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# Pesticide retention by buffer strips receiving simulated runoff containing different sized sediment

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**Pesticide retention by buffer strips receiving simulated runoff  
containing different sized sediment**

by

**Kapil Arora**

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

**DOCTOR OF PHILOSOPHY**

Major: Agricultural Engineering (Soil and Water Resources)

Program of Study Committee:  
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Ames, Iowa

2014

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**DEDICATION**

I dedicate this dissertation to my wife Renuka, as her support is the key for me in completing this work, and to my daughter Aisha, who is the source of my motivation. I also dedicate this dissertation to my deceased parents who had been a constant encouragement for me. Lastly, I dedicate this work to Almighty God, for making me worthy of this achievement.

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**NOMENCLATURE**

|       |   |
|-------|---|
| a.i.  | Active Ingredient   |
| APR   | Average Pesticide Retention                                 |
| AR    | Area Ratio  |
| AR10  | Area Ratio of 10:1  |
| AR30  | Area Ratio of 30:1  |
| ASABE | American Society of Agricultural and Biosystems Engineering |
| BS    | Buffer Strips   |
| CAS   | Chemical Abstracts Service                                  |
| CR    | Carrier Phase Retention                                     |
| D0    | No Sediment in Simulated Runoff                             |
| D1    | Fine Sand Particles in Simulated Runoff                     |
| D2    | Fine Aggregates in Simulated Runoff                         |
| D3    | Clay Particles in Simulated Runoff                          |
| FAO   | Food and Agriculture Organization of the United Nations     |
| GC    | Gas Chromatograph   |
| ISU   | Iowa State University                                       |
| JEQ   | Journal of Environmental Quality                            |
| MS    | Mass Spectrometer   |
| NIST  | National Institute of Standards and Technology              |
| NOAA  | National Oceanic and Atmospheric Administration             |
| NRCS  | Natural Resources Conservation Service                      |

|          |  |
|----------|--|
| PM       | Pesticide Mass   |
| PPDB     | Pesticide Properties Data <i>Base</i>                      |
| PRVR     | Percent Runoff Volume Retention                            |
| PVC      | Poly-Vinyl Chloride  |
| SA       | Study Average  |
| SPAW     | Soil – Plant – Air – Water Model                           |
| SSR      | Sediment Sorption Ratio                                    |
| TA       | Treatment Average  |
| TOF      | Time of Flight   |
| USDA     | United States Department of Agriculture                    |
| US       | United States  |
| VBS      | Vegetative Buffer Strips                                   |
| VFSMOD   | Vegetative Filter Strip Modeling System                    |
| VFSMOD-W | Vegetative Filter Strip Modeling System with Water Quality |

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## ABSTRACT

Infiltration water and sediment mass retained are the two key processes for pesticide mass retention by buffer strips from agricultural runoff, based on the review of 106 published articles. Estimates, based on average published data for runoff volume and sediment mass retention, show that the average pesticide retention is 46, 51, and 70 % for the three sorption classes ( $K_{oc} < 100$ ,  $100 < K_{oc} < 1000$ , and  $K_{oc} > 1000$ , respectively). Source area to buffer area ratios ranging between 10:1 to 50:1 are more practical and effective under field applications of buffer strips. Buffer strips have an upper area where larger particles settle and a lower area where runoff containing fine particles passes through. Rainfall-runoff experiments were conducted on 1.0 m wide x 5.6 m long switchgrass buffer strips to measure pesticide mass transport through buffer strips receiving runoff containing different sized sediment under steady-state rainfall intensity of 6.35 cm/h. Twenty four strips were used to provide three replications each of the sediment type treatments of fine sand, fine aggregates, clay-sized particles, and no sediment; and two treatments of flow convergence represented by source area to buffer area ratios of 10:1 and 30:1. Atrazine, chlorpyrifos, and linuron were used in the experiments at the label recommended rates using field formulations. When receiving runoff mixed with fine sand, buffer strips retained 73% and 53% atrazine, 87% and 80% chlorpyrifos, and 81% and 54% linuron for the two area ratios of 10:1 and 30:1 respectively. The corresponding numbers, when receiving runoff mixed with fine aggregates, were 72% and 54% atrazine, 87% and 71% chlorpyrifos, and 76% and 58% linuron respectively for the two area ratios. Switchgrass buffer strips retained, on average, 70.1% and 49.2% atrazine, 83.0% and 57.6% chlorpyrifos, and 71.2% and

50.4% linuron, respectively for the two area ratios of 10:1 and 30:1 when receiving simulated runoff containing clay-sized particles. Linuron data presented in these experiments is an estimate and readers are cautioned when interpreting linuron data. Results were significantly different for atrazine when the two area ratios were compared for all three sediment types. Results for chlorpyrifos and linuron were not significantly different between the two area ratios indicating the strips performed equally well under both flow conditions in case of sediment type fine sand and fine aggregates. In case of clay-sized particles, results for atrazine and linuron were significantly different for the two area ratios indicating flow convergence can impact atrazine and linuron retention by buffer strips. In case of fine sand, outflow from the buffer strips showed some re-entrainment of sediment from previously deposited sediment, buffer strip soil, or erosion at the exit point, which needs to be further investigated. Infiltration and sediment retention were the key processes for pesticide retention in case of fine aggregates, whereas infiltration alone was the key process in case of fine sand and clay-sized particles. VFSMOD-W, embedded with the empirical linear-additive pesticide mass retention model was used to predict atrazine, chlorpyrifos and linuron retention by the switchgrass buffer strips studied in the experiments. Saturated hydraulic conductivity ( $K_{sat}$ ) of the switchgrass soil was the key parameter in calibrating the model to the experimental conditions, indicating type of buffer strip vegetation and timing of calibration data collection are important factors. Predicted pesticide mass retention results indicate that the performance of buffer strips receiving runoff from farm fields containing large proportions of fine sand or clay-sized particles needs to be further investigated.

## **CHAPTER 1. OVERVIEW OF PESTICIDE TRANSPORT THROUGH BUFFER STRIPS WITH DIFFERENT SIZED SEDIMENT**

### **1.1 General Introduction**

Buffer strips, also known as filter strips or just filters, are an agricultural conservation practice designed to reduce the transport of runoff from source areas (agricultural fields) to the receiving water bodies. No farm chemical application occurs on these strips. Buffer strips are able to reduce the runoff water mass and sediment mass, the two phases of agricultural runoff. These two phases carry with them any farm chemicals that might be lost from the source areas. Pesticides applied to the source areas, included in farm chemicals, are lost from the source areas. The dissolved phase of pesticides (carried with runoff water) and the sorbed phase of pesticides (carried with sediment) are both reduced as the runoff travels through the buffer strips. Published research has shown a varying degree of reduction in both the dissolved and sorbed phases of pesticides. One of the key pesticide properties, sorption, determines how much pesticide is in the dissolved phase and the sorbed phase. Sediment mass to which the pesticide is sorbed has been studied as a single carrier phase. Sediment mass in runoff comprises particles (sand, silt, and clay) and aggregates of varying sizes. Variable sizes of these particles and aggregates have different surface area which effects pesticide sorption. Specifically, different sized sediment can be present or absent from the runoff under field conditions. This can influence pesticide transport through the buffer strips as different sized sediment varies in specific surface area and organic matter. In order to better understand buffer strip performance, the transport of different sized sediment (fine sand, fine aggregates without sand, and clay-sized particles) with the runoff water

through buffer strips needs to be studied. As runoff containing only the clay-sized particles is introduced into the buffer strips, there is a potential for the runoff to re-entrain sediment from within the strip. As such, the introduction of runoff containing no sediment into the buffer strips also needs to be simultaneously evaluated. Secondly, specific sized sediment transport through the buffer strips can be influenced by converging flow resulting from changes in topography. Controlled experimental conditions, where the effects of flow convergence can be evaluated, need to be included in the study. Results from such a study can help to calibrate and/or validate existing models for the transport of runoff through the buffer strips.

## **1.2 Dissertation Organization**

A review of published research on buffer strips was conducted. Literature included all articles in which pesticide transport had or had not been studied. As runoff water mass and sediment mass are the two carrier phases for pesticides, data on the retention of these two carrier phases was summarized. The retention of these two carrier phases was then used with the pesticide property of sorption to develop a simple mathematical model for pesticide retention by buffer strips. Chapter 2 of this dissertation presents an in-depth perspective of the published research in terms of pesticide retention processes occurring in the buffer strips.

Review of literature revealed various gaps in the available research data. The majority of studies have observed buffer strip performance under small source to buffer area ratios (typically less than 10). Flow convergence, due to changes in micro-topography in the buffer strips, causes the area ratios to change. Area ratios of less than 10 are not likely to exist in real field applications. None of the studies have observed



how sorption affects the transport of pesticides with different sized sediment in the buffer strips. As such, a dual experiment was conducted in September 2013 to evaluate pesticide transport through buffer strips with different sized sediment for area ratios of 10:1 (AR10) and 30:1 (AR30).

Chapter 3 of this dissertation presents the how the experiment was conducted. It explains why fine sand (sediment type D1) and fine aggregates (sediment type D2) were chosen for comparison for transport of atrazine, chlorpyrifos, and linuron through buffer strips. Using switchgrass buffer strips, results of this randomized experiment with three replications ( $n=3$ ) each for AR10-D1, AR30-D1, AR10-D2, and AR30-D2 treatments are presented in Chapter 3.

Clay particles are very fine in comparison to fine sand and fine aggregates and do not settle quickly. There is the possibility of clay-sized particles being re-entrained into runoff from the buffer strip soil itself. The second part of the experiment conducted compared pesticide transport with clay-sized particles (sediment type D3) with runoff containing no sediment (sediment type D0) and no pesticide. AR10 and AR30 were compared as well to see the effects of concentrated flow caused by flow convergence. Treatments AR10-D3, AR30-D3, AR10-D0, and AR30-D0 were used in the randomized experiment and the results obtained are presented and discussed in Chapter 4.

Vegetative Filter Strip Modeling System with Water Quality (VFSSMOD-W) has an empirical model embedded in it for determining pesticide mass retention by buffer strips. VFSSMOD-W was used to predict how the buffer strips respond to receiving simulated runoff containing specific-sized sediment under the two flow convergence

condition studied in Chapters 3 and 4. Comparisons of the measured and the predicted pesticide mass retentions using a calibrated VFSSMOD-W are discussed in Chapter 5.

Chapter 6 of this dissertation provides a general discussion of the research performed and provides suggestions for future research work.

## CHAPTER 2. REVIEW OF PESTICIDE RETENTION PROCESSES OCCURRING IN BUFFER STRIPS RECEIVING AGRICULTURAL RUNOFF

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Kapil Arora<sup>2,3,4</sup>, Steven K. Mickelson<sup>2</sup>, Matthew J. Helmers<sup>2</sup>, and James L. Baker<sup>2</sup>

### 2.1 Abstract

Review of the published results shows that the retention of the two pesticide carrier phases (runoff volume and sediment mass) influences pesticide mass transport through buffer strips. Data averaged across different studies showed that the buffer strips retained 45% of runoff volume (ranging between 0% and 100%) and 76% of sediment mass (ranging between 2% and 100%). Sorption (soil sorption coefficient,  $K_{oc}$ ) is one key pesticide property affecting its transport with the two carrier phases through buffer strips. Data from different studies for pesticide mass retention for weakly ( $K_{oc} < 100$ ), moderately ( $100 < K_{oc} < 1,000$ ), and strongly sorbed pesticides ( $K_{oc} > 1,000$ ) averaged (with ranges) 61 (0-100)%, 63 (0-100)%, and 76 (53-100)%, respectively. Because there are more data for runoff volume and sediment mass retention, the average retentions of both carrier phases were used to calculate that the buffer strips would retain 45% of weakly to moderately sorbed and 70% of strongly sorbed pesticides on an average basis. As pesticide mass retention presented is only an average across several studies with

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<sup>2</sup> Graduate Student and Field Agricultural Engineer, Professor and Chair, Professor, and University Professor Emeritus, respectively.

<sup>3</sup> Primary researcher and author.

<sup>4</sup> Author for correspondence.

different experimental setups, the application of these results to actual field conditions should be carefully examined.

## **2.2 Introduction**

Nonpoint source losses of pollutants to surface waters from agricultural lands in the United States are of continued concern. Agricultural runoff, in addition to carrying sediment and nutrients, has been documented to transport pesticides. Pesticide losses from agricultural lands have been reported in the literature since the early 1970s. These losses have been reported as generally being one to five percent of the amount applied. Wauchope (1978) provided a review of early studies on pesticide losses from agricultural fields. Several publications since 1978 show similar data on pesticide losses from agricultural fields (Rohde et al., 1980; Hall et al., 1983; Glenn and Angle, 1987; Hall et al., 1991; Paterson and Schnoor, 1992; Shipitalo et al., 1997; Gaynor et al., 2001). These losses have been shown to be dependent on in-field tillage practices and site-specific conditions (Hall et al., 1972, 1974; White et al., 1976; Baker and Johnson, 1979; Baker and Laflen, 1979; Wu et al., 1983; Shipitalo et al., 1997). One of the key factors reported in these studies is the timing of a runoff event after application of pesticides. Losses of pesticides have been reported to be higher with runoff events happening immediately or within a short time duration after application. Many of the studies have suggested the use of practices such as buffer strips and/or wetlands to control/reduce the offsite transport of pesticides from agricultural lands.

Buffer strips have been studied worldwide for the last four decades as a strategy to reduce the environmental impact of agricultural runoff. Buffer strips are non-treated areas of land through which runoff from agricultural fields may pass before entering

surface waters. These areas, generally, are either cropped or have close grown vegetation planted in them. Several researchers such as Young et al., 1980; Dickey et al., 1981; Cooper et al., 1987; Magette et al., 1989; Dillaha et al., 1989; Chaubey et al., 1994, 1995; Coyne et al., 1995; Daniels and Gillian, 1996; Edward et al., 1996; Lee et al., 2000; Pandey et al., 2001; Lee et al., 2003; Blanco – Canqui et al., 2004b; Helmers et al., 2005; and Deletic, 2005; have shown buffer strips to be effective in reducing off-site transport of sediment, animal waste suspended solids, and nutrients. In addition, the U. S. Department of Agriculture Natural Resource Conservation Service (USDA - NRCS, 2000) recommends use of vegetative filter (buffer) strips as a best management practice to reduce non-point source pollution.

Pesticide retention by buffer strips has also been studied in the past four decades by several researchers (Asumussen et al., 1977; Baker & Mickelson, 1994; Baker et al., 1995; Arora et al., 1996; Misra et al., 1996; Mickelson et al., 1998; Lowrance et al., 1997; Patty et al., 1997; Baker et al., 2000; Rankins et al., 2001; Seybold et al., 2001; Vellidis et al., 2002; Arora et al., 2003; Boyd et al., 2003; Mickelson et al., 2003; Krutz et al., 2003, 2004). In these studies, the main processes for pesticide retention have been identified as infiltration, sediment deposition, and sorption. The main phenomenon occurring in buffer strips has been reported as the reduction of flow velocity due to the resistance to flowing water caused by the vegetation. In addition, the runoff source area is usually a tilled area subject to potentially greater soil surface sealing from rainfall energy. As such, the infiltration rate within the buffer strip area is greater and more constant than the source area.

Pesticide movement from treated fields with runoff may occur with rainfall, irrigation, and/or snow melt. Each runoff event results in a loss of both sediment and water from the treated field. Pesticide properties affect pesticide behavior, and therefore it's transportation in the water phase and sediment phase. One key pesticide property affecting pesticide loss with runoff is its soil sorption coefficient,  $K_{oc}$ . According to the Food and Agriculture Organization of the United Nations (FAO, 2000), the soil sorption coefficient, or simply the partitioning coefficient,  $K_{oc}$ , is the ratio of pesticide concentration as adhered or sorbed to soil solid phase (normalized to the organic carbon content of the soil) to the dissolved water concentration. A larger  $K_{oc}$  value means that the pesticide of interest will have a higher concentration in soil or sediment, and therefore, is strongly sorbed. Likewise, a very low  $K_{oc}$  value means that the pesticide will have a higher concentration in soil water or is weakly sorbed. FAO (2000) uses  $K_{oc}$  values to classify the mobility of pesticides. A pesticide with a  $K_{oc}$  value of less than 100 L/kg is classified as highly mobile to mobile; a  $K_{oc}$  value between 100 and 1000 L/kg is classified as moderately mobile; and a  $K_{oc}$  value greater than 1000 L/kg is classified as being slightly mobile to immobile. Hornsby et al. (1996) summarized that pesticides that are highly sorbed to soil are mainly carried by sediment in runoff. Buffer strips may trap such pesticides simply by trapping sediment. On the other hand, pesticides that are weakly to moderately sorbed to soil particles are carried mainly with the water phase of runoff (Wauchope, 1978). Trapping of such pesticides with buffer strips may occur either by infiltration of runoff or by removal of the pesticide from the water phase of the runoff by sorption to the buffer strip soil or vegetation. Therefore, an attempt to review

buffer strip effectiveness in retaining pesticides must examine what happens to both components (pesticide carrier phases) of runoff, i.e. water and sediment.

A comprehensive search of literature on buffer strips (also designated as vegetative filter strips, vegetative filters, buffer zones, and filter strips) was conducted. Databases for the different agricultural research journals were searched and a list of publications was compiled. This list was trimmed to include only those publications that reported collection of field data as related to either or both the water and sediment components of runoff. Only field data presented at meetings, published in technical reports or published in research journals were included. Any experimental data that was not presented or published and was contained in MS thesis or Ph D dissertation was not included. Any paper listed both as a presentation at a meeting and as published in a journal was also trimmed to exclude the presented paper, as the peer reviewed publication of the same presented paper was considered a better representation of the reported data. Using these criteria for paper selection, a list of thirty-five studies was compiled for review of field data. These studies have evaluated pesticide retention by buffer strips in either or both carrier phases of runoff. Twenty-two additional studies did not evaluate pesticide retention but were found to have evaluated buffer strips for retention of either runoff water or sediment or both. As explained in the previous paragraph, pesticide retention by buffer strips is dependent upon transport of both carrier phases. These additional twenty-two studies provided for unique experimental conditions of runoff source area to buffer strip area ratios, source area tillage practices, and buffer strip vegetation which were not available in the pesticide retention studies dataset. Thus, they were included in the review to expand the dataset for pesticide retention studies.

Field data from the compiled list of studies was extracted and analyzed. This dataset consisted of buffer strip performance results reported under a wide range of sampled experimental conditions across different studies. An attempt was made to summarize this dataset to best represent the performance characteristics of buffer strips. To achieve this task, the retention of both pesticide carrier phases (runoff water and sediment) was estimated from the expanded dataset of fifty-seven studies. These estimates and their minimum and maximum values, thus, represent the entire range of experimental conditions studied including those unique to the non-pesticide retention studies. Using these synthesized retention estimates for both carrier phases, a simple mathematical model was then developed to calculate the overall pesticide retention for the three different pesticide classes (based on sorption coefficient,  $K_{oc}$ ). This modeled pesticide retention, thus includes the experimental setups of the studies that have not studied pesticide retention by buffer strips. Lastly, a comparison was made between the model calculated overall retention and the overall retention as reported in the pesticide retention studies. This was done to see how inclusion of non-pesticide retention studies affected the model calculations when compared with data from the pesticide retention studies.

This article presents several advances over the Reichenberger et al. (2007) paper, a review paper on the effectiveness of different strategies for reducing pesticide transport to ground and surface waters. The authors of this previously published paper presented a summary of a limited number of publications addressing edge-of-field buffer strips as a sub-set of their review. The authors did not include edge-of-field buffer strips that existed as a part of a riparian forest buffer system, a grassed waterways, or as contoured.



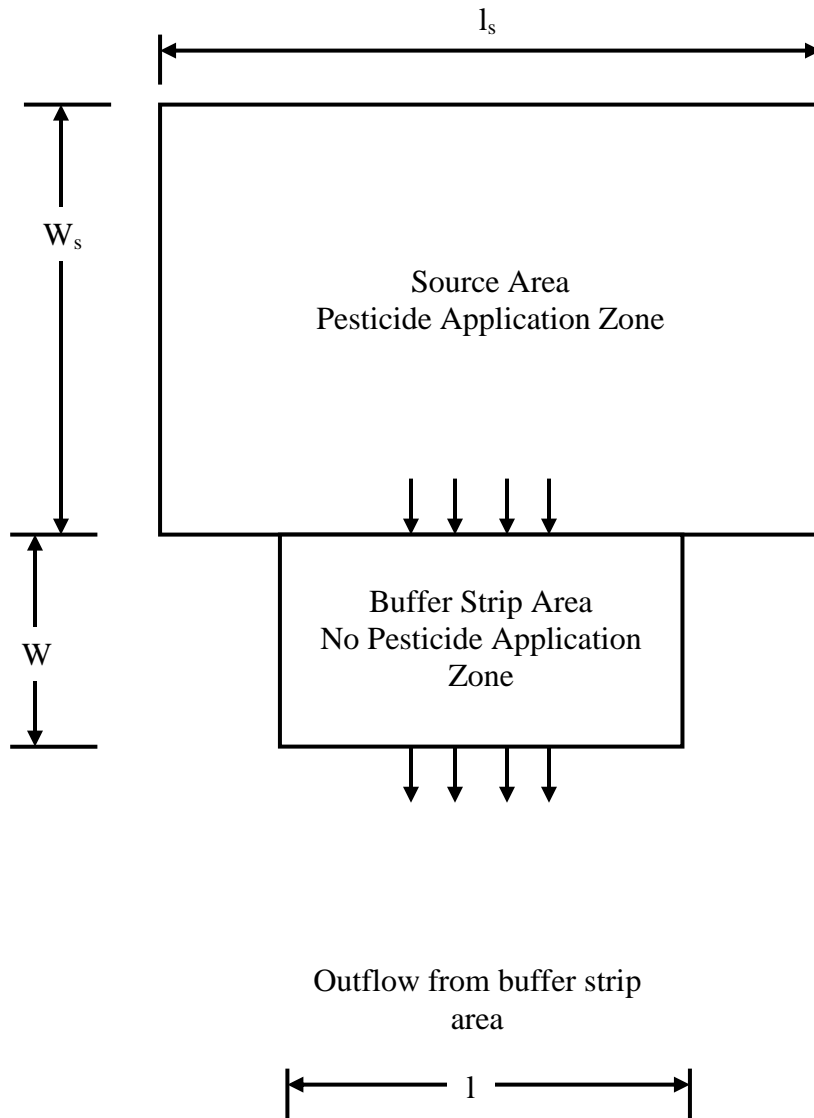
Edge-of-field buffer strip placement within an agricultural watershed is a mix of different locations subject to similar runoff conditions. The current article uses data from the studies representing different applications of buffer strips to estimate pesticide retention. Secondly, the summary presented by Reichenberger et al. (2007) only showed the range of pesticide retention for different studies. It did not include any estimate of the minimum, average, and maximum retention of either component of runoff (water and sediment). Their review also did not summarize publications that evaluate retention of individual components of the runoff by buffer strips. Since estimates were not calculated for retention of individual components of the runoff, no comparisons have been drawn between calculated retention and reported pesticide retention by the buffer strips. The current article calculates an estimate for pesticide retention by buffer strips with individual components of runoff, calculates overall pesticide retention, and then compares it with published data.

### **2.3 Buffer Strip Processes**

As reported in research studies, runoff from the agricultural fields or the source area is generally passed over a specified area of the buffer strips. The source area consists of the pesticide application zone, which is generally cropped and tilled as shown in a simplified schematic in Figure 2.1. Runoff generated in this zone generally flows down slope along the width,  $W_s$ , of the source area. This runoff then enters the buffer strip area as inflow. This inflow travels the width,  $W$ , of the buffer strip area and exists as outflow from the buffer strip. The length of the buffer strip area ( $l$ , perpendicular to flow) may or may not be same as the length of the source area ( $l_s$ , perpendicular to flow). The resulting ratio of the source area to the buffer strip area has generally been termed as

“Area Ratio”. Most commonly, different area ratios have been achieved by simply changing the width of the buffer strip while keeping the size of the source area constant. In these cases, the length of the buffer strip perpendicular to the flow is same as that of the source area and is maintained constant when changing the area ratio. A few studies on the other hand have kept the buffer strip area size the same but have achieved different area ratios by varying runoff flow rates from the source area. This has been achieved in these experimental designs by the use of a flow divider where the runoff from the source area is split in proportion for the desired area ratio.

Runoff from the source area consists of two components or pesticide carrier phases, i.e. water and sediment. In addition, water as rainfall may be added to the buffer strip as runoff passes through it. Thus, the water mass inputs into the unit cell of buffer strip, as shown in Figure 2.2, are rainfall,  $R_i$  (L) and inflow runoff water,  $M_i$  (L). Rainfall water has been measured for its pesticide concentrations (Nations and Hallberg, 1992). These concentrations are generally low enough where they could be ignored in the buffer strip runoff retention studies. Thus, the rainfall water,  $R_i$  (L), is considered to have negligible pesticide mass in it, whereas the inflow runoff water has a dissolved pesticide concentration of  $C_i$  (mg/L). The sediment component of the runoff entering the buffer strip is represented by  $S_i$  (kg), as the sediment mass input in to the unit cell. This sediment has a sorbed pesticide concentration of  $C_{si}$  (mg/kg). Outputs leaving the buffer strip unit cell are: the mass of water,  $M_{out}$  (L), with a dissolved pesticide concentration of  $C_{out}$  (mg/L); sediment mass specified as  $S_{out}$  (kg), with sorbed pesticide concentration of  $C_{sout}$  (mg/kg); and infiltration water mass,  $M_x$  (L), with a dissolved pesticide concentration of  $C_x$  (mg/L). Under certain conditions, it is possible for shallow

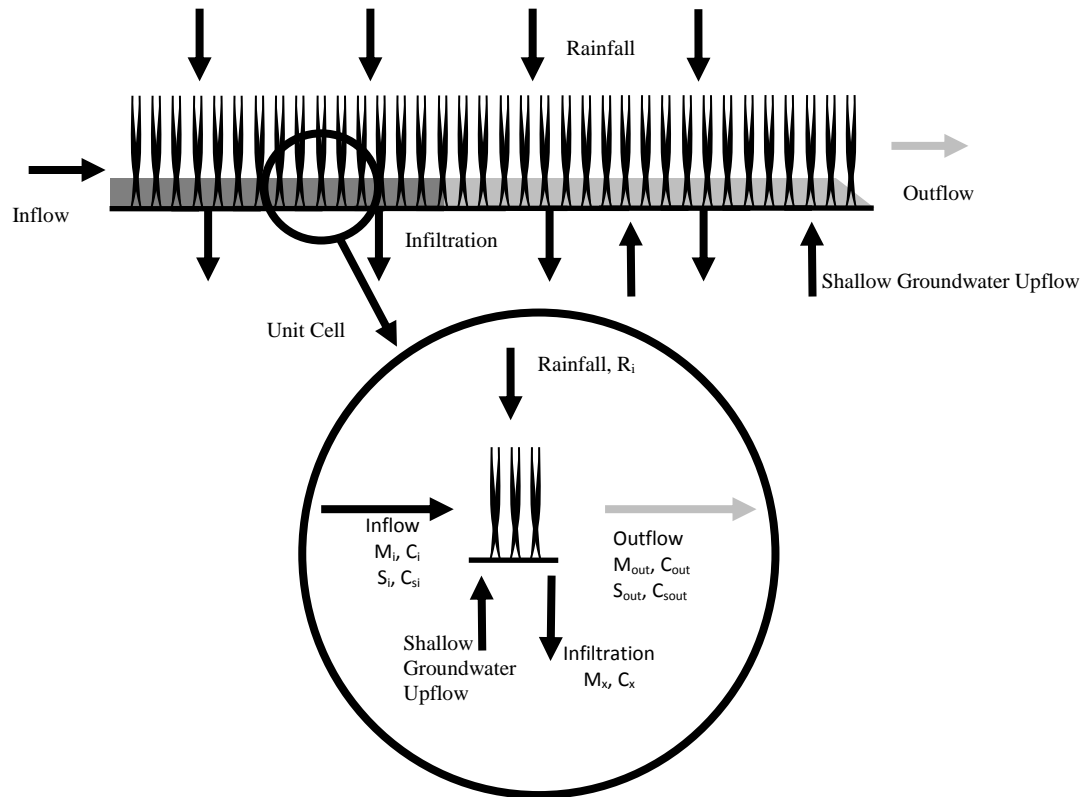


$W_s$  = Width of source area in the direction of flow  
 $W$  = Width of buffer strip area in the direction of flow  
 $l_s$  = Length of the source area perpendicular to flow  
 $l$  = Length of buffer strip area perpendicular to flow  
 Area Ratio = Source Area / Buffer Strip Area

Figure 2.1: Simplified schematic showing source area and buffer strip area dimensions under a typical field application of buffer strips

groundwater to flow to the surface in low areas due to up gradient pressure from new or existing rain-water. In these cases, infiltration water mass is reduced by the amount of shallow groundwater that comes out on the soil surface. Studies that have evaluated pesticide retention by buffer strips have measured the input pesticide mass by measuring the mass contained in either or both carrier phases. The pesticide mass leaving the buffer strips has been similarly measured. Studies have then estimated the amount of pesticide mass retained in buffer strips by calculating the difference between the input and output pesticide masses of either or both carrier phases. This pesticide retention has been attributed mainly to the processes of infiltration, sediment deposition, and sorption (Arora et al., 1996; Misra et al., 1996; Kloppel et al., 1997; Lowrance et al., 1997; Patty et al., 1997; Arora et al., 2003).

In this review article, an attempt was made to estimate pesticide retention by buffer strips associated with infiltration, sediment deposition, and sorption processes based on data reported in literature. First, information contained in the expanded dataset of fifty-seven studies was extracted. Runoff volume retention was synthesized from runoff data available in thirty-seven out of fifty-seven studies. This runoff volume retained has commonly been attributed to infiltration in these studies. Secondly, sediment mass retained (commonly attributed to sediment deposition) was synthesized from sediment data available in thirty-two studies of the same expanded dataset. Effect of sorption was then evaluated to see how it impacts pesticide concentrations, and consequently, the pesticide mass retained. Using the synthesized retentions of both carrier phases, a simple mathematical model was developed to calculate the overall pesticide retention. This model was based on published data and selected assumptions of



$R_i$  = Rainfall

$M_i$  = Inflow Runoff Volume

$C_i$  = Dissolved Pesticide

Concentration in Inflow

$C_{si}$  = Sorbed Pesticide

Concentration in Inflow

$S_i$  = Sediment Mass in Inflow

$M_{out}$  = Outflow Runoff Volume

$C_{out}$  = Dissolved Pesticide

Concentration in Outflow

$C_{sout}$  = Sorbed Pesticide

Concentration in Outflow

$S_{out}$  = Sediment Mass in Outflow

$M_x$  = Infiltration Water Mass

$C_x$  = Dissolved Pesticide

Concentration in Infiltration Water

Figure 2.2: Schematic showing various processes, inputs and outputs from a buffer strip unit cell.

pesticide properties as discussed in the literature. Pesticide retention values, calculated using this simple model, were then compared with the reported data from thirty-five studies that have evaluated pesticide retention by buffer strips.

#### **2.4 Infiltration Water Mass ( $M_x$ )**

Pesticide mass that moves into the soil with infiltration in a buffer strip unit cell (Figure 2.2) is the product of infiltration water mass,  $M_x$  (Carrier) and the dissolved concentration of the pesticide in infiltrating water,  $C_x$ . Infiltration has been reported as the key process by which buffer strip mitigates weakly and moderately sorbed pesticides (Baker and Mickelson, 1994; Patty et al., 1997; USDA - NRCS, 2000; Vellidis et al., 2002; Arora et al., 2003). In estimating infiltration, studies have measured inflow ( $M_i$ ), and outflow ( $M_{out}$ ) runoff volume, and rainfall volume ( $R_i$ ). Infiltration then has been estimated by subtraction of outflow from the sum of inflow and rainfall. This infiltration, so determined, in fact represents the total runoff volume retained by ponding due to micro-topography, any increase in soil moisture content, and actual infiltration in the buffer strip. In addition, under certain conditions, it is possible for subsurface water to come out of the surface in low lying areas due to the up-gradient pressure from new rain water. This process can impact net infiltration into buffer strips as they tend to be located on the lower end of farm slopes adjacent to streams. In this review article, no attempt was made to isolate any of the processes, as they are not reported separately in the literature. All of the processes have been combined together as the runoff volume retained.

Review of the reported data and studies show that the group of contributing factors affecting runoff volume retention can be grouped into two categories, which are site factors and hydrologic factors. The first category of site factors includes area ratio

(Srivastava et al., 1996; Misra et al., 1996; Arora et al., 1996, 2003; Boyd et al., 2003) and/or buffer strip length (Thom & Blevins, 1996; Patty et al., 1997; Barfield et al., 1998; Antonious, 1999; Abu - Zreig, 2001; Mickelson et al., 2003; Antonious, 2004); slope of the buffer area; age, type and density of vegetation in the buffer area (Dillaha et al., 1988, 1989; Patty et al., 1997; Schmitt et al., 1999; Rankins et al., 2001); and buffer strip area soil type. Most frequently studied site factors (Tables 2.1 and 2.2) were found to be silty loam soil type for both source and buffer areas, and grassed vegetation in the buffer area. The second category of contributing factors is the storm intensity and the rainfall amount, and the hydrologic conditions of the site. Variable rainfall intensities (Webster and Shaw, 1996; Kloppel et al., 1997; Boyd et al., 2003; Mickelson et al., 2003), rainfall and runoff amounts and rates (Misra et al., 1996; Arora et al., 1996; Dosskey et al., 2002; Arora et al., 2003), and antecedent soil moisture conditions (Assmussen et al., 1977; Rohde et al., 1980), explain the variability in runoff volume retentions as reported. The first category of contributing factors, i.e. the site factors, can be designed and/or controlled to a certain extent; however, the second set of contributing factors, i.e. the hydrologic factors, are temporal in nature. In the Krutz et al. (2005) review, authors summarized that the natural rainfall studies generally reported data gathered under various field conditions of runoff and rainfall intensities. They concluded that these conditions are more realistic to occur in actual applications of buffer strips. As such, data from such studies are more realistic indicators of buffer strip performance. It should be noted that the most natural rainfall studies have been conducted under controlled experimental conditions using bordered test plots where runoff from one plot does not cross over into other plots. These bordered conditions do not exist in actual field

Table 2.1: Runoff and Sediment retained by buffer strips as reported in natural rainfall studies (1983-2005).

| Literature Citation         | Duration Events           | Source Area Characteristics |   | Buffer Area Characteristics               |   | Runoff Volume Retained        |                             | Sediment Retained                 |                                   |
|-----------------------------|---------------------------|-----------------------------|---|---|---|-------------------------------|-----------------------------|-----------------------------------|-----------------------------------|
|                             |                           | Area & Width                | Vegetation (Tillage)                    | Dimensions                                | Vegetation                                    | Source & Buffer Area          | Area                        | Study Average Data-points (Range) | Study Average Data Points (Range) |
| Hall et al. (1983)          | 1 year<br>11 events       | 0.003 ha, w = 16 m          | Corn (n/a)<br>14                        | w = 6 m, l = 1.8 m                        | Oats<br>14                                    | Silty Clay<br>Loam            | 2.67                        | 66 %<br>4<br>(43 - 85)            | 76 %<br>4<br>(66 - 99)            |
| Parsons et al. (1994)       | 2 years<br>9 events       | 0.015 ha, w = 36.6 m        | n/a (n/a)<br>1.9                        | w = 4.3 & 8.5 m, l = 4 m                  | Grass<br>1                                    | Sandy<br>Loam                 | 4.35 &<br>8.6               | 68 %<br>34<br>(0 - 100)           | 79 %<br>34<br>(4 - 100)           |
| Arora et al. (1996)         | 2 years<br>6 events       | 0.41 ha, w = 154 m          | Corn (Conv. Till)<br>3                  | w = 20.12 m, l = 1.52 m                   | Smooth Bromegrass<br>2                        | Silty Clay<br>Loam            | 15 & 30                     | 60 %<br>36<br>(3 - 100)           | 60 %<br>36<br>(41 - 100)          |
| Daniels & Gilliam (1996)    | 2 years<br>26 events      | 0.05 ha w = 84 m            | n/a (n/a)<br>1.1 & 1.2                  | w = 3 & 6 m, l = 6 m                      | Fescue<br>4.9 & 2.1                           | Sandy<br>Loam to<br>clay loam | 14.33 &<br>28.67            | n/a<br>n/a<br>n/a                 | 56 %<br>4<br>(45 - 61)            |
| Robinson et al. (1996)      | 2 years<br>13 events      | 0.057 ha, w = 18.3 m        | Fallow (Tilled every 3 wks)<br>7 & 12   | w = 3.1, 6.1, 9.2, 12.2 & 18.3 m, l = 31m | Bromegrass<br>7 & 12                          | Silt Loam                     | 1, 1.5, 2,<br>3 & 6         | n/a<br>n/a<br>n/a                 | 80 %<br>4<br>(70 - 85)            |
| Webster & Shaw (1996)       | 3 years<br>24 events      | 0.009 ha, w = 22 m          | Soybeans, (NT, CT & Disked)<br>3        | w = 2 m, l = 4 m                          | Tall fescue<br>3                              | Silty Clay                    | 11                          | 48 %<br>24<br>(0 - 100)           | n/a<br>n/a<br>n/a                 |
| Patty et al. (1997)         | 1 to 2 years<br>16 events | 0.025 ha, w = 50 m          | Corn / Wheat (Plowing)<br>7 - 15        | w = 6, 12, & 18 m, l = 5 m                | Rye grass<br>7 - 15                           | Silt Loam                     | 2.77,<br>4.17, &<br>8.33    | 82 %<br>9<br>(42 - 97)            | 97 %<br>9<br>(87 - 100)           |
| Tingle et al. (1998)        | 3 years<br>1 event        | 0.009 ha, w = 22 m          | Soybean, tilled<br>3                    | w = 0.5, 1, 2, 3 & 4 m, l = 4 m           | Tall fescue<br>3                              | Silty Clay<br>Loam            | 5.5, 7.3,<br>11, 22 &<br>44 | 58 %<br>5<br>(47 - 69)            | 87 %<br>5<br>(82 - 94)            |
| Mendez et al. (1999)        | 2 years<br>35 events      | 0.009 ha, w = 24.7 m        | Corn, tilled<br>18                      | w = 4.3 & 8.5 m, l = 3.7 m                | Tall fescue<br>18                             | Silt Loam                     | 2.91 &<br>5.74              | 56 %<br>2<br>(40 - 71)            | 86 %<br>2<br>(82 - 90)            |
| Muñoz-Carpena et al. (1999) | 3 years<br>7 events       | 0.015 ha, w = 37 m          | n/a (n/a)<br>5 - 7                      | w = 4.3 & 8.5 m, l = 4 m                  | Fescue, bluegrass, and bermuda grass<br>5 - 8 | Silt Loam                     | 4.35 &<br>8.6               | 26 %<br>7<br>(8 - 53)             | 88 %<br>7<br>(57 - 98)            |
| Sheridan et al. (1999)      | 3 years<br>104 events     | 0.93 ha, n/a                | Corn, Pearl Millet, Peanuts, n/a<br>3.5 | w = 8 m, l = 39 m                         | Bermudagrass and Bahiagrass<br>3.5            | Loamy<br>Sand                 | 29.8                        | 64 %<br>2<br>(56 - 72)            | 81 %<br>2<br>(78 - 83)            |

w = width of source area or buffer area in the direction of flow, l = length of buffer perpendicular to direction of flow, area ratio is source area (ha) divided by buffer area (ha), study average is (total input minus total output) divided by total input, n/a is not reported in the study.



