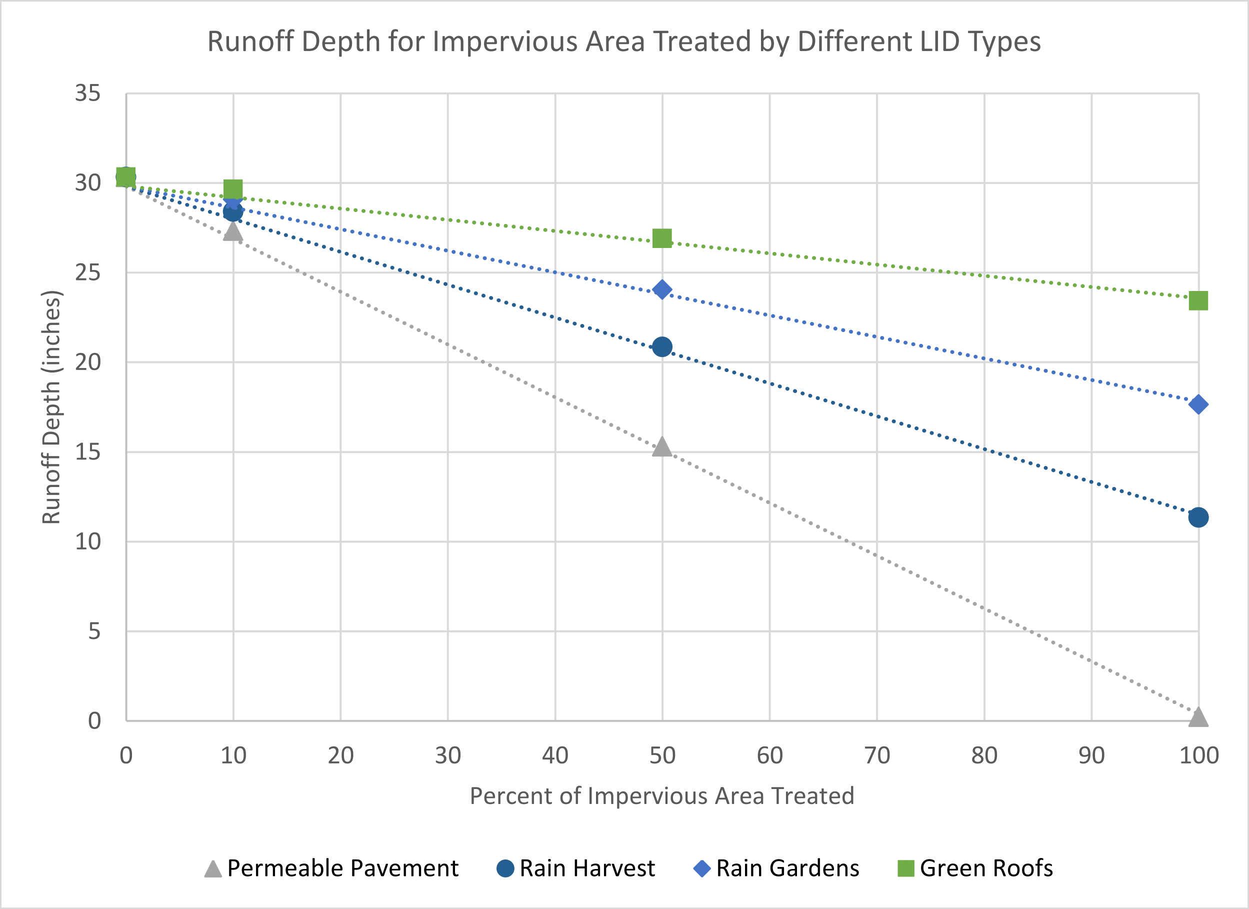


Figure 4.5 – Regression equations for Case Study II.

Optimization Spreadsheet. Two scenarios were run, the first was simply to find a combination that maximized runoff reduction while minimizing cost and the second was to minimize installation cost while achieving a 50% runoff reduction over the base model. As with Case Study I, permeable asphalt and rain gardens achieved high volume reduction at low cost compared to other LID types. The second scenario only treated 89% of the impervious area, however this was sufficient to achieve a 50% runoff reduction (Table 4.7).

Table 4.7 - Different scenarios and the accompanying LID combinations and results for Case Study II, the commercial area of downtown Stillwater, OK. Permeable asphalt and rain gardens are the primary practices selected.

Scenario	Primary LID Types Used and Percent of Impervious Area Treated	Percent Volume Reduced	Total Cost/ Volume Reduction ($/gal)	Installation Cost/ Volume Reduction ($/gal)	Total Cost ($)	Total Volume Reduction (gallons)
Original case study - minimize total cost and maximize volume reduction	Permeable Asphalt – 63.2%, Rain Harvesting – 33.8% Rain Garden – 0.4%, Pervious Concrete – 2.6%	83%	0.14	0.52	4,900,000	34,730,000
Minimize Installation Cost/Volume Reduced, Runoff volume must be reduced by at least 50% from the base model-current condition	Permeable Asphalt – 26.6%, Rain Garden – 62.5%	50%	0.11	0.36	1,200,000	20,800,000

4.6 Discussion

The optimization method presented here is a simple tool that does not require significant software investment or technical expertise. This method can quickly and easily investigate multiple scenarios with different objectives and constraints. The base model determines runoff depth with no implementation of LID and the pre-development model replaces impervious area with a different land use type based on user judgement. The watershed characteristics and design of each LID type determine the runoff reduction performance for each type. Relationships for performance and cost are then input to the optimization spreadsheet to determine a combination of LID practice that optimizes the objective function of the user's choosingwhile satisfying constraints. The different scenarios of the two case studies illustrate that different combinations of LID type are sometimes necessary to achieve different goals.