Table 2.1 (continued):

| Literature Citation    | Duration Events             | Source Area Characteristics<br>Area & Width<br>Vegetation (Tillage)<br>Percent Slope | Buffer Area Characteristics<br>Dimensions<br>Vegetation<br>Percent Slope | Source & Buffer Area<br>Soil Type | Area Ratio     | Runoff Volume Retained<br>Study Average<br>Data-points<br>(Range) | Sediment Retained<br>Study Average<br>Data Points<br>(Range) |
|------------------------|-----------------------------|--|--|-----------------------------------|----------------|---|--|
| Rankins et al. (2001)  | 3 years<br>16 + 6<br>events | 0.009 ha, w = 4 m<br>Cotton (Disked)<br>3  | w = 0.3 m, l = 22 m<br>Diff. Grasses<br>3                                | Silty Clay                        | 73.33          | 57 %<br>4<br>(46 - 76)  | 74 %<br>4<br>(66 - 80)                                       |
| Hoffman et al. (2002)  | 2 years<br>2 events         | 0.17 ha, w = 46.7 m<br>Corn / Wheat (Conv. Till)<br>4                                | w = 9 m, l = 45 m<br>Wheat / Costal Bermudagrass<br>4                    | Black Clay                        | 4.2            | 9 %<br>2<br>(0 - 27)  | n/a<br>n/a<br>n/a  |
| Boyd et al. (2003)     | 2 years<br>5 events         | 0.41 ha, w = 154 m<br>Corn (Conv. Till)<br>4   | w = 20.12 m, l = 1.52 m<br>Smooth Bromegrass<br>3                        | Silty Clay<br>Loam                | 15 & 45        | 71 %<br>30<br>(54 - 100)  | 82 %<br>30<br>(53 - 100)                                     |
| Lee et al. (2003)      | 2 years<br>19 events        | 0.005 ha, w = 22.1 m<br>Soybean / Corn (n/a)<br>8                                    | w = 7.1 & 16.3 m, l = 4.1 m<br>Switchgrass<br>5                          | Fine Loam                         | 1.36 &<br>3.11 | 59 %<br>1<br>n/a  | 92 %<br>1<br>n/a   |
| Helmerts et al. (2005) | 1 year<br>1 event           | n/a, w = 670 m<br>Corn (n/a)<br>1  | w = 13, l = n/a<br>Bluestem, Switchgrass, and Indiangrass<br>1           | Silt Loam                         | 51.5           | 29 %<br>2<br>(2 - 56)   | 79 %<br>2<br>(74 - 83)                                       |
| Vianello et al. (2005) | 2 years<br>16 events        | 0.07 ha, w = 35 m<br>Corn, Soybeans (Plowed)<br>1.8                                  | w = 6 m, l = 20 m<br>Grass + Shrub + Trees<br>1.8                        | Silty Loam                        | 5.83           | 17 %<br>12<br>(9 - 31)  | n/a<br>n/a<br>n/a  |

w = width of source area or buffer area in the direction of flow, l = length of buffer perpendicular to direction of flow, area ratio is source area (ha) divided by buffer area (ha), study average is (total input minus total output) divided by total input, n/a is not reported in the study.

Table 2.2: Runoff and Sediment retained by buffer strips as reported in simulated rainfall / runoff / irrigation studies (1977-2005).

| Literature Citation    | Duration Events    | Source Area Characteristics |                                | Buffer Area Characteristics   |                                     | Runoff Volume Retained |                         | Sediment Retained                 |                                   |
|------------------------|--------------------|-----------------------------|--------------------------------|-------------------------------|-------------------------------------|------------------------|-------------------------|-----------------------------------|-----------------------------------|
|                        |                    | Area & Width                | Vegetation (Tillage)           | Dimensions                    | Vegetation                          | Source & Buffer Area   | Area                    | Study Average Data-points (Range) | Study Average Data Points (Range) |
| Asmussen et al. (1977) | 1 year<br>2 events | 0.003 ha, n/a               | Corn, Bedded                   | w = 24.4 m, l = 4.5 m         | bermudagrass, bahiagrass            | Loamy<br>Sand          | 0.27                    | 27 %<br>2<br>(3 - 51)             | 96 %<br>2<br>(94 - 98)            |
| Brockway et al. (1977) | 1 year<br>3 events | 0.6 ha, w = 140 m           | Wheat on Irrigation Furrows    | w = 2.44, l = 42.86           | Wheat, single & double band planted | Silt Loam              | 57.38                   | 6 %<br>12<br>(0 - 41)             | 70 %<br>12<br>(59 - 86)           |
| Hayes et al. (1984)    | n/a<br>5 events    | 0.001 ha, n/a               | mine spoil from erosion table  | w = 28.8, 33.1 & 33.9 m, n/a  | Fescue                              | Silt Loam              | n/a                     | 76<br>5<br>(55 - 93)              | 94 %<br>5<br>(93 - 99)            |
| Dillaha et al. (1988)  | 1 year<br>6 events | 0.01 ha, w = 18.3 m         | Bare & compacted               | w = 4.6 & 9.1 m, l = 5.5 m    | Orchard Grass                       | Silt Loam              | 2.01 &<br>3.98          | 12 %<br>12<br>(0 - 37)            | 71 %<br>12<br>(20 - 97)           |
| Dillaha et al. (1989)  | 1 year<br>6 events | 0.01 ha, w = 18.3 m         | Bare soil, conv. tilled        | w = 4.6 & 9.1 m, l = 5.5 m    | Orchard Grass                       | Silt Loam              | 2.01 &<br>3.98          | 18 %<br>12<br>(0 - 66)            | 77 %<br>12<br>(34 - 99)           |
| Magette et al. (1989)  | n/a<br>6 events    | 0.012 ha, w = 22 m          | Fallow, broiler litter applied | w = 4.6 & 9.1 m, l = 5.5 m    | Fescue                              | Sandy<br>Loam          | 2.39 &<br>4.78          | 21 %<br>12<br>(0 - 46)            | 63 %<br>12<br>(3 - 92)            |
| Coyne et al. (1995)    | 1 year<br>2 events | 0.01 ha, w = 22.1 m         | n/a                            | w = 9 m, l = 4.6 m            | Fescue & Kentucky Blue Grass        | Silt Loam              | 2.46                    | 88 %<br>2<br>(88 - 89)            | 99 %<br>2<br>(98.5 - 99.5)        |
| Misra et al. (1996)    | 1 year<br>6 events | n/a, n/a                    | n/a                            | w = 12.2 m, l = 1.48 m        | Bromegrass                          | Loam                   | 15 & 30                 | 31 %<br>12<br>(17 - 38)           | n/a<br>n/a<br>n/a                 |
| Thom & Blevins (1996)  | 1 year<br>2 events | n/a, conv. & no-till        | n/a                            | w = 15, 30 & 45 m, l = n/a    | Fescue-Bluegrass Mixture            | n/a                    | n/a                     | 95 %<br>6<br>(91 - 97)            | 98 %<br>6<br>(91 - 97)            |
| Van Dijk et al. (1996) | n/a<br>2 events    | n/a, n/a                    | n/a                            | w = 1, 4, 5 & 10 m, l = 0.5 m | n/a                                 | n/a                    | n/a                     | 38 %<br>24<br>(0 - 86)            | 81 %<br>24<br>(49 - 99)           |
| Barfield et al. (1998) | 1 year<br>2 events | 0.01 ha, w = 22.1 m         | Bare (Conv. & No-till)         | w = 4.57, 9.14 & 13.72 m      | Bluegrass & Fescue                  | Silt Loam              | 1.61,<br>2.42 &<br>4.84 | 94 %<br>12<br>(88 - 100)          | 98 %<br>12<br>(92 - 100)          |

w = width of source area or buffer area in the direction of flow, l = length of buffer perpendicular to direction of flow, area ratio is source area (ha) divided by buffer area (ha), study average is (total input minus total output) divided by total input, n/a is not reported in the study.

Table 2.2 (continued):

| Literature Citation    | Duration Events    | Source Area Characteristics  |  | Buffer Area Characteristics               |                                   | Runoff Volume Retained      |   | Sediment Retained                       |  |
|------------------------|--------------------|--|--|---|-----------------------------------|-----------------------------|---|---|--|
|                        |                    | Area & Width<br>Vegetation (Tillage)<br>Percent Slope                | Percent Slope  | Dimensions<br>Vegetation<br>Percent Slope | Source & Buffer Area<br>Soil Type | Area<br>Ratio               | Study Average<br>Data-points<br>(Range) | Study Average<br>Data Points<br>(Range) |  |
| Pearce et al. (1998)   | 2 years<br>1 event | n/a, n/a   | n/a  | w = 10 m, l = 3 m                         | Sandy to Clay<br>Loam             | n/a                         | n/a                                     | 93 %                                    |  |
|                        |                    | n/a  | n/a  | Grass Community                           |                                   |                             | n/a                                     | 2                                       |  |
|                        |                    | n/a  | n/a  | (3 - 5)                                   |                                   |                             | n/a                                     | (92 - 95)                               |  |
| Tingle et al. (1998)   | 3 years<br>1 event | 0.009 ha, w = 22 m   | 0.009 ha, w = 22 m   | w = 0.5, 1, 2, 3 & 4 m, l = 4 m           | Silty Clay<br>Loam                | 5.5, 7.3,<br>11, 22 &<br>44 | 88 %                                    | 94 %                                    |  |
|                        |                    | Soybean, tilled  | Soybean, tilled  | Tall fescue                               |                                   |                             | 5                                       | 5                                       |  |
| Mendez et al. (1999)   | 1 year<br>3 events | 3  | 3  | 3   | Silt Loam                         | 2.91 &<br>5.74              | (83 - 93)                               | (88 - 98)                               |  |
|                        |                    | 0.009 ha, w = 24.7 m   | 0.009 ha, w = 24.7 m   | w = 4.3 & 8.5 m, l = 3.7 m                |                                   |                             | 56                                      | 86 %                                    |  |
| Mersie et al. (1999)   | 1 year<br>3 events | Corn, tilled   | 18   | Tall fescue                               | Loamy Fine<br>Sand                | 15                          | 2                                       | 2                                       |  |
|                        |                    | n/a, n/a   | n/a  | w = 2 m, n/a                              |                                   |                             | 60 %                                    | n/a                                     |  |
|                        |                    | n/a  | n/a  | Switchgrass & tall fescue                 |                                   |                             | 6                                       | n/a                                     |  |
| Schmitt et al. (1999)  | 1 year<br>1 event  | n/a  | n/a  | 3   | Silty Clay<br>Loam                | 5.4 &<br>10.8               | (20 - 100)                              | n/a                                     |  |
|                        |                    | n/a, n/a   | n/a, n/a   | w = 7.5 & 15 m, l = 3 m                   |                                   |                             | 56 %                                    | 93 %                                    |  |
|                        |                    | n/a  | n/a  | Mixed grasses                             |                                   |                             | 6                                       | 6                                       |  |
| Gilley et al. (2000)   | 1 year<br>2 events | n/a  | n/a  | (6 - 7)                                   | Fine Silt                         | 14.86                       | (36 - 82)                               | (84 - 99)                               |  |
|                        |                    | 0.004 ha, w = 10.7 m   | 0.004 ha, w = 10.7 m   | w = 0.72 m, l = 3.7 m                     |                                   |                             | 7 %                                     | 61 %                                    |  |
|                        |                    | Corn residue with no crop, NT,<br>Disked, Manure applied<br>(8 - 16) | Corn residue with no crop, NT,<br>Disked, Manure applied<br>(8 - 16) | Switchgrass<br>(9 - 16)                   |                                   |                             | 12                                      | 12                                      |  |
| Melville et al. (2001) | 1 year<br>1 event  | 8.75   | 8.75   | 8.75                                      | Sandy Loam                        | 6                           | (6 - 9)                                 | (2 - 100)                               |  |
|                        |                    | 0.002 ha, w = 6 m  | 0.002 ha, w = 6 m  | w = 1 m, l = 3 m                          |                                   |                             | 3 %                                     | 93 %                                    |  |
| Seybold et al. (2001)  | n/a<br>4 events    | n/a  | n/a  | Fescue and Medow Grass                    | Loam                              | 15                          | (1 - 4)                                 | (70 - 98)                               |  |
|                        |                    | n/a  | n/a  | w = 3 m, l = 0.9 m                        |                                   |                             | 61 %                                    | n/a                                     |  |
|                        |                    | n/a  | n/a  | Switchgrass & bare soil                   |                                   |                             | 4                                       | n/a                                     |  |
| Arora et al. (2003)    | 1 year<br>1 event  | n/a  | n/a  | 1   | Silty Clay<br>Loam                | 15 & 30                     | (53 - 73)                               | n/a                                     |  |
|                        |                    | n/a  | n/a  | w = 20.12 m, l = 1.52 m                   |                                   |                             | 35 %                                    | 88 %                                    |  |
|                        |                    | n/a  | n/a  | Smooth Bromegrass                         |                                   |                             | 6                                       | 6                                       |  |
|                        |                    | n/a  | n/a  | 2   |                                   |                             | (30 - 39)                               | (87 - 90)                               |  |

w = width of source area or buffer area in the direction of flow, l = length of buffer perpendicular to direction of flow, area ratio is source area (ha) divided by buffer area (ha), study average is (total input minus total output) divided by total input, n/a is not reported in the study.

Table 2.2 (continued):

| Literature Citation          | Duration Events    | Source Area Characteristics                               |  | Buffer Area Characteristics  |  | Runoff Volume Retained               |                | Sediment Retained                       |   |
|------------------------------|--------------------|---|--|--|--|--------------------------------------|----------------|---|---|
|                              |                    | Area & Width<br>Vegetation (Tillage)<br>Percent Slope     |  | Dimensions<br>Vegetation<br>Percent Slope  |  | Source &<br>Buffer Area<br>Soil Type | Area<br>Ratio  | Study Average<br>Data-points<br>(Range) | Study Average<br>Data Points<br>(Range) |
| Ludovice et al. (2003)       | 1 year<br>4 events | 0.03 ha, w = 10 m<br>Corn<br>n/a                          |  | w = 5.7, 10 m, l = 3 m<br>Grass<br>n/a   |  | n/a                                  | 1 & 2          | 95 %<br>8<br>(88 - 99)                  | n/a<br>n/a<br>n/a                       |
| Mersie et al. (2003)         | 1 year<br>3 events | n/a, n/a<br>n/a<br>n/a                                    |  | w = 2 m, n/a<br>Switchgrass & tall fescue<br>3                                     |  | Loamy Fine<br>Sand                   | 15             | 60 %<br>6<br>(20 - 100)                 | n/a<br>n/a<br>n/a                       |
| Mickelson et al. (2003)      | 1 year<br>3 events | n/a<br>n/a<br>n/a   |  | w = 4.6 & 9.1 m, l = 1.52 m<br>Smooth Brome/Kent. Blue/Kent.<br>Tall Fescue<br>4.6 |  | Silt Loam                            | 5 & 10         | 42 %<br>4<br>(33 - 56)                  | 79 %<br>2<br>(71 - 87)                  |
| Blanco-Canqui et al. (2004a) | 1 year<br>1 event  | 0.001 ha, w = 8 m<br>Fallow<br>4.9                        |  | w = 0.7, 4 & 8 m, l = 1.5 m<br>Fescue & Switchgrass<br>4.9                         |  | Silt Loam                            | 1, 2 &<br>11.4 | 24 %<br>9<br>(2 - 45)                   | 90 %<br>9<br>(75 - 96)                  |
| Blanco-Canqui et al. (2004b) | 1 year<br>1 event  | 0.001 ha, w = 8 m<br>Fallow with Concentrated Flow<br>4.9 |  | w = 0.7, 4 & 8 m, l = 1.5 m<br>Fescue & Switchgrass<br>4.9                         |  | Silt Loam                            | 1, 2 &<br>11.4 | 25 %<br>6<br>(13 - 37)                  | 91 %<br>6<br>(72 - 99)                  |
| Helmets et al. (2005)        | 1 year<br>5 events | n/a, w = 670 m<br>Corn (n/a)<br>1                         |  | w = 13, l = n/a<br>Bluestem, Switchgrass, and Indiangrass<br>1                     |  | Silt Loam                            | 51.5           | 1 %<br>10<br>(0 - 43)                   | 84 %<br>10<br>(73 - 93)                 |
| Vianello et al. (2005)       | 2 years<br>2 event | 0.07 ha, w = 35 m<br>Corn, wheat, soybeans<br>1.8         |  | w = 6 m, l = 20 m<br>Grass + Shrub + Trees<br>1.8                                  |  | Silty Loam                           | 5.83           | 23 %<br>2<br>(19 - 28)                  | n/a<br>n/a<br>n/a                       |

w = width of source area or buffer area in the direction of flow, l = length of buffer perpendicular to direction of flow, area ratio is source area (ha) divided by buffer area (ha), study average is (total input minus total output) divided by total input, n/a is not reported in the study.

applications. Therefore, this creates some uncertainty as to how representative the results from such studies are of actual field conditions. Runoff from different locations with the same source area may enter into the buffer strip at multiple locations and converge within the buffer strip in actual field conditions.

Several studies have reported runoff volume retention as a response under different combinations of site factors and hydrologic factors as treatments using natural or simulated rainfall/runoff events. A median response across such conditions would best represent the performance of buffer strips. This median value would, however, be skewed by similarities in experimental setups as the sampled field conditions are not equitably represented in these studies. An average value would, thus, be the most appropriate summary statistic capable of reflecting the effects of the wide range of sampled field conditions on buffer strips performance. Secondly, the studies in the expanded dataset have reported rainfall, inflow, and outflow for varying number of events observed under different treatments used in the experimental designs. To give a more balanced representation of the diversity of conditions among the treatments and events reported, it was necessary to calculate event weighted treatment averages (TA) and treatment weighted study averages (SA) to estimate overall runoff volume retention in this review article. This was accomplished by the use of equations 2.1 and 2.2 as shown below for calculating TA and SA. Percent runoff volume retained (PRVR) was first calculated as amount retained (rainfall plus inflow minus outflow) divided by input (rainfall plus inflow) for each reported event and treatment type. Rainfall over the buffer area was considered as a direct input to the system when calculating this PRVR for each event. PRVR was then averaged for the number of events reported using equation 2.1 to

calculate TA. TAs were then averaged across treatments to calculate the SA using equation 2.2.

$$TA_j = \frac{\sum_{i=1}^n (PRVR)_i}{E_n} \quad 2.1$$

$$SA = \frac{\sum_{j=1}^n (TA)_j}{T_n} \quad 2.2$$

where  $TA$  is the treatment average (%) for each unique treatment in a study,  $PRVR$  represents the percent runoff volume retention for each event,  $i$  represents different events with in a study from 1 to  $n$ ,  $E_n$  is the total number of events reported in a study,  $SA$  is the study average (%),  $j$  represents the different treatments with in a study from 1 to  $n$ , and  $T_n$  are the total number of treatments for the same study.

A few studies did not report event-by-event data but provided treatment averages based on the number of observed events. In these cases, the runoff volume retention reported was used as-is to calculate the SA using equation 2.2. In addition to these studies, a few special cases were observed as the data was synthesized. A few studies reported runoff volume retention based on a calculation of total inputs and total outputs from all events. A few more studies reported runoff volume retention averaged across events but did not report the number of events used to calculate the average. A few studies reported measurement errors due to experimental setup and cautioned that the results reported were only estimates. SA in these special cases was considered as having been reported from a single event. Each SA calculated thus either represented a unique number of events as reported or a single event if it was a special case.

Percent runoff volume retention from individual studies was averaged across studies to calculate an event and treatment weighted average response. Equation 2.3 was

used to account for the number of events and treatments represented in each study average to calculate this average.

$$AR = \frac{\sum_{k=1}^n ((TA)_j \times E_x)_k}{\sum_{k=1}^n (E_x)_k} \quad 2.3$$

where  $AR$  is the average retention (%) across studies,  $k$  represents the different studies from 1 to  $n$ ,  $TA$  is the treatment average (%) as reported or calculated using equation 2.1,  $j$  represents different treatments within a study,  $E_x$  is number of events a study represents, and  $n$  is the total number of studies. The number of events was set to 1 when using equation 2.3 for the studies that were considered special cases as per earlier discussion. The same procedure of calculating the  $TA$ ,  $SA$ , and event and treatment weighted average across studies was used to average data for sediment mass retention and pesticide retention as discussed later in this article.

Runoff volume retention was 45% when averaged across studies that reported percent infiltration data collected from field studies (natural rainfall, simulated rainfall/runoff/irrigation). Natural rainfall studies showed an average of 50% runoff volume retention (Hall et al., 1983; Parsons et al., 1994; Arora et al., 1996; Webster & Shaw, 1996; Patty et al., 1997; Tingle et al., 1998; Mendez et al., 1999; Muñoz - Carpena et al., 1999; Sheridan et al., 1999; Rankins et al., 2001; Hoffman et al., 2002; Lee et al., 2003; Boyd et al., 2003; Helmers et al., 2005; Vianello et al., 2005). The simulated runoff studies showed an average of 38% runoff volume retention (Assmussen et al., 1977; Brockway et al., 1977; Hays et al., 1984; Dillaha et al., 1988, 1989; Magette et al., 1989; Coyne et al., 1995; Misra et al., 1996; Thom and Blevins, 1996; Van Dijk et al., 1996; Barfield et al., 1998; Tingle et al., 1998; Mersie et al., 1999, 2003; Schmitt et al., 1999; Gilley et al., 2000; Melville et al., 2001; Seybold et al., 2001; Arora et al., 2003;

Ludocice et al., 2003; Mickelson et al., 2003; Blanco - Canqui et al., 2004a, 2004b; Helmers et al., 2005; Vianello et al., 2005). This average runoff volume retention accounts for the different number of events and treatments reported, but does not include any differences due to experimental setup. This average runoff volume retention is an average across different combinations of site factors and hydrologic factors to the extent reported in different studies.

The amount of runoff volume retention as a percent of total input (rainfall plus inflow) was determined for each reported event and plotted against area ratio. This plot was made since several studies have concluded that longer buffer strips (smaller area ratios) can greatly increase the amount of runoff volume retained. Figure 2.3 shows the percent runoff volume retained on an event basis for different area ratios as reported or calculated from the data included in various studies. This figure shows a wide range for percent runoff volume retention (from 0% to 100%), including negative values. The possible reasons for negative values for runoff volume retention are measurement error, shallow groundwater appearing on the surface due to up gradient pressure, neglecting rainfall over the buffer area as an input in calculations, and/or experimental design where output runoff volume from a buffered plot is compared to runoff volume from a non-buffered plot. Runoff volume retention in the source area is assumed similar for both the buffered and the non-buffered plots in these studies, which is not the case, resulting in negative numbers. In the case of wide buffer strips, there is a potential for runoff generation from within the buffer strip, under natural rainfall conditions and prior to runoff from source area, reaching the buffer area. None of the studies included in this



review article measured this runoff generation as an output and as such, it is not included in any calculations for determining runoff volume retention.

Several additional studies (Dillaha et al., 1989; Tim et al., 1994; Hoffman et al., 1995; Tim et al., 1995; Srivastava et al., 1996; Boyd et al., 2003) have concluded that the amount of runoff water that is retained in the buffer strip greatly depends on the length and/or the area of the strip over which the flow occurs. Consequently, longer buffers can significantly reduce runoff volume. However, it is not feasible to maintain uniform flow across the buffer strips due to changes in topography as reported by Dillaha et al. (1989) and Thom and Blevins (1996). Some of the more recent studies (Helmets et al., 2005; Bansal et al., 2006) have shown that flow convergence or concentrated flow occurs in the case of field scale buffer strips. This happens due to formation of flow paths within the buffer strip area in relationship to variable micro topography of the specific site. As such, the buffer strip area over which the flow occurs is actually smaller than the actual area of the buffer strip. The resulting area ratio, i.e. source area to the buffer strip area (actual flow path area), is a relatively higher area ratio. Different studies have used different experimental setups (simulated rainfall, simulated runoff, natural rainfall, etc.) as reported by Krutz et al. (2005); however, each study has used some ratio of source area to buffer strip area.

Four studies listed in Table 2.1 and 2.2 did not report on the area ratios used in the experimental design, whereas fourteen studies used an area ratio of greater than ten. Over half of the studies (twenty-four) have used an area ratio of less than ten in their experimental setups. Flow convergence or concentrated flow, as discussed earlier, happens in field scale buffer strips. As such, it can result in variable runoff volume

retention as the entire area of the buffer strip is not exposed to uniform overland flow. Bansal et al. (2006) have shown, through grid analysis using elevation data that flow convergence happens due to development of flow paths within the field and the buffer. As such, area ratios of 10 or smaller are unlikely to be implemented for field scale buffer strips. The USDA - NRCS (2003) filter strip practice standard recommends limiting area ratios to about 50 when designing field scale filter/buffer strips, although no lower limit is assigned. Under a strip cropping situation, area ratios can be as low as one, as in the theoretical case of a two strip rotation. In such cases, low area ratios or small source areas and therefore low runoff flow volumes, are less likely to occur in field conditions due to flow convergence. As such, results from studies with low area ratios or low runoff flow volumes are likely an over estimation of the actual field performance of buffer strips. Average runoff volume retention is 40% if results related with area ratios less than 10 are excluded. This average retention is an average across different combinations of site factors and hydrologic factors to the extent reported in the different studies; and it does not include any differences due to experimental setup.

Minimum runoff volume retention, on an event-by-event basis as reported in these studies (Tables 2.1 and 2.2), is of the order of one to five percent. Saturated hydrologic conditions have been reported as the key factor for such low percent retention. Maximum runoff volume retention is 100% as reported by Parsons et al., 1994; Arora et al., 1996; Barfield et al., 1998; Boyd et al., 2003; Mersie et al., 2003; and Blanco - Canqui et al., 2004a under both natural and simulated rainfall/runoff experimental setups. Authors of these studies have concluded that such high percent infiltration occurs during dry antecedent moisture conditions accompanied by a low flow rate and/or volume of

runoff from source areas. In summary, runoff volume retention varies with different site specific combinations of site and hydrologic factors on an event-by-event basis as reported in Tables 2.1, 2.2, and Figure 2.3. This event variability for runoff volume retention plotted for different area ratio ranges is evident in Figure 2.3. Both the mean and median values along with the percentile ranges are shown for each area ratio range plotted. Median value is skewed towards the studies with similar source area to buffer area ratios, source area tillage practices, buffer strip vegetation, and slope. Area ratios of less than 10 are represented by 142 data points, area ratios from 10 to 30 are represented by 35 points, and area ratios of greater than 30 are represented by 30 data points in Figure 2.3. An overall median value will skew the final value of runoff volume retention towards smaller area ratios which is not representative of field conditions where flow converges in buffer strips. Thus, an event and treatment weighted average value is more accurate representation of the range of values than the median value. An average performance of buffer strips across different conditions more likely represents the performance potential of buffer strips in reducing runoff volume. This average performance, however, is sensitive to the effects of larger area ratios.

## **2.5 Dissolved Pesticide Concentration ( $C_{out}$ )**

Dissolved pesticide concentration in the outflow from the buffer strips, represented by  $C_{out}$  in Figure 2.2, is a result of interactions between the input pesticide mass and the effect of rainfall dilution and sorption or desorption of the pesticide with organic matter/soil in the buffer strip. An interesting point to consider is what water infiltrates: is it just runoff or is it some mixture of runoff mixed with rainwater (a dilution effect)? Only runoff will infiltrate when there is no rain falling on the buffer strips as

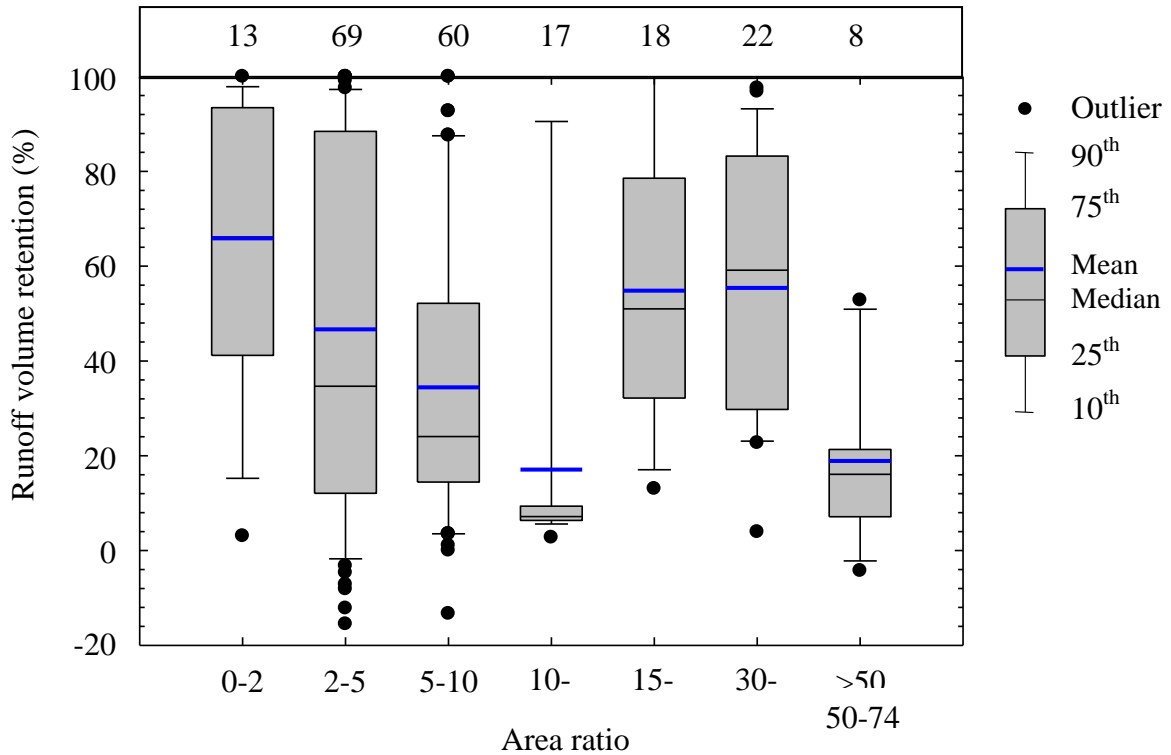


Figure 2.3: Percent runoff volume reduction as a function of area ratio. Percent reduction numbers (used in this figure) are on event basis as reported or calculated from data reported in studies listed in Table 2.1 and 2.2 where area ratio data were available. Note: Two data points at ~90% for 10-15 range pull the mean up. Dots are outliers. Numbers above the box plots indicate sample size.

runoff passes through it, and therefore, a change in pesticide concentration can directly be attributed to sorption and/or desorption. On the other hand, if rainfall is occurring on the buffer strip as runoff from the source area passes through it, a change in concentration is a net effect of rain water dilution and sorption/desorption.

A few studies have quantified the changes in dissolved pesticide concentration due to rainfall as the runoff passes through the buffer strips. These studies show that different combinations of site and hydrologic factors result in different rainfall dilution effects. Variations to area ratios (Misra et al., 1996), rainfall intensities (Lowrance et al., 1997; Vellidis et al., 2002); and buffer strip lengths (Schmitt et al., 1999) result in

variable rainfall dilution factors for dissolved pesticide concentrations. Thus, it is important to note that the concentration change due to dilution is sensitive to rainfall intensities, surface roughness, buffer strip length and slope, and area ratio.

In addition to rainfall dilution, the change in the dissolved pesticide concentration in outflow depends on how much pesticide gets sorbed or desorbed to dead organic matter content (age and amount), live vegetation (height and thickness), and soil particles (size and distribution) of the buffer strips. These three components represent the total sorption sites that may be available for sorption within the buffer strips. As such, one may assume that longer buffer strips with wider effective flow widths will have larger sorption capacity than shorter buffer strips with narrower effective flow widths. Large sorption capacities found in relation to large organic matter content of the buffer strip soils supports this assumption (Reungsang et al., 2001). However, a few researchers have found no clear relation between moderately sorbed pesticide concentration reduction and length of buffer strips (Patty et al., 1997; Tingle et al., 1998; and Syversen and Bechmann, 2004). Evaluating sorption sites in terms of the age and vegetation density of the buffer strips, Schmitt et al. (1999) showed that outflow dissolved moderately and strongly sorbed pesticide concentrations were significantly lower in buffer strips which were 10 times older than the newly established two year old buffer strips. Older buffer strips are likely to have greater pools of surface residue and organic matter in the soil. Increased surface residue is likely to reduce flow velocity due to greater resistance to flow whereas increased organic matter content is likely to provide greater pesticide sorption sites. The study did not clearly specify if the pesticide concentration reduction observed was caused by increased organic matter content in the soil or due to reduced

travel time, i.e. greater contact time for the pesticides to get sorbed. Evaluating sorption sites in terms of contact with live vegetation, Arora et al. (1996) and Misra et al. (1996) found no effect on the dissolved moderately sorbed pesticide concentrations when the flow depth was doubled, doubling the contact area with live vegetation. These two studies tried to estimate mathematically from experimental data as to how much sorption was taking place in the buffer strips. The authors estimated that the net effect of sorption and desorption was of the order of five percent of the input pesticide mass for atrazine, metolachlor, and cyanazine for 15:1 and 30:1 area ratio buffer strips. Other researchers have found mixed results where outflow dissolved concentrations have either decreased or increased (Cole et al., 1997; Mickelson et al., 1998; Mersie et al., 1999; Arora et al., 2003). These studies have not been able to clearly establish how much sorption or desorption is taking place as the flow passes through the buffer strips.

Krutz et al. (2005) have summarized the environmental fate of over twenty pesticides and/or their metabolites as they pass through the buffer strip area. Sorption of non-ionic pesticides to the buffer strip soil occurs at a greater degree than its desorption. The amount of net sorption is relatively small (Lacas et al., 2005) as the flow in buffer strips is transient and sorption/desorption is not an instantaneous process. Anionic pesticides, on the other hand, show no difference in sorption to and desorption from buffer strip soil when compared with cultivated field soils. Krutz et al. (2005) concluded that mobility of herbicides is not significantly impeded by larger percent organic matter in the soils.

In summary, sorption and desorption of pesticides does occur in the buffer strips. Owing to differences in pesticide properties, lack of direct measurements (indirect

measurements for atrazine, metolachlor, and cyanazine by Arora et al., 1996; Misra et al., 1996), and differences in reported results, the net effect of this process on pesticide retention in buffer strips cannot be accurately predicted. Outflow dissolved pesticide concentrations, when compared with outflow as sorbed to sediment pesticide concentrations, show that pesticide partitioning coefficient's do not significantly vary between inflow and outflow as expected. In addition, most of the studies have measured the outflow dissolved pesticide concentrations. This concentration has been used to estimate the pesticide mass output in the water phase by multiplying the concentration with the outflow volume. Percent pesticide mass retained (calculated in the studies is a difference between input and output masses as a percent of input), represents the net retention of pesticide within the buffer strips. Therefore, outflow dissolved pesticide concentration and percent mass retained represent the net effect of infiltration, rainfall dilution and sorption/desorption. Therefore, the percent pesticide mass retained in the buffer strips with runoff volume can be considered directly proportional to the percent runoff volume retained and the pesticide partitioning coefficient.

## **2.6 Sediment Mass Retained**

Sediment mass retained is the mass of eroded sediment from the source area that deposits within the buffer strip. This deposited mass is generally calculated as the difference between inflow ( $S_i$ ) and outflow ( $S_{out}$ ) sediment masses (Figure 2.2). Percent sediment mass retention as reported in different studies is shown in Figure 2.4. This figure shows sediment mass retention as a function of area ratio. Similar to Figure 2.3, Figure 2.4 also shows the event by event variability in the reported data where the sediment mass retention varies between 2% to 100%.

Sediment mass retention was 76% when averaged across studies that have reported data collected from field studies (natural rainfall, simulated rainfall/runoff/irrigation). Natural rainfall studies showed an average of 75% retention (Hall et al., 1983; Parsons et al., 1994; Arora et al., 1996; Daniels and Gilliam, 1996; Robinson et al., 1996; Patty et al., 1997; Tingle et al., 1998; Mendez et al., 1999; Muñoz - Carpena et al., 1999; Sheridan et al., 1999; Rankins et al., 2001; Boyd et al., 2003; Lee et al., 2003; Helmers et al., 2005). The simulated rainfall/runoff/irrigation studies showed an average of 76% retention (Asmussen et al., 1977; Brockway et al., 1977; Dillaha et al., 1988, 1989; Magette et al., 1989; Coyne et al., 1995; Van Dijk et al., 1996; Thom & Blevins, 1996; Barfield et al., 1998; Pearce et al., 1998; Tingle et al., 1998; Mendez et al., 1999; Schmitt et al., 1999; Gilley et al., 2000; Melville et al., 2001; Arora et al., 2003; Mickelson et al., 2003; Blanco - Canqui et al., 2004a, 2004b; Helmers et al., 2005). This average percent sediment mass retention, so calculated, includes the number of different events and treatments reported in the study but does not include any differences due to experimental setup. Some of the studies again have reported sediment mass retention by using a comparison basis between buffered plots and non-buffered plots. Output from a non-buffered plot is considered as input into the buffered plot when making calculations. Actual input into the buffered plots is not measured in these studies due to their experimental setup and is the likely reason for low sediment mass retention numbers reported. The reported numbers (Figure 2.4) show a combined effect of three processes, i.e. sedimentation ahead of the buffer strip, physical filtering of the sediment in the buffer strip, and co-deposition (penetration) of particles into the soil surface of the buffer strip along with infiltrating water.



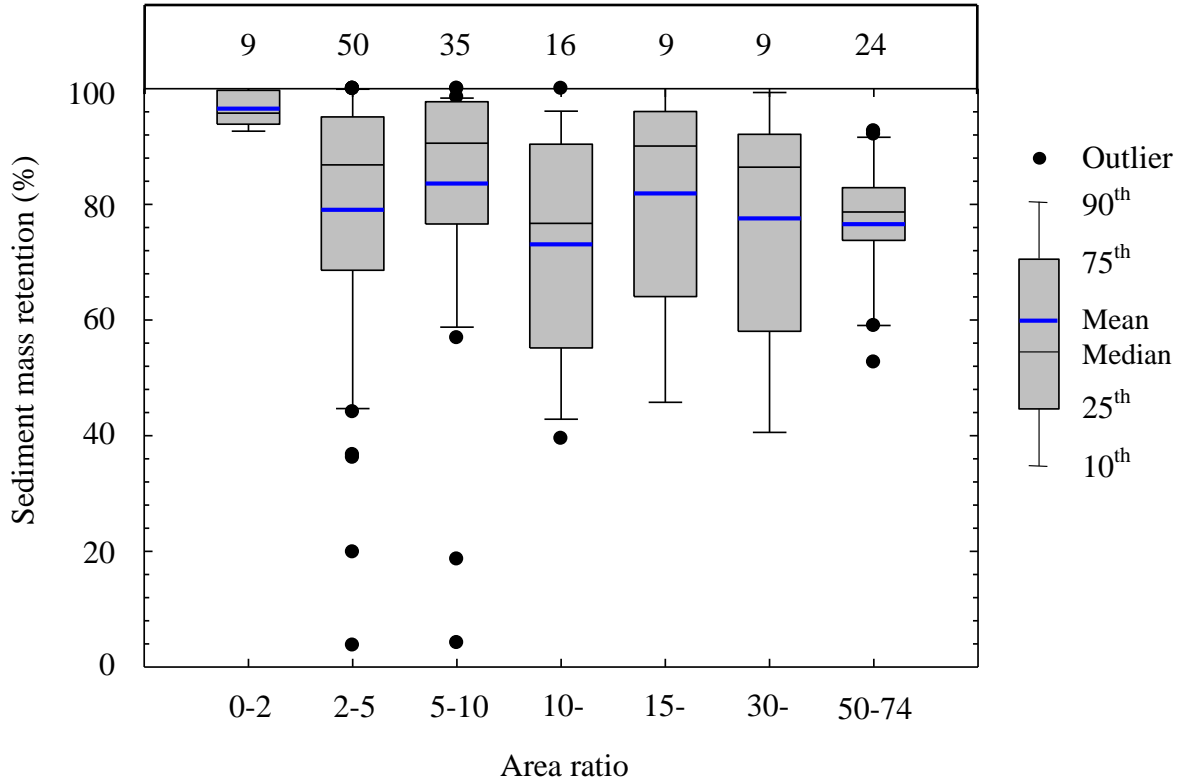


Figure 2.4: Percent sediment mass retention as a function of area ratio. Percent reduction numbers (used in this figure) are on event basis as reported or calculated from data reported in studies listed in Table 2.1 and 2.2 where area ratio data were available. Dots are outliers. Numbers above the box plots indicate sample size.

Deposition ahead of the buffer strip has been shown by Dillaha et al. (1989), Dabney et al. (1995), and Meyer et al. (1995) as one of the factors in sediment mass reduction. Physical filtering effect of the buffer strip is a function of the sediment transport capacity of the water flowing through the buffer strip and its effectiveness in offering resistance to flow (Dabney et al., 1995; Jin et al., 2001). None of the studies have determined whether or not the deposited sediment becomes a part of flow through buffer strip for subsequent events. Lastly, penetration of very fine particles into the buffer strip soil may occur resulting in sediment retention (Misra, 1995; Mickelson et al.,

2003; Lacas et al., 2005). This penetration of fine particles results in reduced runoff volume retention when compared to the non-sediment mixed simulated runoff (Misra, 1995; Mickelson et al., 2003). In summary, the studies reviewed have not reported sediment mass retention for the three processes individually. As such, total sediment mass retention is considered as the combined effect of the above mentioned three processes in this review article.

Data presented in the natural rainfall studies, when averaged for low sediment mass retention (data points with values less than 50%), showed a 25% sediment mass retention. The average for simulated rainfall/runoff studies was 19% sediment mass retention. Authors from the studies cited no till or minimum till practices and/or sufficient canopy cover in the source area as the key factors for low sediment mass retentions. Minimum sediment mass retention, as reported in both natural rainfall and simulated rainfall studies, was the order of 2% to 10% (Magette et al., 1989; Parsons et al., 1994; Muñoz - Carpena et al., 1999; Gilley et al., 2000; Jin et al., 2001). Similar data averages for high sediment retention (data points with values greater than 50%) for natural rainfall studies averaged 88%. This average was 95 % for simulated runoff studies, with a maximum of 100% sediment mass retention reported for either experimental setup. Authors reported dry antecedent moisture conditions and/or very low runoff producing storms as the key factors for such high sediment mass retentions.

In summary, buffers strips can be expected to retain 76% sediment mass based on an average of studies reviewed. This is comparable to USDA information of 75% retention stated in the on - line document Buffer Strips: Common Sense Conservation (USDA - NRCS, 2008). Sediment mass retention across various studies for different area

ratios shows at least 40% retention, provided the numbers that are related with negative infiltration and for area ratios less than 10 are excluded. Buffer strips may only retain 2% to 10% of the incoming sediment mass on the minimum basis. This extreme of minimum sediment mass retention should not be viewed as the inability of buffer strips to perform appropriately. Similarly, maximum sediment mass retention of 100% by buffer strips should not be viewed as if buffer strips can completely stop sediment export from small scale fields/watersheds.

## **2.7 Sorbed Pesticide Concentration**

Sediment mass that enters the buffer strip has a particle size distribution and a sorbed pesticide concentration. Enrichment of this sediment occurs as the runoff flows through the buffer strips. Larger particles settle out first and the outflow consists mostly of smaller particles (Lee et al., 2000). These smaller particles can have higher sorbed pesticide concentrations, up to ten times higher as reported in the review by Lacas et al. (2005). This is most likely as smaller particles have larger specific surface area, and subsequently, more pesticide mass sorbed to them. Thus, sorbed pesticide concentrations in outflow should theoretically increase as enrichment occurs. None of the studies reviewed have evaluated sorbed pesticide concentrations between inflow and outflow based on particle size classes. Krutz et al. (2005) summarized that it is difficult to differentiate between inflow and outflow sorbed concentrations for field studies due to differences in inflow nominal concentrations, solubility, hydrophobicity, and ionic nature. Consequently, the effects of enrichment were not quantified in this paper by Krutz et al. (2005). A few studies have reported inflow and outflow sorbed pesticide concentrations on an overall basis but not based on particle size classes (Webster and

Shaw, 1996; Arora et al. (1996); and Arora et al., 2003). These studies have found negligible or insignificant differences between the inflow and outflow overall sorbed pesticide concentrations for all three sorption classes (weakly, moderately, and strongly sorbed pesticides). As the effects of the enrichment process are reportedly negligible, the retained sediment sorbed pesticide concentrations are, therefore, similar to both inflow and outflow sorbed pesticide concentrations.

Inflow sorbed pesticide concentration is proportional to the sorption coefficient of the pesticide. As inflow and retained sediment sorbed pesticide concentrations are similar, the retained sediment sorbed pesticide concentration is also proportional to the sorption coefficient. The sorbed pesticide mass is generally measured as a product of sediment mass and the sorbed pesticide concentration. The retained sorbed pesticide mass, therefore, is proportional to the sorption coefficient and the retained sediment mass.

## **2.8 Estimating Average Pesticide Mass Retention (%) in Buffer Strips**

Average retentions of both carrier phases of pesticides (runoff volume and sediment mass) have been calculated and presented in this paper. These average retentions include unique experimental setups not used by studies that have exclusively studied pesticide retention by buffer strips. Using these average carrier retentions, average pesticide retention was estimated and compared with pesticide retention data reported in literature. A simple mathematical model was considered to estimate average pesticide retention (%) for the three different pesticide classes (based on sorption coefficient,  $K_{oc}$ ). This model can be used to estimate average pesticide retention under field conditions which fall within the range of the experimental setups of the expanded

dataset. Furthermore, the model can be used to estimate overall pesticide retention for any pesticide not studied.

Using pesticide sorption or the partitioning coefficient ( $K_{oc}$ ) as the key pesticide property, a simple model can be written as a function of carrier mass retained (%) and the pesticide mass (%) within the carrier. This results in the following equation for determining average pesticide retention (%) within the buffer strips.

$$APR_k = (CR \times PM_k)_w + (CR \times PM_k)_s \quad 2.4$$

where  $APR_k$  is average pesticide retention (%),  $k$  represents three pesticide sorption classes,  $CR$  is carrier phase retention (%), and  $PM$  is pesticide mass with the specific carrier (%),  $w$  and  $s$  are the water and sediment phase of runoff, respectively.  $PM_k$ , pesticide mass in the carrier phase, will depend on the partitioning coefficient ( $K_{oc}$ ) of the pesticide. Equation 2.4, therefore, will result in separate percent retention by buffer strips for different pesticides.

As discussed earlier in the paper, the effect of sorption and desorption on pesticide mass retained in buffer strips is difficult to determine based on published data. This model assumes that the net effect of sorption and desorption is negligible or zero. Secondly, the model also assumes that the net effect of enrichment is negligible or zero. As explained earlier, the model considers the pesticide mass retained with either carrier phase of runoff as directly proportional to the carrier mass retained and the pesticide mass contained in this carrier phase based on the sorption coefficient. This model is parameterized to account for synthesized data for the average runoff volume (%) and sediment mass retention (%) in the buffer strips. By quantifying pesticide mass ( $PM$ )

contained in each carrier phase, the model can calculate a pesticide mass retention (%) when the carrier retention (%) is multiplied with the pesticide mass (%) it carries.

Parameter  $PM_k$  of equation 2.4 simply stated represents three classes of pesticides i.e. weakly sorbed ( $K_{oc} < 100$  L/kg), moderately sorbed ( $100 < K_{oc} < 1000$  L/kg), and strongly sorbed ( $K_{oc} > 1000$  L/kg). This results in a separate value of  $PM_k$  for each class of pesticide synthesized for pesticide retention. Pesticide mass ( $PM_k$ ) contained in either carrier phase (water or sediment) entering the buffer strips depends on specific pesticide properties. Pesticide formulation, solubility in water, volatilization, sorption to infield soil, method of application, and half - life affects the amount of pesticide that is lost from source area (Baker and Mickelson, 1994). In summarizing these characteristics, Wauchope (1978) concluded that for pesticides with relatively low solubility and high sorption coefficients, only 10 - 30 % of the total loss from the source area occurred with runoff water. Rohde et al. (1980) reported a 5% to 25% of total loss of trifluralin with runoff water. Boyd et al. (2003) reported chlorpyrifos losses in the range of 10% to 40% of the total loss from source area. On the other hand, for moderately sorbed pesticides with medium solubility, Wauchope (1978) summarized that 60% to 100% of total loss from source area was with runoff water. Hall et al. (1972, 1974) showed 80% to 98% of total loss of atrazine with runoff water. Arora et al. (1996) showed 85% to 99% of total loss of atrazine, metolachlor, and cyanazine being with runoff water. Pesticide loss with runoff water as a percent of total loss for atrazine, alachlor, cyanazine, carbaryl, and fonofos varied between 65% to 95% in the results reported by Hall et al., 1972; Ritter et al., 1974; Caro et al., 1974; Bailey et al., 1974; Baker et al., 1978; and Rohde et al., 1980. In summary, for strongly sorbed pesticides, an average of only 20% of loss from

source area with runoff occurs in runoff water. The remaining 80% of the loss occurs with runoff sediment. For moderately sorbed pesticides, this average loss is 80% with runoff water and only 20% with runoff sediment. Almost 95% to 100% of the total loss of weakly sorbed pesticides occurs with runoff water. These average values of pesticide mass ( $PM_k$ ) in runoff from source area and entering the buffer strips for the three pesticide classes for both water and sediment carrier phases are presented in Table 2.3.

The second parameter (CR) in equation 2.4 represents carrier phase retention of runoff volume and/or sediment mass in buffer strips. As presented in the “Infiltration Water Mass” section earlier, CR for runoff volume was 45% when averaged across studies that reported percent infiltration data collected from field studies (natural rainfall, simulated rainfall/runoff/irrigation). This average of 45% runoff volume retention is used as CR for water in equation 2.4 and Table 2.3. Similarly, as presented in the “Sediment Mass Retained” section earlier, buffers strips can be expected to retain 76% sediment mass based on an average of studies reviewed. This average of 76% sediment mass retention is used as CR for sediment in calculating the average percent retention in equation 2.4 and Table 2.3. Ranges of either carrier mass retentions are presented in parenthesis in Table 2.3. Table 2.3 also represents the lower and upper end of pesticide mass retention (in parenthesis) in buffer strips for the three different types of pesticides. A lower end of 10% runoff volume retention and 20% of sediment mass retention is used in calculating the average percent retention for both total and with either carrier phase. An upper end of 95% runoff volume retention and 90% of sediment mass retention is used in calculating this percent retention for both total and with either carrier phase.

The model calculated estimate of the pesticide retention quantified (Table 2.3) by the review performed in this article represents varying situations of area ratios, buffer strips lengths and slopes, buffer vegetation density and age, rainfall intensities, and dry and saturated antecedent conditions of buffer soils. This estimate, so quantified, is based on the average retention of either pesticide carrier phase and does not take into consideration experimental error of individual studies. Table 2.4 shows pesticide retention by buffer strips under different agricultural applications of buffer strips. Strongly sorbed pesticides, such as chlorpyrifos and trifluralin (both with  $K_{oc} > 1000$  L/kg) can be retained on the average of 70% ( $0.2 \times 0.45 + 0.8 \times 0.76$ ) with minimum and maximum retentions of 18% and 91% respectively (calculated using equation 2.4 and listed in Table 2.3). This calculated average is lower than the individual study averages but is within the range of strongly sorbed pesticide retentions reported (Table 2.4). This calculated average pesticide retention for strongly sorbed pesticides is lower than the average among natural rainfall studies which showed an average of 75% retention by the buffer strips (Antonious and Byers, 1997; Patty et al., 1997; Antonious, 1999; Boyd et al., 2003; Antonious, 2004; Syversen, 2005; 8 pesticides). The model calculated average is lower when compared with the simulated studies which averaged 78% (Rohde et al., 1980; Kloppel et al., 1997; Schmitt et al., 1999; Arora et al., 2003; Mersie et al., 2003; 5 pesticides). The overall average for both natural and simulated studies averaged 76% retention (10 pesticides) by buffer strips. The average pesticide retention for both experimental data sets, separately and combined, exceeds the model calculated average pesticide retention of 70% for the strongly sorbed pesticides as listed in Table 2.3. The model makes two assumptions that the net effects of sorption/desorption and enrichment



in buffer strips on pesticide mass retention is negligible or zero. Model calculated averages being lower than the reported averages, shows that these processes do affect strongly sorbed pesticide mass retention. The difference between study average of 76% retention and model calculated average of 70% shows that the effect of sorption/desorption and enrichment is relatively small (~6%) in this case.

Model calculated averages were also compared with study averages for moderately sorbed pesticides which are transported mainly with water. In case of these

Table 2.3: Average pesticide mass retention (%) in buffer strips with average retention of both carrier phases (%) as modeled using equation 2.4. Lower and upper end pesticide mass retentions are included in parenthesis.

| <i>Type of Pesticide</i>   | <i>Carrier Phase in Runoff</i> | <i>Pesticide Mass in Carrier Phase<sup>1</sup> (%)</i> | <i>Average Carrier Retention<sup>2</sup> (%)</i> | <i>Pesticide Mass Retention in Carrier (%)</i> |
|--|--------------------------------|--|--|--|
| <i>Weakly Sorbed (<math>K_{oc} &lt; 100</math> L/kg)</i>               | <i>Water</i>                   | 95   | 45 (10 – 95)                                     | 43 (9 – 90)                                    |
|  | <i>Sediment</i>                | 5  | 76 (20 – 90)                                     | 4 (1 – 5)                                      |
|  | <i>Total</i>                   | 100  |  | 46 (10 – 95)                                   |
| <i>Moderately Sorbed (<math>100 &lt; K_{oc} &lt; 1000</math> L/kg)</i> | <i>Water</i>                   | 80   | 45 (10 – 95)                                     | 36 (8 – 76)                                    |
|  | <i>Sediment</i>                | 20   | 76 (20 – 90)                                     | 15 (4 – 18)                                    |
|  | <i>Total</i>                   | 100  |  | 51 (12 – 95)                                   |
| <i>Strongly Sorbed (<math>K_{oc} &gt; 1000</math> L/kg)</i>            | <i>Water</i>                   | 20   | 45 (10 – 95)                                     | 9 (2 – 19)                                     |
|  | <i>Sediment</i>                | 80   | 76 (20 – 90)                                     | 61 (16 – 72)                                   |
|  | <i>Total</i>                   | 100  |  | 70 (18 – 91)                                   |

<sup>1</sup> Average pesticide mass in the carrier phase is an average over the  $K_{oc}$  range from the reported studies.

<sup>2</sup> Average retention of both carrier phases is calculated from studies listed in Table 2.1 and Table 2.2, majority of which have been conducted on silt loam soils.

Table 2.4: Pesticide retention (%) by buffer strips as reported by different studies as related to agricultural runoff (1977-2005).

| Literature Citation, Location<br>Duration / Events   | Source Area<br>Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Buffer Area<br>Dimensions<br>Vegetation<br>Slope (percent) | Soil Type<br>& Area<br>Ratio | Name, Formulation<br>Rate kg a.i./ha, Method<br>K <sub>oc</sub> , Half-life (days)  | Pesticide Retention<br>Study Average<br>Data Points<br>(Range)                            | Comments  |
|--|---|--|------------------------------|---|---|---|
| <b>Application: Buffer Strips Intercropped in Vegetable Row Crops, Natural Rainfall Studies</b>                      |   |  |                              |   |   |   |
| Antonious and Byers (1997), USA<br>1 year, 4 events  | 0.008 ha, w = 22 m<br>Tomatoes, roto-tilled<br>10                           | w = 1.5 & 3 m, l = 3.7 m<br>Fescue<br>10                   | Silty Loam<br>7.2 & 14.2     | Endosulfan, EC<br>0.61, sprayed<br>12400, 50  | 78 (T)<br>2<br>(56-99)  | Natural rainfall events recorded on a 5 % O.M. soil.  |
| Antonious (1999)<br>USA<br>n/a, n/a  | 0.008 ha, w = 22 m<br>Capsicum / Tomatoes,<br>n/a<br>10                     | w = 1.5 & 3 m, l = 3.7 m<br>Festuca sp. Kentucky 31<br>10  | Silty Loam<br>7.2 & 14.2     | Dacthal, W-75<br>3.44, banded<br>5000, 100  | 88 (T)<br>4<br>(72 - 100)   | Total retention by both water and sediment phase not reported. Natural rainfall events recorded on a 2 % O.M. soil.   |
| Antonious (2004)<br>USA<br>1 year, 3 events  | 0.008 ha, w = 22 m<br>Tomatoes, n/a<br>10                                   | w = 0.7 m, l = 3.7 m<br>Tall Fescue<br>10                  | Silty Loam<br>31             | Trifluralin, EC<br>0.84, sprayed<br>8000, 60  | 86 (W)<br>n/a<br>(n/a)  | Only retention in dissolved phase reported as an average of three natural rainfall events on a 2.8 % O.M. soil.   |
| <b>Application: Edge of Field Buffer Strips as Setbacks for Tile Inlet Terraces, Natural Rainfall Studies</b>        |   |  |                              |   |   |   |
| Mickelson et al. (1998), USA<br>2 years, 5 events  | 0.75 ha, n/a<br>Corn, disked<br>7.5   | w = 20.1 m, l = 40.2 m<br>Source area crop<br>7.5          | Silty Clay<br>Loam<br>9.3    | Atrazine, 4L<br>2.2, broadcast<br>100, 60<br>Metolachlor, 8E<br>2.8, broadcast<br>200, 90<br>Cyanazine, 4L<br>3.4, broadcast<br>190, 14 | 1.8 (T)<br>15<br>(-18 - 25)<br>4.8 (T)<br>15<br>(-15 - 26)<br>5.6 (T)<br>15<br>(-10 - 25) | Buffer strips as cropped areas with no pesticide application on a 3 % O.M. soil were used in this study. Due to ponding at the tile inlet, setbacks were submerged by different depths and uniform flow through the setback buffers was not achieved.     |
| <b>Application: Edge of Field Buffer Strips as Zone 3 of Riparian Forest Buffer System, Natural Rainfall Studies</b> |   |  |                              |   |   |   |
| Lowrance et al. (1997), USA<br>3 years, > 18 events  | 2.5 ha, n/a<br>Corn (Conv. Till)<br>n/a                                     | w = 8 m, l = 55 m<br>Bermudagrass and Bahia grass<br>n/a   | Loamy<br>sand<br>56.82       | Atrazine<br>2.85, sprayed<br>100, 60<br>Alachlor<br>3.42, sprayed<br>170, 15  | 70 (T)<br>2<br>(n/a)<br>81 (T)<br>2<br>(n/a)  | Similar to Vellidis et al. (2002) below except this is a three year study with a larger source area planted to corn.  |
| Vellidis et al. (2002), USA<br>2 years, > 10 events  | n/a, w = 10 m<br>Pasture<br>n/a   | w = 8 m, l = 100 m<br>Bermudagrass and Bahia grass<br>n/a  | Loamy<br>sand<br>n/a         | Atrazine<br>17.1, sprayed<br>100, 60<br>Alachlor<br>20.5, sprayed<br>170, 15  | 95 (T)<br>2<br>(n/a)<br>96 (T)<br>2<br>(n/a)  | Pesticide mass retention is total input v/s total output over two years of study. It is not an average across different events recorded. Events recorded include events occurring after first 250 mm of rainfall up to next year's pesticide application. |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events   | Source Area<br>Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Buffer Area<br>Dimensions<br>Vegetation<br>Slope (percent) | Soil Type<br>& Area<br>Ratio  | Name, Formulation<br>Rate kg a.i./ha, Method<br>K <sub>oc</sub> , Half-life (days) | Pesticide Retention<br>Study Average<br>Data Points<br>(Range) | Comments   |
|---|---|--|-------------------------------|--|--|--|
| <b>Application: Edge of Field Buffer Strips as a part of Grassed Waterway, Simulated Rainfall Studies</b> |   |  |                               |  |  |  |
| Assmussen et al.<br>(1977), USA<br>1 year, 2 events   | 0.003 ha, n/a<br>Corn (Conv. Till)<br>2                                     | w = 24.4 m, l = 4.6 m<br>bermudagrass, bahiagrass<br>2     | Loamy<br>sand<br>0.27         | 2,4-D<br>0.56, sprayed<br>20, 10   | 71 (T)<br>2<br>(69 - 72)                                       | Simulated rainfall intensity of 25.4 cm/h was used to apply 12.7 cm of rainfall over the source area for both events.  |
| Rohde et al. (1980),<br>USA<br>2 years, 2 event   | 0.003 ha, w = 6.1 m<br>n/a<br>n/a   | w = 24.4 m, l = 4.6 m<br>Bermudagrass/Bahiagrass<br>3      | Loamy<br>sand<br>0.25         | Trifluralin, n/a<br>1.12, surface applied &<br>incorporated<br>8000, 60            | 92 (W)<br>2<br>(86 - 96)                                       | Simulated rainfall intensity of 19.1 cm/h was used to apply 14.9 cm of rainfall under dry (42.7 % Soil M.C.) conditions and 15.7 cm under wet (28.6 % Soil M.C.) conditions.   |
| <b>Application: Edge of Field Buffer Strips on Contours, Natural Rainfall Studies</b>                     |   |  |                               |  |  |  |
| Hoffman et al. (1995),<br>USA<br>2 years, > 2 events  | 0.17 ha, w = 36.7 m<br>Corn / Wheat (Conv. Till)<br>4                       | w = 9 m, l = 45 m<br>Wheat / Costal Bermudagrass<br>4      | Black Clay<br>5.2             | Atrazine, n/a<br>2.24, pre-emergence<br>100, 60                                    | 47 (T)<br>2<br>(44 - 50)                                       | Three sections of source area and contour grass filter strips established within each watershed (0.6 ha).  |
| Hoffman et al. (2002),<br>USA<br>2 years, 2 events  | 0.17 ha, w = 36.7 m<br>Corn / Wheat (Conv. Till)<br>4                       | w = 9 m, l = 45 m<br>Wheat / Costal Bermudagrass<br>4      | Black Clay<br>4.2             | Atrazine, n/a<br>n/a, n/a<br>100, 60   | 52 (T)<br>4<br>(46 - 59)                                       | Project report from Blackland Prairie Demonstration Program has not been published. Three sections of source area and contour grass filter strips established within each watershed (0.6 ha).                          |
| Arora et al. (1996),<br>USA<br>2 years, 6 events  | 0.41 ha, w = 154 m<br>Corn (Conv. Till)<br>3                                | w = 20.12 m, l = 1.52 m<br>Smooth Bromegrass<br>2          | Silty Clay<br>Loam<br>15 & 30 | Atrazine, 4L<br>2.12, broadcast spray<br>100, 60                                   | 61 (T)<br>36<br>(11-100)                                       | Concentrations and masses for each carrier phase were measured but are not reported. Flow distributor was used at the inflow end of buffer strips to achieve replications and to regulate inflow based on area ratios. |
|   |   |  |                               | Metolachlor, 8E<br>2.8, broadcast spray<br>200, 90                                 | 63 (T)<br>36<br>(16 - 100)                                     |  |
|   |   |  |                               | Cyanazine, 4L<br>3.36, pre-emergence spray<br>190, 14                              | 61 (T)<br>36<br>(8 - 100)                                      |  |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in study or from Hornsby *et al.* (1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events     | Source Area<br>Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Buffer Area<br>Dimensions<br>Vegetation<br>Slope (percent) | Soil Type<br>& Area<br>Ratio       | Name, Formulation<br>Rate kg a.i./ha, Method<br>K <sub>oc</sub> , Half-life (days) | Pesticide Retention<br>Study Average<br>Data Points<br>(Range) | Comments   |
|---|---|--|------------------------------------|--|--|--|
| Webster and Shaw<br>(1996), USA<br>3 years, 24 events     | 0.009 ha, w = 22 m<br>Soybeans, (Nt, CT &<br>Disked)<br>3                   | w = 2 m, l = 4 m<br>Tall fescue<br>3                       | Silty Clay<br>11                   | Metolachlor, n/a<br>3.4, pre emergence<br>sprayed<br>200, 90                       | 51 (W)<br>63<br>(0 - 100)                                      | Only runoff water samples were<br>analyzed. Three events are simulated<br>rainfall events.   |
|   |   |  |                                    | Metribuzin, n/a<br>0.42, pre emergence<br>sprayed<br>60, 40                        | 59 (W)<br>50<br>(0 - 100)                                      |  |
| Patty et al. (1997),<br>France<br>1 to 2 years, 11 events | 0.025 ha, w = 50 m<br>Corn / Wheat (Plowing)<br>( 7 - 15 )                  | w = 6, 12, & 18 m, l = 5 m<br>Rye grass<br>( 7 - 15 )      | Silt Loam<br>2.77, 4.17,<br>& 8.33 | Atrazine, n/a<br>1.25, broadcast sprayed<br>100, 60                                | 83 (T)<br>6<br>(44 -100)                                       | Buffer strips at three different<br>locations studied based on crop<br>rotations and combination of<br>natural/simulated rainfall events.<br>Atrazine and Lindane were considered<br>at two locations (2 & % O.M. soils)<br>whereas the other two pesticides were<br>considered at the third site (2-3 % O.<br>M. soils). K <sub>oc</sub> and half-life for<br>pesticides are as reported in the study.<br>Runoff collection tanks overflowed<br>during rainfall events. Reported data<br>are estimates. |
|   |   |  |                                    | Lindane, n/a<br>1.35, soil-incorporated<br>1100, 400                               | 94 (T)<br>6<br>(72 -100)                                       |  |
|   |   |  |                                    | Diflufenican, n/a<br>0.16, broadcast sprayed<br>1990, 200                          | 99 (T)<br>5<br>(97 -100)                                       |  |
|   |   |  |                                    | Isoproturon, n/a<br>1.25, broadcast sprayed<br>120, 30                             | 99.8 (T)<br>5<br>(99.8 -99.9)                                  |  |
| Rankins et al. (2001),<br>USA<br>3 years, 16 + 6 events   | 0.009 ha, w = 22 m<br>Cotton (Disked)<br>3                                  | w = 0.3 m, l = 4 m<br>Diff. Grasses<br>3                   | Silty Clay<br>73.3                 | Fluometuron<br>1.7, broadcast sprayed<br>100, 85                                   | 71 (T)<br>4<br>(59 - 84)                                       | Four different grass species as<br>treatments considered under a mix of<br>natural and simulated rainfall events.  |
|   |   |  |                                    | Norflurazon<br>1.7, broadcast sprayed<br>700, 30                                   | 61 (T)<br>4<br>(45 - 86)                                       |  |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events | Source Area<br>Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Buffer Area<br>Dimensions<br>Vegetation<br>Slope (percent)           | Soil Type<br>& Area<br>Ratio  | Name, Formulation<br>Rate kg a.i./ha, Method<br>Koc, Half-life (days)  | Pesticide Retention<br>Study Average<br>Data Points<br>(Range) | Comments   |
|---|---|--|-------------------------------|--|--|--|
| Boyd et al. (2003),<br>USA<br>2 years, 5 events       | 0.41 ha, w = 154 m<br>Corn (Conv. Till)<br>4                                | w = 20.12 m, l = 1.52 m<br>Smooth Bromegrass<br>3                    | Silty Clay<br>Loam<br>15 & 45 | Atrazine (4L)<br>1.68, broadcast spray<br>100, 60                      | 86 (T)<br>30<br>(63 - 100)                                     | Concentrations and masses for each carrier phase were measured but are not reported. Flow distributor was used at the inflow end of buffer strips to achieve replications and to regulate inflow based on area ratios. Data averaged has been extracted from Boyd, P. MS Thesis (1999) |
|   |   |  |                               | Acetochlor (4L)<br>1.96, broadcast spray<br>n/a, 90                    | 84 (T)<br>30<br>(69 - 100)                                     |  |
|   |   |  |                               | Chlorpyrifos (15G)<br>1.22, banded<br>6070, 30                         | 86 (T)<br>30<br>(62 - 100)                                     |  |
|   |   |  |                               |  |  |  |
| Syversen (2005)<br>Norway<br>4 years, > 6 events      | 0.45 ha, w = 45 m<br>Barley (Harrowed in<br>Winter)<br>14                   | w = 5 m, l = 10 m<br>Fescue, timothy, thistle,<br>common couch<br>14 | Silty Clay<br>Loam<br>9       | Glyphosate, n/a<br>1.08, n/a<br>24000, 47                              | 48 (T)<br>1<br>(n/a)   | A correction equation was developed and applied to correct runoff volumes for reference runoff from control plots. Only average over four years for each pesticide provided in the study. Event by event data not reported.  |
|   |   |  |                               | Propiconazole, n/a<br>0.125, n/a<br>650, 110                           | 85 (T)<br>1<br>(n/a)   |  |
|   |   |  |                               | Fenpropimorph, n/a<br>0.375, n/a<br>4300, 30                           | 34 (T)<br>1<br>(n/a)   |  |
|   |   |  |                               | AMPA, n/a<br>n/a, n/a<br>>1200, 150                                    | 67 (T)<br>1<br>(n/a)   |  |
|   |   |  |                               |  |  |  |
|   |   |  |                               |  |  |  |
| Vianello et al. (2005),<br>Italy<br>2 years, 8 events | 0.07 ha, w = 35 m<br>Corn, Wheat, Soybeans<br>(Plowed)<br>1.8               | w = 6 m, l = 20 m<br>Grass + Shrub/Trees<br>1.8                      | Silty Loam<br>5.83            | Metolachlor<br>2.25, sprayed, pre<br>emergence<br>200, 90              | 99 (T)<br>4<br>(97 - 100)                                      | Total of 13 natural rainfall events recorded. Five events as outliers or no results were excluded. Site consisted of two rows of shrub/trees planted at 1.5 and 4.5 m from the edge of the buffer. Both grass and shrub/trees were planted three years prior to the experiment.        |
|   |   |  |                               | Terbuthylazine<br>1.13 & 1, pre & post<br>emergence sprayed<br>600, 27 | 99 (T)<br>4<br>(99 - 100)                                      |  |
|   |   |  |                               | Isoproturon<br>1, pre-emergence<br>120, 30                             | 69 (T)<br>5<br>(0 - 99)  |  |
|   |   |  |                               |  |  |  |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase,  $K_{oc}$  = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events                                 | Source Area<br>Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Buffer Area<br>Dimensions<br>Vegetation<br>Slope (percent)   | Soil Type<br>& Area<br>Ratio                         | Name, Formulation<br>Rate kg a.i./ha, Method<br>K <sub>oc</sub> , Half-life (days) | Pesticide Retention<br>Study Average<br>Data Points<br>(Range) | Comments  |
|---|---|--|--|--|--|---|
| <b>Application: Edge of the Grain Row Crop Field Buffer Strips, Simulated Studies</b> |   |  |  |  |  |   |
| Misra et al. (1996), USA<br>1 year, 6 events  | n/a, n/a  | w = 12.2 m, l = 1.48 m                                       | Loam<br>15 & 30                                      | Atrazine,<br>n/a, mixed with water   | 39 (W)<br>12   | No sediment was mixed with runoff water. Pesticides were added to runoff water to achieve nominal concentrations and therefore two treatments of 0.1 mg/L and 1.0 mg/L of each compound. Six rainfall simulations were done of set of 2 buffer strips each  |
|   | n/a   | Bromegrass<br>2.5  |  | 100, 60  | (24 - 74)  |   |
|   | n/a   |  |  | Metolachlor, n/a<br>n/a, mixed with water  | 37 (W)<br>12   |   |
|   |   |  |  | 200, 90  | (22 - 75)  |   |
|   |   |  | Cyanazine, n/a<br>n/a, mixed with water              | 36 (W)<br>12   |  |   |
|   |   |  | 190, 14  | (23 - 73)  |  |   |
| Thom and Blevins<br>(1996), USA<br>1 year, 2 events                                   | n/a, conv. & no-till<br>n/a   | w = 15, 30 & 45 m, l = n/a<br>Fescue-Bluegrass Mixture       | n/a  | Atrazine, n/a<br>2.24, broadcast   | 97(T)<br>3   | Pesticide was applied 24-h prior to rainfall simulation (6.35 cm/h) as 1 hour rain, 24-h rest, 30 min rain, 30 min rest, and 30 min rain.   |
|   | 9   | 9  | n/a  | 100, 60  | (93 - 99)  |   |
| Kloppel et al. (1997),<br>Germany<br>1 year, 7 events                                 | n/a, n/a<br>Triticale (Cultivated)  | w = 10, 15 & 20 m, l = 10<br>Mixed grasses                   | Silty<br>Loam  | Terbuthylazine<br>n/a, mixed with water  | 86 (T)<br>7  | Simulated rainfall (1.4 cm/h) was applied on buffer strips during runoff simulations. Runoff was added to the top of the strips at rates of 400, 1500, and 2000 L/h. Runoff simulations were carried with 50 and 200 µg/L concentrations of each pesticide. |
|   | 8   | 5  | n/a  | 600, 27  | (70 - 98)  |   |
|   |   |  |  | Isoproturon<br>n/a, mixed with water   | 85 (T)<br>7  |   |
|   |   |  |  | 120, 30  | (70 - 98)  |   |
|   |   |  |  | Dichloroprop - P<br>n/a, mixed with water  | 82 (T)<br>7  |   |
|   |   |  |  | 1000, 10   | (61 - 98)  |   |
| Barfield et al. (1998),<br>USA  | 0.01 ha, w = 22.1 m<br>Bare (Conv. & No-till)                               | w = 4.57, 9.14 & 13.72 m, l =<br>4.57m<br>Bluegrass & Fescue | Silt<br>Loam,<br>1.61,<br>2.42 &<br>4.84             | Atrazine, n/a<br>2.24, broadcast   | 98 (W)<br>12   | No rainfall applied on buffer strips during simulation; however, strips were saturated prior to test runs.  |
|   |   |  |  | 100, 60  | (94 - 100)   |   |
| Tingle et al. (1998),<br>USA<br>3 years, n/a  | 0.009 ha, w = 22 m<br>Soybean, tilled                                       | w = 0.5, 1, 2, 3 & 4 m, l = 4 m<br>Tall fescue               | Silty<br>Clay<br>Loam<br>5.5, 7.3,<br>11, 22<br>& 44 | Metolachlor, n/a<br>2.8, pre emergence sprayed                                     | 80 (T)<br>5  |   |
|   |   |  |  | 200, 90  | (67 - 90)  |   |
|   |   |  |  | Metribuzin, n/a<br>0.42, pre emergence<br>sprayed                                  | 85 (T)<br>5  |   |
|   |   |  |  | 60, 40   | (73 - 96)  |   |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.* (1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events                                 | Source Area  | Buffer Area                                 | Soil<br>Type &<br>Area<br>Ratio | Name, Formulation<br>Rate kg a.i./ha, Method<br>K <sub>oc</sub> , Half-life (days) | Pesticide Retention                     | Comments  |
|---|--|---|---------------------------------|--|---|---|
|   | Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Dimensions<br>Vegetation<br>Slope (percent) |                                 |  | Study Average<br>Data Points<br>(Range) |   |
| <b>Application: Edge of the Grain Row Crop Field Buffer Strips, Simulated Studies</b> |  |   |                                 |  |   |   |
| Schmitt et al. (1999),<br>USA<br>1 year, 1 event                                      | n/a  | w = 7.5 & 15 m, l = 169 m                   | Silty<br>Clay                   | Atrazine, n/a  | 62 (T)                                  | Pesticides were applied to achieve peak concentrations as would be found from a post plant corn field runoff. Runoff application manifold was used in conjunction with a runoff mixing tank.  |
|   | n/a  | Mixed grasses                               | Loam                            | n/a, mixed with water  | 6                                       |   |
|   | n/a  | 6.5   | 5.4 &<br>10.8                   | 100, 60  | (32 - 90)                               |   |
|   |  |   |                                 | Alachlor, n/a  | 68 (T)                                  |   |
|   |  |   |                                 | n/a, mixed with water  | 6                                       |   |
|   |  |   |                                 | 170, 15  | (42 - 93)                               |   |
|   |  |   |                                 | Permethrin, n/a  | 80 (T)                                  |   |
|   |  |   |                                 | n/a, mixed with water  | 6                                       |   |
|   |  |   |                                 | 100000, 30   | (53 - 97)                               |   |
| Arora et al. (2003),<br>USA<br>1 year, 1 event  | n/a  | w = 20.12 m, l = 1.52 m                     | Silty<br>Clay                   | Atrazine, n/a  | 50 (T)                                  | Pesticides were applied to the sediment to achieve a nominal concentration of 100 mg of pesticide per kg of soil. Flow distributor was used at the inflow end of buffer strips to achieve replications and to regulate inflow based on area ratios.   |
|   | n/a  | Smooth Bromegrass                           | Loam                            | n/a, sprayed on sediment   | 6                                       |   |
|   | n/a  | 2   | 15 & 30                         | 100, 60  | (47 - 53)                               |   |
|   |  |   |                                 | Metolachlor, n/a   | 51 (T)                                  |   |
|   |  |   |                                 | n/a, sprayed on sediment   | 6                                       |   |
|   |  |   |                                 | 200, 90  | (48 - 54)                               |   |
|   |  |   |                                 | Chlorpyrifos, n/a  | 80 (T)                                  |   |
|   |  |   |                                 | n/a, sprayed on sediment   | 6                                       |   |
|   |  |   |                                 | 6070, 30   | (77 - 83)                               |   |
| Krutz et al. (2003), USA<br>2 years, 2 events   | 0.003 ha, w = 3 m  | w = 3 m, l = 1 m                            | Black<br>clay                   | Atrazine, n/a  | 22 (W)                                  | No sediment was mixed with runoff water. Pesticides were added to water to achieve a nominal concentration of 0.1 µg / ml of each compound. A nurse tank in conjunction with a recirculation pump and a sheet flow runoff applicator was used to apply runoff to buffer strips. Buffer strips were saturated prior to runoff addition |
|   | n/a  | Buffalograss                                |                                 | n/a, mixed with water  | 2                                       |   |
|   | 2  | 2   | 10                              | 100, 60  | (n/a)                                   |   |
|   |  |   |                                 | Diaminotrazine, n/a  | 20 (W)                                  |   |
|   |  |   |                                 | n/a, mixed with water  | 2                                       |   |
|   |  |   |                                 | Deisopropylatrazine, n/a   | 20 (W)                                  |   |
|   |  |   |                                 | n/a, mixed with water  | 2                                       |   |
|   |  |   |                                 | Desethylatrazine, n/a  | 19 (W)                                  |   |
|   |  |   |                                 | n/a, mixed with water  | 2                                       |   |
|   |  |   | Hydroxyatrazine, n/a            | 18 (W)   |   |   |
|   |  |   | n/a, mixed with water           | 2  |   |   |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

Table 2.4 (continued):

|  | Source Area  | Buffer Area   | Soil Type & Area     | Pesticide Retention  |   |
|--|--|---|----------------------|--|---|
| Literature Citation, Location, Duration / Events                               | Area & Dimensions, Vegetation (Tillage), Slope (percent) | Dimensions, Vegetation, Slope (percent)                                     | Ratio                | Name, Formulation, Rate kg a.i./ha, Method, K <sub>oc</sub> , Half-life (days) | Study Average, Data Points (Range), Comments  |
| Application: Edge of the Grain Row Crop Field Buffer Strips, Simulated Studies |  |   |                      |  |   |
| Ludovice et al. (2003), Brazil, 1 year, 4 events                               | 0.03 ha, w = 10 m, Corn, n/a                             | w = 5, 7, & 10 m, l = 3 m, Grass, n/a                                       | n/a, 1 & 2           | Atrazine, 1.3, broadcast spray, 100, 60  | 60 (T), 4, (2 - 93), Simulated rainfall with intensity of 6 cm/h was used to apply 11 cm of rainfall for each event.  |
| Mickelson et al. (2003), USA, 1 year, 3 events                                 | n/a, n/a, n/a  | w = 4.6 & 9.1 m, l = 1.52 m, Smooth Brome/Kent. Blue/Kent. Tall Fescue, 4.6 | Silt Loam, 5 & 10    | Atrazine, 4L, n/a, mixed with water, 100, 60                                   | 51 (T), 4, (27 - 84), Two runoff mixes, experimental treatments as with and without sediment, were introduced at the top of buffer strips. Atrazine was applied to achieve a nominal concentration of 1 mg/L. Simulated rainfall with intensity of 6.6 cm/h was used to approximately 5.5 cm of rainfall. |
| Krutz et al. (2004), USA, 2 years, 2 events                                    | 0.003 ha, w = 30 m, n/a, 2                               | w = 3 m, l = 1 m, Buffalograss, 2   | Black clay, 10       | Metolachlor, n/a, n/a, mixed with water, 200, 90                               | 25 (W), 2, (n/a)  |
|  |  |   |                      | Metolachlor ESA, n/a, n/a, mixed with water, 5, n/a                            | 16 (W), 2, (n/a)  |
|  |  |   |                      | Metolachlor OA, n/a, n/a, mixed with water, 7, n/a                             | 14 (W), 2, (n/a), Same as Krutz et al. (2003), different pesticide and metabolites. K <sub>oc</sub> for metabolites as reported in the study.   |
| Vianello et al. (2005), Italy, 2 years, 2 events                               | 0.07 ha, w = 35 m, Corn, wheat, soybeans, 1.8            | w = 6 m, l = 20 m, Grass + Shrub + Trees, 1.8                               | Silty Loam, 5.83     | Metolachlor, 2.25, sprayed, pre emergence, 200, 90                             | 82 (T), 1, (n/a)  |
|  |  |   |                      | Isoproturon, 1, pre-emergence sprayed, 120, 30                                 | 92 (T), 1, (n/a), One outlier event not included in averages. One event for Metolachlor & Isoproturon each. Study site is same as Vianello et al. (2005) reported under natural rainfall studies.   |
| Popov et al. (2006), Australia, 1 year, 7 events                               | n/a, n/a, n/a  | w = 4 m, l = 1.25 m, Mixed grasses, 5.3                                     | Clay (vertisol), n/a | Atrazine, n/a, n/a, sprayed on sediment, 100, 60                               | 55 (T), 7, (40 - 85), Pesticides were applied to the sediment with tank mix having concentration of 100 µg a.i. /L of each pesticide. Water tank with mixing tank used to deliver runoff  |
|  |  |   |                      | Metolachlor, n/a, n/a, sprayed on sediment, 200, 90                            | 66(T), 7, (44 - 86)   |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.