4.61 Case Studies

The primary differences between the two case studies were the runoff potential of each watershed's soil and the amount of impervious area. Both factors affected the runoff depth of the base model. In the base model for Case Study I, about 73% of rainfall became runoff and in the base model for Case Study II, 84% of rainfall became runoff. Even though the soil for Case Study II had a higher capacity to infiltrate runoff, the high amount of impervious area led to higher amounts of runoff. This also led to an unachievably low pre-development runoff depth of about 82% of annual precipitation (6.6 inches from 35 inches of precipitation).

In both case studies, the regression equation for permeable asphalt had the highest slope of any of the LID types. Even though permeable asphalt had only the third lowest cost, the combination of high runoff reduction and relatively low cost made it the best option. Rain gardens also had a relatively high slope and were fourth least expensive so were the next best tool to optimize for both runoff reduction and cost. The second scenario of Case Study I required reducing installation cost be reduced while maintaining a certain runoff reduction. Permeable asphalt was still the tool that treated the most impervious area. However downspout disconnection came into play to treat about 36% of the impervious area. Downspout disconnection has very little capacity to reduce runoff, but is the cheapest tool to implement. The third scenario reduced the runoff reduction constraint further and again set the objective to reduce installation cost. This resulted in about 95% of impervious area being treated by downspout disconnection. While this scenario resulted in a combination that cost only $91,000, it had a runoff reduction of only 7% from the base model-current condition.

4.6.2 Optimization Method

The simplicity and flexibility of the optimization method allows planners to get a rough estimate of feasibility of meeting certain objectives at certain price points. There is some setup required outside of the SWC and the optimization spreadsheet to determine land use. Within the SWC, there is also some setup required to input watershed characteristics and then to execute the calculator multiple times to develop the regression equations. While cost estimates are included in the spreadsheet, they are based on data available online and may not reflect local pricing. Users are able to modify cost estimates based on knowledge of local costs for both installation and maintenance.

The EPA Stormwater Calculator uses SWMM, a robust model that incorporates long-term weather data and physical characteristics to estimate runoff depth. While the EPA Stormwater Calculator is based on robust methods, its relative simplicity leads to a few limitations that users must consider. Specifically, it is not able to incorporate routing. Case Study I contained a stormsewer within the watershed that was not accounted for. While this likely had some effect on runoff depth, it is unlikely that the effect was large because LID is designed to treat runoff near its source. Runoff that is treated by LID was likely intercepted prior to entering the stormsewer. The inability to incorporate routing also means that the same impervious area cannot be treated by more than one type of LID. For example, overflow from a rainwater harvesting system could not be designed to be captured by a rain garden, it would instead become runoff. Treating the same impervious area with multiple LID practices could have improved runoff reduction in both case studies. Another limitation of the EPA Stormwater Calculator is related to watershed size and variability. If a watershed is large and consists of different slopes or soil types, then the watershed must be broken into subwatersheds with homogenous slope and soil type. The watersheds in both case studies were relatively homogenous so this limitation did not affect results from either case study.

4.7 Summary

A simple, accessible tool to help urban planners choose LID practices based on user-defined optimization criteria was developed. The user inputs watershed characteristics into the EPA Stormwater Calculator, a simple yet robust tool freely available online. Regression equations are then developed for each LID type and then input to the optimization spreadsheet. Area constraints are added that limit the available area for each treatment type. Finally, an objective is specified and the solver routine executed. To ensure that the resulting LID types and amounts are the optimal solution, the user should rerun the solver routine with high, medium, and low starting points for all LID types. The resulting combination is an optimization of both cost and volume reduction. The case studies demonstrate that different objectives result in different practices being chosen.

The optimization tool is intended to be a screening tool for urban planners to determine LID solutions for small watersheds. While the tool lacks some capability such as routing, it is robust and does not require significant technical expertise. The target audience is smaller municipalities and developers that can use this tool to perform preliminary analysis and determine what types of LID they should pursue in new or existing developments.

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CHAPTER V

CONCLUSIONS

Runoff from both agricultural and urban sources is a potential threat to aquatic resources. Landscape modification and anthropogenic influences increase the diversity and quantity of pollutants. Pesticides, while not in the public consciousness, are known to be ubiquitous in many urban and agricultural water bodies, often at concentrations toxic to aquatic organisms. Nutrients, specifically nitrogen and phosphorus, are one of the primary causes of algal blooms leading to the long-term detriment of water quality. Land use modification also dramatically alters the hydrologic response of a watershed.

Low impact development is a technology that utilizes natural physical, chemical, and biological processes to mitigate the impact of urban and agricultural runoff. The overall goal of the research presented in this dissertation was to evaluate and develop low impact development for runoff management. A field study investigated the use of constructed wetland systems for pesticide and nutrient removal in nursery runoff.

A lab study examined the effects of different hydrologic conditions on pesticide removal. Finally, a simple tool was developed that enables stormwater professionals to choose combination of LID types that optimize runoff reduction and cost.

1. The field study was performed to meet the first research objective, Evaluate pesticide, nutrient, and sediment removal performance of a two different types of constructed wetlands at two nurseries in Oklahoma. Conclusions and future work for the field study are:
    - Most of the pesticide compounds analyzed for were detected above reporting limits multiple times at both nursery sites, however only one pesticide at each site had a concentration that was higher than an aquatic health benchmark (either acute or chronic). While most measured influent pesticide concentrations were below published aquatic health benchmarks, frequent irrigation in conjunction with pesticide and fertilizer application could lead to chronic pollutant loading into receiving bodies of water and should be managed using constructed wetlands or similar treatment practices.
    - Both constructed wetland systems were effective at reducing non-pesticide analytes. The SFCW was effective at reducing the most commonly detected pesticides however the FSCW did not demonstrate significant mass reduction for any pesticide compound analyzed for. This could be due in part to a limited sample size and to relatively low influent concentrations.
    - Constructed wetlands can be implemented using equipment and materials typically available to nurseries. The SFCW in this study cost between $5,000 and $6,000 to construct.
    - The FSCW in this study was undersized which likely negatively impacted performance. To achieve satisfactory treatment performance, FSCWs require a relatively large area. If

limited land area is available, implementing a large-scale FSCW can take land out of production.

- Constructed wetlands are able to treat pollutants with a wide range of transport properties and can be implemented with relatively little input. It is recommended that constructed wetlands be used to treat nursery runoff.
- Future research should investigate how these systems perform over time. Future work should also include a more in-depth economic analysis and feasibility of implementation for nursery operators. While performance was demonstrated for both an SFCW and a FSCW, the two systems were in different settings. There is limited research directly comparing pollutant removal performance for the two different systems.

2. The lab-scale column study was performed to meet the second research objective to examine the effects of saturation conditions and irrigation patterns on pesticide removal. Conclusions and recommendations for future work for the lab study are:
    - Due to a relatively short time period, this study does not necessarily reflect conditions found in established constructed wetland systems. However, the hydrology of wetland systems is cyclical, going between wet and dry, and this study is similar to conditions found in wetland systems during the transition period.
    - On the time-scale of the study, saturation did not affect pesticide removal.
    - Overall, longer antecedent period led to higher pesticide removal.
    - The volume of water that was stored within the system between runs had higher removal than water that was not stored between runs.
    - Other studies have demonstrated that sorption processes are time-dependent. This study demonstrated that water remaining in the system between runs had higher removal than

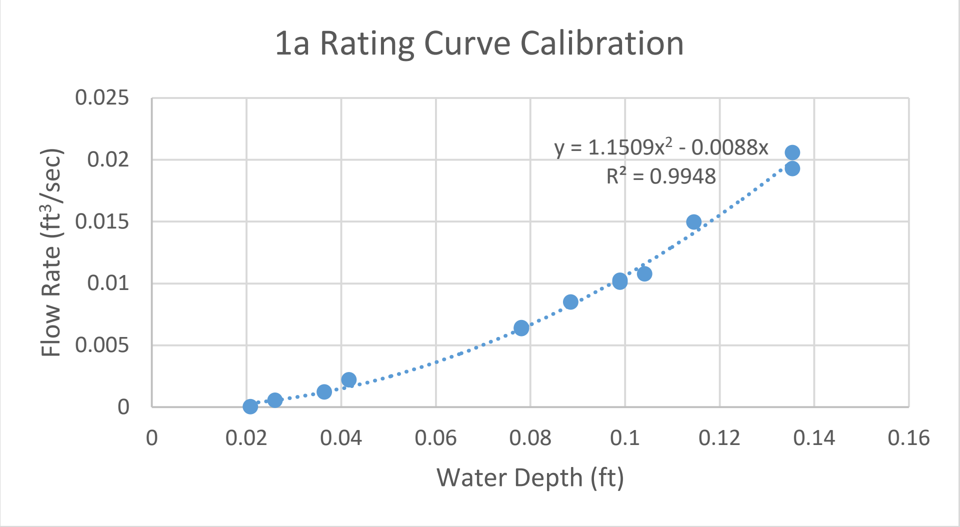
water that only flowed through the column and did not remain in the column for the period of time between runs. While this study is exploratory in nature and will not result directly in design guidance, this result should be explored further. Runoff best management practices that store water between storm or irrigation events could potentially improve removal efficiency by increasing storage volume or extending storage time.

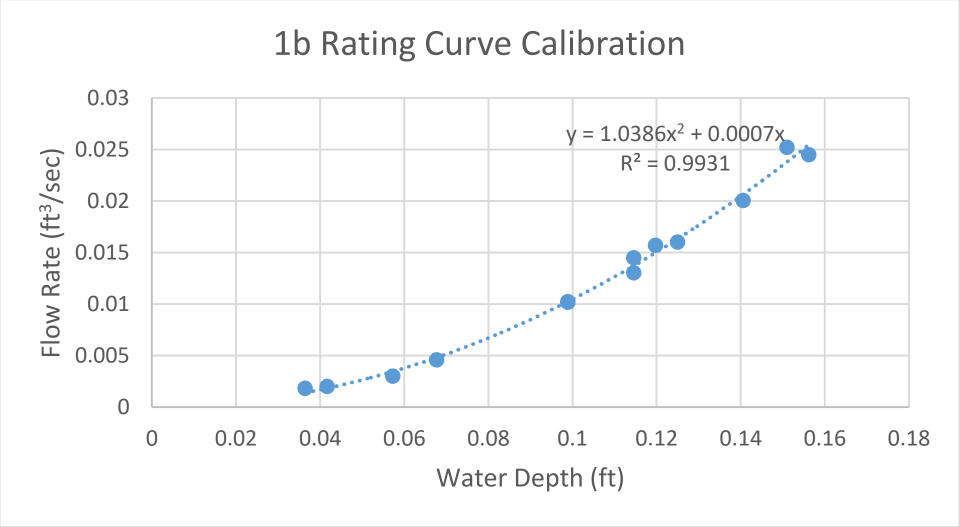
3. The third research objective was to develop a simple optimization procedure that enables stormwater professionals to choose combinations of low impact development that optimize runoff volume reduction and cost. The summary and recommendations for future work are:
    - The procedure is relatively simple, requires little time to set up, and uses available software.
    - The user can achieve different runoff reduction or cost goals by modifying the objective function of the optimization routine and/or by adding or changing constraints.
    - Because the optimization procedure does not require significant technical expertise in programming or hydrology, it is accessible to developers or municipalities that may lack the technical resources required to use more complex runoff modeling procedures.
    - The procedure is limited to smaller watersheds that have homogenous slope and soil characteristics. Due to the simplicity of the EPA Stormwater Calculator, routing and location of practices cannot be accounted for.
    - Future work could be done to make the optimization procedure more automated.