Table 2.4 (continued):

| Literature Citation,<br>Location<br>Duration / Events                             | Source Area  | Buffer Area  | Soil<br>Type &<br>Area<br>Ratio               | Pesticide Retention   | Study Average<br>Data Points<br>(Range)              | Comments   |
|---|--|--|---|---|--|--|
|   | Area & Dimensions<br>Vegetation (Tillage)<br>Slope (percent) | Dimensions<br>Vegetation<br>Slope (percent)              |   |   |  |  |
| Application: Edge of Field Buffer Strips as Strip Crops, Natural Rainfall Studies |  |  |   |   |  |  |
| Hall et al. (1983), USA<br>1 year, 11 events                                      | 0.003 ha, w = 16 m<br>Corn (n/a)<br>14                       | w = 6 m, l = 1.8 m<br>Oats<br>14                         | Silty<br>Clay<br>Loam<br>2.67                 | Atrazine, 80W<br>2.2 & 4.5, pre<br>emergence &<br>incorporated<br>100, 60 | 78 (T)<br>11<br>(65 - 91)                            | Buffer strips are setup as strip crop  |
| Application: Orchard Floor Inter-row Buffer Strips, Laboratory Study              |  |  |   |   |  |  |
| Watanabe et al.<br>(2001), USA<br>1 year, 3 events                                | 0.00005 ha, n/a<br>n/a<br>3                                  | w = 2 m, l = 1 m<br>Fallow & Fescue<br>3                 | Silt<br>Loam<br>1 & 2                         | Diazinon, n/a<br>2.8, broadcast spray<br>400, 45                          | 53 (T)<br>2<br>(33 - 73)                             | Buffer strips intercropped in orchard<br>trees, expressed as 50 % and 100 % of<br>the floor area. Simulated rainfall (5<br>cm/h) was applied for 60 min for each<br>event. |
| Application: Edge of the Field Buffer Strips, Laboratory Studies                  |  |  |   |   |  |  |
| Mersie et al. (1999),<br>USA<br>1 year, 3 events                                  | n/a<br>n/a<br>n/a  | w = 2 m, l = 0.9 m<br>Switchgrass & bare soil<br>1       | Sandy<br>loam<br>(Emporia<br>series)<br>15    | Atrazine<br>2.2, n/a<br>100, 60<br>Metolcahlor<br>3.5, n/a<br>200, 90     | 41 (W)<br>3<br>(39 - 44)<br>47 (W)<br>3<br>(42 - 53) | Same as Seybold et al. (2001) below<br>with narrower tilted beds and different<br>soil.  |
| Seybold et al. (2001),<br>USA<br>n/a, 4 events                                    | n/a<br>n/a<br>n/a  | w = 3 m, l = 0.9 m<br>Switchgrass & bare soil<br>1       | Loam<br>(Cullen<br>series)<br>15              | Atrazine<br>2.2, n/a<br>100, 60<br>Metolcahlor<br>3.5, n/a<br>200, 90     | 57 (W)<br>4<br>(53 - 69)<br>61 (W)<br>4<br>(58 - 73) | Lab experiment using tilted bed set up<br>simulating field conditions as<br>receiving runoff from conventionally<br>tilled corn field.                                     |
| Mersie et al. (2003),<br>USA<br>2 years, 3 events                                 | n/a<br>n/a<br>n/a  | w = 2 m, l = 0.9 m<br>Fescue, Switchgrass, and bare<br>3 | Loamy<br>fine sand<br>(Bojac<br>series)<br>15 | Endosulfan ( $\alpha$ and $\beta$ )<br>n/a, n/a<br>12400, 50              | 74 (W)<br>3<br>(40 - 100)                            | Same as Seybold et al. (2001) above<br>with narrower tilted beds, different<br>soil, and pesticide.  |

O.M. = organic matter, n/a is not available or not reported in the study, (T) = total pesticide mass, (W) = pesticide mass with water carrier phase, (S) = pesticide mass with sediment carrier phase, K<sub>oc</sub> = soil organic carbon sorption coefficient (values as reported in Study or from Hornsby *et al.*(1996), a.i. = active ingredient of the pesticide, Soil M.C. = Soil Moisture Content.

pesticides, the runoff volume retention by buffer strips is important. Different studies (Table 2.4) have not shown a substantial difference in mass retention between weakly and moderately sorbed pesticides. Based on model calculated retentions as listed in Table 2.3, such pesticides ( $100 < K_{oc} < 1000$  L/kg) can be retained on average 51% by the buffer strips with a range of 12% to 95%. This model calculated average is lower than the individual study averages but is within the range of moderately sorbed pesticide retentions reported (Table 2.4). An average for moderately sorbed pesticides among natural rainfall studies showed a 66% retention by buffer strips (Hall et al., 1983; Hoffman et al., 1995; Arora et al., 1996; Webster and Shaw, 1996; Lowrance et al., 1997; Patty et al., 1997; Mickelson et al., 1998; Rankins et al., 2001; Hoffman et al., 2002; Vellidis et al., 2002; Boyd et al., 2003; Syversen, 2005; Vianello et al., 2005; 10 pesticides). This average for simulated studies was calculated as 60% (Misra et al., 1996; Thom and Blevins, 1996; Kloppel et al., 1997; Tingle et al., 1998; Mersie et al., 1999; Schmitt et al., 1999; Seybold et al., 2001; Watanabe et al., 2001; Arora et al., 2003; Krutz et al., 2003; Ludovice et al., 2003; Mersie et al., 2003; Mickelson et al., 2003; Krutz et al., 2004; Vianello et al., 2005; Popov et al., 2006; 6 pesticides). The overall average for both the natural and simulated rainfall/runoff studies averaged 64% retention (10 pesticides) by buffer strips. The average pesticide retention for both of the experimental data sets, separately and combined, exceeds the model calculated average pesticide retention of 51% for the moderately sorbed pesticides as listed in Table 2.3. The difference between study average of 64% retention and model calculated average of 51% shows that the effect of sorption/desorption and enrichment in case of moderately sorbed pesticides is relatively larger (~13%) than the strongly sorbed pesticides.

Study averages for weakly sorbed pesticides ( $K_{oc} < 100$  L/kg) were calculated and compared with the model calculated averages. An average for weakly sorbed pesticides among natural rainfall studies showed a 59% retention by buffer strips (Webster and Shaw, 1996; one pesticide (metribuzin)). This average for simulated studies was calculated as 81% (Assmussen et al., 1977; Tingle et al., 1998; two pesticides (2, 4-D and metribuzin)). The overall average for both the natural and simulated studies calculated as 61% retention (two pesticides) by the buffer strips. The average pesticide retention for both of the experimental data sets, separately and combined, again exceeds the model calculated average pesticide retention of 46% for the weakly sorbed pesticides as listed in Table 2.3. In comparison, retention of the bromide anion ( $K_{oc} = 0$ ), as studied by Misra, 1995 and Mickelson et al., 2003 (both simulation studies), averaged 48% with a minimum and maximum range of 20% to 77%. Two natural rainfall studies (Vellidis et al., 2002 and Lowrance et al., 1997) studied bromide anion transport through buffer strips (as Zone 3 of the riparian forest buffer system, (USDA - NRCS, 1997)), but did not report retention in the buffer strip. The averages for bromide anion retention are within the range of data reported and estimated (Table 2.3) for weakly sorbed pesticides. The difference between study average of 61% retention and model calculated average of 46% is greater than the same difference for both strongly and moderately sorbed pesticides. The model assumptions are likely to hold true in the case of weakly sorbed pesticides. The effect of sorption/desorption and enrichment in this case is negligible as majority of the pesticide is transported as dissolved in water carrier phase. Model calculated average of 46% pesticide retention closely follows the average runoff volume retention of 45%. This average runoff volume retention includes several different experimental setups of

buffer strips evaluation which are not included in the three studies that have evaluated weakly adsorbed pesticides (Tables 2.1, 2.2 and 2.3). As such, model calculated average retention is different from study averaged retention for weakly sorbed pesticides.

Percent pesticide mass retentions as reported in different studies were plotted on an event basis. Figure 2.5 shows strongly sorbed pesticide mass retention as a function of source to buffer area ratio. This figure shows event-by-event variability similar to Figures 2.3 and 2.4, but also shows that none of the studies have evaluated area ratios larger than 50 for strongly sorbed pesticides. Very few data points exist for the 30 to 50 area ratio range and the pool of data for the 10 to 30 area ratio range is limited as well. Larger area ratios (greater than 10) are likely to occur in field scale buffers due to convergence of flow as the micro-topography changes. As such, larger area ratios should be considered when evaluating strongly sorbed pesticides. Figure 2.6 shows the pesticide mass retention for weakly to strongly sorbed pesticides by buffer strips as a function of area ratio. This figure closely follows Figure 2.3 for runoff volume retention. As such, runoff volume retention (water carrier phase) plays a key role in weakly to moderately sorbed pesticides retention, whereas both runoff volume and sediment mass retention are of importance for strongly sorbed pesticides.

Developing an estimate of the average pesticide retention and comparing it with published data, as done above in this review article, has its limitations. All studies conducted with buffer strips have found them to be effective (to a varying degree) in reducing runoff volume and controlling sediment yields to surface water bodies. Retention of both of these carriers, i.e. runoff water and sediment, has been identified as the main mechanisms for pesticide retention within buffer strips. These studies, however,

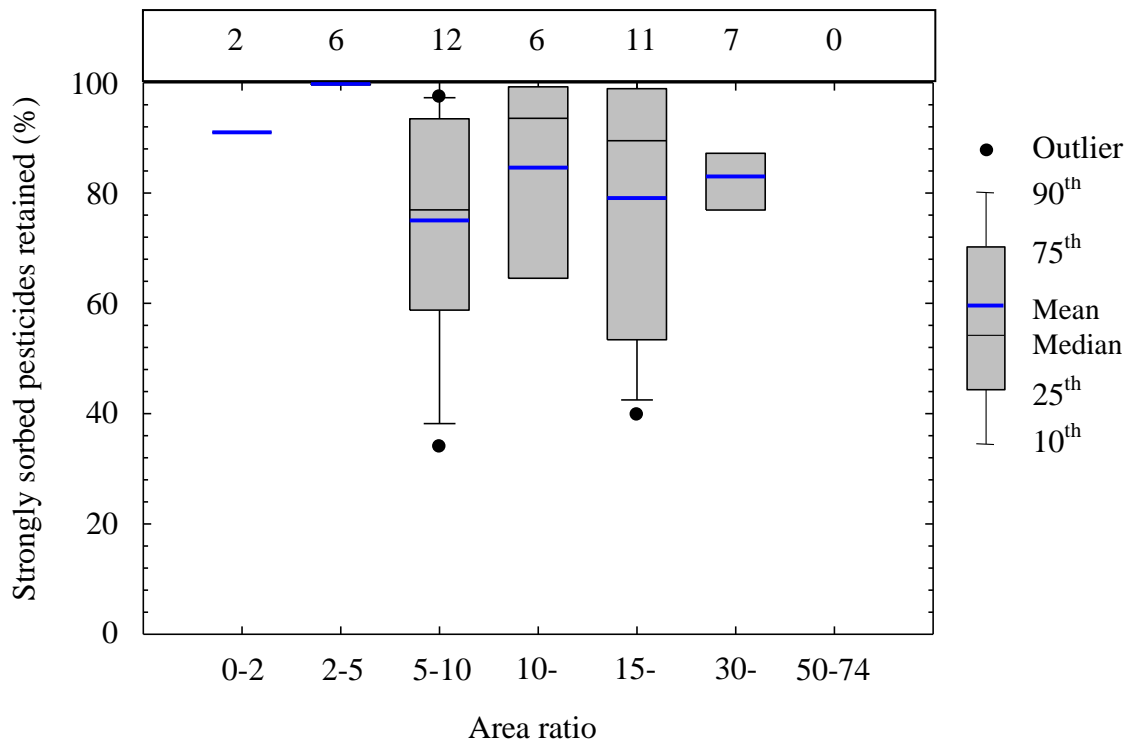


Figure 2.5: Percent pesticide (strongly sorbed,  $K_{oc} > 1000$  L/kg) mass retention as a function of area ratio. Percent reduction numbers (used in this figure) are on event basis as reported or calculated from data reported in studies listed in Table 2.4 where area ratio data were available. Dots are outliers. Numbers above the box plots indicate sample size.

represent different experimental setups (natural or simulated) and different combinations of hydrologic factors (storm intensity and duration, and runoff flow rates), site factors (area ratio/length, slope, age, soil type, and antecedent moisture conditions), and pesticide properties (pesticide formulation, solubility in water, volatilization, sorption to in-field soil, method of application, and half-life). Pesticide retention as shown in Table 2.3 is synthesized as an average across these studies and therefore, models the reported experimental data. Several of the simulation studies have used extreme conditions under which the experiments were conducted. Extreme conditions, such as very high rainfall

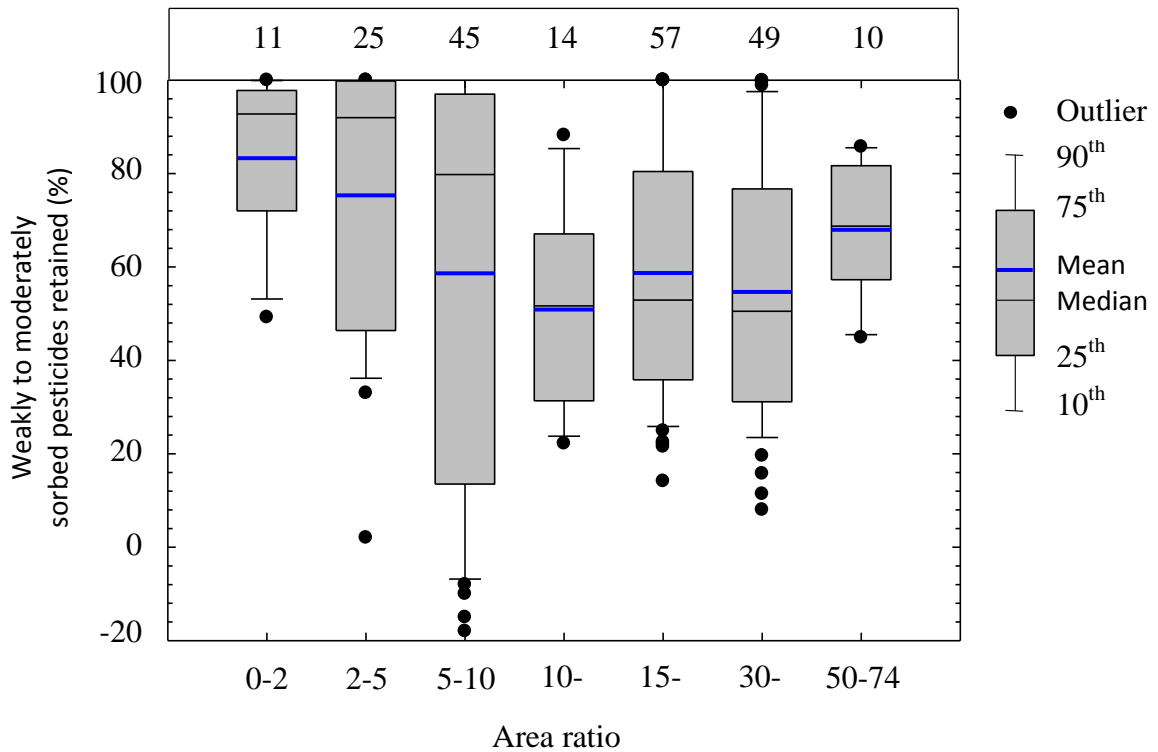


Figure 2.6: Percent pesticide (weakly to moderately sorbed,  $K_{oc} < 1000$  L/kg) mass retention as a function of area ratio. Percent reduction numbers (used in this figure) are on event basis as reported or calculated from data reported in studies listed in Table 2.4 where area ratio data were available. Dots are outliers. Numbers above the box plots indicate sample size.

intensities and/or dry antecedent moisture conditions represent unusual or worst case scenarios which have limited applicability to field conditions. As such, future studies should consider practical field conditions in their experimental designs. Dry antecedent moisture conditions in the buffer area are unlikely to occur once runoff initiates in the source area. Future simulated experimental designs should consider adding rain on the buffer area to reach similar hydrologic balance with the source area. In case high rainfall intensities are used, it will be helpful to quantify what fraction of annual pesticide mass is likely to move through a buffer under extreme portion of flow. In addition, the studies

must consider flow convergence in the buffer areas and how it impacts the area ratio. As flow converges, it flows through a smaller buffer area than designed, resulting in a larger area ratio. Area ratios in the experimental designs should be carefully evaluated based on the local topography. Small area ratios of less than 10 should be avoided unless it is adequately justified to do so.

One of the main summaries of the natural rainfall/runoff studies is the temporal pattern of hydrologic conditions and their impact on pesticide retention. This event by event variability is bound to happen in field conditions. Figures 2.5 and 2.6 for pesticide mass retention correspond with the event-by-event variability as seen in Figures 2.3 and 2.4 for runoff volume retention and sediment mass retention. Best and worst runoff events should not be considered as performance indicators as they only represent either extreme. At the same time, it is practically impossible to evaluate all combinations of site factors, hydrologic factors, and pesticide properties on field scale basis. Therefore, a process-based model that can analyze these combinations needs to be developed and validated. Studies performed to date can, however, serve the purpose of validating the model. Validation of such a process-based model will, however, require additional studies to be undertaken, as several of the past studies have used very small test plots and area ratios. Development and validation of such a model is beyond the scope of this review article.

Most of the data extracted from the studies reviewed in this paper represent buffer strips established on loamy/silty soils. Sandy soils can have higher infiltration rates just based on soil texture. Clayey soils on the other hand can have cracks or large macropores developed through them due to insect/earthworm populations or due to root mass

decay, thus increasing the infiltration rates. The average retention shown in Table 2.3 does not include much variability in soil textures. Another similarity among several studies is the analysis of data considering outflow from non-buffered plots as inputs for buffered plots. Variability in non-buffered plots due to micro-topography and/or soil type difference has in certain cases led to outflow from non-buffered plots being lower in mass than the outflow from the buffered plots. In addition, some of the studies have not included rainfall over the buffer area in the mass balance. Such experimental designs do not accurately represent field conditions. Future studies should consider measuring both inflow into and the outflow from the buffer strips.

## **2.9 Conclusions**

Seventeen natural rainfall studies and twenty three simulated rainfall / runoff / irrigation studies were reviewed and 359 data points were extracted to estimate runoff volume and sediment mass retention. Runoff volume retention commonly termed as infiltration in these studies, averaged (with ranges) 45 (0 – 100)% across the different studies under both natural and simulated experimental conditions, whereas the sediment mass retention averaged 76 (2 – 100)%. The studies, from which the data has been averaged, represent different combinations of hydrologic factors (storm intensity and duration, and runoff flow rates) and site factors (area ratio/length, slope, age, soil type, and antecedent moisture conditions). Consequently, the average runoff volume and sediment mass retention only represents the average of the reported data and do not take into account experimental error of different studies. In addition, results from research studies are mainly obtained under controlled conditions whereas field scale buffer strips



perform in uncontrolled conditions. Therefore, actual field performance of buffer strips may be different, and if so, probably less.

Overall pesticide retention by buffer strips from natural and simulated studies for weakly ( $K_{oc} < 100$  L/kg), moderately ( $100 < K_{oc} < 1000$  L/kg), and strongly sorbed pesticides ( $K_{oc} > 1000$  L/kg) averaged (with ranges) 61 (0 - 100), 63 (0 - 100), and 76 (53 - 100)% respectively. The pool of these studies is limited in scope and more studies need to be undertaken to expand this pool of data, keeping in mind that it is not feasible to conduct field scale natural rainfall studies for all possible combinations of site factors, hydrologic factors, and pesticide properties. More specifically, larger area ratios (greater than 10) need to be considered in future evaluations as flow convergence occurs due to changes in micro-topography in field applications of buffer strips.

Model calculated average pesticide mass retention using average runoff volume retention of 45% and average sediment mass retention of 76%, was 70% for strongly sorbed and 46% for weakly to moderately sorbed pesticides (Equation 2.4 and Table 2.3). This calculated pesticide mass retention is an average across different studies with different treatments. This calculated average is sensitive to the treatment combinations not studied. The majority of studies have used tilled source area conditions or silty loam buffer strip area soil types when evaluating pesticide retention by buffer strips. As such, application of calculated averages to no till source area conditions or different soil type in buffer strip area should be carefully evaluated.

The model assumption that the net effect of sorption/desorption and enrichment processes in buffer strips is negligible does not appear to be valid for moderately and

strongly sorbed pesticides. As such, the model calculated average pesticide mass retention was lower than the average pesticide mass retention reported in studies for these two pesticide classes. In the case of weakly sorbed pesticides, the model calculated pesticide retention very closely followed the runoff volume retention. As such, the above mentioned model assumption is valid for this category of pesticides. The reason for the model calculated pesticide retention to be lower than the average reported in studies is inclusion of the expanded dataset. This expanded dataset includes unique experimental conditions of source area to buffer area ratios, source area tillage practices, and buffer area vegetation, which are not available in the pesticide retention studies.

Experimental studies that use dry antecedent moisture conditions in buffer strip soil, sediment free runoff, zero infiltration, simulated vegetation, and excessively high rainfall intensities, usually do not represent practical field conditions. These studies have experimental value as they set boundary limits to buffer strip performance. Natural rainfall studies, those that more closely mimic actual field conditions, represent data that would be expected to provide a reasonable indicator of buffer strip performance.

Minimal pesticide retention for moderately sorbed pesticides is of the order of 5% to 10% whereas the maximum retention is of the order of 94% to 100%. Runoff volume retention by buffer strips is the key process for retention of moderately sorbed pesticides. Minimal and maximum retention for strongly sorbed pesticides is of 10% to 20% and 90% to 100% respectively. Sediment mass retention in the buffer strips plays the key role in retention of strongly sorbed pesticides.

Minimum and maximum performance characteristics of buffer strips represent event-by-event variability. Maximum performance may occur when all runoff from source area containing pesticides is retained within the buffer. Minimum performance may occur when the buffer strip is fully saturated prior to runoff entry. Subsequently, such performance data do not indicate that buffer strips are either an absolute solution or a complete failure in reducing environmental impacts of agricultural runoff.

Different studies representing different experimental setups were used to synthesize the performance data for buffer strips. Due to the lack of adequate monitoring for the range of physical conditions with studies and the differences among experimental designs across studies, the average pesticide retention of the reported data more closely represents the actual performance of buffer strips.

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### **CHAPTER 3. COMPARISON OF PESTICIDE RETENTION BY BUFFER STRIPS RECEIVING SIMULATED RUNOFF CONTAINING FINE SAND AND FINE AGGREGATES**

A paper written for submittal to the Transactions of the American Society of Agricultural Biosystems Engineering (ASABE)

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#### **3.1 Abstract**

Pesticide retention in both dissolved and sorbed phase by buffer strips depends upon several factors, including pesticide chemistry, sediment type (texture), and the ratio of the contributing source area to the buffer area. A rainfall-runoff study was conducted to develop a better understanding of these factors by comparing the transport of three different pesticides with two different sediment types under two different source area to buffer area ratios. Simulated runoff water, mixed with pesticide-applied sediment, was applied to 1.0 m wide and 5.6 m long switchgrass buffer strips under 6.35 cm/h steady state rainfall conditions. Twelve strips were used for providing three replications each of the sediment type treatments of fine sand, D1 and fine aggregates, D2; and the source area to buffer area ratio treatments of 10:1, AR10 and 30:1, AR30. Atrazine, chlorpyrifos, and linuron were applied at the label recommended rates using field formulations to each sediment type prior to mixing with the simulated runoff water. When receiving runoff mixed with fine sand, buffer strips retained 73% and 53% atrazine, 87% and 80% chlorpyrifos, and 81% and 54% linuron for the two area ratios of

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10:1 and 30:1 respectively. The corresponding numbers, when receiving runoff mixed with fine aggregates, were 72% and 54% atrazine, 87% and 71% chlorpyrifos, and 76% and 58% linuron respectively for the two area ratios. Differences in percent retention for atrazine were significant between the two area ratios for both D1 and D2 treatments. Chlorpyrifos and linuron percent retentions were not significantly different between the smaller and the larger area ratios for either sediment type; however, the trend was higher retention at lower area ratio. When comparing between D1 and D2 sediment types for either area ratio, the percent retention for atrazine and chlorpyrifos was not significantly different. This indicates that the buffer strips retained either pesticide equally for the experimental conditions studied. Linuron mass in the sorbed phase for either sediment type was below the detection limit indicating linuron does not sorb well to sediment with negligible to low organic carbon content. Linuron data presented in this experiment is an estimate and readers are cautioned on the interpretation of linuron data. For the simulated runoff mixed with fine sand for either area ratio, re-entrainment of sediment was observed. In these treatments, the sediment transport capacity of the water flowing through the buffer strips was not reduced to zero. This resulted in re-entrainment of sediment even though all of the fine sand in the simulated runoff settled in the buffer strips. Re-entrained sediment in the runoff exiting the buffer strips, showed quantifiable amounts of atrazine and chlorpyrifos sorbed with it, however, the total sorbed mass of either pesticide was very small.

### **3.2 Introduction**

Pesticide transport with runoff can be mitigated with the help of off-site practices, such as buffer strips. Buffer strips are vegetative areas to which no pesticide has been

applied. These vegetative areas act as filters of pollutants being carried by the runoff. Arora et al. (2010) summarized several pesticide retention studies that have reported experimental data for pesticide retention by buffer strips, concluding that the pesticide retention by buffer strips is greatly dependent on the partitioning coefficient of the pesticide. Pesticide partitioning coefficient or simply adsorption coefficient ( $K_{oc}$ ) causes pesticides masses to be different in runoff water and sediment phase. Weakly adsorbed ( $0 < K_{oc} < 100 \text{ L/kg}$ ) and moderately adsorbed ( $100 \text{ L/kg} < K_{oc} < 1000 \text{ L/kg}$ ) pesticides are mainly lost from application fields with water phase. Strongly adsorbed ( $K_{oc} > 1000 \text{ L/kg}$ ) pesticides are mainly carried in the runoff sediment phase from the fields where applied. The authors also summarized that the key processes occurring in the buffer strips are infiltration, sediment deposition (both just before the strip and within the strip) and pesticide sorption to the plant matter and buffer strip soil. Infiltration was identified as the key process for weakly to moderately adsorbed pesticides whereas sediment deposition was the key process for strongly adsorbed pesticides. They also found in their review that none of the studies had reported experimental data that shows the effect of different sized sediment on the pesticide retention within the buffer strip. Smaller or finer soil particles have greater specific area and therefore can have higher concentrations of sediment adsorbed pesticide concentrations. On the other hand, larger soil particles have less specific area in comparison to finer particles, and, thus, have lower sediment adsorbed pesticide concentrations. It needs to be determined how the presence of specific sized sediment impacts the total pesticide mass retained by the buffer strips.

Another factor affecting the pesticide retention by buffer strips identified by Arora et al. (2010) is area ratio. Application area or source area, typically, consists of the

farm field to which a pesticide is applied. The buffer strip is the area downstream from the source area to which no pesticide has been applied. The ratio of source area to buffer area or simply area ratio influences the quantity of runoff that may pass through a buffer strip. In comparison to smaller source area, large source areas can yield greater volumes of runoff to a buffer strip both in terms of runoff water and runoff sediment. Secondly, flow convergence within the buffer strips under field conditions can cause the area ratio to be greater than the design area ratio. Helmers et al. (2005) and Bansal et al. (2008) showed that flow convergence can easily increase the area ratios by 2 to 10 times of the design area ratios. Arora et al. (2010) suggested that future buffer strip studies should consider area ratios of at least 10:1 or higher.

Converging flow can cause the flow volume to change and can subsequently cause the sediment load being transported by runoff water to change. Thus, the sediment particle size distribution can be subject to change. Particles of different sizes are likely to behave differently in the buffer strips. Larger, heavier particles may deposit quickly in the buffer strips, whereas the fine particles may not settle at all in a buffer strip. Jin and Romkens (2001) studied the movement of fine sand, silt loam, and coarse sand soil particle fractions in simulated vegetative filter strips in a laboratory setup. The authors reported that the simulated vegetative filter strips were not effective in retaining particles smaller than 150  $\mu\text{m}$  in size. They also reported that 80% of the particles deposited in the approach channel and the upper half to the vegetative filter strip.

The particle size distribution of the sediment in runoff entering the buffer strip can be influenced by the size of the source area or the area ratio, type of tillage practices being used in the source area, rainfall intensity, crop or residue cover, and soil type. All



of these factors can influence the mass of different particle sizes in runoff sediment. Cogo et al. (1983), using simulated rainfall, investigated the effects of residue cover, tillage-induced roughness, and runoff velocity on eroded sediment size distribution in terms of aggregate sizes ranging between 2 to 2000  $\mu\text{m}$ . The authors reported that the size distributions of the eroded sediment under chisel plow plus disk, moldboard plow plus disk, no-till, and chisel plow tillage systems were not greatly different when the soil was covered with residue. However, the  $D_{50}$  size (the aggregate size which 50% of the aggregates exceed) in the eroded sediment without cover was 33, 32, 20, and 11  $\mu\text{m}$  respectively for the four tillage systems. In comparison with the eroded sediment for soils with cover for the respective tillage treatments, the  $D_{50}$  was 12  $\mu\text{m}$  for all four tillage systems. Authors also reported that the percentage of aggregates with size  $> 50 \mu\text{m}$  decreased exponentially with an increase in residue cover for no-till soils. Under tillage plow tillage system, the percentage of larger aggregates in runoff was not effectively reduced by an increase in residue cover. Increase in runoff flow velocity resulted in the percentage of eroded aggregates  $> 50 \mu\text{m}$  to linearly increase for chisel plow tillage conditions.

Poor to no residue cover conditions can influence the sediment size distributions of the eroded sediment. Elberts et al. (1980) tested runoff samples from formed rills and interrills for particle size distributions under simulated rainfall of 6.40 cm/h. Bare rill plots, established on an 8% slope with Miami silt loam soil type, also received inflow at different flow rates to simulate runoff from upslope lands. Results showed that the highest enrichment of sand particles was found in the size classes of  $> 2000 \mu\text{m}$  and 50 - 210  $\mu\text{m}$ . For both rill and interrill plots, the highest percentage of silt and clay was

reported for the size class of  $< 50 \mu\text{m}$ . In this size class, silt and clay particles were 70% and 30% of the total sediment mass.

Effect of sediment size distribution on pesticide loss from source area was evaluated by Wu et al. (2003). Authors studied the effects of size distribution of eroded sediment on propiconazole lost from agricultural farm fields in Norway. Runoff samples were collected from the entry point of a farm pond which received eroded sediment from an adjacent farm field. Results reported showed that about 80% of propiconazole in sorbed phase was attached to aggregates with sizes between 2 to  $250 \mu\text{m}$ . The authors concluded that environmental transport of propiconazole could be reduced with quick settling of such aggregates.

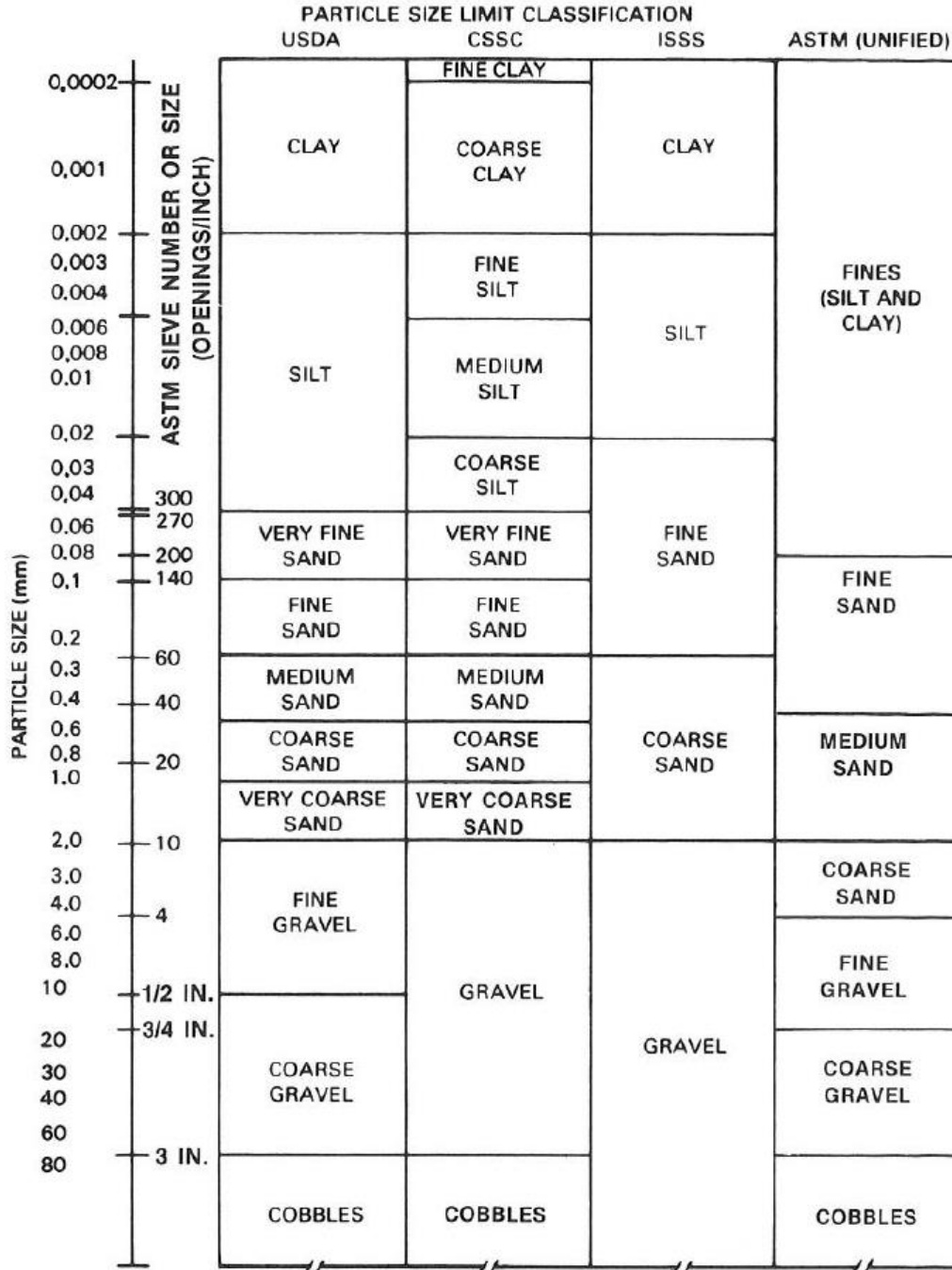
All of the studies summarized by Arora et al. (2010) have evaluated sorbed pesticide transport through buffer strips as lumped together for all sediment and aggregate classes. Different sized sediment can have variable pesticide sorption due to differences in surface area and organic matter content. None of the studies published have researched how the pesticide retention by buffer strips is influenced by different sized sediment. Runoff from a farm field consists of sediment as a mixture of fine organic matter, sand, silt, clay, and aggregates. Treatments in an experiment with specific sized sediment in runoff entering the buffer strips can only be achieved in a simulation study. Secondly, flow convergence can alter the source area to buffer area ratios as the runoff travels through the strip. This can cause the flow volumes and flow velocities to change affecting the sediment transport capacity of the water moving through the buffer strips. When evaluating different sized sediment for pesticide transport through the buffer strips, effects of flow convergence in the form of area ratio

changes need to be studied as well. A rainfall-runoff simulation study was thus proposed with the overall objective to evaluate pesticide transport through buffer strips with specific sized sediment in the runoff entering the strips under different source area to buffer area ratios.

To study pesticide transport with different sized sediment, an attempt was made to select size classes that were reasonably achievable. USDA (1982) classifies soil particles with size 50 - 2000  $\mu\text{m}$  as sand and particles 50 - 250  $\mu\text{m}$  as fine sand (Figure 3.1). Particle size classification from other sources identify soil textural classes differently, however, the USDA classification was used in this experiment. In laboratory settings, soil aggregates can be dispersed by chemical means followed by sand separation by sieving or sedimentation methods (Gee & Bauder, 1986). This separation is not feasible for any soil without destroying the sorption sites needed for pesticide transport. Mechanical sieving can only provide sediment smaller than a particular size, which includes both particles and aggregates. Chemical dispersion is accomplished by first removing cementing substances, such as organic matter and iron oxides, and then replacing calcium and magnesium ions (which tend to bind soil particles together into aggregates) with sodium ions (which surround each soil particle with a film of hydrated ions). The calcium and magnesium ions are then removed from solution by treating with oxalate or hexametaphosphate (Calgon) anions (Baver et al., 1972; Gee & Bauder, 1986; Sheldrick & Wang, 1993), resulting in discrete particles. Chemical dispersion would have destroyed existing pesticide sorption sites on the sand particles. As sand particles cannot be separated from the soil aggregates, naturally occurring sands should be considered in such a study. Coarse sand particles, 250 - 2000  $\mu\text{m}$ , should not be

considered in a buffer strip study as prior research shows that coarse sands settle in the approach areas just prior to the entry into the buffer strips. Thus, fine sand particles, with size ranging from 50 - 250  $\mu\text{m}$  were considered for evaluation in this research study.