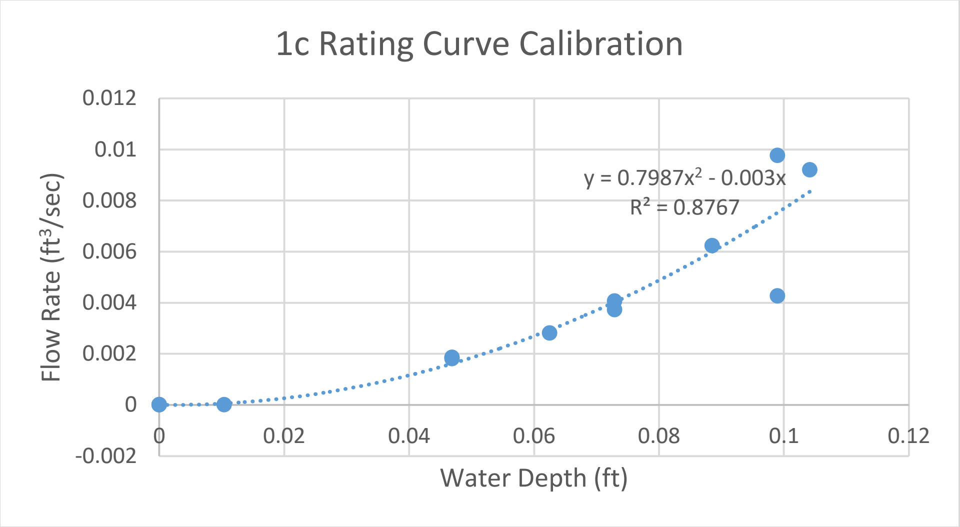
In conclusion, runoff in both agricultural and urban settings can have negative impacts on water resources. Pollutants such as pesticides and nutrients can be transported to receiving bodies of water. Constructed wetlands are a runoff management practice that can treat runoff. In urban areas, runoff can be can be managed with a suite of low impact development practices. The developed optimization procedure is a useful tool to enable developers and stormwater professionals to choose combinations of practices that maximize runoff reduction and minimize cost.

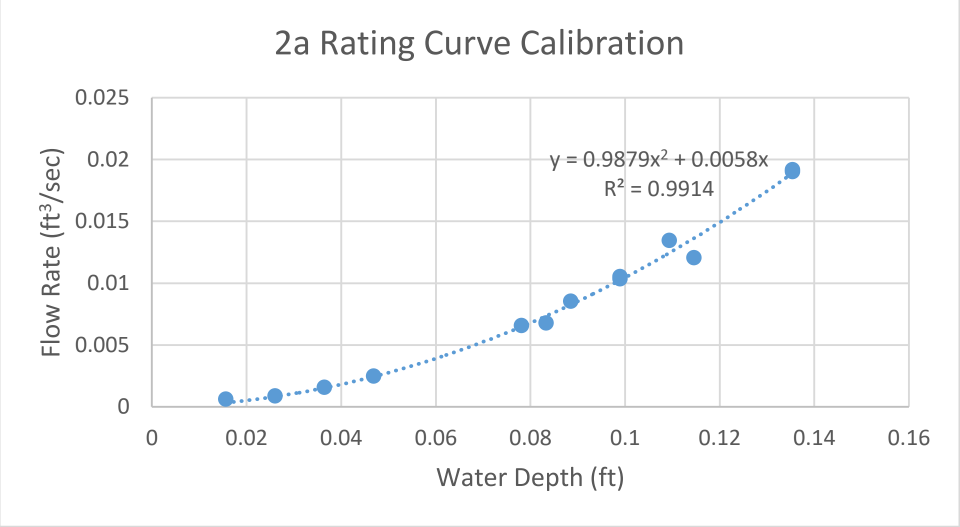
Appendix A

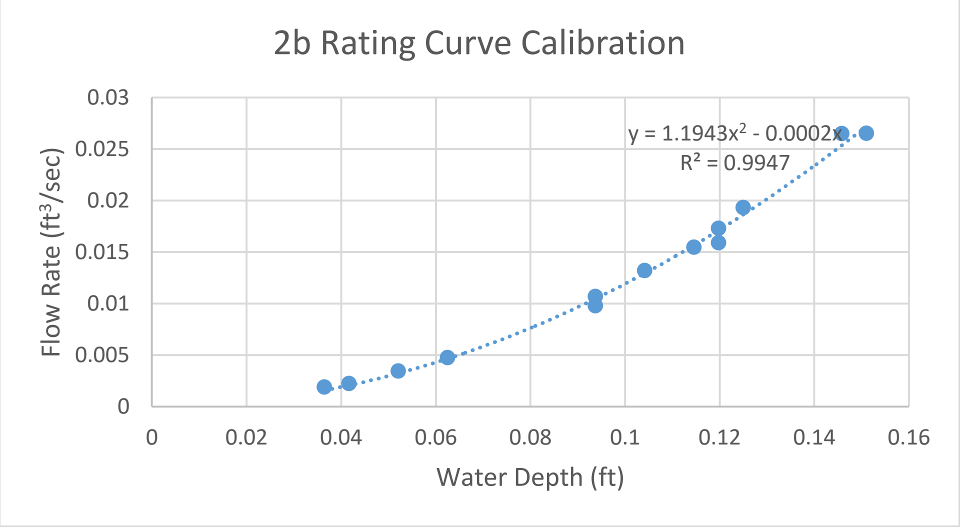
The rating curves were determined by measuring the time to fill a bucket and then the final weight of the bucket. Each cell of the free-surface constructed wetland had three openings indicated in each figure title as a,b, or c. For example, the second opening in the third cell is indicated as 3b. Since only one equation could be programmed into each auto sampler, the three openings were combined into one graph for programming purposes, however each individual curve was used to determine flow during analysis.

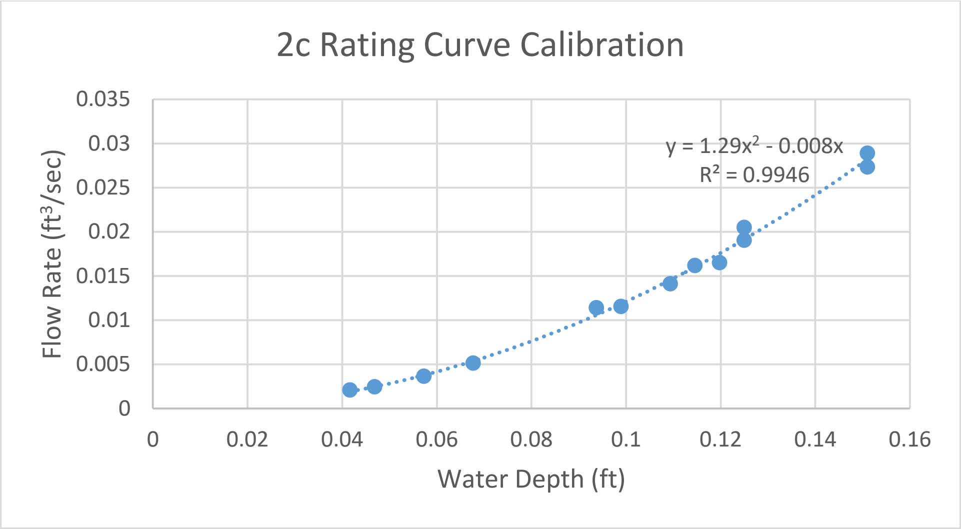


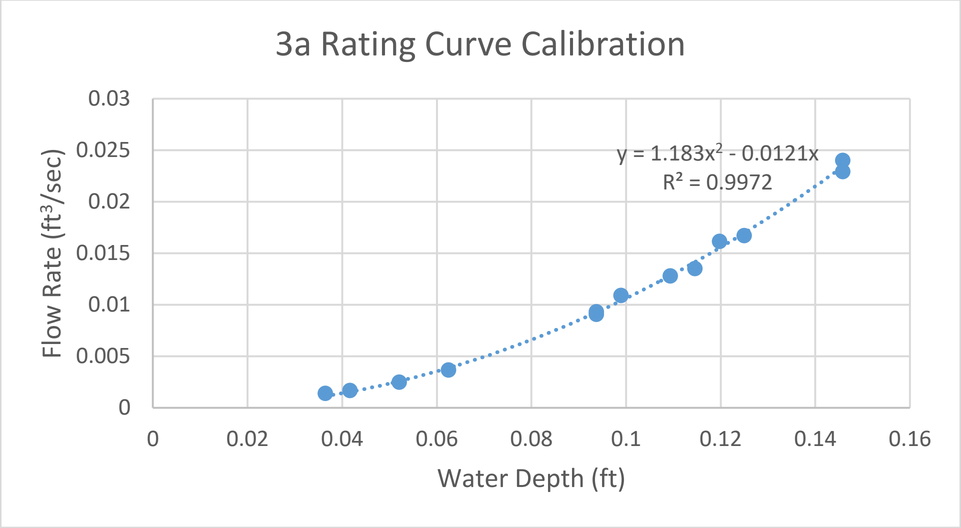


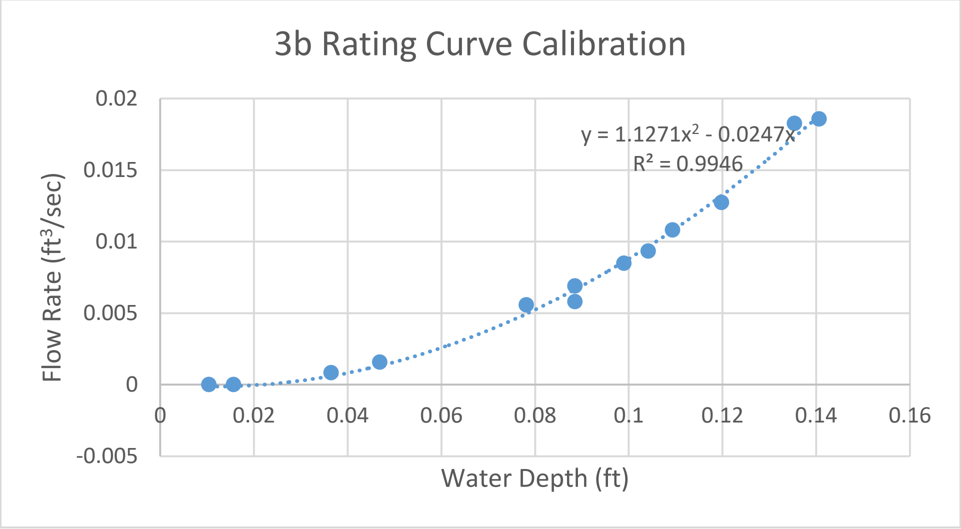

1c Rating Curve Calibration
Flow Rate (ft³/sec)
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
0
0.02
0.04
0.06
0.08
0.1
0.12
Water Depth (ft)
y = 0.7987x² - 0.003x
R² = 0.8767

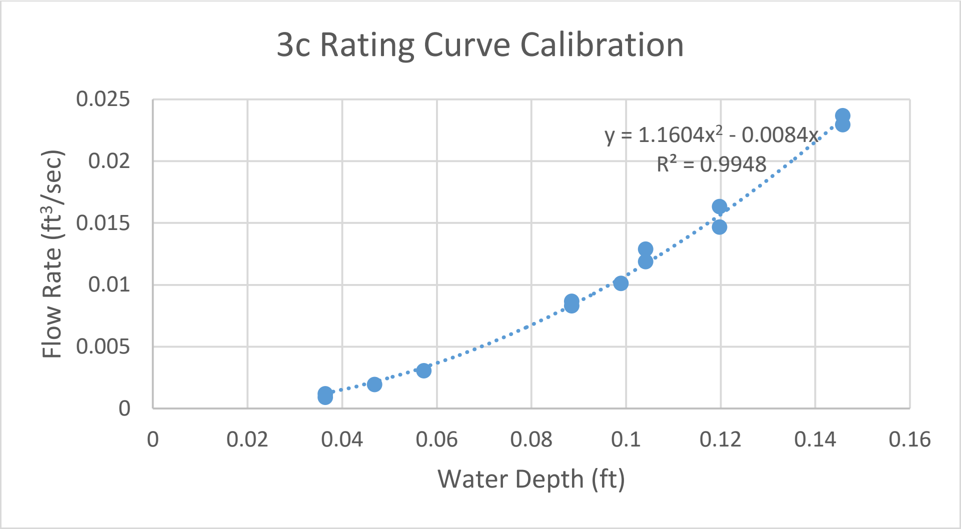

2a Rating Curve Calibration
Flow Rate (ft³/sec)
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)
y = 0.9879x² + 0.0058x
R² = 0.9914