USDA classification identifies particles  $< 50 \mu\text{m}$  as silt and clay. In a laboratory setting, particles passing USA Sieve # 60 ( $< 250 \mu\text{m}$ ) and retained above USA Sieve # 270 ( $> 53 \mu\text{m}$ ) are classified as fine sand. Particles passing through a USA Sieve # 270 ( $< 53 \mu\text{m}$ ) are typically classified as silt and clay. Mechanically grinding and sieving the ground soil through a USA Sieve # 270 can yield sediment type smaller than 53  $\mu\text{m}$  in size. This sediment type will be a mix of particles (silt and clay) and fine aggregates, here-in-after classified together as fine aggregates. Further size separation of this sediment type cannot be achieved without destroying the pesticide sorption sites. This sediment type will have different surface area and organic matter content in comparison to fine sand particles. Thus, it will have different amounts of pesticide sorbed to it in comparison to sediment type consisting of fine sand. These two sediment types, i.e. fine sands (53 - 250  $\mu\text{m}$ ) and fine aggregates ( $< 53 \mu\text{m}$ ) were selected for comparison in this study as they are a part of the runoff entering the strip but travel differently through the strip. Transport of different sediment types can be impacted by flow convergence. Flow convergence, coupled with different sediment types, can affect how the pesticide transport occurs through the buffer strips. Flow convergence in an experimental setup can be evaluated by comparing different area ratios. Based on recommendations by Arora et al. (2010), a smaller area ratio of 10:1 was selected for evaluation. For comparison purposes, a larger area ratio of 30:1 was selected based on experimental feasibility. The larger area ratio represented a flow convergence magnitude of 3, which is



USDA—U.S. DEPARTMENT OF AGRICULTURE, (SOIL SURVEY STAFF, 1975)  
 CSSC—CANADA SOIL SURVEY COMMITTEE, (McKEAGUE, 1978)  
 ISSS—INTERNATIONAL SOIL SCI. SOC. (YONG AND WARKENTIN, 1966)  
 ASTM (UNIFIED)—AMERICAN SOCIETY FOR TESTING & MATERIALS (ASTM, D-2487, 1985a)

Figure 3.1: USDA and other methods of soil particle size classification. Source: Gee & Bauder, 1986.

within the range of magnitudes observed by Helmers et al. (2005) and Bansal et al. (2006). Thus, the specific objectives of this experiment were to:

1. Evaluate pesticide retention by buffer strips receiving simulated runoff consisting only of fine sand (53 - 250  $\mu\text{m}$ ) under two different area ratios of 10:1 and 30:1;
2. Evaluate pesticide retention by buffer strips receiving simulated runoff consisting only of fine aggregates (< 53  $\mu\text{m}$ ) under two different area ratios of 10:1 and 30:1;
3. Compare pesticide retention by buffer strips between the fine sand particles (53 - 250  $\mu\text{m}$ ) and fine aggregates (< 53  $\mu\text{m}$ ).

### **3.3 Materials and Methods**

Fine aggregates with no sand, (sediment type D2 in this experiment), were prepared by using the top soil adjacent to the buffer strip site and removing sand particles/large aggregates from it. The top 5.1 cm of the soil surface just upslope of the switchgrass plots was scrapped with a loader bucket to obtain the source soil. This source soil was air dried under a roof to reduce moisture and for easy handling. The dried soil was sieved through a 1.27 cm soil sieve to remove large organic matter fragments and large soil aggregates. Sieved source soil was then further dried in the sun at 98°F for 6 hours to further reduce its moisture. The sun dried soil was then ground in a Humboldt soil grinder. About 100 gm of the ground source soil, passing through a 2000  $\mu\text{m}$  size sieve, was analyzed for its particle size distribution to obtain a percent finer particle classification. The percent finer classification can be used to reference experimental results for comparison with other studies and for modeling purposes. The

USDA Textural Classification of the Clarion 138C source soil, as provided on Web Soil Survey and as obtained in laboratory analysis, is listed in Table 3.1.

As evident from the laboratory analysis,  $D_{60}$  (60% particles finer than a particular size) refers to the separation of sand and silt/clay for the source area soil. Mechanical separation of aggregates finer than 53  $\mu\text{m}$  was performed by sieving the ground soil. Approximately 23 kg of fine aggregates passing through Sieve # 270 were collected for

Table 3.1: Particle size classification of the source soil (Clarion 138C).

| USDA Textural Class                   | USDA Composition | Laboratory Analysis (n=3) | Percent Finer Based on Laboratory Analysis |
|---------------------------------------|------------------|---------------------------|--|
| Sand (53 - 2000 $\mu\text{m}$ ):      | 41.6%            | 40.0%                     | 60.0% ( $D_{60} = 53 \mu\text{m}$ )        |
| Silt (2 - 53 $\mu\text{m}$ ):         | 37.4%            | 34.4%                     | 25.6% ( $D_{26} = 2 \mu\text{m}$ )         |
| Clay (smaller than 2 $\mu\text{m}$ ): | 21%              | 25.6%                     | 0.0% ( $D_0 = 0 \mu\text{m}$ )             |

use in this experiment. Fine aggregates were mixed in a stainless steel stock pot by placing the sealed stock pot on a bucket rotator for 30 min. About 100 gm of the mixed fine aggregates were analyzed utilizing the Pipette Method and consisted of 70% silt and 30% clay (n=3).

Fine sand particles (sediment type D1 in this experiment) were obtained by sieving Ames Golf Sand available from the Hallett Materials Quarry located in south east Ames, Iowa. Ames Golf Sand is produced from the naturally occurring sand in the quarry which is dredged up from a 3 to 10 m depth. The quarried sand is then processed using cells to separate the fine sand material from the production of concrete sand. The fine sand is then further run through cells to obtain the gradation needed for PGA TOUR Golf Sand specifications. The specifications for the Ames Golf Sand showed that the

fine sand (53 - 250  $\mu\text{m}$ ) ranged from 5% to 10% in mid-August 2013. These specifications showed that the Ames Golf Sand had the highest percentage of fine sand in comparison to other naturally occurring sands available. Approximately 23 kg of fine sand particles passing through Sieve # 60 and retained above Sieve # 270 was collected for use in this experiment. The fine sand particles were mixed in a stainless steel stock pot by placing the sealed stock pot on a bucket rotator for 30 min. About 100 gm of the mixed fine sand particles were analyzed and consisted of 99% sand and 1% fines (n=3). Figure 3.2 shows the percent finer particle classification for the source area soil (Clarion 138C) for comparison between the treatments. Treatment D1 thus represents fine sand particles ranging from  $D_{84}$  to  $D_{60}$  and treatment D2 (discussed earlier) represents fine aggregates smaller than  $D_{60}$  for the source soil.

Two herbicides, atrazine and linuron, and an insecticide, chlorpyrifos, were studied in this experiment and their chemical characteristics are listed in Table 3.2. Pesticides were applied at the label recommended rates of 2.8 kg active ingredient (a.i.) per hectare for atrazine, 2.2 kg a.i. per hectare for linuron, and 1.1 kg a.i. per hectare for chlorpyrifos. A known volume of each of the three pesticides was obtained from the commercially available formulations for use in the experiment.

A known volume of pesticide was mixed with water and the mixture was sprayed on to the sieved particles and aggregates using a fine tip hand sprayer. After pesticide application, the particles were mixed together in a stainless steel stock pot by placing the sealed stock pot on the bucket rotator for 30 min. After mixing, either sediment type was transferred into individual 18.9 L buckets, sealed, and stored in a dark cooler designated for pesticide storage.



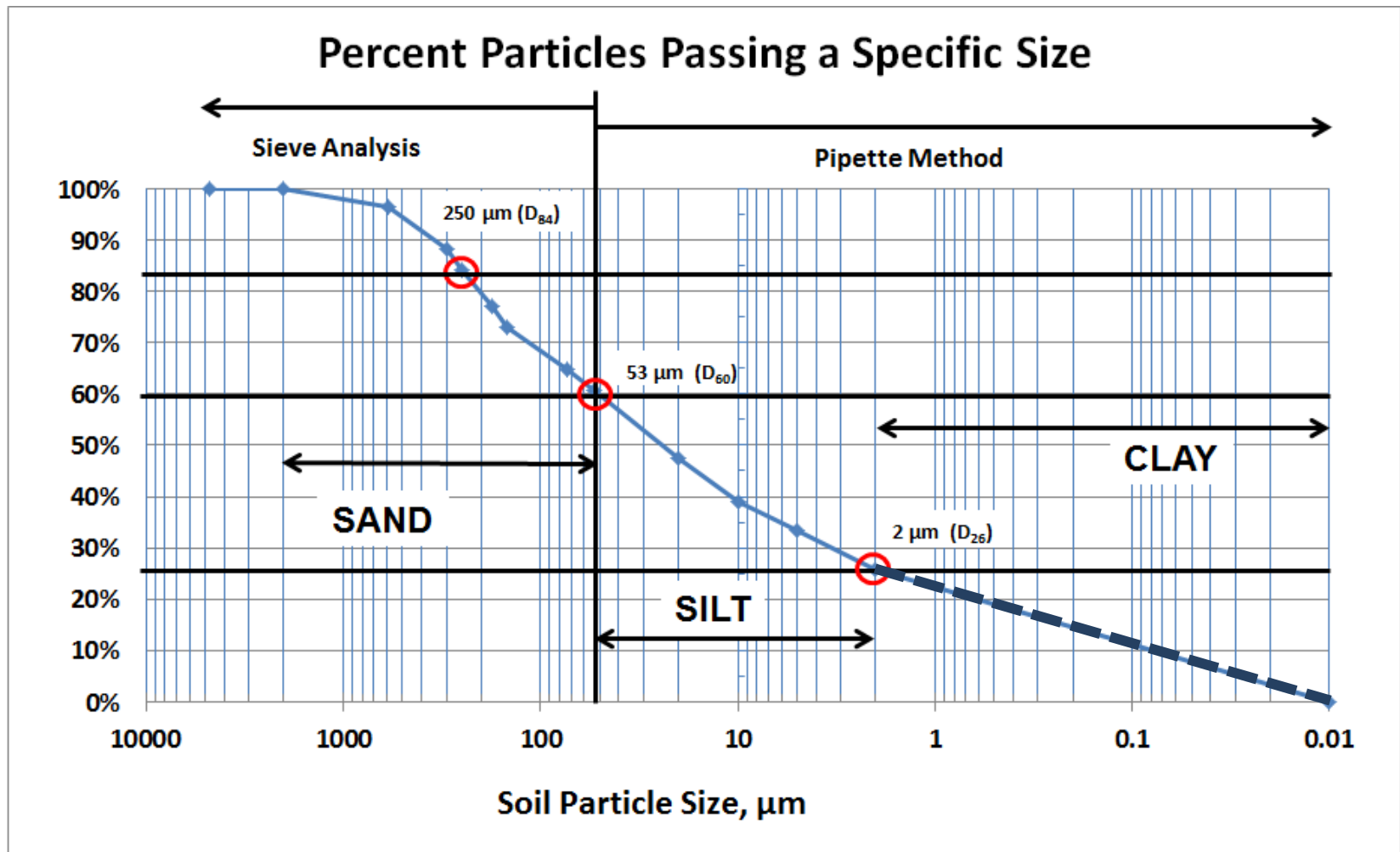


Figure 3.2: Particle size distribution for the source area soil (Clarion 138C). Dotted line indicates estimated particle size for  $D_0$ .

Table 3.2. Names, half-lives, and sorption coefficients for the three pesticides studied. [a]

| Common Name  | Trade Name   | Chemical Formulae  | Field Half Life (days) | Adsorption Coefficient [a] $K_{oc}$ (L/kg) | Partitioning Coefficient $K_d = K_{oc} \times f_{oc}$ [b] |
|--------------|--------------|--|------------------------|--|---|
| Atrazine     | AAtrex       | C <sub>8</sub> H <sub>14</sub> ClN   | 60                     | 100  | 4   |
| Linuron      | Linex, Lorox | C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> | 48                     | 400  | 16  |
| Chlorpyrifos | Lorsban      | C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS            | 30                     | 6070                                       | 243   |

[a] Source: Hornsby et al., 1996, pp. 6–16.

[b]  $K_d$  values are calculated for 4% average fractional organic carbon content of soil ( $f_{oc}$ ).

The buffer strip area on which the experiment was conducted is located at the Iowa State University (ISU) Agricultural Engineering and Agronomy Research Farm, 11.3 km west of Ames, Iowa. Switchgrass plots, 7.62 m wide x 22.86 m long, with a 2% to 3% slope, were available for use in 2013. These plots, established in April 2007, had been a part of nutrient loss and biomass harvest study from 2007 to 2012. A layout of these plots is shown in Figure 3.3. These switchgrass plots had sub-surface drain lines installed in the lower 10.7 m of the plot, thus reducing the usable size of the plots to 7.6 m wide by 12.2 m long. The area was surveyed to verify the slope on these plots using a transit and a ranging rod. The rainfall simulator (Norton and Savabi, 2010) used in this study was only 8 m long. During the rainfall simulator calibrations, it was determined that in one setting of the simulator, rainfall uniformity of 90% and higher could only be achieved over an area 1.02 m wide x 5.79 m long due to lack of overlap for the end nozzles. Thus, buffer strips of size 1.02 m wide x 5.79 m long were selected for use in the experiment due to sub-surface drainage, slope, and rainfall simulator size (described later) limitations. Based on the total switchgrass area available, it was decided to use a 0.61 m separation distance between each strip to minimize rainfall overlap from the simulator.

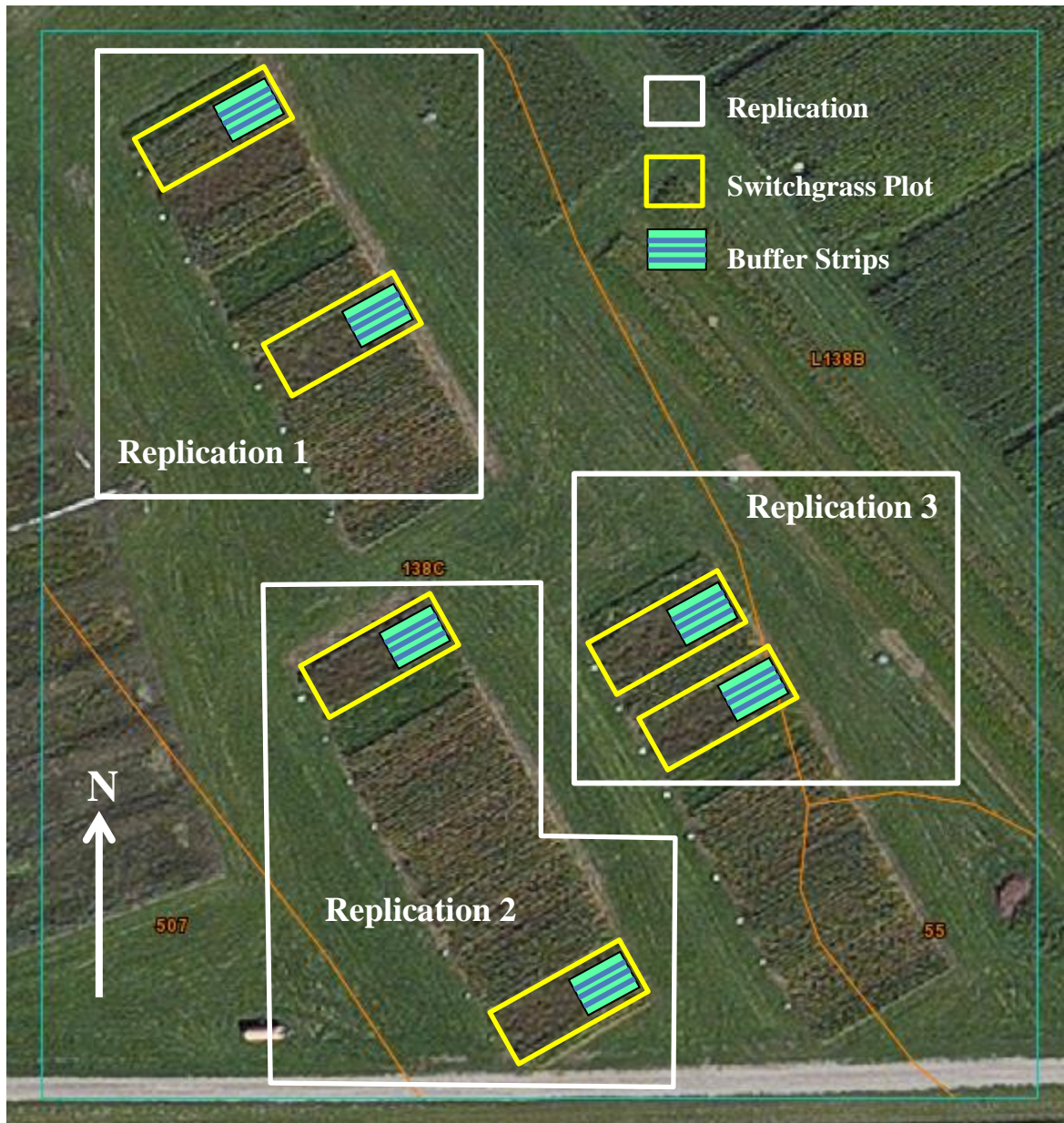


Figure 3.3: Location of the Switchgrass Buffer Strips on Field 5A, predominately on Clarion 138C Soil Type (Soil Map and Aerial Image Source: USDA Web Soil Survey, 2014). Plot and buffer strip dimensions are for reference and not to scale with the aerial image.

The buffer strip plots were installed by using a rectangular frame constructed of PVC pipe with inner dimensions of 1.02 m wide x 5.79 m long. The frame was adjusted

according to the topography such that the two top edges were at similar elevations. The frame was adjusted again to achieve the same for the two bottom edges. Switchgrass within the frame was trimmed to 25.4 cm height. Switchgrass outside the frame was trimmed down to the ground surface. Excess biomass, resulting from trimming of switchgrass, was removed from both areas. Grass, both in the strip and outside of the strip, was kept trimmed to the mentioned heights until the simulations were conducted. A second frame of same dimensions, using 0.61 m long PVC pipe spacers, was laid down and adjusted for topography prior to trimming the grass in-between the strips. The process was repeated until all strip boundaries were marked with flags on the top edge, the bottom edge, and both sides. Flags were placed on inside edge of the pipe frame. Galvanized steel borders were installed on the flagged edges of the buffer strips to avoid runoff from leaving the strip area. Slight adjustments to the dimensions of the buffer strips were performed during border installation to adjust for dry soil and impenetrable root mass. A galvanized steel V-shaped runoff collection gutter, with a 10 degree slope, was installed on the downstream end of the buffer strips to concentrate the outflow to one point for sample collection and flow measurement. Trenches, 9.1 m long x 0.61 m wide x 0.61 m deep, were dug using a backhoe on the downstream end of each buffer strip. This was done to allow for free flow of the outflow and to retain all flow exiting the buffer strips on the plots. Using this strip installation methodology and taking into consideration the experimental limitations as explained earlier, a total of 24 strips were installed on switchgrass plots. These buffer strips were assigned numerical identifiers starting with number one for the northern-most buffer strip and twenty-four for the southern-most buffer strip. Twelve of these twenty four strips were randomly selected

for use in this experiment for three replications each of AR10-D1, AR30-D1, AR10-D2, and AR30-D2 treatments.

The type of tiller species and population in the buffer strips was determined by randomly tossing a 0.05 m<sup>2</sup> wooden rectangle (0.30 m x 0.17 m) at three different locations along the length of the buffer strip. These three approximate locations were determined by dividing the length of the strip into two halves, upslope half and downslope half, respectively. Mid-point of the upslope half and the downslope half, and the mid-point of the buffer strip were used as the three location for determining vegetation densities. The tillers were then counted by species within the wooden rectangle for each of the three locations within each strip, resulting in three sets of populations per strip. These three numbers were averaged for the sediment type treatment and then scaled on a per hectare basis to determine average tiller population and percentage composition of each species. Vegetation in strips used for the fine sand treatment (D1) was 58% switchgrass (*Panicum virgatum*), 40% fox tail (*Setaria lutescens*), and 2% other. The average tiller population was determined to be 9.92 M tillers/ha. The corresponding numbers for the vegetation in strips used for the fine aggregates treatment (D2) was 58% switchgrass (*Panicum virgatum*), 37% fox tail (*Setaria lutescens*), and 5% other. The average tiller population was determined to be 8.47 M tillers/ha. The population densities were comparable to 9.00 (Helmets et al., 2005), 10.46 (Mickelson et al., 2003), 7.01 (Misra et al. 1996), and 8.82 (Arora et al., 1996) M tillers/ha. These population densities classified the buffer strips as having a poor to fair cover based on the criteria provided by Temple et al. (1987) and Haan et al. (1994).

The water used for the chemical applications on the ISU research farm was used as the source water for this simulation project. Water was supplied to the three 9463 L poly-tanks on-site which served as reservoirs for the rainfall-runoff simulations. The site experienced extremely dry conditions with only 5.41 cm of rainfall in July and August prior to September 2013. As such, it was decided to flood irrigate the strips to create field capacity conditions in the strip prior to conducting the simulation experiment. Water from the reservoir tanks was applied by gravity as irrigation water using a flow distributor to the upstream end of the strips with an approximate flow rate of 11.36 Lpm. Irrigation was stopped when the water showed up at the downstream end of the strip. Typically, a time period of 12 hours elapsed between the end of irrigation and start of simulation experiment on any particular strip. A covered runoff collector was installed at the outflow end of the buffer strips into the wet soil in order to minimize soil disturbance, immediately prior to start of the simulation.

A 26.25-m-long oscillating linear-overhead-boom rainfall simulator, as described by Norton and Savabi (2010), was used to apply simulated rainfall at 6.35 cm/h for 60 min on one strip in a single setting. For the Ames 8 WSW recording station for the National Weather Service, the rainfall intensity in terms of recurrence interval for a 10 year-1 hour storm is 5.82 cm/h and for a 25 year-1 hour storm is 7.16 cm/h (NOAA, 2013). The Norton Rainfall Simulator has several advantages over its predecessors including the ability to almost continuously apply rainfall over the entire length of the test plot across the slope. In comparison, nozzles of the rotating overhead boom rainfall simulator, as described by Swanson (1965), only apply rainfall to a part of the test plot over which they pass.

Prior to conducting the simulation experiments, the Norton rainfall simulator was calibrated to ensure it delivered the intended rainfall intensity over the entire strip area. First, the nozzle flow rate was calibrated by capturing the discharge from each nozzle at a specific pressure for a given time period. Each nozzle discharge was measured three times to get an average flow rate at a specific pressure. The flow rates were measured at three different pressures to verify nozzle performance across the oscillating boom. Based on the measured flow rates, pressures across the oscillating boom sections were adjusted and tested to achieve  $\pm 5\%$  of the mean flow rate across all nozzles.

After the nozzle flow rates had been calibrated, the simulator was hoisted and calibrated for obtaining the design rainfall intensity of 6.35 cm/h. For calibration purposes, the rainfall simulator was setup over an area of same dimensions as the buffer strips. Eighteen rain gauges were setup underneath the simulator and rainfall was collected for 10 minutes. The procedure was repeated until the desired operating pressures were obtained for delivering the design rainfall intensity. The rainfall simulator operating procedures, as described in Norton and Savabi (2010), were followed.

A photograph of a rainfall-runoff simulation in progress during September 2013 is shown in Figure 3.4. A typical rainfall-runoff simulation setup used in the experiment consisted of three poly-tanks mounted on a 14.6 m long flatbed trailer. The three poly-tanks comprised of a 4542 L rainfall water supply tank, a 1987 L runoff supply tank, and a 1230 L runoff supply tank. An additional 1230 L poly-tank was placed on the ground at the outflow end of the buffer strip to catch excess water from the rainfall simulator. Excess rain water was recirculated back into the rainfall supply tank as the catch tank filled up during the experiment. Prior to the start of the simulation, water from the

reservoir tanks was pumped into the rainfall tank to feed the rainfall simulator. Using a Neptune in-line water flow meter, approximately 1931 L and 777 L, of water was metered into the larger and smaller runoff supply tanks, respectively. Metered quantity of water was used to calculate the mass of sediment needed to achieve the desired sediment mass concentration in simulated runoff. This set-up provided adequate quantities of water needed to complete two rainfall-runoff simulations in one day. A simple schematic of this setup is provided in Figure 3.5. Approximately about 4.83 kg of sediment (corrected for moisture content) was mixed in 1931 L of water to obtain a sediment concentration of 2500 mg/L in the AR30 treatment simulated runoff. The corresponding sediment mass for the AR10 treatment was 1.90 kg mixed in 777 L of water to obtain similar sediment mass concentration. The addition of sediment mass to water in the runoff supply tank took place 30 min prior to start of rainfall on the buffer strip. The sediment and water mixture was thoroughly mixed for 30 min in the inflow supply tank to provide an opportunity for the pesticide mass to equilibrate between the sediment and water phases. The agitation took place by utilizing four TeeJet Vortex Agitation Nozzles (Model Y-33-I-80) mounted on a manifold attached on the return end of the flow from the pump. The nozzles were pointed towards the bottom of the tank to keep sediment in suspension.

After the sediment and water had been mixed for 30 min, it was introduced as inflow to the upper end of the buffer strips. An additional pipe mounted on the outflow end of the agitation pump served as the inflow line to the buffer strips. This inflow line was attached to a specially designed PVC distributor consisting of a 0.61 m long PVC pipe, a Great Plains industries digital flow meter, a gate valve for flow control, and a



perforated PVC pipe, 1.91 cm in diameter and 1.5 times as wide as the 1.01-m-wide upper end of the buffer strips. This construction minimized turbulence for flow readings while providing for an effective method of flow control and distribution. Perforations in the PVC pipe were performed using a 0.64 cm bench drill. The number of perforations drilled into the PVC pipe were determined to insure that the flow was neither too slow to carry sediment nor too fast to cause erosion on the inflow end of the buffer strip. The terminal end of the distributor had a 90-degree elbow attached to it to allow for free flow such that the distributor did not accumulate any sediment within itself. Discharge from the distributor openings was allowed to fall on flat metal piece placed in the buffer strip grass to further spread out the flow.

The buffer strip inflow was introduced at a rate of 13.25 Lpm for the AR10 strip and 39.75 Lpm for the AR30 strips. This calculation for runoff volume was based on the assumption that 22.5% of the 6.35 cm/h rainfall would run off from the source area. Typical runoff from agricultural fields ranges from 15 to 25% of the rainfall amount. The design buffer strip area was 1.01 m by 5.49 m, equaling 5.57 square meters. Source Area 1 is 10 times bigger or 55.74 square meters. The runoff rate of 1.43 cm/h calculates as 0.80 cubic meters of water in one hour or 796.41 L of water in one hour or 13.27 Lpm. Source Area 2 is 30 times bigger or 167.23 square meters. This equates to inflow rate of 2389.23 L of water in one hour or 39.82 Lpm. The flow rates were increased by approximately 0.50 Lpm to account for volume of water removed from inflow during sampling.

Two rainfall simulations were conducted each day during the field experiment in September 2013. Each simulation run included a 60 min rainfall with inflow being added



Figure 3.4: Photograph of a rainfall-runoff simulation in progress showing the experimental setup.

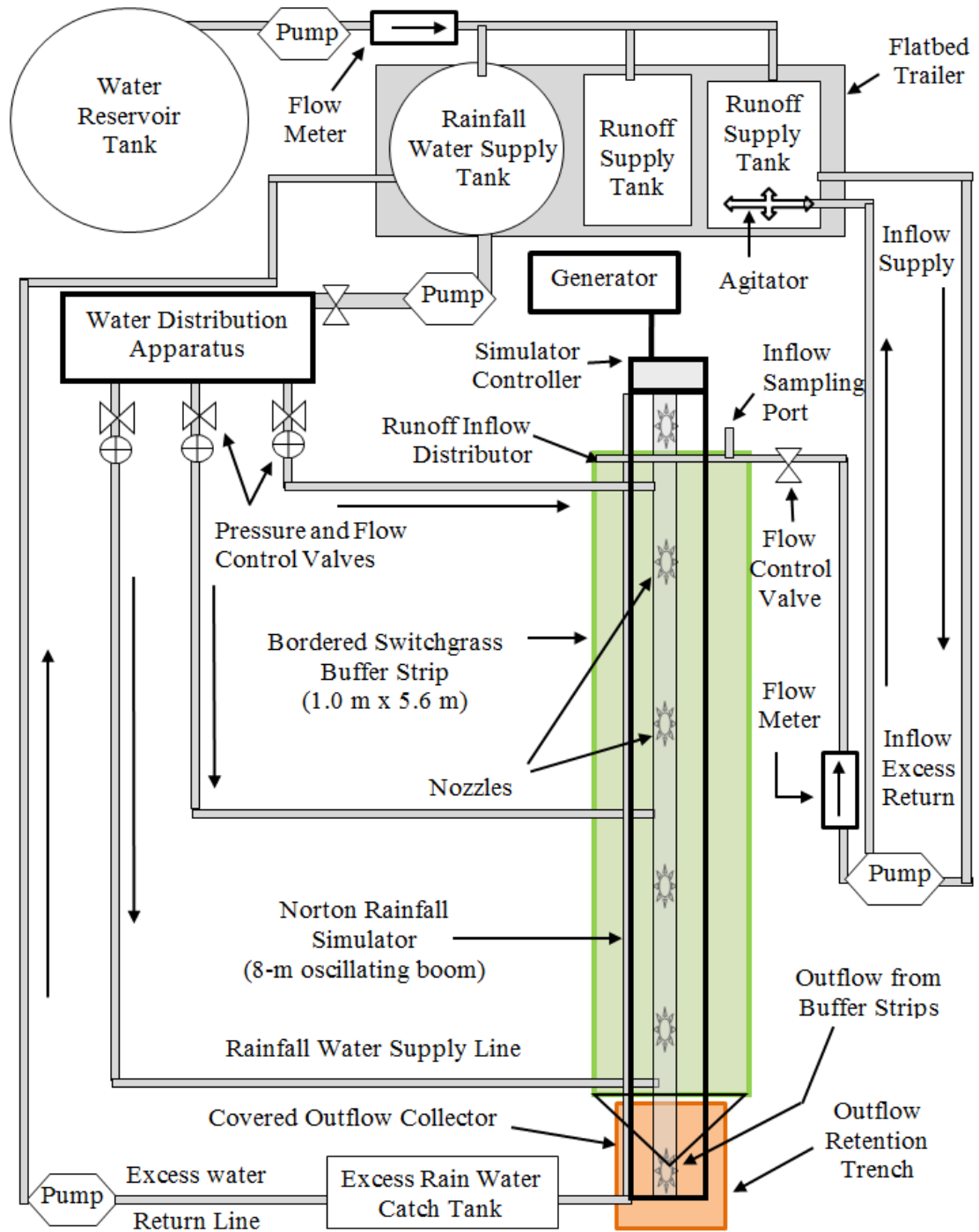


Figure 3.5: Rainfall-Runoff Simulation Setup for Switchgrass Buffer Strip Study (not to scale).

to upstream end of the buffer strips 15 min after the start of rainfall. Sediment mixing started 15 min prior to start of the rainfall in case of the treatments where inflow with sediment was added. Six to seven rain gauges, with 0.25 cm accuracy were setup on the plots to measure the rainfall depth and intensity. Two rain gauges were setup outside the wetted perimeter of the simulator to capture any natural rainfall that might have occurred during the simulation.

Inflow was metered into the upstream end of the buffer strips using a Great Plains Industries digital flow meter. The gate valve placed after the flow meter in the distributor set-up provided with a flow control adjustment to achieve the desired flow rate. Digital flow rate readouts were recorded at the onset of inflow and then every 10 min to calculate the volume of inflow into the buffer strip. This calculated volume was compared with the total volume readout provided by the flow meter. The total volume of inflow used for comparison, in both cases, was corrected for the volume of water taken for inflow samples and for particle size analysis, as the sampling port was mounted after the flow meter. The inflow volume was within  $\pm 3\%$  of each other; however, corrected flow volume calculated using flow meter readings was used to perform the hydrologic analysis. Samples were taken at 10 min intervals from sampling port with time counted from the start of inflow. Two, 0.95 L samples, were collected from inflow to ensure sediment was obtained for sediment adsorbed pesticide concentration analysis. Due to infiltration within the buffer strip, the outflow was expected to be variable. One 0.95 L sample was collected every two minutes after the start of outflow from the buffer strips. In between the sampling times and other tasks for the simulation, flow measurements were performed to estimate the rate of outflow. Outflow was collected in a 4.73 L bucket

and weighed on a stainless steel bench scale with 0.002 kg accuracy. Time to fill about 1/2 to 2/3 of the bucket was recorded using a stop clock. The temperature of the water was recorded to convert the weight of water recorded to volume of water based on density. Temperature was recorded with a Fischer Scientific Multi-Thermometer with a 20.32 cm long stainless steel stem with an accuracy of 0.1 degrees Centigrade or Fahrenheit. Samples were composited to ensure enough sediment (~ 1 to 5 gm) was available to analyze for sediment adsorbed pesticide concentrations. All equipment used for delivery and sampling of inflow and outflow was flushed with water from the reservoir tank at the end of each run. A Sharp Digital Atomic Clock was used to record the time of start of sediment mixing, rainfall, inflow, and outflow sampling. Rain water collected in rain gauges was collected as a single sample for rainfall analysis. The inflow, outflow, and rain samples were immediately transported to a refrigerated storage room at 4°C in the Department of Agricultural and Biosystems Engineering. All analysis of the collected samples was completed within eight months of collection.

Sediment mass concentrations were determined to complete the sediment mass balance. Total solids concentration in inflow, outflow, and rainfall samples was determined by placing a 20 mL aliquot in a labeled tin and over drying the sample for 24 h at 90°C (to avoid boiling action) and then at 105°C for 1 h. The aliquot was obtained by using a 20 mL disposable glass pipette from a thoroughly stirred sample. The weight of the empty tin, the volume of sample placed in the tin, and the weight of tin with the dry sample were used in calculating total solids concentration. The pipette was rinsed with distilled de-ionized water when obtaining aliquot from samples within the same set of inflow or outflow samples. A new pipette was used at the start of obtaining aliquots

from each set of samples. Each sample was tested in duplicates and difference between the total solids concentrations was calculated. Samples failing the 5% permissible difference were retested until the difference was below the permissible limit. For each set of inflow and outflow samples, the sediment mass concentrations were corrected for total solids concentration in the rainfall sample for the respective treatment.

Pesticide concentrations in the samples (both water and sediment phase) were determined using gas–liquid chromatography. The pesticide mass was extracted into toluene (purity = 99.99%) and toluene extracts were analyzed on the gas chromatograph. Toluene was chosen as the solvent for extraction as all three pesticides have relatively high solubility in toluene (Table 3.3).

Table 3.3: Solubility of the three pesticides used in the study in water and toluene.

| Pesticide    | CAS # [c] | Solubility at 20°C (mg/L) [a] |           | Solubility Ratio [b] |
|--------------|-----------|-------------------------------|-----------|----------------------|
|              |           | Water                         | Toluene   | Toluene : Water      |
| Atrazine     | 1912-24-9 | 35                            | 4000      | 114                  |
| Linuron      | 330-55-2  | 63.8                          | 75,000    | 1175                 |
| Chlorpyrifos | 2921-88-2 | 1.05                          | 4,000,000 | 3,809,524            |

[a] PPDB, 2006, USDA-ARS and PPDB, 2013, University of Hertfordshire, UK.

[b] Solubility ratio of >100 indicates potential to extract 100% of pesticide from water into toluene.

[c] Chemical Abstracts Service Identification Number, American Chemical Society, 2014.

Pesticide extraction procedures used in this experiment were similar to those used by Arora et al. (2003), Boyd et al. (2003), Misra et al. (1996), and Arora et al. (1996). To develop sediment extracts, the water from the refrigerated samples was decanted such that the settled sediment was not re-suspended. The decanted water was poured into a clean quart jar rinsed with de-ionized water. The sediment mass and the remaining water were then stirred and the shaken sample with sediment was transferred into stainless steel

cups. Stainless steel cups were then centrifuged at 4300 rpm for 15 minutes. Water was decanted and the stainless steel cups containing the wet sediment were weighed.

Pesticide mass from the wet sediment was extracted by adding a known weight of toluene into the stainless steel cups. Ten to fifteen, 4 mm dia., glass beads were added to the wet sediment-toluene mixture to lift the sediment into suspension in the toluene. The cups were then rotated for 1 h in a horizontal orientation and then for 1 h in a vertical orientation. Toluene from the stirred mixture was decanted into amber silanized glass vials to the extent possible. The remaining mixture was dried for 24 h in an externally vented oven to obtain the dry weight of the sediment. To develop water extracts, a subsample of the mixed water remaining after centrifuging out the sediment was filtered through 0.45  $\mu\text{m}$  membrane filter paper under a vacuum to obtain water free of sediment. A known weight of this filtered water subsample was extracted with a known weight of toluene by shaking the mixture in a clean, 250 mL flat bottom flask on an orbital shaker for 60 min. After shaking, distilled de-ionized water was added to the flask to allow toluene to rise into the neck of the flask, as toluene is lighter than water. The water-toluene mixture was then allowed to separate for 15 min, and the separated toluene was decanted into screw-top glass test tubes using individually wrapped borosilicate glass pipettes. Volumetrically, about 200 ml of the filtered water subsample was extracted with 10 mL of toluene. Glass tubes and vials containing the toluene extracts were stored in a dark refrigerator at 4°C prior to analysis.

Prior to analysis, 1 mL of the toluene extracts (calibrated by weight) were pipetted into amber silanized glass vials. Benzophenone was used as an internal standard for analysis. Ten  $\mu\text{L}$  of known concentration of benzophenone was added to the sample in

each glass vial. Toluene extracts containing the internal standard were analyzed on the Waters GCT accurate-mass Time-of-Flight (TOF) Mass Spectrometer (MS) coupled with a Model 6890 Gas Chromatograph (GC) from Agilent, which was equipped with a Model 7683 Auto-injector from Agilent. Two micro-liters of the extract were injected using the front inlet in split-less mode into the GC with an injector temperature of 260°C. The column used on the GC was a Restek Rxi-5 Sil MS, 30 m long with an internal diameter of 0.25 mm having a film thickness of 0.25 µm. Carrier gas was Helium (purity = 99.9995%) with a constant flow rate of 1.0 mL/min. Temperature of the column was kept at 100°C for the first minute, then ramped to 160°C at a rate of 30°C per minute, then ramped to 250°C at a rate of 10°C per minute, and finally ramped to 310°C at a rate of 30°C per minute and baked out for four minutes. The TOF-MS was operated in the electron ionization positive (EI+) mode with electron energy of 70 eV, a source temperature of 150°C, trap current of 100 micro amps, scan range of 45 to 650 Daltons with a scan rate of one scan per sec. The mass measurement precision was +/- 1 milliDalton. Mass peaks produced in the chromatograms were processed using respective accurate-mass quantitation ions and total ion current for the three pesticides on the MassLynx 4.1 software. The libraries used in the software for mass identification were Wiley 7th Edition (McLafferty, 2000) and NIST 2011 which included ion identification for each CAS number provided in Table 3.4.