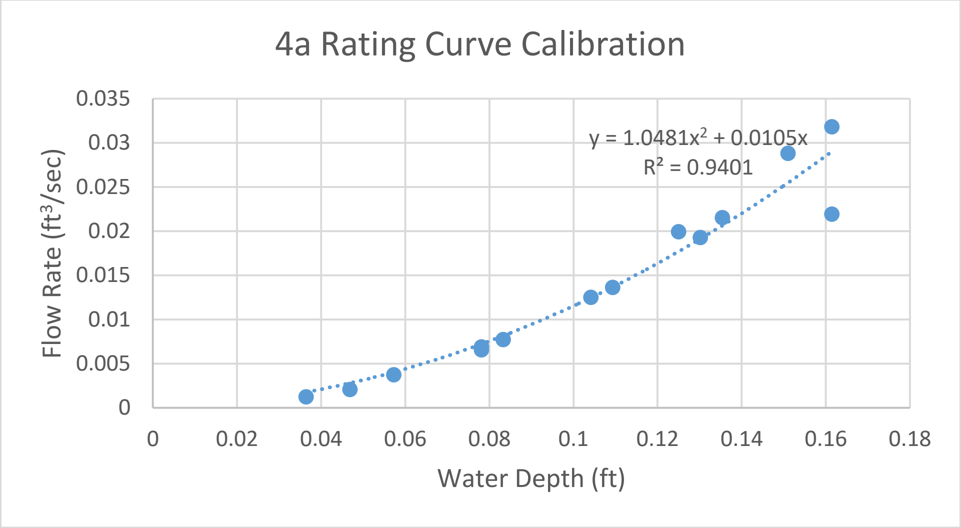

2b Rating Curve Calibration
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)
y = 1.1943x² - 0.0002x
R² = 0.9947

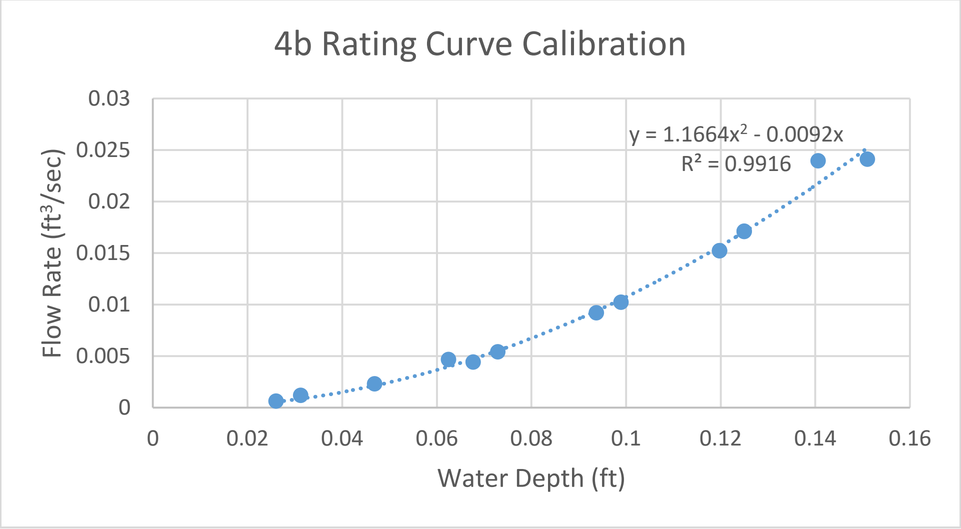

2c Rating Curve Calibration
y = 1.29x² - 0.008x
R² = 0.9946
Flow Rate (ft³/sec)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

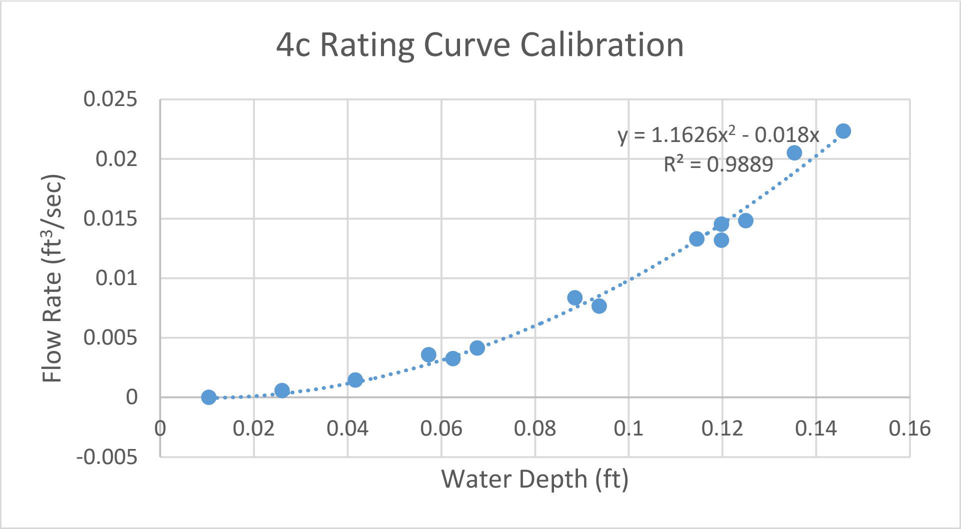

3a Rating Curve Calibration
y = 1.183x² - 0.0121x
R² = 0.9972
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