An inflow-outflow-rainfall mass balance was performed to calculate the amount of infiltration water mass using equation 3.1 below:

$$M_x = M_i + R_i - M_{out} \quad (3.1)$$



where  $M_x$  is the infiltration water mass as shown in Figure 2.2 in mm,  $M_i$  is the inflow water mass in mm,  $R_i$  is the rainfall water mass in mm, and  $M_{out}$  is the outflow water mass in mm. Measurements in mm were obtained by converting the volumetric mass (L) to mm of depth over the strip area, to account for variations in the strip dimensions. Sediment mass retentions were obtained by using the sediment mass concentration with the respective flow volume to obtain the sediment mass in inflow and outflow. The pesticide mass retained in the strip in the water carrier phase was calculated by using the dissolved pesticide mass concentrations with the respective flow volumes for both inflow and outflow. The dissolved pesticide mass concentrations in outflow were analyzed for about one half of the samples taken every two minutes due to budget restrictions. Intermediate concentration values were linearly interpolated for calculation purposes. The pesticide mass retained with the sediment carrier phase was calculated by using the sorbed pesticide concentrations with the respective sediment mass in inflow and outflow. The sediment mass in the outflow samples was combined to ensure adequate pesticide mass was available for detection and quantitation. As such, the same value for sorbed pesticide concentration was used for the samples combined in performing the calculations. Total pesticide mass retained was then obtained by adding the pesticide mass retained in the water phase and in the sediment phase. The percent pesticide retention values were analyzed for significant differences among area ratios and between sediment types for the three pesticides using a randomized block design (Cochran and Cox, 1992).

### 3.4 Results and Discussion

Simulation experiments were conducted approximately 12 h after the irrigation was stopped on each strip. The duration of irrigation and the amount of water applied was variable for each strip. These durations and amounts along with strip dimensions are presented in Table 3.4. The flow rate used ranged between 9.2 to 11.2 Lpm as the irrigation water was gravity applied from the reservoir tank and the flow rate varied due to change in height of water in the tank. The infiltration rates, for the duration of irrigation over the strip area, averaged between 10.2 to 11.7 cm/h. Without the irrigation, it would not have been feasible to conduct the experiment as all inflow and rainfall would have infiltrated.

#### 3.4.1 Infiltration water mass ( $M_x$ )

Dissolved pesticide mass that is transported with the water carrier phase through the buffer strip is retained with the infiltration water mass ( $M_x$ ). Sorbed pesticide mass that is transported with the sediment carrier phase through the buffer strip is retained with the sediment mass. Table 3.5 shows the mass balance for percent infiltration for three replications each of the 10:1 (AR10) and 30:1 (AR30) area ratios; and D1 and D2 sediment types. The percentage of infiltration water mass for the AR10 buffer strips was similar, with an average of 71.5% for D1 strips, when compared with the same area ratio buffer strips for D2 strips (average of 73.6% for three strips). There was no statistically significant difference between the two averages at  $\alpha = 0.05$  in the two-tailed t-test. For the AR30 strips, D1 strips had an average infiltration water mass retention of 48.9% when compared with the D2 strips with an average of 53.4%. The average infiltration water mass retention percentage was statistically significant when the AR10 and AR30

strips were compared for both sediment types (D1 and D2). The difference between the two area ratios for the infiltration water mass retention is likely due to greater depth of water flow and not due to type of sediment introduced with inflow into the strips. The results, therefore, indicate that flow convergence, resulting in higher area ratios as the flow passes through the buffer strips, can cause the infiltration percentage to be lower. As a special case, the first 15 min of rainfall was excluded from the mass balance to estimate percent infiltration without the rainfall wetting period. This mass balance is also presented in Table 3.5. This caused the rainfall amounts to be lower and percent infiltration water mass to be lower than the mass balance in which the entire amount of rainfall was included. This exclusion of 15 min of rainfall did not change the differences among treatments as explained earlier.

Flow rates (average inflow and outflow for each replication) and average rainfall rates for AR10 strips are presented graphically as a function of time in Figure 3.6. The time scale represented in these figures starts at zero to mark the start of the rainfall on the buffer strip. Inflow on each strip was started 15 min after the rainfall had started (wetting period). Time for the outflow to appear at the downstream end of the buffer strips averaged 13.5 min ranging between 5 to 19 min for the AR10 strips. The corresponding travel time for the AR30 strips (Figures 3.6) was 5.3 min ranging between 3 to 8 min. Under concentrated flow conditions represented by AR30, the travel time was less than half in comparison to AR10 strips. When compared within the same area ratio of 10:1, the average travel time for sediment type D1 was 15.5 min ranging between 13 to 19 min whereas for sediment type D2, the average was 10.3 min ranging between 5 to 19 min. The corresponding numbers for the 30:1 area ratio for D1 sediment type were 5 min

Table 3.4: Buffer strip dimensions and area, amount and duration of irrigation applied for each replication of two area ratios and sediment types.

| Replication        | Sediment<br>Type | Strip<br># | Run<br># | Date      | Strip         |              |                           | Irrigation    |              |
|--------------------|------------------|------------|----------|-----------|---------------|--------------|---------------------------|---------------|--------------|
|                    |                  |            |          |           | Length<br>(m) | Width<br>(m) | Area<br>(m <sup>2</sup> ) | Amount<br>(L) | Duration (h) |
| AR10 - D1 - Rep 1  | Fine Sand        | 2          | 3        | 9/11/2013 | 5.6           | 1.0          | 5.6                       | 2432          | 4.0          |
| AR10 - D1 - Rep 2  | Fine Sand        | 24         | 14       | 9/23/2013 | 5.6           | 1.0          | 5.6                       | 2846          | 5.0          |
| AR10 - D1 - Rep 3  | Fine Sand        | 19         | 19       | 9/30/2013 | 5.6           | 1.0          | 5.6                       | 2861          | 4.5          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.6                       | 2713          | 4.5          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.0                       | 243           | 0.5          |
| AR30 - D1 - Rep 1  | Fine Sand        | 5          | 5        | 9/12/2013 | 5.6           | 1.0          | 5.6                       | 6391          | 10.0         |
| AR30 - D1 - Rep 2  | Fine Sand        | 9          | 7        | 9/13/2013 | 5.6           | 1.0          | 5.6                       | 4277          | 7.0          |
| AR30 - D1 - Rep 3  | Fine Sand        | 14         | 18       | 9/25/2013 | 5.6           | 1.0          | 5.4                       | 2668          | 4.5          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.6                       | 4446          | 7.2          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.1                       | 1867          | 2.8          |
| AR10 - D2 - Rep 1  | Fine Aggregates  | 6          | 6        | 9/12/2013 | 5.6           | 1.0          | 5.7                       | 7386          | 11.0         |
| AR10 - D2 - Rep 2  | Fine Aggregates  | 11         | 9        | 9/16/2013 | 5.6           | 1.0          | 5.6                       | 2652          | 4.5          |
| AR10 - D2 - Rep 3  | Fine Aggregates  | 13         | 17       | 9/25/2013 | 5.6           | 0.9          | 5.1                       | 3181          | 5.5          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.7                       | 2838          | 4.7          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.1                       | 425           | 0.8          |
| AR30 - D2 - Rep 1  | Fine Aggregates  | 1          | 4        | 9/11/2013 | 5.6           | 1.0          | 5.8                       | 3284          | 5.5          |
| AR30 - D2 - Rep 2  | Fine Aggregates  | 21         | 13       | 9/23/2013 | 5.6           | 1.0          | 5.6                       | 2439          | 4.0          |
| AR30 - D2 - Rep 3  | Fine Aggregates  | 20         | 20       | 9/30/2013 | 5.7           | 1.0          | 5.7                       | 2792          | 4.5          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.5                       | 4406          | 7.0          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.1          | 0.3                       | 2594          | 3.5          |

Table 3.5: Inflow, outflow, rainfall, and infiltration for two area ratios (AR10 and AR30) and two sediment types (D1 and D2).

| Replication #        | Strip # | Area (m <sup>2</sup> ) | Inflow <sup>1</sup> (mm) | Outflow (mm) | Rainfall (mm) | Infiltration (%) | Modified Rainfall <sup>2</sup> (mm) | Modified Infiltration <sup>2</sup> (%) |
|----------------------|---------|------------------------|--------------------------|--------------|---------------|------------------|-------------------------------------|--|
| AR10 - D1 - Rep 1    | 2       | 5.6                    | 106.3                    | 36.9         | 62.2          | 78.1%            | 46.7                                | 75.9%                                  |
| AR10 - D1 - Rep 2    | 24      | 5.6                    | 107.3                    | 53.0         | 63.5          | 69.0%            | 47.6                                | 65.8%                                  |
| AR10 - D1 - Rep 3    | 19      | 5.6                    | 107.7                    | 54.6         | 63.5          | 68.1%            | 47.6                                | 64.9%                                  |
| Average <sup>3</sup> |         | 5.6                    | 107.1                    | 48.2         | 63.1          | 71.7% a          | 47.3                                | 68.8% a                                |
| Standard Deviation   |         | 0.0                    | 0.7                      | 9.8          | 0.7           |                  | 0.5                                 |  |
| AR30 - D1 - Rep 1    | 5       | 5.6                    | 318.6                    | 191.9        | 63.5          | 49.8%            | 47.6                                | 47.6%                                  |
| AR30 - D1 - Rep 2    | 9       | 5.6                    | 317.9                    | 182.0        | 63.1          | 52.2%            | 47.4                                | 50.2%                                  |
| AR30 - D1 - Rep 3    | 14      | 5.4                    | 332.2                    | 218.2        | 64.2          | 45.0%            | 48.2                                | 42.6%                                  |
| Average              |         | 5.6                    | 322.9                    | 197.4        | 63.6          | 48.9% b          | 47.7                                | 46.7% b                                |
| Standard Deviation   |         | 0.1                    | 8.1                      | 18.7         | 0.6           |                  | 0.4                                 |  |
| AR10 - D2 - Rep 1    | 6       | 5.7                    | 106.1                    | 56.4         | 62.7          | 66.6%            | 47.0                                | 63.2%                                  |
| AR10 - D2 - Rep 2    | 11      | 5.6                    | 108.0                    | 43.3         | 64.2          | 74.8%            | 48.2                                | 72.3%                                  |
| AR10 - D2 - Rep 3    | 13      | 5.1                    | 119.5                    | 38.0         | 62.0          | 79.1%            | 46.5                                | 77.1%                                  |
| Average              |         | 5.5                    | 111.2                    | 45.9         | 63.0          | 73.6% a          | 47.2                                | 71.0% a                                |
| Standard Deviation   |         | 0.3                    | 7.2                      | 9.5          | 1.1           |                  | 0.8                                 |  |
| AR30 - D2 - Rep 1    | 1       | 5.8                    | 314.0                    | 165.4        | 62.8          | 51.6%            | 47.1                                | 54.2%                                  |
| AR30 - D2 - Rep 2    | 21      | 5.6                    | 321.7                    | 204.3        | 63.5          | 47.0%            | 47.6                                | 44.7%                                  |
| AR30 - D2 - Rep 3    | 20      | 5.7                    | 313.0                    | 183.4        | 62.8          | 51.2%            | 47.1                                | 49.1%                                  |
| Average              |         | 5.7                    | 316.3                    | 184.3        | 63.0          | 51.4% b          | 47.3                                | 49.3% b                                |
| Standard Deviation   |         | 0.1                    | 4.7                      | 19.5         | 0.4           |                  | 0.3                                 |  |

<sup>1</sup> Flow converted to mm of water depth over the strip area. Flow for area ratio 30:1 is about 3 times the flow for 10:1 due to design of the experiment.

<sup>2</sup> Rainfall for the first 15 min of the experiment excluded from total rainfall for a modified infiltration mass balance.

<sup>3</sup> t-test H0: Mean (10:1) = Mean (30:1), no significant difference between the same letters at  $\alpha = 0.05$  in the two-tailed test.

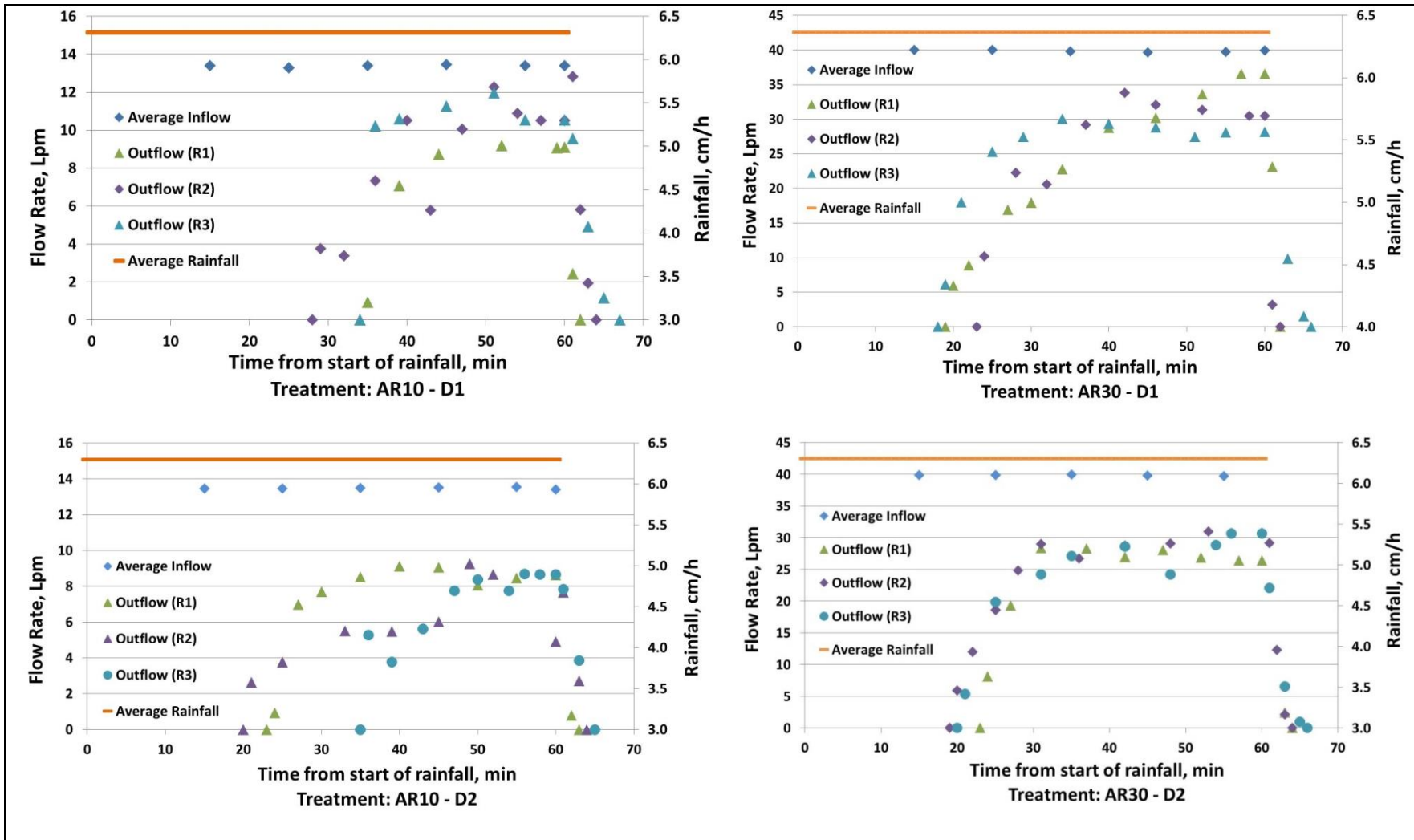


Figure 3.6: Average inflow and outflow from three replications, and average rainfall for all four treatments.

(ranging between 3 - 8 min) and for D2 sediment type were 5.3 min (ranging between 4 - 8 min). In the case of the AR10 strips, the travel time was reduced when comparing D1 to the D2 strips. In case of the AR30 strips, the travel time was similar when comparing D1 to the D2 strips. The main reason for quicker travel times for the AR30 strips for either sediment type is due to increased inflow volume. Figure 3.6 shows similar trends for outflow, which after starting from zero, first increased gradually, then reached somewhat of a steady-state condition, and then rapidly stopped after the inflow and rainfall were stopped. These results indicate that the infiltration capacity of the soil did not reach a constant value during the rainfall period only. The increasing limbs of the outflow hydrographs indicate the infiltration capacity of the soil decreased during this time period before reaching somewhat of a steady-state condition. Considering the mass balance for the last 10 min of the rainfall, to represent a steady-state condition, infiltration for this time period of 10 min calculated as 46.1% for AR10-D1, 59.4% for AR10-D2, 31.4% for AR30-D1, and 33% for AR30-D2 treatments, respectively.

In comparison with previously conducted simulation studies, Tingle et al. (1998) and Blanco-Canqui et al. (2004a and 2004b) have reported an average infiltration water mass of 15.2 percent for close to 11:1 area ratio strips. Misra et al. (1995) and Arora et al. (2003) have conducted rainfall simulation studies and reported an average infiltration water mass of 29.4% for 30:1 area ratio strips. These studies are summarized in Table 2.2. These results are lower than the results obtained in this experiment for both area ratios, respectively. Possible reason for higher infiltration achieved in this experiment is the extensive dry period which existed prior to conducting the experiment. This could have caused the moisture at lower depths of the buffer strips to be lower than what it can

be under periods of repeated rainfalls. Obtaining deep cores of soil samples prior to start of simulation in the buffer strips was not feasible in this experiment as it would have created preferential flow paths. Differences in experimental design, especially how the infiltration water mass is calculated by comparing a buffered plot with a non-buffered plot, is the second reason for study averages explained above, for 11:1 area ratio to be low.

### **3.4.2 Dissolved pesticide concentration ( $C_{out}$ )**

Dissolved pesticide concentration ( $C_i$ ) in the inflow into the buffer strips is subject to interaction with the rainfall water; and sorption to the organic carbon contained in the living and dead organic matter on the strip surface, and organic matter in the top 2.5 cm of the soil (surface mixing zone). In addition, as the flow passes through the strip, pesticide molecules are subject to sunlight exposure, pH changes due to surface interactions, and surface soil temperature changes. All these factors cause the dissolved pesticide concentrations to be different in outflow ( $C_{out}$ ).

Figure 3.7 shows the dissolved atrazine concentrations in inflow (averaged for 3 replications) and in outflow for each of the three replications for the four treatments of AR10-D1, AR30-D1, AR10-D2, and AR30-D2, respectively. When compared between D1 and D2 treatments, the average inflow atrazine concentrations were slightly higher for D2 treatments. As fine sand is more porous than fine aggregates, atrazine mass could have been lost to a higher degree during mixing after pesticide application. When the atrazine concentrations for all four treatments in the rising limb time duration of the outflow hydrograph were compared, the concentrations gradually increased over time. This increase in concentrations was more obvious in the AR10 treatment strips for both



D1 and D2 sediment type. The effect of rainfall dilution and sorption to organic matter are the two likely reasons for the rising limb of the dissolved atrazine concentration graph. This effect is more marked in AR10 strips as the inflow rate was lower than the AR30 strips.

Dissolved chlorpyrifos concentrations in inflow (averaged for 3 replications) and in outflow for each of the three replications for the four treatments of AR10-D1, AR30-D1, AR10-D2, and AR30-D2, respectively, are plotted in Figure 3.8. As in the case of atrazine, dissolved chlorpyrifos concentrations in inflow were higher for D2 sediment than for D1 sediment for both area ratios. For all four treatments, the outflow concentrations were lower than the average inflow concentrations for chlorpyrifos. For treatment AR30-D2, the concentrations gradually increased with the rising limb of the hydrograph. A similar trend was observed for AR1-D2 treatment. This trend was not clear for the AR10-D1 and AR30-D1 treatments for the dissolved chlorpyrifos concentrations in outflow.

Figure 3.9 shows the dissolved concentrations for linuron in inflow (averaged for 3 replications) and in outflow for each of the three replication for the four treatments of AR10-D1, AR30-D1, AR10-D2, and AR30-D2, respectively. Linuron concentrations in toluene, when processed on the gas chromatograph-mass spectrometer, showed two peaks for the accurate-mass ions and for the total ion current. The presence of two peaks on the chromatogram indicates decomposition, disintegration, and/or degradation of linuron into a second compound with a similar chemical structure to linuron. Linuron standards at different concentrations showed the presence of same two peaks at the same time on the chromatogram. The masses for the two peaks were added together to determine the

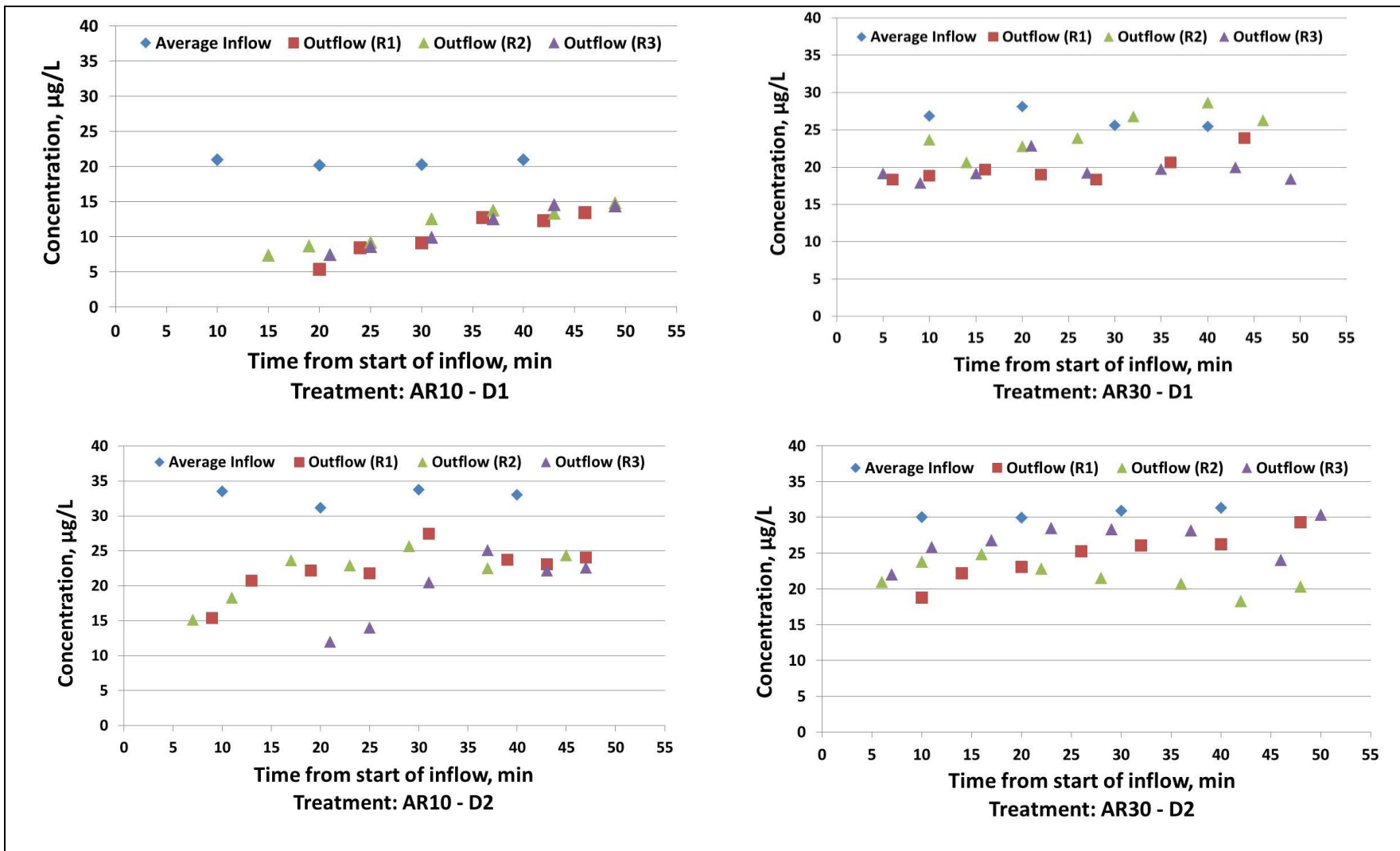


Figure 3.7: Dissolved atrazine concentrations in inflow (average) and in outflow for each replication.

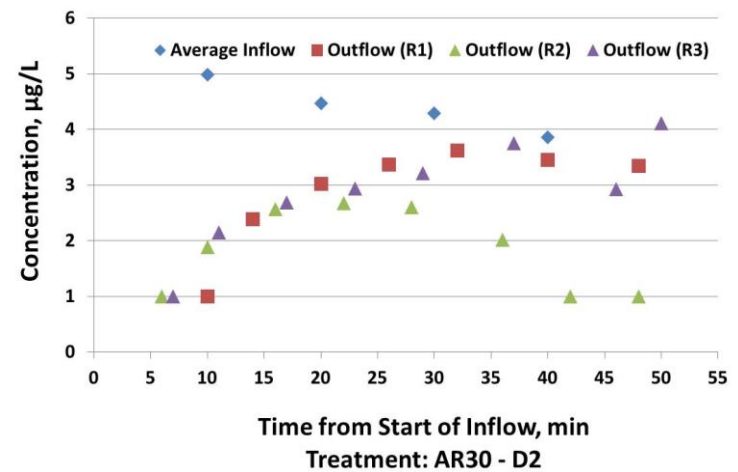
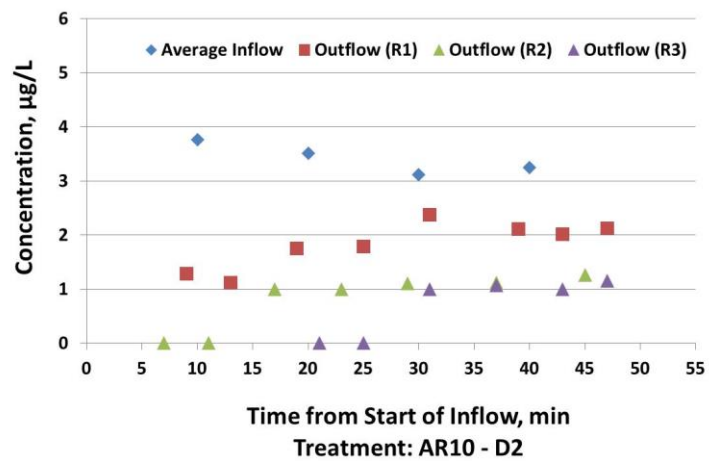
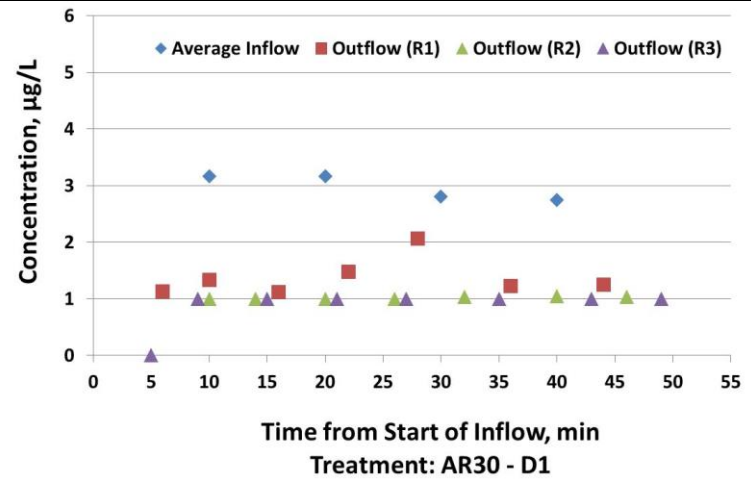
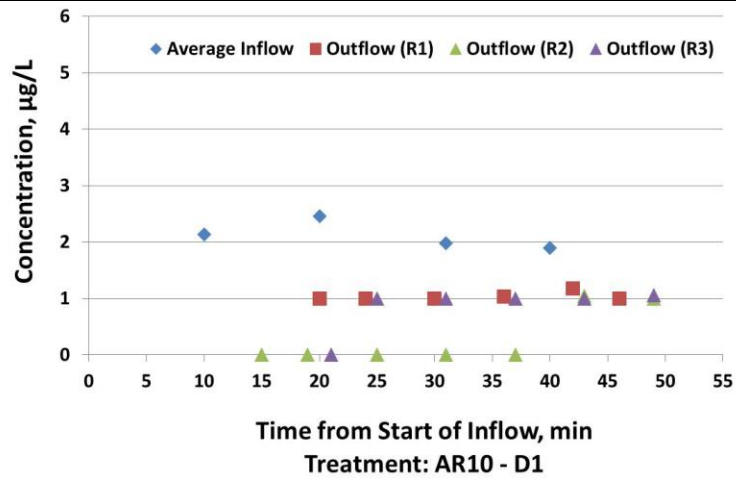


Figure 3.8: Dissolved chlorpyrifos concentrations in inflow (average) and in outflow for each replication.

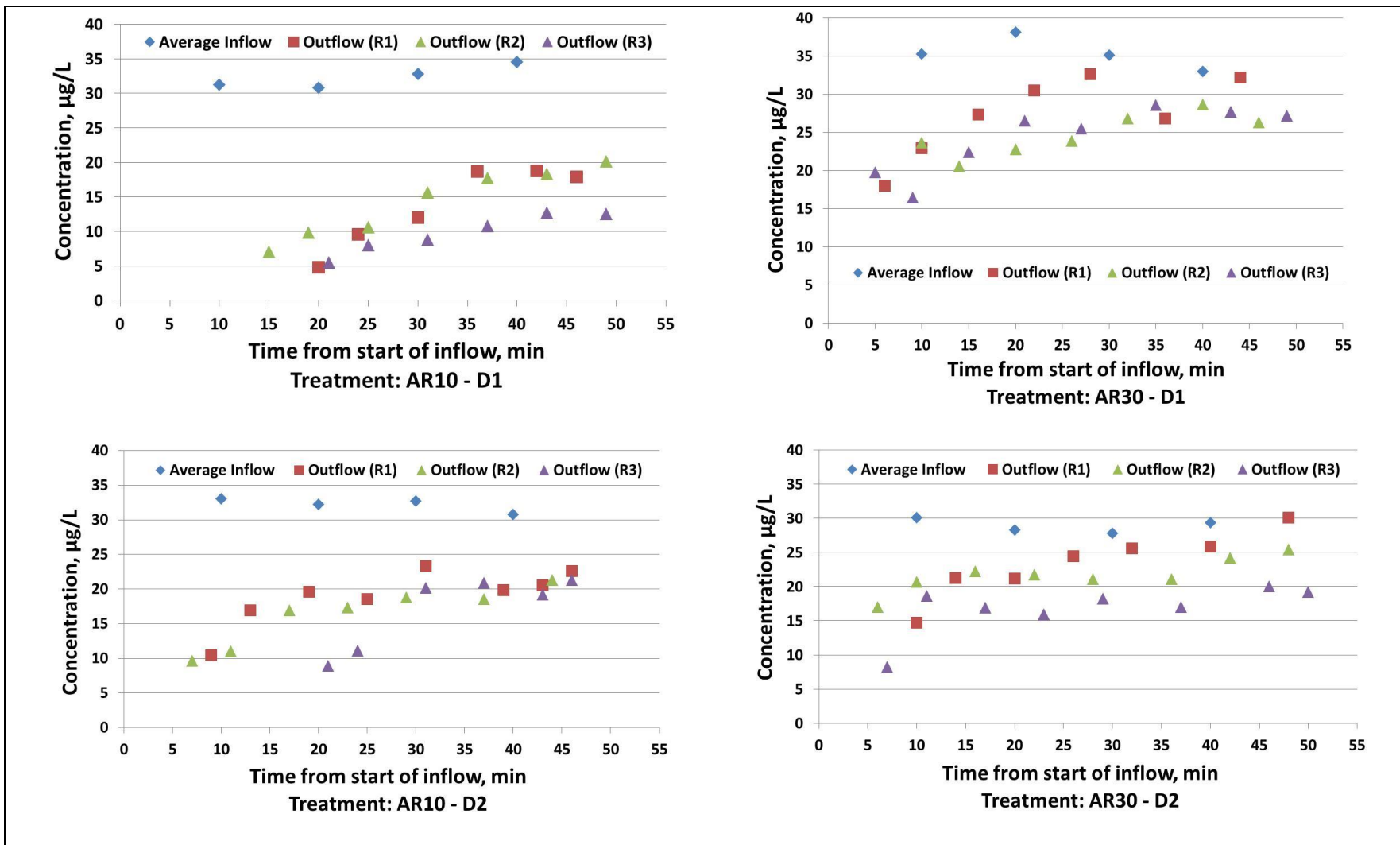


Figure 3.9: Dissolved linuron concentrations in inflow (average) and in outflow for each replication.

linuron concentrations. The extent to which decomposition, disintegration, and/or degradation of linuron had occurred could not be determined. As such, the results for linuron are estimates and the reader is advised to use caution when interpreting linuron data from this experiment. Dissolved concentration data presented in Figure 3.9 shows that the linuron concentrations were low when the outflow began from the strips and then the concentrations gradually increased with the rising limb of the hydrograph. Similar trends were observed for atrazine and chlorpyrifos as mentioned earlier.

Rainfall on the downstream end of the buffer strip has a smaller chance of infiltrating than the rainfall on the upstream end. Dissolved pesticide concentrations in outflow can simply be lower than the inflow concentrations due to dilution from rainfall. Calculations were made to determine a maximum dilution factor due to rainfall considering all of the water mass infiltrating was exclusively inflow only and not a mixture of inflow plus rainfall. In other words, how much of the outflow water mass is comprised of rainfall. In the case of AR10 strips for both D1 and D2 sediment type, the outflow water mass was lower than the mass of water applied from rainfall. Assuming infiltration of inflow only in this case, the outflow will have no dissolved concentration of the three pesticides. Detection of dissolved pesticide concentrations above zero indicates that the infiltrating water mass is a mixture of inflow and rainfall. In the case of AR30 strips, the outflow water mass exceeded the rainfall water mass applied for both D1 and D2 sediment types (Table 3.5). Using an average modified rainfall amount of 47.7 mm for the 45 min time interval for AR30-D1 strips and an average outflow amount of 197.4 mm, the maximum dilution factor calculates as 0.24 ( $47.7/197.4$ ). The corresponding dilution factor for AR30-D2 is 0.26 using the average modified rainfall

and outflow amounts. Using the average 0.25 rainfall dilution factor for AR30 strips, the pesticide concentrations will be reduced by 25% if all modified rainfall water mass was part of the outflow. Average inflow concentrations for chlorpyrifos, when multiplied by 0.75 (1 minus 0.25), show concentration values higher than the observed outflow concentrations. This indicates that sorption of chlorpyrifos to the organic matter in the strip is occurring along with dilution from rainfall. It could not be determined, due to the experimental setup, if the sorption was permanent or if both sorption and desorption of the pesticides were occurring. In the case of atrazine and linuron, the calculated outflow concentrations (due to dilution) were slightly higher than the observed outflow concentrations. This indicates that the sorption of atrazine and linuron may not be permanent and both sorption and desorption processes are occurring in the strips for these two pesticides.

### **3.4.3 Sediment mass retained**

Sediment mass retained in the buffer strips was determined by subtracting the output sediment mass from the input sediment mass. In making this calculation, sediment mass concentrations were determined and corrected, and are shown in Figure 3.10. Average inflow sediment mass concentrations were slightly above the design concentration of 2500 mg/L. Sediment mass concentrations in outflow were significantly lower in outflow when compared with inflow concentrations for all four treatments. Due to reduced flow velocity, sediment deposition occurs within the buffer strips resulting in sediment retention. Visual observations during the experiment showed that majority of fine sand (sediment type D1) settled in the first meter length of the buffer strip. Outflow from the strips used in sediment type D1, thus, consisted of none of the fine sand used as

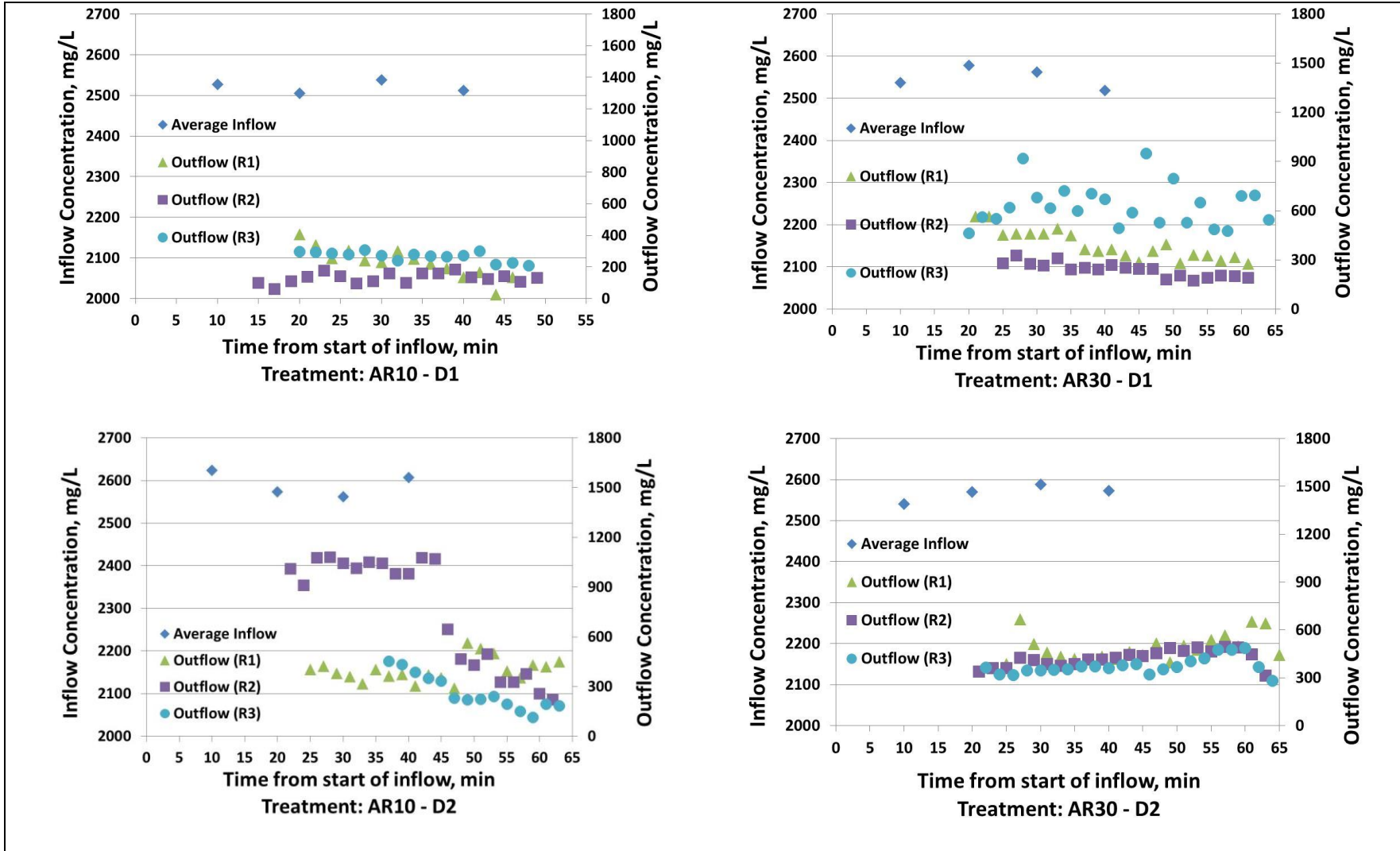


Figure 3.10: Sediment mass concentrations in inflow (average) and in outflow for each replication.

treatment. The majority of sediment in outflow was re-entrained from within the buffer strips and potentially at the exit point of the buffer strip. Potential existed for the installation of the covered outflow collector to disturb the soil at the exit point. This disturbance was minimized due to the covered outflow collector's installation into the wet soil. Furthermore, any disturbed particles and aggregates would have flushed out in the initial 2 min of the outflow prior to any sample collection. For sediment type D1, outflow concentrations for AR30 were slightly higher than AR10. For sediment type D2, outflow concentrations for AR30 were also slightly higher when compared to the outflow concentrations for AR10 with the exception of one replication (R2).