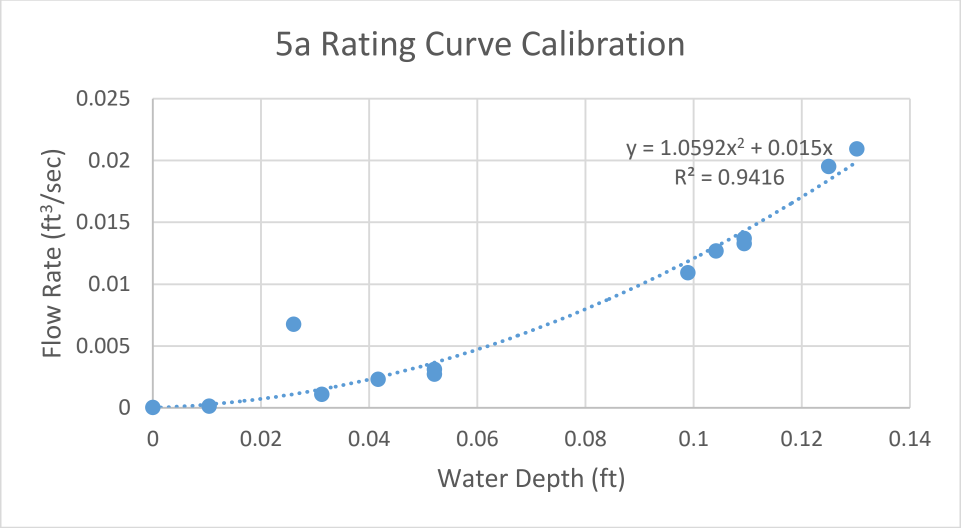

3b Rating Curve Calibration
y = 1.1271x² - 0.0247x
R² = 0.9946
Flow Rate (ft³/sec)
0.02
0.015
0.01
0.005
0
-0.005
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

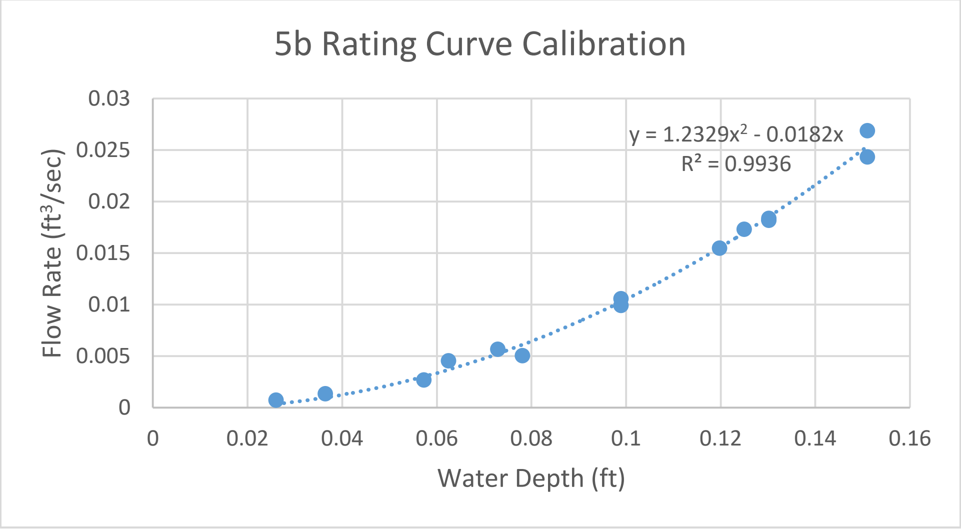

3c Rating Curve Calibration
y = 1.1604x² - 0.0084x
R² = 0.9948
Flow Rate (ft³/sec)
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

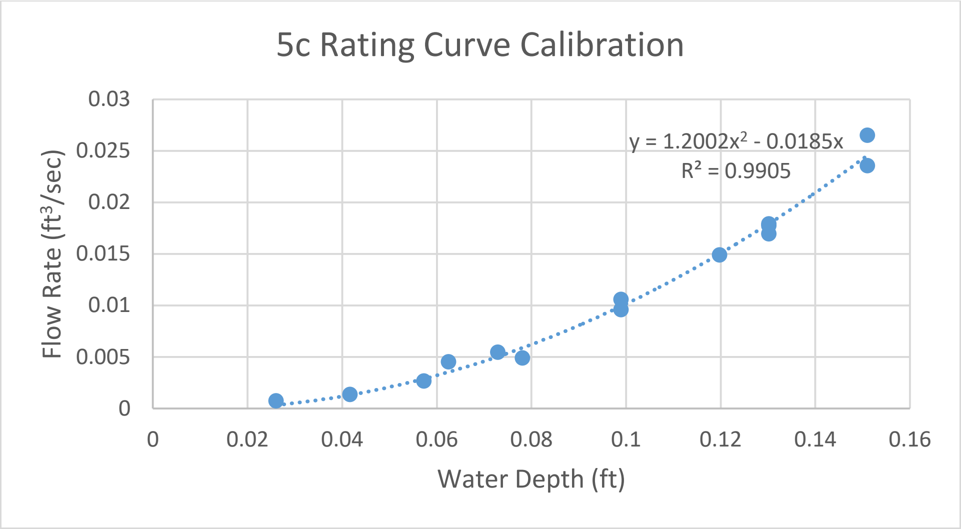

4a Rating Curve Calibration
y = 1.0481x² + 0.0105x
R² = 0.9401
Flow Rate (ft³/sec)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Water Depth (ft)