Sediment mass retention for sediment type D1 was 96.4% and 89.8% for the AR10 and AR30 strips, respectively (Table 3.6). Sediment mass retention for sediment type D2 was 92.8% and 90.2% for the AR10 and AR30 strips, respectively. For sediment type D1, the sediment mass retention is nearly 100%, as the majority of fine sand particles settled with the strips. Since sediment re-entrainment most likely occurred from within the strip, the sediment mass retention is lower than 100%. The AR30 area ratio strips received three times the flow volume, which likely increased the flow velocity. This is the most likely reason for AR30 sediment mass retention to be lower than for AR10 in case of sediment type D2. These differences in sediment mass retention were not significantly different in the two-tailed t-test at  $\alpha = 0.05$ .

#### **3.4.4 Sorbed pesticide concentration**

Sediment sorbed pesticide concentrations ( $C_{si}$  and  $C_{sout}$ ) were determined for inflow samples and for combined sediment mass outflow samples. Sediment mass in the outflow samples had to be combined to ensure enough pesticide mass was available for



Table 3.6: Sediment mass in inflow and outflow from the buffer strips, and percent sediment retained for two area ratios (AR10 and AR30) and two sediment types (D1 and D2).

| Replication        | Strip | Strip Area        | Sediment In <sup>1</sup> | Sediment Out | Sediment Retained <sup>3</sup> |
|--------------------|-------|-------------------|--------------------------|--------------|--------------------------------|
| #                  | #     | (m <sup>2</sup> ) | kg/ha <sup>2</sup>       | kg/ha        | (%)                            |
| AR10 - D1 - Rep 1  | 2     | 5.6               | 2690.8                   | 75.2         | 97.2%                          |
| AR10 - D1 - Rep 2  | 24    | 5.6               | 2736.3                   | 73.1         | 97.3%                          |
| AR10 - D1 - Rep 3  | 19    | 5.6               | 2669.7                   | 147.2        | 94.5%                          |
| Averages           |       | 5.6               | 2698.9                   | 98.5         | 96.4% b                        |
| Standard Deviation |       | 0.0               | 34.1                     | 42.2         |                                |
| AR30 - D1 - Rep 1  | 5     | 5.6               | 8130.8                   | 687.4        | 91.5%                          |
| AR30 - D1 - Rep 2  | 9     | 5.6               | 7999.0                   | 429.1        | 94.6%                          |
| AR30 - D1 - Rep 3  | 14    | 5.4               | 8536.6                   | 1431.0       | 83.2%                          |
| Averages           |       |                   | 8222.2                   | 849.1        | 89.8% b                        |
| Standard Deviation |       | 0.1               | 280.2                    | 520.2        |                                |
| AR10 - D2 - Rep 1  | 6     | 5.7               | 2720.3                   | 227.4        | 91.6%                          |
| AR10 - D2 - Rep 2  | 11    | 5.6               | 2811.6                   | 293.1        | 89.6%                          |
| AR10 - D2 - Rep 3  | 13    | 5.1               | 3138.5                   | 90.0         | 97.1%                          |
| Averages           |       | 5.5               | 2890.1                   | 203.5        | 92.8% b                        |
| Standard Deviation |       | 0.3               | 219.9                    | 103.7        |                                |
| AR30 - D2 - Rep 1  | 1     | 5.8               | 8140.5                   | 795.2        | 90.2%                          |
| AR30 - D2 - Rep 2  | 21    | 5.6               | 8217.2                   | 883.8        | 89.2%                          |
| AR30 - D2 - Rep 3  | 20    | 5.7               | 8012.7                   | 707.1        | 91.2%                          |
| Averages           |       | 5.7               | 8123.5                   | 795.4        | 90.2% b                        |
| Standard Deviation |       | 0.1               | 103.3                    | 88.3         |                                |

<sup>1</sup> Sediment mass is determined by multiplying sediment concentration with flow volume. Sediment mass in inflow for area ratio 30:1 is about 3 times the flow for 10:1 due to design of the experiment.

<sup>2</sup> Sediment mass converted to kg/ha over the strip area to account for variations in strip size.

<sup>3</sup> t-test H0: Mean (10:1) = Mean (30:1), no significant difference between the same letters at  $\alpha = 0.05$  in the two-tailed test.

extraction, detection, and quantification. These concentrations are tabulated in Appendix C along with the respective dissolved concentrations. Sorption coefficient (K) values (ratio of sorbed concentration to dissolved concentration) were determined and are tabulated in Appendix C.

Sorption coefficients for atrazine for the AR10-D1 treatment averaged in inflow as 1 (ranged from 0.5 to 1.5) and in outflow as 2 (ranged from 1 to 3). For AR30-D1 treatment, the respective averages and ranges were 1 (0.5 to 1.5) in inflow and 0 (0 to 1)

in outflow. Sorption coefficients for chlorpyrifos for the AR10-D1 treatment averaged in inflow as 27 (ranged from 11 to 47) and in outflow as 39 (ranged from 25 to 105). For AR30-D1 treatment, the respective averages and ranges were 14 (9 to 21) in inflow and 20 (10 to 25) in outflow. Linuron concentrations in sorbed phase were not detected both in inflow and outflow samples. As such, sorption coefficients could not be determined. Sediment type D1 tested at 0.4% for organic matter and thus is likely to have low K values. Using  $K_{oc}$  values from Table 3.2, a sorption coefficient for atrazine is 0.2 and chlorpyrifos is 14. Observed data for K values in inflow for both atrazine and chlorpyrifos is consistent with the tabulated values. This was not the case in outflow. Higher K values in outflow indicate a stronger sorption of the two pesticides to the sediment in outflow. As the majority of fine sand settled out in the buffer strips, high K values indicate that the sorption of the two pesticides to the re-entrained sediment and organic matter is occurring in the runoff.

In case of sediment type D2 (fine aggregates), atrazine sorption coefficients for the AR10-D2 treatment averaged 5 in the inflow (range from 3 – 9) and 19 in the outflow (ranged from 9 – 41). The respective averages and ranges for the AR30-D2 treatment were 4 (3 - 5) in inflow and 19 (8 to 30) in outflow. Sorption coefficients for chlorpyrifos for the AR10-D2 treatment averaged in inflow as 181 (ranged from 126 to 272) and in outflow as 375 (ranged from 138 to 953). For AR30-D2 treatment, the respective averages and ranges were 145 (109 to 212) in inflow and 288 (122 to 317) in outflow. Sediment type D2 tested at 4% for organic matter and thus is likely to have low K values. Using  $K_{oc}$  values from Table 3.2, a sorption coefficient for atrazine is 2.4 and chlorpyrifos is 143. For both atrazine and chlorpyrifos, adsorption coefficient values

were higher in outflow than in inflow. As fine aggregates are trapped in the buffer strips, some enrichment of sediment is likely to occur. This means that the outflow consists of even finer aggregates and fine clay particles, thus leading to higher sorption coefficient in outflow. Linuron concentrations in sorbed phase were not detected both in inflow and outflow samples for the sediment type D2 as well. Linuron has a higher  $K_{oc}$  value than atrazine. Lack of linuron sorption to both sediment types D1 and D2 indicates that linuron does not easily attach to sediment particles with low organic content.

### 3.4.5 Pesticide mass retained

Table 3.6 shows the total pesticide masses, which is a sum of the dissolved phase and sorbed phase pesticide masses for sediment type D1. Table 3.7 shows the same data for sediment type D2. For sediment type D1, the AR10 strips retained an average of 73.0% of total atrazine in comparison with AR30 strips which retained an average of 52.5%. This difference was statistically different in the two tailed t-test at  $\alpha = 0.05$ . The average sorbed atrazine mass was less than 0.5% of the total mass (dissolved plus sorbed) in inflow. In case of both area ratios, the strips retained over 95% of the sediment sorbed atrazine.

Average retention for total chlorpyrifos was 87.2% and 79.5% for the AR10-D1 and AR30-D1 treatments, respectively. These two averages were not statistically different at  $\alpha = 0.05$ . The average sorbed chlorpyrifos mass was about 6% of the total mass in inflow for AR10-D1 strips in comparison to about 3% for AR30 strips. This higher sorption of chlorpyrifos than atrazine is mainly due to higher sorption coefficient of chlorpyrifos ( $K_{oc} = 6070$ ) in comparison with atrazine ( $K_{oc} = 100$ ). Both treatment

strips retained about 97% of sediment sorbed chlorpyrifos. The difference between the two area ratios for the sorbed chlorpyrifos was not statistically different ( $\alpha = 0.05$ ). Average linuron retention in case of the AR10-D1 treatment was 80.5% in comparison with the AR30-D1 treatment where it was 53.9%. These two averages were not statistically different at  $\alpha = 0.05$ . In spite of the insignificant statistical difference for chlorpyrifos and linuron for the two area ratios, lower area ratio strips retained a greater percentage of total pesticide mass. This is likely due to increased infiltration at low flow depths. Infiltration is further increased by potential surface storage in case of switchgrass strips. Switchgrass tends to grow in clumps which are very stiff and dense, and such vegetation is likely to create a dam effect. This dam effect can create temporary surface storage conditions leading to increased infiltration. For sediment type D2 (Table 3.7), AR10 strips retained an average total mass of 71.5% for atrazine, 87.4% for chlorpyrifos, and 75.5% for linuron. In comparison, AR30 strips retained an average of 53.7% atrazine, 71.3% chlorpyrifos, and 57.5% linuron total mass, respectively. The difference between the two area ratio treatments for sediment type D2 for atrazine, chlorpyrifos, and linuron was statistically different in the two tailed t-test at  $\alpha = 0.05$ . Significantly different infiltration between the AR10-D1 and AR30-D2 strips is the likely reason for atrazine, chlorpyrifos, and linuron retentions to be significant as 70 to 100% of their mass was in the dissolved phase in input to the strips.

The sorbed phase for sediment type D2 comprised an average of 1.2% of total atrazine input mass and 30% of total chlorpyrifos input mass. This sorbed mass for atrazine and chlorpyrifos was 4 to 5 times higher than the sorbed mass for sediment type D1 in input to the buffer strips. If a spherical particle with radius  $r$ , volume  $V$ , and

Table 3.7: Percent retained and dissolved, sorbed, and total pesticide masses in inflow and outflow of the AR10 and AR30 buffer strips for sediment type D1.

| Replication       | Mass             | Atrazine Mass [1] |            |         | Chlorpyrifos Mass |         |         | Linuron Mass |        |         |
|-------------------|------------------|-------------------|------------|---------|-------------------|---------|---------|--------------|--------|---------|
|                   |                  | Dissolved [2]     | Sorbed [2] | Total   | Dissolved         | Sorbed  | Total   | Dissolved    | Sorbed | Total   |
| #                 | Inflow / Outflow | g/ha              | g/ha       | g/ha    | g/ha              | g/ha    | g/ha    | g/ha         | g/ha   | g/ha    |
| AR10 - D1 - Rep 1 | Inflow           | 20.1              | 0.057      | 20.2    | 2.7               | 0.256   | 3.0     | 36.4         | -      | 36.4    |
|                   | Outflow          | 4.0               | 0.002      | 4.0     | 0.4               | 0.006   | 0.4     | 5.6          | -      | 5.6     |
|                   | Retained (%)     | 79.9%             | 96.7%      | 80.0%   | 86.4%             | 97.6%   | 87.4%   | 84.6%        | -      | 84.6%   |
| AR10 - D1 - Rep 2 | Inflow           | 22.9              | 0.060      | 22.9    | 1.7               | 0.127   | 1.9     | 37.4         | -      | 37.4    |
|                   | Outflow          | 6.3               | 0.002      | 6.3     | 0.1               | 0.003   | 0.1     | 8.0          | -      | 8.0     |
|                   | Retained (%)     | 72.3%             | 97.2%      | 72.3%   | 95.8%             | 97.7%   | 95.9%   | 78.5%        | -      | 78.5%   |
| AR10 - D1 - Rep 3 | Inflow           | 18.2              | 0.048      | 18.2    | 1.8               | 0.057   | 1.9     | 23.7         | -      | 23.7    |
|                   | Outflow          | 6.2               | 0.004      | 6.2     | 0.4               | 0.005   | 0.4     | 5.4          | -      | 5.4     |
|                   | Retained (%)     | 66.0%             | 92.4%      | 66.1%   | 77.7%             | 91.5%   | 78.1%   | 77.3%        | -      | 77.3%   |
| Average           | Inflow           | 20.4              | 0.055      | 20.4    | 2.1               | 0.147   | 2.2     | 32.5         | -      | 32.5    |
|                   | Outflow          | 5.5               | 0.002      | 5.5     | 0.3               | 0.005   | 0.3     | 6.3          | -      | 6.3     |
|                   | Retained (%)     | 72.9% a [3]       | 95.6% a    | 73.0% a | 86.5% a           | 96.9% a | 87.2% a | 80.5%        | -      | 80.5% a |
| Standard Dev. [4] | Inflow           | 2.4               | 0.006      | 2.4     | 0.54              | 0.101   | 0.63    | 7.6          | -      | 7.6     |
|                   | Outflow          | 1.3               | 0.001      | 1.3     | 0.18              | 0.002   | 0.18    | 1.5          | -      | 1.5     |
|                   |                  |                   |            |         |                   |         |         |              |        |         |
| AR30 - D1 - Rep 1 | Inflow           | 81.2              | 0.136      | 81.4    | 10.6              | 0.334   | 10.9    | 110.5        | -      | 110.5   |
|                   | Outflow          | 39.2              | 0.007      | 39.2    | 2.7               | 0.011   | 2.7     | 56.1         | -      | 56.1    |
|                   | Retained (%)     | 51.8%             | 95.2%      | 51.8%   | 74.3%             | 96.8%   | 75.0%   | 49.3%        | -      | 49.3%   |
| AR30 - D1 - Rep 2 | Inflow           | 87.4              | 0.129      | 87.5    | 9.9               | 0.297   | 10.2    | 119.9        | -      | 119.9   |
|                   | Outflow          | 39.2              | 0.005      | 39.2    | 1.7               | 0.010   | 1.7     | 45.9         | -      | 45.9    |
|                   | Retained (%)     | 55.2%             | 96.1%      | 55.2%   | 82.9%             | 96.5%   | 83.3%   | 61.7%        | -      | 61.7%   |
| AR30 - D1 - Rep 3 | Inflow           | 87.1              | 0.153      | 87.2    | 7.9               | 0.340   | 8.3     | 109.7        | -      | 109.7   |
|                   | Outflow          | 43.2              | 0.005      | 43.2    | 1.6               | 0.021   | 1.6     | 54.8         | -      | 54.8    |
|                   | Retained (%)     | 50.4%             | 96.5%      | 50.5%   | 80.3%             | 93.8%   | 80.9%   | 50.1%        | -      | 50.1%   |
| Average           | Inflow           | 85.2              | 0.139      | 85.4    | 9.5               | 0.324   | 9.8     | 113.4        | -      | 113.4   |
|                   | Outflow          | 40.5              | 0.006      | 40.5    | 2.0               | 0.014   | 2.0     | 52.3         | -      | 52.3    |
|                   | Retained (%)     | 52.5% b           | 95.9% a    | 52.5% b | 79.0% a           | 95.6% a | 79.5% a | 53.9%        | -      | 53.9% a |
| Standard Dev.     | Inflow           | 3.5               | 0.012      | 3.5     | 1.4               | 0.024   | 1.4     | 5.7          | -      | 5.7     |
|                   | Outflow          | 2.3               | 0.0008     | 2.3     | 0.63              | 0.006   | 0.63    | 5.5          | -      | 5.5     |

[1] Mass of pesticides is converted to g/ha over the strip area, [2] Dissolved mass refers to pesticide mass retained with infiltration water. Sorbed mass refers to pesticide mass retained with Sediment, [3] Two-tailed t-test with unequal variances with H0(mean AR10) = H1(mean AR30); no significant difference between same letters at  $\alpha = 0.05$ , [4] Standard deviation for inflow and outflow masses.

Table 3.8: Percent retained and dissolved, sorbed, and total pesticide masses in inflow and outflow of the AR10 and AR30 buffer strips for sediment type D2.

| Replication       | Mass             | Atrazine Mass [1] |            |         | Chlorpyrifos Mass |         |         | Linuron Mass |        |         |
|-------------------|------------------|-------------------|------------|---------|-------------------|---------|---------|--------------|--------|---------|
|                   |                  | Dissolved [2]     | Sorbed [2] | Total   | Dissolved         | Sorbed  | Total   | Dissolved    | Sorbed | Total   |
| #                 | Inflow / Outflow | g/ha              | g/ha       | g/ha    | g/ha              | g/ha    | g/ha    | g/ha         | g/ha   | g/ha    |
| AR10 - D2 - Rep 1 | Inflow           | 36.5              | 0.631      | 37.1    | 4.6               | 1.6     | 6.2     | 35.7         | -      | 35.7    |
|                   | Outflow          | 13.1              | 0.075      | 13.2    | 1.1               | 0.160   | 1.2     | 11.3         | -      | 11.3    |
|                   | Retained (%)     | 64.1%             | 88.1%      | 64.5%   | 76.4%             | 90.3%   | 80.1%   | 68.3%        | -      | 68.3%   |
| AR10 - D2 - Rep 2 | Inflow           | 37.7              | 0.506      | 38.2    | 3.5               | 2.0     | 5.5     | 32.1         | -      | 32.1    |
|                   | Outflow          | 10.0              | 0.085      | 10.1    | 0.428             | 0.115   | 0.543   | 7.8          | -      | 7.8     |
|                   | Retained (%)     | 73.4%             | 83.2%      | 73.5%   | 87.8%             | 94.2%   | 90.1%   | 75.7%        | -      | 75.7%   |
| AR10 - D2 - Rep 3 | Inflow           | 34.1              | 0.336      | 34.4    | 3.3               | 2.0     | 5.3     | 38.9         | -      | 38.9    |
|                   | Outflow          | 7.9               | 0.051      | 8.0     | 0.301             | 0.052   | 0.353   | 7.0          | -      | 7.0     |
|                   | Retained (%)     | 76.7%             | 84.7%      | 76.8%   | 90.8%             | 97.4%   | 93.3%   | 82.0%        | -      | 82.0%   |
| Average           | Inflow           | 36.1              | 0.491      | 36.6    | 3.8               | 1.9     | 5.6     | 35.5         | -      | 35.5    |
|                   | Outflow          | 10.4              | 0.071      | 10.4    | 0.602             | 0.109   | 0.712   | 8.7          | -      | 8.7     |
|                   | Retained (%)     | 71.3% a [3]       | 85.6% a    | 71.5% a | 84.1% a           | 94.2% a | 87.4% a | 75.5% a      | -      | 75.5% a |
| Standard Dev. [4] | Inflow           | 1.8               | 0.16       | 1.9     | 0.69              | 0.19    | 0.51    | 3.4          | -      | 3.4     |
|                   | Outflow          | 2.6               | 0.02       | 2.6     | 0.42              | 0.05    | 0.47    | 2.3          | -      | 2.3     |
| AR30 - D2 - Rep 1 | Inflow           | 88.0              | 0.905      | 88.9    | 14.4              | 4.8     | 19.2    | 96.0         | -      | 96.0    |
|                   | Outflow          | 41.1              | 0.240      | 41.3    | 5.2               | 0.555   | 5.8     | 39.8         | -      | 39.8    |
|                   | Retained (%)     | 53.3%             | 73.5%      | 53.5%   | 63.8%             | 88.4%   | 69.9%   | 58.6%        | -      | 58.6%   |
| AR30 - D2 - Rep 2 | Inflow           | 92.5              | 0.939      | 93.5    | 12.9              | 4.9     | 17.8    | 95.7         | -      | 95.7    |
|                   | Outflow          | 44.1              | 0.346      | 44.5    | 4.1               | 0.380   | 4.5     | 44.8         | -      | 44.8    |
|                   | Retained (%)     | 52.3%             | 63.1%      | 52.4%   | 68.3%             | 92.2%   | 74.8%   | 53.2%        | -      | 53.2%   |
| AR30 - D2 - Rep 3 | Inflow           | 110.0             | 0.869      | 110.8   | 13.8              | 5.5     | 19.3    | 83.0         | -      | 83.0    |
|                   | Outflow          | 49.4              | 0.444      | 49.9    | 5.5               | 0.401   | 5.9     | 32.1         | -      | 32.1    |
|                   | Retained (%)     | 55.1%             | 48.9%      | 55.0%   | 60.2%             | 92.7%   | 69.4%   | 61.4%        | -      | 61.4%   |
| Average           | Inflow           | 96.8              | 0.904      | 97.7    | 13.7              | 5.1     | 18.8    | 91.6         | -      | 91.6    |
|                   | Outflow          | 44.9              | 0.343      | 45.2    | 4.9               | 0.445   | 5.4     | 38.9         | -      | 38.9    |
|                   | Retained (%)     | 53.7% b           | 62.0% a    | 53.7% b | 64.0% b           | 91.2% a | 71.3% b | 57.5% b      | -      | 57.5% b |
| Standard Dev.     | Inflow           | 11.6              | 0.04       | 11.6    | 0.73              | 0.38    | 0.83    | 7.4          | -      | 7.4     |
|                   | Outflow          | 4.2               | 0.10       | 4.3     | 0.74              | 0.10    | 0.78    | 6.4          | -      | 6.4     |

[1] Mass of pesticides is converted to g/ha over the strip area, [2] Dissolved mass refers to pesticide mass retained with infiltration water. Sorbed mass refers to pesticide mass retained with Sediment, [3] Two-tailed t-test with unequal variances with H0(mean AR10) = H1(mean AR30); no significant difference between same letters at  $\alpha = 0.05$ , [4] Standard deviation for inflow and outflow masses.

surface area  $A$  is divided into small spheres, such that the new spheres have a new radius equal to  $r/2$ , it yields eight small spheres to make up the same volume  $V$  of the original sphere but doubles the surface area. Further subdividing the small spheres into even smaller spheres such that the new radius is  $r/4$ , it yields sixty four smaller spheres to make up the same volume  $V$ , but the surface area is increased by four times of the original sphere. Greater organic matter content and larger surface area are the two main reasons for the sorbed atrazine and chlorpyrifos mass in input of the sediment type D2 (smaller sized aggregates) to be higher than sediment type D1 (larger sized particles). Difference in the sediment sorbed atrazine and chlorpyrifos mass for AR10 and AR30 strips was insignificant for both D1 and D2 sediment. This indicates that these two pesticides in the treatments were attached to particles which settled out irrespective to follow depth difference between AR10 and AR30 strips.

For weakly sorbed pesticides ( $K_{oc} < 100$ ), natural rainfall and simulated rainfall/runoff studies averaged by Arora et al. (2010) show that buffer strips will retain, on average, 61% of the total input mass. The corresponding number for moderately sorbed pesticides ( $100 < K_{oc} < 1,000$ ) is 63% retention, and 76% retention for strongly sorbed pesticides ( $K_{oc} > 1,000$ ), respectively. For sediment type D1, average retention of total atrazine mass between AR10 and AR30 strips was 62.8%, was 67.2% for linuron, and 83.3% for chlorpyrifos, respectively. In this case, atrazine data matched very well with the study averages as atrazine is the most common pesticide studied in the previously published buffer strip studies. Using the mathematical model (equation 2.4) and data from Table 2.3, the percent retention for atrazine is predicted as 46%, 51% for linuron, and 70% chlorpyrifos. Data for sediment type D1 shows higher percent

retentions as the mass sorbed to sediment was very low. The process of infiltration played a major role in atrazine, linuron, and chlorpyrifos retention in case of sediment type D1.

For sediment type D2, average retention of total atrazine mass between AR10 and AR30 strips was 62.6%, was 66.5% for linuron, and 79.4% for chlorpyrifos, respectively. In this case, atrazine data again matched very well with the study averages provided by Arora et al. (2010). The data for sediment type D2 shows higher percent retentions for linuron and chlorpyrifos for than the model predicted retentions (equation 2.4 and Table 2.3). Both processes of infiltration and sediment retention were important for linuron and chlorpyrifos retention in case of sediment type D2.

### **3.5 Conclusions**

This experiment represents a case of a rainfall-runoff simulation where runoff from the source area consists either only of fine sand particles or fine aggregates without sand. Runoff consisting of specific sized particles eliminated any complications in interpretation of results which otherwise would be the case with a study comprising of runoff with all sediment particle sizes mixed together. Under these specific experimental conditions, buffer strips, receiving only fine sand as sediment in inflow, retained 73% and 53% of atrazine mass for the 10:1 and 30:1 area ratios respectively. In case of buffer strips receiving sediment free of fine sand, atrazine retention was 72% and 54% respectively, for the two area ratios. The differences in retention for the two area ratios were significant ( $\alpha = 0.05$ ) indicating atrazine retention is reduced with an increased area ratio for either sediment type.



Chlorpyrifos and linuron retentions by the switchgrass buffer strips were 83% and 73%, for fine sand, averaged for both 10:1 and 30:1 area ratios. For fine aggregates, these averages for the two pesticides were 79% and 67%, respectively. The differences between the two treatments of area ratios were not significant for these two pesticides ( $\alpha = 0.05$ ). However, the trend was higher retention at lower area ratios for both pesticides for either sediment type.

Linuron mass, sorbed to fine sand and fine aggregates, was below the experimental detection limit conditions, indicating linuron transport is not affected by the processes of sedimentation in the buffer strips. Infiltration was the key factor for linuron retention in buffer strips. As reported in this study, the linuron mass retained in the buffer strips is an estimate and the readers are advised to interpret linuron results accordingly.

Differences in pesticide retention between fine sand and fine aggregates were not significant for atrazine and chlorpyrifos for both 10:1 and 30:1 area ratios. Even though fine aggregates had 4 to 5 times higher mass of the two pesticides sorbed to them in comparison with fine sand, buffer strips were able to retain a similar amount of total pesticide mass with either sediment type under both area ratio conditions. This indicates the atrazine and chlorpyrifos transport through the buffer strips was similar for the two sediment types studied under the given experimental conditions.

Sediment retention was over 90% for all four treatments studied in this experiment with no significant difference between sediment type and area ratios. Visual observations showed that fine sand particles settled within the first couple meters of the buffer strip length as expected. Fine aggregates, on the other hand, settled over the entire length of

the buffer strips. In the case of fine aggregates, results from this study indicate that the 5.6-m length of the buffer strips was adequate to retain atrazine and chlorpyrifos equally in comparison to fine sands.

Fine sand treatment results revealed that after the sediment from the inflow is retained in the buffer strip, the sediment transport capacity of the water flowing through the strip is not reduced to zero. Re-entrainment of sediment into the runoff from within the strip occurs. Source of this re-entrained sediment can be previously deposited sediment or the buffer strip soil itself. The exit point, where the runoff leaves the buffer strip, can be an additional source of re-entrainment, especially if the flow velocity increases due to slope changes resulting in erosion. Re-entrained sediment, in the runoff exiting the buffer strips, showed quantifiable amounts of atrazine and chlorpyrifos sorbed with it, however, the total mass of either pesticide was very small. These results indicate that the sorption of the pesticide to the sediment originating from within the buffer strips is possible.

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## CHAPTER 4. PESTICIDE RETENTION BY BUFFER STRIPS RECEIVING SIMULATED RUNOFF CONTAINING CLAY-SIZED PARTICLES

A paper written for submittal to the Transactions of the American Society of Agricultural and Biosystems Engineering (ASABE)

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### 4.1 Abstract

Clay-sized particles are highly mobile and their transport through the buffer strips can be influenced by several factors. Switchgrass buffer strips were studied to develop an understanding of these factors by evaluating the retention of three pesticides under two different source area to buffer area ratios, receiving simulated runoff containing clay-sized particles. Six strips, 1.0 m wide x 5.6 m long, received pesticide and clay-sized particles mixed simulated runoff, while six similar strips received simulated runoff containing no sediment and no pesticide. Two source area to buffer area ratios of 10:1 and 30:1 were studied under 6.35 cm/h steady-state rainfall conditions for two sediment types D3 (clay-sized particles) and D0 (no sediment). Atrazine, chlorpyrifos, and linuron were applied at the label recommended rates, using field formulations, to the simulated runoff water containing clay-sized particles. Switchgrass buffer strips retained, on average, 70.1% and 49.2% atrazine, 83.0% and 57.6% chlorpyrifos, and 71.2% and 50.4% linuron, respectively, for the two area ratios of 10:1 and 30:1 when receiving simulated runoff containing clay-sized particles. Results for atrazine and linuron were

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significantly different between the two area ratios. Results were not significantly different for chlorpyrifos. Results indicate that flow convergence can greatly reduce switchgrass buffer strips capacity to reduce atrazine and linuron from runoff containing clay-sized particles. Switchgrass buffer strips receiving no sediment in runoff showed an average of 113 and 72 mg/L sediment mass concentration in outflow for the 10:1 and 30:1 area ratio buffer strips, respectively. Sediment mass concentration results show that re-entrainment of sediment occurs in the buffer strips. The source of re-entrained sediment is the buffer strips soil and/or erosion at the exit point of the outflow from the strips. The infiltration water mass retention was 71.1% and 51.4%, respectively, for the lower and higher area ratios in strips receiving clay-sized particles in runoff. In comparison, the corresponding numbers for the two area ratio strips receiving no sediment in runoff were 67.9% and 47.0%, respectively. Clay-sized particles can penetrate into the soil pores and potentially reduce the infiltration rate of the soil. Lack of difference in infiltration between the two sediment types for the respective area ratios indicates that presence of clay-sized particles in simulated runoff did not impede infiltration. Results of this experiment indicate that infiltration is the key process for pesticide retention with clay-sized particles, as both the dissolved phase and the sorbed phase are carried with water.

## **4.2 Introduction**

Clay-sized particles are an integral part of the agricultural surface runoff occurring from croplands. Clay-sized particles are classified as a mix of particles and aggregates with sizes smaller than two micrometers ( $< 2 \mu\text{m}$ ; Theng and Yuan, 2008; Gee & Bauder, 1986). This class of particles and aggregates is a mixture of organic,

inorganic, and biological materials with sizes ranging from just less than 2  $\mu\text{m}$  to nanoscale ( $10^{-9}$  m) (Navortsky, 2003). One particular characteristic of clay-sized particles is the larger specific surface area in comparison with silt- (2 - 50  $\mu\text{m}$ ) and sand-sized (50 - 2000  $\mu\text{m}$ ) particles. A larger specific surface area for soil particles can have a greater amount of nutrients and pesticides sorbed to them. This can result in nutrient and pesticides concentrations to be higher in clay-sized particles than the silt- and sand-sized particles. The clay-sized particles are likely to travel long distances with agricultural runoff as they require very little energy to stay in suspension. The mass of clay-sized particles in the agricultural runoff is impacted by slope, tillage, and crop residue cover in the cropped areas. Rhoton et al. (2002) compared no-till and conventional tillage practices for their effect on runoff and soil loss from Midwestern and Southeastern United States silt loam soils. By comparing runoff, soil loss, bulk density of field soils (0-3.8 cm depth), and soil organic matter under the two tillage systems, authors concluded that long term cultivation and runoff results in preferential erosion of the fine silt and clay-sized particles.

Meyer et al. (1992) studied the size distributions of eroded sediment for twenty two soils in Mississippi, Iowa, and Alabama as undispersed sediment and secondly by dispersing the sediment. Runoff samples were obtained in late spring and summer from bare, initially dry, tilled fields which were otherwise under intensive cropping. Samples were collected after steady state runoff conditions had been achieved under simulated rainfall of 6.70 cm/h. The authors found that the sandy loam and loam textured soils produced eroded sediment similar to clayey soils under undispersed conditions. When results from the twenty two different soils were compared, undispersed eroded sediment



consisted of less than 20 percent clay irrespective of the clay content of the source soil. Data reported for Clarion Loam soil in the study showed size distribution of the eroded sediment as 1.8 percent ( $> 1000 \mu\text{m}$ ), 24.4 percent (250 - 1000  $\mu\text{m}$ ), 36.2 percent (36 - 250  $\mu\text{m}$ ), 15.2 percent (16 - 63  $\mu\text{m}$ ), 8.3 percent (4 - 16  $\mu\text{m}$ ), and 14.1 percent ( $< 4 \mu\text{m}$ ). Respective numbers reported for Tama Silty Clay Loam soil were 1.7%, 25.6%, 17.5%, 26.1%, 13.9%, and 15.2%. Data indicates that under typical 10,000 mg/L sediment mass concentrations of eroded sediment in runoff, less than 1500 mg/L corresponds to size smaller than 4  $\mu\text{m}$ .

The amount of clay-sized particles that can be naturally dispersed in the runoff from a source area can be influenced by tillage systems. Deizman et al. (1987) studied the size distributions of eroded sediment in agricultural runoff under no-till and conventional tillage systems. Simulated rainfall at 5.0 cm/h was applied on Groseclose silt loam plots with 3.7% organic matter and 1.39 g/cm<sup>3</sup> bulk density. Approximately 100 mm of rainfall was applied over each plot as 50 mm for 60 min (dry run), a 24-h delay, 25 mm for 30 min (wet run), a 30 min delay followed by 25 mm for 30 min (very wet run). Plots (0.01 ha) under no-till had slope ranging between 8.6% to 15.1%, and residue level ranging between 1.1 to 3.4 kg/ha. The corresponding numbers for conventional tillage were 8.5% to 9.7% for slope and zero kg/ha as residue level. Runoff samples were collected and analyzed for sediment size distributions. Under undispersed conditions of the eroded sediment, averaged for three runs, no-till plots showed size distribution of 2.5% aggregates larger than 2000  $\mu\text{m}$ , 39.8% aggregates between 50 - 2000  $\mu\text{m}$ , 52.4% aggregates between 2 - 50  $\mu\text{m}$ , and 5.3% aggregates smaller than 2  $\mu\text{m}$ . Conventional tillage plots showed 2.2% aggregates larger than 2000  $\mu\text{m}$ , 29.9%

aggregates (50 - 2000  $\mu\text{m}$ ), 60.0% aggregates (2 - 50  $\mu\text{m}$ ), and 7.9% (< 2  $\mu\text{m}$ ), respective, for the undispersed eroded sediment size distribution. Data indicates that under typical 10,000 mg/L sediment mass concentrations of eroded sediment in runoff, less than 800 mg/L corresponds to size smaller than 2  $\mu\text{m}$ .

Wu et al. (2003) evaluated the effects of size distribution of eroded sediment on propiconazole ( $K_{oc} = 650$ , Hornsby et al., 1996) lost from agricultural farm fields in Norway. Runoff samples were collected from the entry point of a farm pond which received eroded sediment from an adjacent farm field. In the undispersed samples of the eroded sediment, aggregates with size between 250 to 2000  $\mu\text{m}$  comprised of 46.6% of sediment by weight, whereas the clay-sized particles (< 2  $\mu\text{m}$ ) comprised only 3.8% of sediment. This fraction of sediment accounted for 20% of total sediment sorbed propiconazole. Authors concluded that the high mobility even under low flow velocity conditions makes clay-sized particles important transporters of sediment bound pesticides in runoff suspensions.

Buffer strips are conservation practices installed on the agricultural landscapes in between the cropped fields and runoff receiving water bodies. The intent of such placement is to intercept runoff leaving the farm fields and alleviate its impact on the water bodies. All of the studies reviewed and summarized by Arora et al. (2010) have looked at sediment sorbed pesticide transport as lumped together for all eroded sediment particles. None of the studies have evaluated pesticide transport through buffer strips with clay-sized particles only. Due to the size of the material comprising the clay-sized particles, little trapping in buffer strips is generally theorized. Research needs to be performed to evaluate the pesticide trapping efficiency of the buffer strips for naturally

dispersed clay-sized particles in the runoff. This research needs to be carefully designed and evaluated as the clay-sized particles ( $< 2 \mu\text{m}$ ) may be re-entrained into the runoff from within the buffer strip.

Studies, summarized by Arora et al. (2010), indicate that flow convergence occurs in buffer strips due to changes in micro-topography. Source area to buffer area ratios, ranging between 10:1 to 50:1, are likely to occur under realistic applications of buffer strips. As flow converges, it increases the flow volume passing through a certain point within the buffer strip. Changes in micro-topography can cause flow velocities to change within the buffer strips. Such changes in flow volume and velocities can impact the retention of clay-sized particles, and subsequently pesticide mass retained by the buffer strips. This impact needs to be quantified, especially to determine what occurs in lower part of the buffer strips if heavier particles and aggregates settle in the upper half. Obtaining runoff containing only of clay-sized particles is only possible under simulated conditions. Clay-sized particles, can thus, be harvested from the source area soil and used in simulated runoff entering the buffer strips. A simulated rainfall/runoff experiment was thus conducted with the following objectives:

1. Evaluate the retention of pesticides in buffer strips receiving runoff containing naturally dispersed clay-sized particles ( $< 2 \mu\text{m}$ );
2. Compare sediment mass retention in buffer strips from runoff containing clay-sized particles ( $< 2 \mu\text{m}$ ) with runoff containing no sediment/pesticide;
3. Evaluate the impact of flow convergence on pesticide retention with clay-sized particles by performing the experiment under simulated source area to buffer area ratios of 10:1 and 30:1.

### 4.3 Materials and Methods

Clay-sized particles from the source soil (Clarion 138C) were obtained by setting a water column on a levelled flatbed trailer. A circular poly tank with 4542 L capacity served as the container for setting up the water column (Figure 4.1). Water, as used on the farm for chemical applications, was pumped into the circular poly tank. The tank was left undisturbed for 24 h in a machine shed on the levelled flatbed trailer to allow any turbulence in the water to subside. Secondly, this did not allow for any hot and cold water currents to develop due to the differential solar heating of the poly tank which could hinder fine sediment/particle settling. A known amount of source soil (Clarion 138C), ground and sieved through 2000  $\mu\text{m}$  sieve, was added to a known amount of water and agitated with a heavy duty pump for 30 min. Approximately 50 kg of ground and sieved soil was added to 454 L of water in a 682 L cylindrical poly tank. The agitated sediment-water slurry was allowed to stand for 5 min to allow heavier sediment and aggregates to settle out. The remaining sediment-water mixture was then added to the water surface of the circular poly tank containing 3400 L water with a specially designed long arm applicator at a rate of 26.5 L per min. After the sediment-water mixture was applied to the water surface, the time for sediment particles ( $> 2 \mu\text{m}$ ) to settle to below the bottom 15 cm of the water column was calculated. This calculation was based on water temperature and the height of the water column in the tank, including the increase in height of water column due to sediment-water mixture addition. After the time to settle sediment particles larger than 2  $\mu\text{m}$  had elapsed, a specially designed siphon constructed from 10.1 cm PVC pipe was placed in the bottom of tank. The siphon consisted of a pivoting arm with multiple inlets drilled into the PVC pipe such that

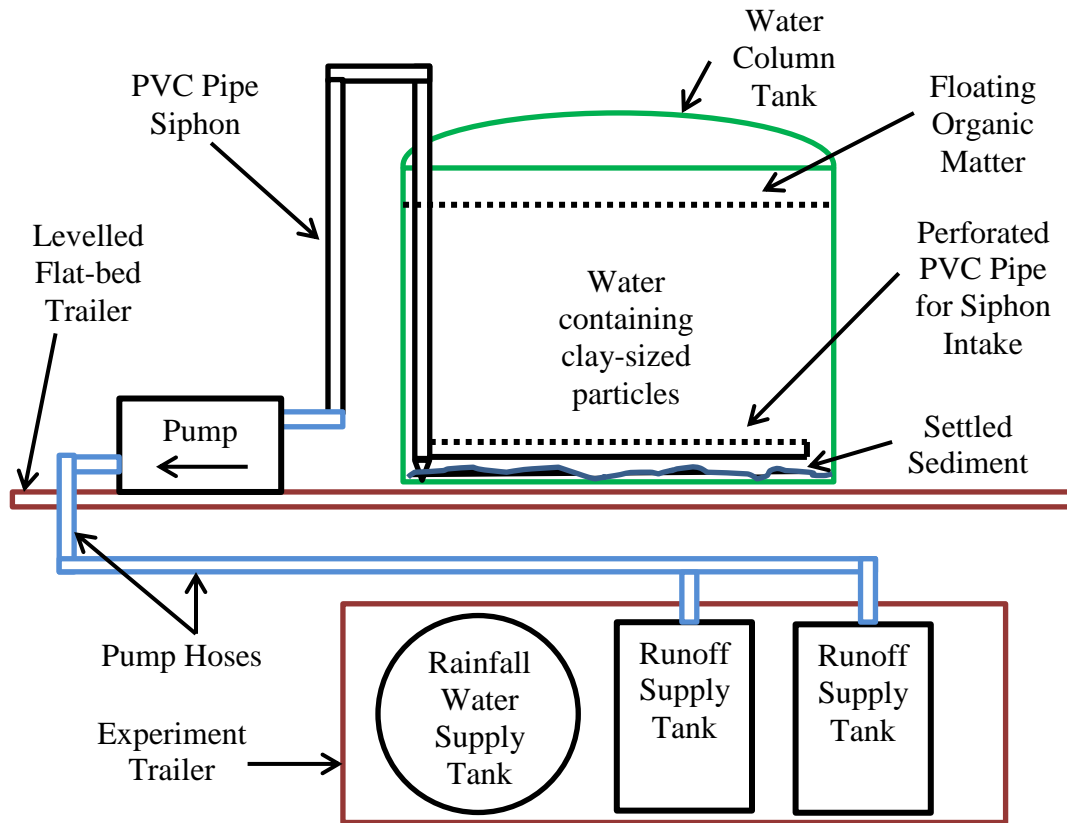


Figure 4.1: Schematic showing the poly tank used to setup the water column on a levelled flat-bed trailer to harvest clay-sized particles (not to scale).

the inlet points were located at 25 cm height from the bottom of the tank. Approximately 2700 L of water containing the clay fraction was siphoned for use in the experiment as simulated runoff from source area. This runoff comprised of sediment class D3 treatment in the experiment.