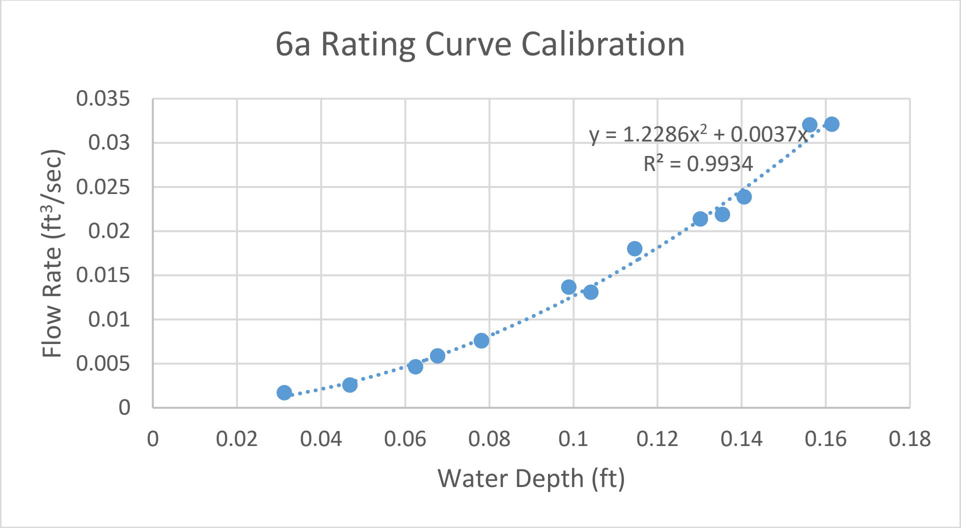

4b Rating Curve Calibration
y = 1.1664x² - 0.0092x
R² = 0.9916
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

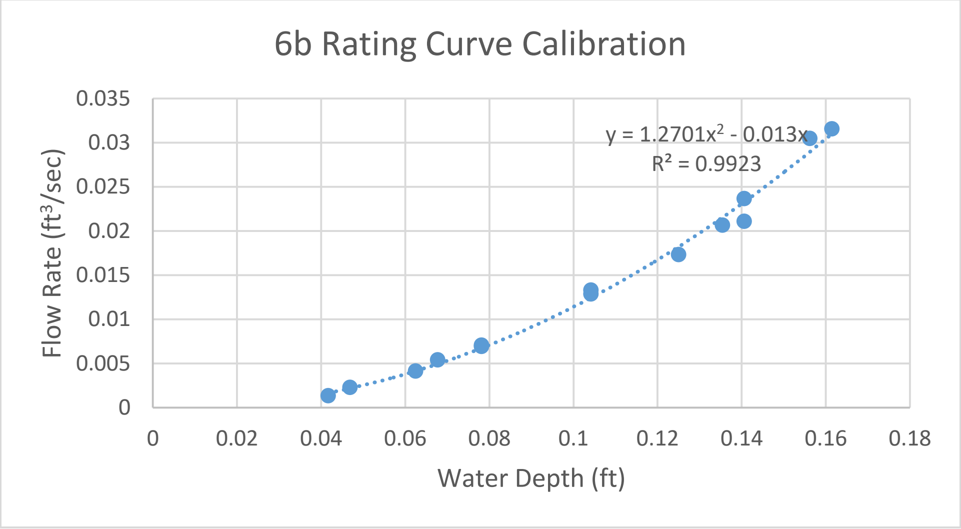

4c Rating Curve Calibration
y = 1.1626x² - 0.018x
R² = 0.9889
Flow Rate (ft³/sec)
0.025
0.02
0.015
0.01
0.005
0
-0.005
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)

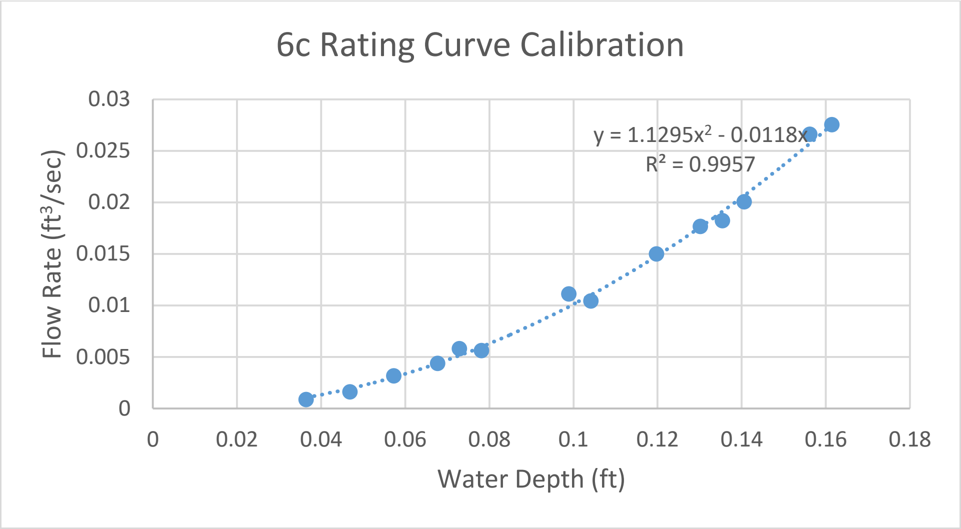

5a Rating Curve Calibration
y = 1.0592x² + 0.015x
R² = 0.9416
Flow Rate (ft³/sec)
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
Water Depth (ft)


5b Rating Curve Calibration
y = 1.2329x² - 0.0182x
R² = 0.9936
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)


5c Rating Curve Calibration
y = 1.2002x² - 0.0185x
R² = 0.9905
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
Water Depth (ft)


6a Rating Curve Calibration
y = 1.2286x² + 0.0037x
R² = 0.9934
Flow Rate (ft³/sec)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Water Depth (ft)


6b Rating Curve Calibration
y = 1.2701x² - 0.013x
R² = 0.9923
Flow Rate (ft³/sec)
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Water Depth (ft)


6c Rating Curve Calibration
y = 1.1295x² - 0.0118x
R² = 0.9957
Flow Rate (ft³/sec)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
Water Depth (ft)

VITA

John Thomas McMaine

Candidate for the Degree of
Doctor of Philosophy

Thesis: DEVELOPMENT AND EVALUATION OF SELECTED LOW IMPACT DEVELOPMENT PRACTICES FOR RUNOFF MANAGEMENT AT THE NURSERY AND WATERSHED SCALES

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2011 – 2013 Graduate Research/Teaching Assistant, University of Kentucky, Lexington, Kentucky
2011 Engineering Technician, Bell Engineering, Lexington, Kentucky

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