Two herbicides, atrazine and linuron, and an insecticide, chlorpyrifos, were studied in this experiment and are listed in Table 3.2. Pesticides were applied to the siphoned off water containing clay-sized particles at the label recommended rates of 2.8 kg active ingredient (a.i.) per hectare for atrazine, 2.2 kg a.i. per hectare for linuron, and

1.1 kg a.i. per hectare for chlorpyrifos. A known volume of each of the three pesticides was obtained from the commercially available formulations for use in the experiment. Amount of pesticide mass used for application was similar to the ones used for the experiment in Chapter 3.

Re-entrainment of clay-sized particles is possible as runoff flows through a buffer strip. To estimate how much of clay-sized particles ( $< 2 \mu\text{m}$ ) can potentially be re-entrained into runoff, water containing no sediment was used as runoff entering the buffer strips for comparison. No pesticides were applied to this water. This runoff with no sediment and no pesticide comprised of sediment type D0 treatment in the experiment.

The experiment was conducted at the same location as described in Chapter 3. Twelve switchgrass buffer strips, separate from the ones used for the experiment described in Chapter 3, but located on the same site, were randomly selected for use in this experiment. Six buffer strips represented the sediment type D0 treatment with three replications each for the 10:1 and 30:1 source area to buffer area ratios. The other six buffer strips represented the sediment type D3 treatment with three replications each for the 10:1 and 30:1 source area to buffer area ratios.

Dimensions of the switchgrass buffer strips were 1.0 m wide x 5.6 m long, similar to buffer strips used in the previous experiment. Establishment and maintenance of the buffer strips was performed in the similar manner as explained in Chapter 3. Type of tiller species and population was determined by counting the tiller species within the randomly tossed  $0.05 \text{ m}^2$  wooden rectangle (0.30 m x 0.17 m) at three different locations along the length of the VBS and counting the tillers within the frame area. The same procedure, as used in the previous experiment to calculate tiller densities, was used.

Vegetation in strips used for treatment with no sediment (D0) was 53% switchgrass (*Panicum virgatum*), 44% fox tail (*Setaria lutescens*), and 3% other. The average tiller population was determined to be 10.64 M tillers/ha. The corresponding numbers for the vegetation in strips used for the clay treatment (D3) was 45% switchgrass (*Panicum virgatum*), 53% fox tail (*Setaria lutescens*), and 2% other. The average tiller population was determined to be 8.75 M tillers/ha.

The same experimental procedures were used for conducting the experiment as explained in Chapter 3. Methodology for collecting inflow, outflow, and rainfall samples; measuring inflow, outflow, and rainfall rates; and the laboratory procedures for analysis of samples were also same. One key point of the analytical methods was the separation of the liquid from the wet sediment in the runoff samples. Nitrocellulose membrane filters, used for liquid separation, had an opening size of 0.45  $\mu\text{m}$ . Thus, the sediment type D3 represents particles with size ranging from 0.45  $\mu\text{m}$  to 2  $\mu\text{m}$ . Mathematical procedures used for determining infiltration, sediment deposition, and pesticide mass retention, both in sorbed and dissolved phase, were the same as explained in Chapter 3.

#### **4.4 Results and Discussion**

This experiment was conducted as a second part of the dual experiment performed in September 2013. A trial experiment was conducted using an inflow flow rate of 11.0 Lpm on a separate part of switchgrass area with dry antecedent soil moisture conditions. This trial experiment failed to produce any outflow from the strip area over the 45 min experimental time period. As such it was decided to irrigate the buffer strips prior to conducting the experiment. Without this irrigation, it would not have been feasible to

conduct the experiment. Table 4.1 lists the durations and amounts of irrigation along with strip dimensions. Each strip consumed variable amount of irrigation water before the water showed up at the downstream end. The duration of irrigation was variable as well. The irrigation water was gravity applied from the reservoir tank and the flow rate varied due to change in height of water in the tank. The flow rate observed for irrigation water ranged between 9.2 to 11.2 Lpm. The irrigation was stopped after the water showed up at the exit point of the buffer strips as it allowed for uniform irrigation over the strip area. Secondly, it allowed for the installation of the covered outflow collector into the wet soil without disturbing the soil at the exit point of the buffer strips. This disturbance of the soil would have been significantly higher if the collector had been installed into the dry soil causing the exit point to act as a source of particles into the outflow from the strips. The infiltration rate, over the duration of the irrigation applied and over the strip area, ranged from 10.0 to 11.6 cm/h.

#### **4.4.1 Infiltration water mass ( $M_x$ )**

Table 4.2 shows the mass balance for percent infiltration for the three replications each of the 10:1 (AR10) and 30:1 (AR30) area ratios; and the D0 and D3 sediment types. The percentage of infiltration water mass for the AR10 buffer strips was similar, with an average of 67.9% for D0 strips, when compared with the same area ratio buffer strips for D3 strips (average of 71.1% for three strips). There was no statistically significant difference between the two averages at  $\alpha = 0.05$  in the two-tailed t-test. For the AR30 strips, D0 strips had an average infiltration water mass retention of 51.4% when compared with the D3 strips with an average of 47.0%. There was no statistically significant difference between these two averages. Thus, the presence of clay-sized



particles in the runoff did not change the infiltration capacity of the strips within a given area ratio. As the clay-sized particles are fine, they are expected to penetrate the soil surface through the soil pores and can potentially reduce the infiltration capacity of the soil as the soil pores get plugged. This did not happen in the case of the strips receiving simulated runoff with clay-sized particles. The average infiltration percentage was statistically significant when the AR10 and AR30 strips were compared for both the D0 and D3 sediment type at  $\alpha = 0.05$  in the two tailed t-test. Within the sediment type, the trend was a greater infiltration with a lower area ratio. Flow difference, as the AR30 strips had three times the design inflow as that of the AR10 strips, is the reason why infiltration percentages are lower for AR30 strips. Time period, when both rainfall and inflow were simultaneous inputs into the buffer strips, was considered to calculate the modified rainfall amount (Table 4.2). During this time period of 45 min, the percent infiltration was reduced by using modified rainfall, but the trends remained the same. This indicates that rainfall during the first 15 min wetting period did not affect the infiltration capacity. The differences among area ratios and among sediment types stayed the same as explained earlier.

Flow rates (average inflow and outflow for each replication) and average rainfall rates for the AR10 strips are presented graphically as a function of time in Figure 4.2. Travel time, time for the runoff to travel the 5.6 m long buffer strips, averaged 10 min (ranged from 9 to 14) and 17min (ranged from 9 to 25) for AR10-D0 and AR10-D3 treatments, respectively. The travel times for the AR30 strips were 4 min (range 4 to 4) and 4 min (range 3 to 5) for the D0 and D3 treatments, respectively. Larger flow volume

Table 4.1: Buffer strip dimensions and area, amount and duration of irrigation applied for each replication of two area ratios and sediment types.

| Replication        | Sediment<br>Type | Strip<br># | Run<br># | Date      | Strip         |              |                           | Irrigation    |              |
|--------------------|------------------|------------|----------|-----------|---------------|--------------|---------------------------|---------------|--------------|
|                    |                  |            |          |           | Length<br>(m) | Width<br>(m) | Area<br>(m <sup>2</sup> ) | Amount<br>(L) | Duration (h) |
| AR30 - D0 - Rep 1  | None             | 4          | 1        | 9/10/2013 | 5.6           | 1.0          | 5.8                       | 4281          | 7.0          |
| AR30 - D0 - Rep 2  | None             | 12         | 10       | 9/16/2013 | 5.6           | 1.0          | 5.5                       | 3856          | 6.0          |
| AR30 - D0 - Rep 3  | None             | 15         | 23       | 10/2/2013 | 5.7           | 1.0          | 5.6                       | 2400          | 4.0          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.6                       | 3512          | 5.7          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.1                       | 986           | 1.5          |
| AR10 - D0 - Rep 1  | None             | 3          | 2        | 9/10/2013 | 5.6           | 1.0          | 5.8                       | 4129          | 7.0          |
| AR10 - D0 - Rep 2  | None             | 10         | 8        | 9/13/2013 | 5.6           | 1.0          | 5.6                       | 4080          | 6.5          |
| AR10 - D0 - Rep 3  | None             | 18         | 24       | 10/2/2013 | 5.6           | 1.0          | 5.6                       | 2453          | 4.0          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.6                       | 3554          | 5.8          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.1                       | 954           | 1.6          |
| AR10 - D3 - Rep 1  | Clay             | 23         | 12       | 9/20/2013 | 5.6           | 1.0          | 5.4                       | 1847          | 3.0          |
| AR10 - D3 - Rep 2  | Clay             | 7          | 16       | 9/24/2013 | 5.7           | 1.0          | 5.8                       | 3571          | 6.0          |
| AR10 - D3 - Rep 3  | Clay             | 16         | 22       | 10/1/2013 | 5.7           | 1.0          | 5.6                       | 1671          | 3.0          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.6                       | 2363          | 4.0          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.2                       | 1050          | 1.7          |
| AR30 - D3 - Rep 1  | Clay             | 22         | 11       | 9/20/2013 | 5.6           | 1.0          | 5.4                       | 3196          | 5.5          |
| AR30 - D3 - Rep 2  | Clay             | 8          | 15       | 9/24/2013 | 5.6           | 1.0          | 5.9                       | 3937          | 6.0          |
| AR30 - D3 - Rep 3  | Clay             | 17         | 21       | 10/1/2013 | 5.6           | 1.0          | 5.8                       | 3414          | 5.5          |
| Average            |                  |            |          |           | 5.6           | 1.0          | 5.7                       | 3516          | 5.7          |
| Standard Deviation |                  |            |          |           | 0.0           | 0.0          | 0.3                       | 381           | 0.3          |

Table 4.2: Inflow, outflow, rainfall, and infiltration for two area ratios (AR10 and AR30) and two sediment types (D0 and D1).

| Replication #        | Strip # | Area (m <sup>2</sup> ) | Inflow <sup>1</sup> (mm) | Outflow (mm) | Rainfall (mm) | Infiltration (%) | Modified Rainfall <sup>2</sup> (mm) | Modified Infiltration <sup>2</sup> (%) |
|----------------------|---------|------------------------|--------------------------|--------------|---------------|------------------|-------------------------------------|--|
| AR10 - D0 - Rep 1    | 3       | 5.8                    | 104.4                    | 57.2         | 63.9          | 66.0%            | 47.9                                | 62.5%                                  |
| AR10 - D0 - Rep 2    | 10      | 5.6                    | 108.1                    | 59.7         | 64.2          | 65.3%            | 48.2                                | 61.8%                                  |
| AR10 - D0 - Rep 3    | 18      | 5.6                    | 110.5                    | 48.4         | 63.1          | 72.1%            | 47.4                                | 69.4%                                  |
| Average <sup>3</sup> |         | 5.6                    | 107.7                    | 55.1         | 63.8          | 67.9% a          | 47.8                                | 64.6% a                                |
| Standard Deviation   |         | 0.1                    | 3.1                      | 6.0          | 0.6           |                  | 0.4                                 |  |
| AR30 - D0 - Rep 1    | 4       | 5.8                    | 309.5                    | 179.5        | 64.5          | 52.0%            | 48.4                                | 49.8%                                  |
| AR30 - D0 - Rep 2    | 12      | 5.5                    | 323.8                    | 174.6        | 63.1          | 54.9%            | 47.4                                | 53.0%                                  |
| AR30 - D0 - Rep 3    | 15      | 5.6                    | 322.3                    | 203.4        | 63.5          | 47.3%            | 47.6                                | 45.0%                                  |
| Average              |         | 5.6                    | 318.5                    | 185.8        | 63.7          | 51.4% b          | 47.8                                | 49.3% b                                |
| Standard Deviation   |         | 0.1                    | 7.9                      | 15.4         | 0.7           |                  | 0.5                                 |  |
| AR10 - D3 - Rep 1    | 23      | 5.4                    | 112.8                    | 53.1         | 64.8          | 70.1%            | 48.6                                | 67.1%                                  |
| AR10 - D3 - Rep 2    | 7       | 5.8                    | 106.5                    | 27.8         | 64.3          | 83.7%            | 48.3                                | 82.0%                                  |
| AR10 - D3 - Rep 3    | 16      | 5.6                    | 108.0                    | 69.7         | 64.8          | 59.6%            | 48.6                                | 55.5%                                  |
| Average              |         | 5.6                    | 109.1                    | 50.2         | 64.6          | 71.1% a          | 48.5                                | 68.1% a                                |
| Standard Deviation   |         | 0.2                    | 3.3                      | 21.1         | 0.2           |                  | 0.2                                 |  |
| AR30 - D3 - Rep 1    | 22      | 5.4                    | 333.9                    | 203.1        | 63.5          | 48.9%            | 47.6                                | 46.8%                                  |
| AR30 - D3 - Rep 2    | 8       | 5.9                    | 305.3                    | 152.1        | 63.5          | 58.8%            | 47.6                                | 56.9%                                  |
| AR30 - D3 - Rep 3    | 17      | 5.8                    | 310.5                    | 249.5        | 63.5          | 33.3%            | 47.6                                | 30.3%                                  |
| Average              |         | 5.7                    | 316.6                    | 201.6        | 63.5          | 47.0% b          | 47.6                                | 44.7% b                                |
| Standard Deviation   |         | 0.3                    | 15.2                     | 48.7         | 0.0           |                  | 0.0                                 |  |

<sup>1</sup> Flow converted to mm of water depth over the strip area. Flow for area ratio 30:1 is about 3 times the flow for 10:1 due to design of the experiment.

<sup>2</sup> Rainfall for the first 15 min of the experiment excluded from total rainfall for a modified infiltration mass balance.

<sup>3</sup> t-test H0: Mean (10:1) = Mean (30:1), no significant difference between the same letters at  $\alpha = 0.05$  in the two-tailed test.

is the reason why these times were quicker for AR30 strips when compared to AR10 strips. All four hydrographs for outflow in Figure 4.1 show that no outflow was detected with rainfall alone during the wetting period. The rising limbs of the hydrographs show a decrease in the infiltration capacity of the buffer strip soil. With time, the infiltration capacity did reach somewhat of a steady state condition, but did not reach a constant value. The recessional limbs of the hydrographs show a sharp decrease in outflow after the rainfall and inflow were stopped, when compared with the rising limbs. This sharp decrease indicates that potentially two processes are occurring, surface storage on the strips and infiltration, to rapidly reduce the outflow to zero.

A steady-state condition can be considered for the last 10 min of the rainfall. Considering only the inflow, rainfall, and outflow for these 10 min, infiltration calculated as 45.3% for AR10-D0, 49.8% for AR10-D3, 48.9% for AR30-D0, and 32.4% for AR30-D3 treatments, respectively. The trend of higher infiltration with lower area ratio in these 10 min was observed for sediment type D3. The trend was reversed for sediment type D0 indicating that infiltration capacity for AR30-D0 strips was higher than the AR10-D0 strips for these 10 min.

#### **4.4.2 Dissolved pesticide concentration ( $C_{out}$ )**

Chlorpyrifos and linuron were not detected in both the inflow and outflow samples for treatments AR10-D0 and AR30-D0. This was expected as no pesticide was added to these two treatments. Trace amounts of atrazine was detected in inflow and outflow samples for these two treatments, but was below the quantitation limits. Atrazine was not added to the inflow water or on the plots for these two treatments. Poly-tanks, flow-lines, and pumps were the same when used for pesticide treatments and when used for the

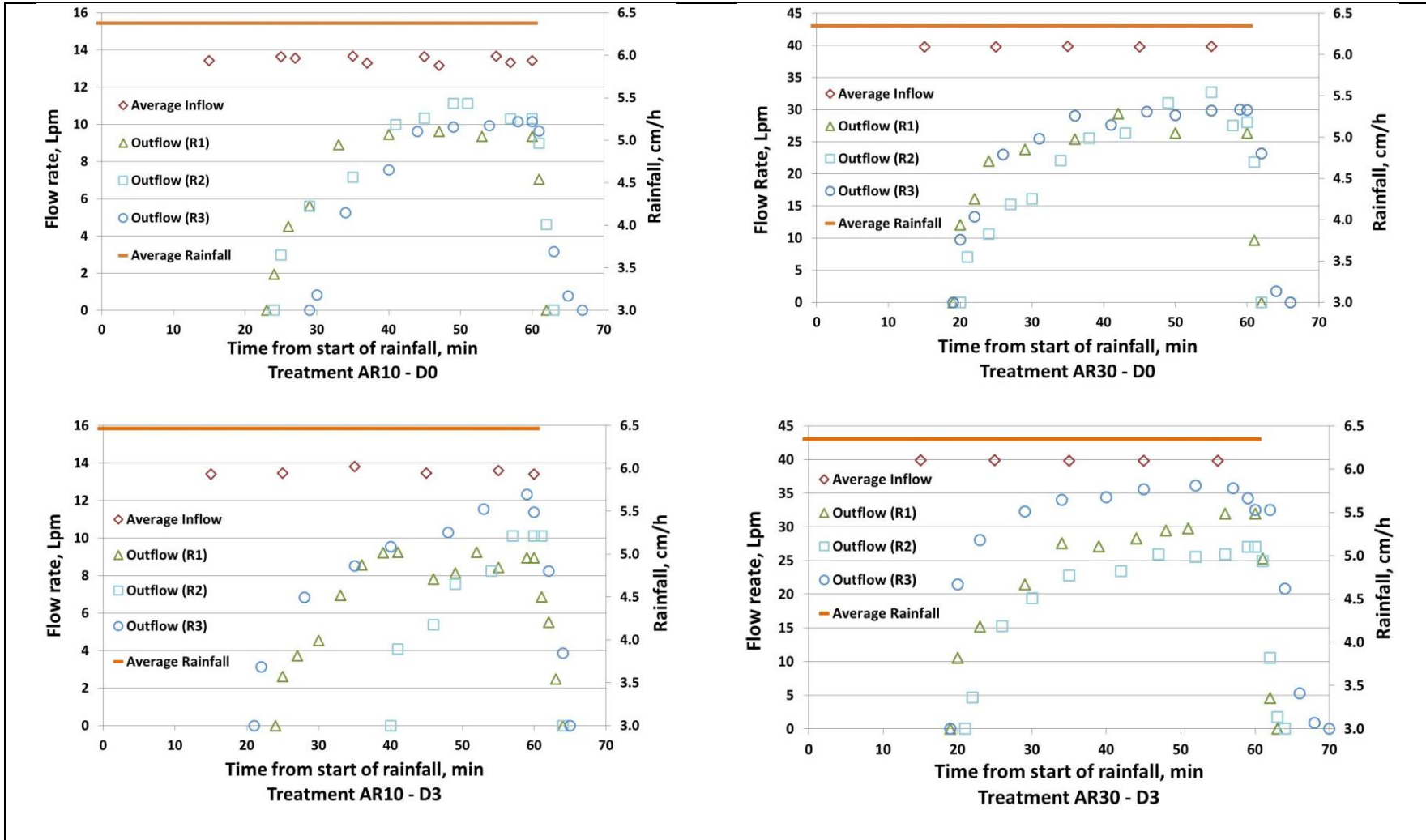


Figure 4.2: Average inflow and outflow for three replications, and average rainfall for AR10-D0, AR30-D0, AR10-D3, and AR30-D3 treatments.

treatment containing no pesticide. All tanks, flow-lines, and pumps were thoroughly rinsed after each run. Detection of atrazine in all inflow samples, for two of the replications, indicates some atrazine is desorbing from the flow lines. Atrazine would have sorbed to the flow line material in the previous runs when pesticide applied sediment was used in the treatment.

For sediment type D3 treatments, atrazine, chlorpyrifos, and linuron dissolved concentrations are plotted as a function of time in Figures 4.3, 4.4, and 4.5, respectively. Atrazine concentrations for the AR10 treatment strips were lower in outflow than inflow. Only one of the three replications showed the trend of increasing concentration with the rising limb of the hydrograph (Figure 4.3). This trend was not visible in any of the three replications in the AR30-D3 treatment for atrazine. Rainfall dilution and sorption to the buffer strip soil are likely to cause the outflow concentrations to be lower earlier than later in the hydrograph. No specific trends in the outflow concentrations indicate negligible effects of these two processes on the outflow concentrations for atrazine. Dissolved chlorpyrifos concentrations in inflow were higher than outflow for both AR10 and AR30 treatment strips (Figure 4.4). Outflow concentrations for both treatments showed an increase with the rising limb of the hydrograph before reaching somewhat of a steady-state concentration. This indicates that both rainfall and sorption processes reached steady-state condition for chlorpyrifos.

Two peaks were observed on the chromatographs when the linuron concentrations in toluene were processed for the accurate-mass ions and for the total ion current. Linuron standards at different concentrations showed the presence of the same two peaks at the same time on the chromatogram. The masses for the two peaks were added

together to determine the linuron concentrations, although the  $R^2$  value for the concentration for the added mass was low (0.78). The reasons for presence of two peaks could be decomposition, disintegration, and/or degradation of linuron into a secondary compound similar in structure to linuron. The two peaks, when processed individually, had even lower  $R^2$  than the masses of the peaks added together. As such, the results for linuron are estimates and the reader is advised to use caution when interpreting linuron data from this experiment. Linuron concentrations in the dissolved phase for sediment type D3 are shown in Figure 4.5. Outflow concentrations for both AR10 and AR30 strips were lower than the inflow strips. Outflow concentrations for AR30, as in case of atrazine and chlorpyrifos, did show the same trend of gradually increasing with the rising limb of the hydrograph.

A rainfall dilution factor can be calculated for the last 10 minutes of the inflow hydrograph, assuming steady-state conditions exist during this time period. A complete mixing of the rainfall water will occur into the inflow, and thus, the infiltration water will be a complete mix of rainfall water and inflow. The dilution factor, in this case of last ten minutes, will be a ratio of inflow divided by the sum of inflow and rainfall. This dilution factor is calculated as 0.69 for the AR10 strips, and as 0.87 for the AR30 strips. Thus, the outflow pesticide concentrations, mathematically, will be equal to the inflow concentrations reduced by 31% for the AR10 strips, and by 23% for the AR30 strips. Table 4.3 shows the average inflow, calculated outflow, and the average outflow pesticide concentrations for the last ten minutes of the rainfall. In the case of dissolved chlorpyrifos concentrations for the AR10-D3 strips, measured outflow concentrations were lower by 45% than the calculated outflow concentrations. The corresponding

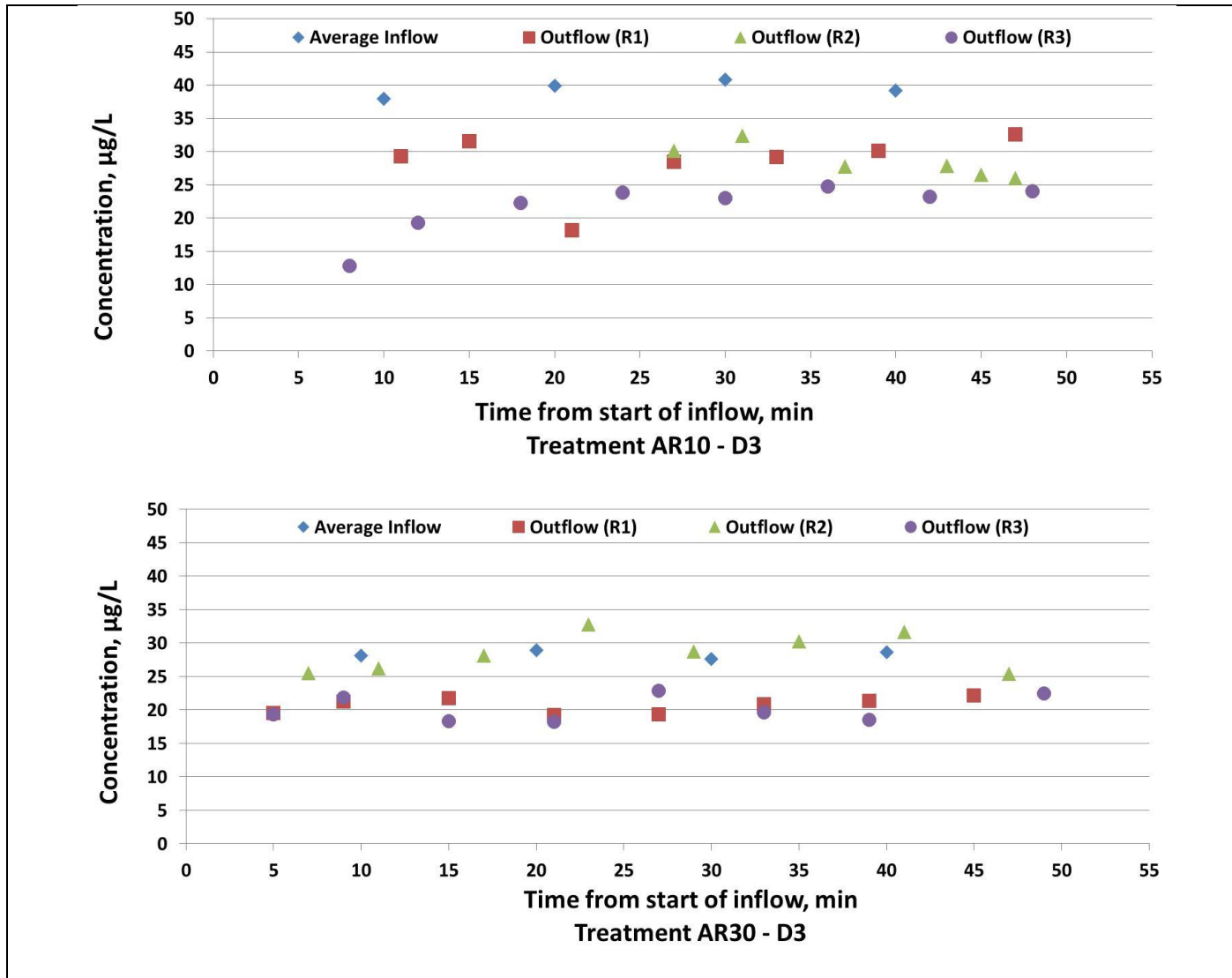


Figure 4.3: Dissolved atrazine concentrations in inflow (average) and in outflow for each replication.



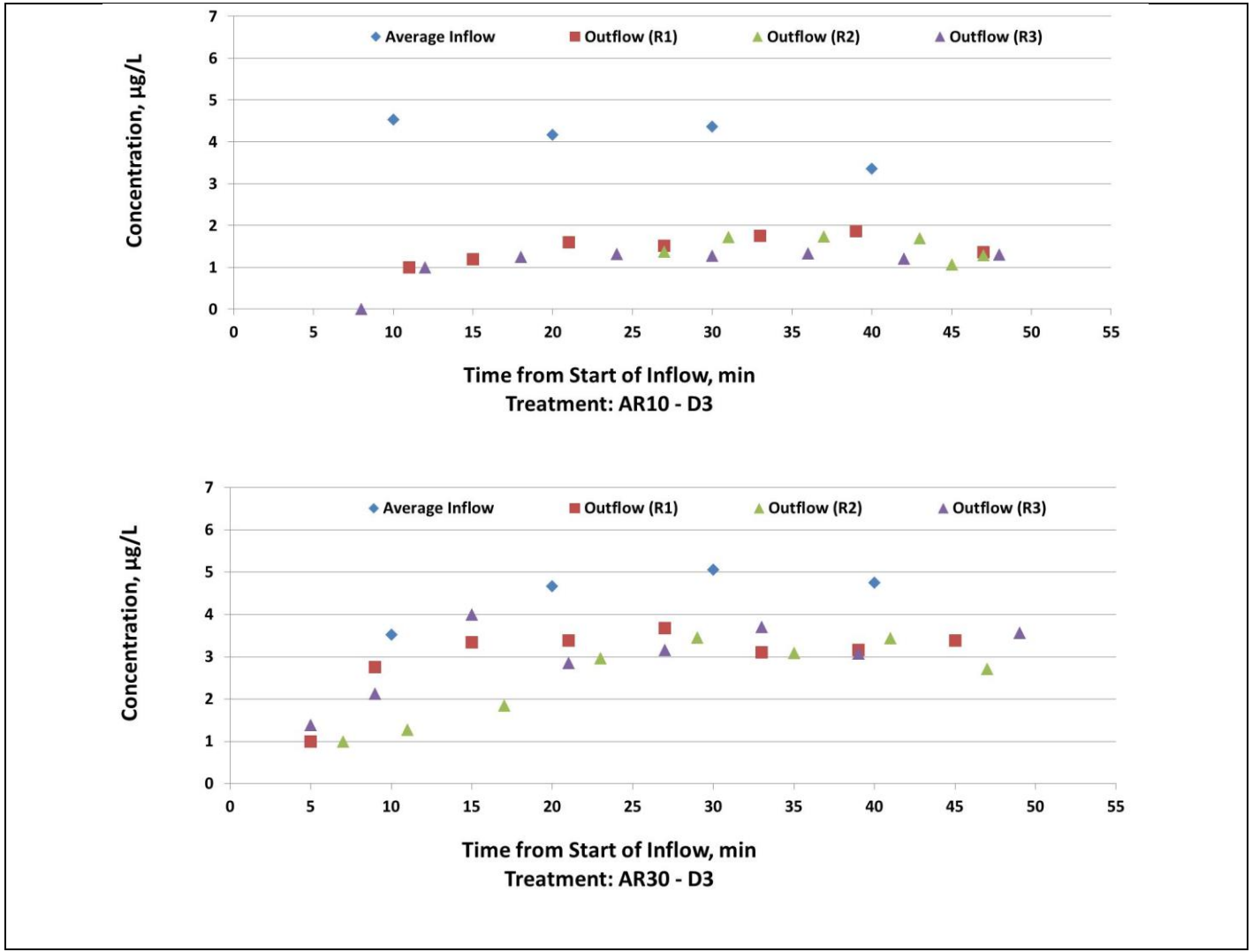


Figure 4.4: Dissolved chlorpyrifos concentrations in inflow (average) and in outflow for each replication.

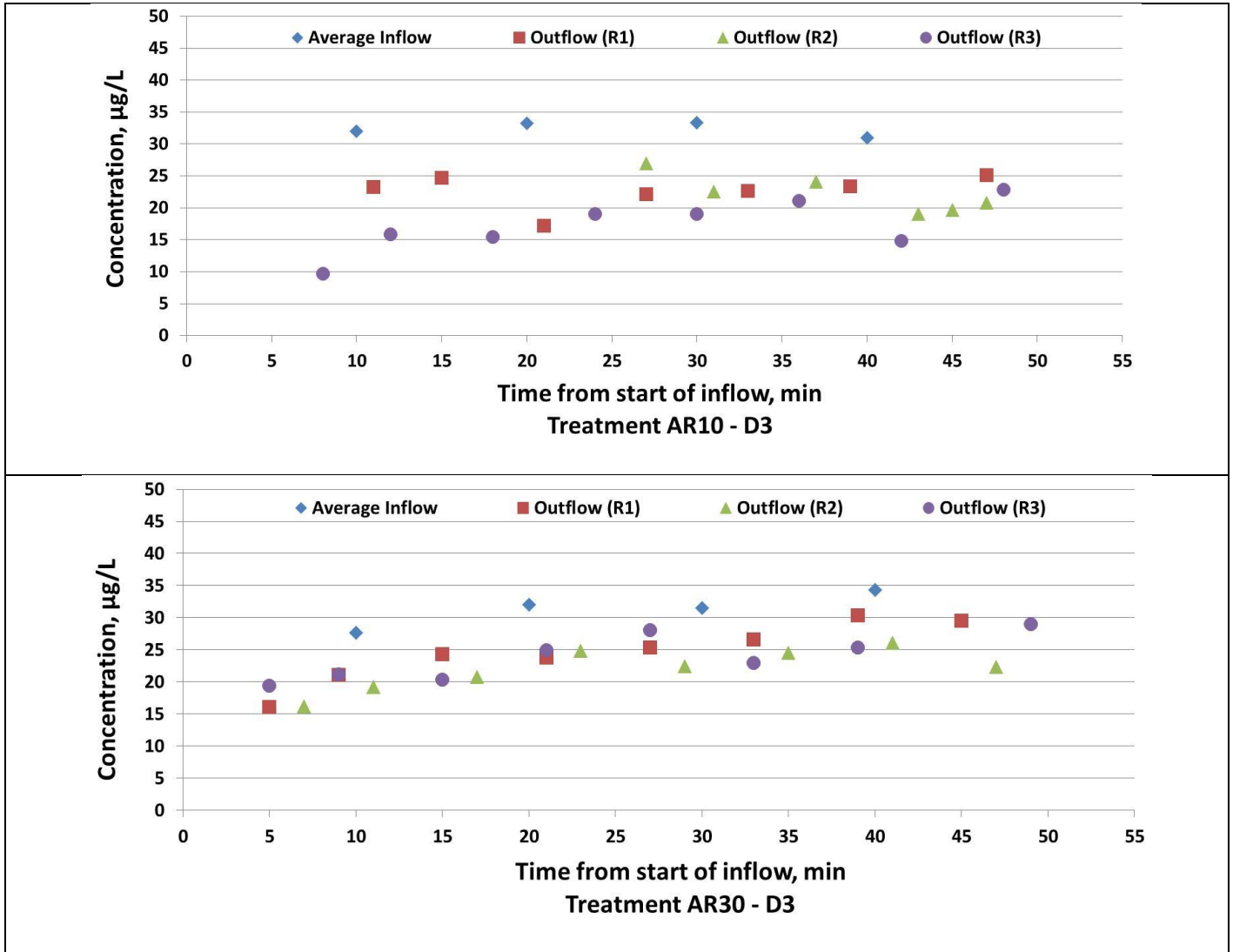


Figure 4.5: Dissolved linuron concentrations in inflow (average) and in outflow for each replication.

Table 4.3: Dissolved pesticide concentrations in inflow, outflow, and outflow diluted for rainfall, for the AR10-D3 and AR30-D3 strips.

| Atrazine Concentration<br>( $\mu\text{g/L}$ ) |                |                | Chlorpyrifos Concentration<br>( $\mu\text{g/L}$ ) |                |                  | Linuron Concentration<br>( $\mu\text{g/L}$ ) |                |                |
|---|----------------|----------------|---|----------------|------------------|--|----------------|----------------|
| Inflow<br>[1]                                 | Outflow<br>[2] | Outflow<br>[3] | Inflow<br>[1]                                     | Outflow<br>[2] | Outflow<br>w [3] | Inflow<br>[1]                                | Outflow<br>[2] | Outflow<br>[3] |
| ----- Treatment AR10-D3 -----                 |                |                |   |                |                  |  |                |                |
| 40  | 27             | 27             | 4   | 3              | 2                | 32   | 22             | 21             |
| ----- Treatment AR30-D3 -----                 |                |                |   |                |                  |  |                |                |
| 28  | 24             | 24             | 5   | 4              | 3                | 33   | 29             | 28             |

[1] Measured inflow concentration is averaged for the last 10 minutes.

[2] Outflow concentration as calculated using the dilution factor of 31% for AR10 strips and 23% for AR30 strips.

[3] Measured outflow concentration, averaged for the three replications and then averaged for the last 10 minutes of inflow time period.

number for the AR30 strips was 23%. Measured concentrations lower than the calculated observations due to rainfall dilution indicates that sorption of chlorpyrifos is occurring to the buffer strip organic matter. This is likely true as chlorpyrifos has a relatively high  $K_{oc}$  of 6070. In the case of the dissolved atrazine and linuron, the measured outflow concentrations are similar to the calculated outflow concentrations. Lack of any difference in these two outflow concentrations, for both sediment type D3 treatments, indicates that very little sorption of atrazine and linuron is occurring to the buffer strips organic matter due to low  $K_{oc}$ . In case sorption is occurring, there is the possibility that the equilibrium between the dissolved mass and sorbed pesticide mass exists. This equilibrium can cause the pesticide mass to shift from the sorbed phase to the dissolved phase resulting in very little difference between the observed dissolved concentration and rainfall diluted calculated concentrations.

#### 4.4.3 Sediment mass retained

Sediment mass concentrations in inflow and outflow, for all four treatments of AR10-D0, AR30-D0, AR10-D3, and AR30-D3, are presented in Figure 4.6. Inflow and outflow sediment mass concentrations were corrected for total solids concentration in the rainfall samples. This resulted in the inflow concentrations for AR10-D0 and AR30-D0 strips to be slightly below zero but were set to zero as no sediment was added in the D0 sediment type treatment. Outflow concentrations for the AR10-D0 and AR30-D0 strips showed sediment mass concentrations ranging from 0 to 450 mg/L, with majority of data points falling in the range of 0 to 200 mg/L (Figure 4.6). As no sediment was added to the simulated runoff into the buffer strips in the D0 treatment, presence of such sediment mass concentration shows that sediment is re-entrained into the flow from with the strips. The source of re-entrainment can be the buffer strip soil, previously deposited sediment or the eroded sediment at the exit point of outflow. Sediment mass concentrations, when average for all outflow samples within a replication, and then averaged for the three replications, were 113 and 72 mg/L, respectively, for the AR10-D0 and AR30-D0 strips. The AR30 strips are likely to have higher flow velocities and can potentially re-entrain larger sediment mass than that for the AR10 strips. Lower sediment mass concentrations are likely due to larger flow volume passing through the strips. Sediment mass concentrations for the AR10-D3 and AR30-D3 strips averaged 412 and 440 mg/L in inflow; and 431 and 426 mg/L in outflow for the two treatments, respectively. Outflow concentrations, for both area ratio treatments for sediment type D3, ranged from 105 to 790 mg/L. This range indicates that both rainfall dilution and re-entrainment processes are occurring in the buffer strips.

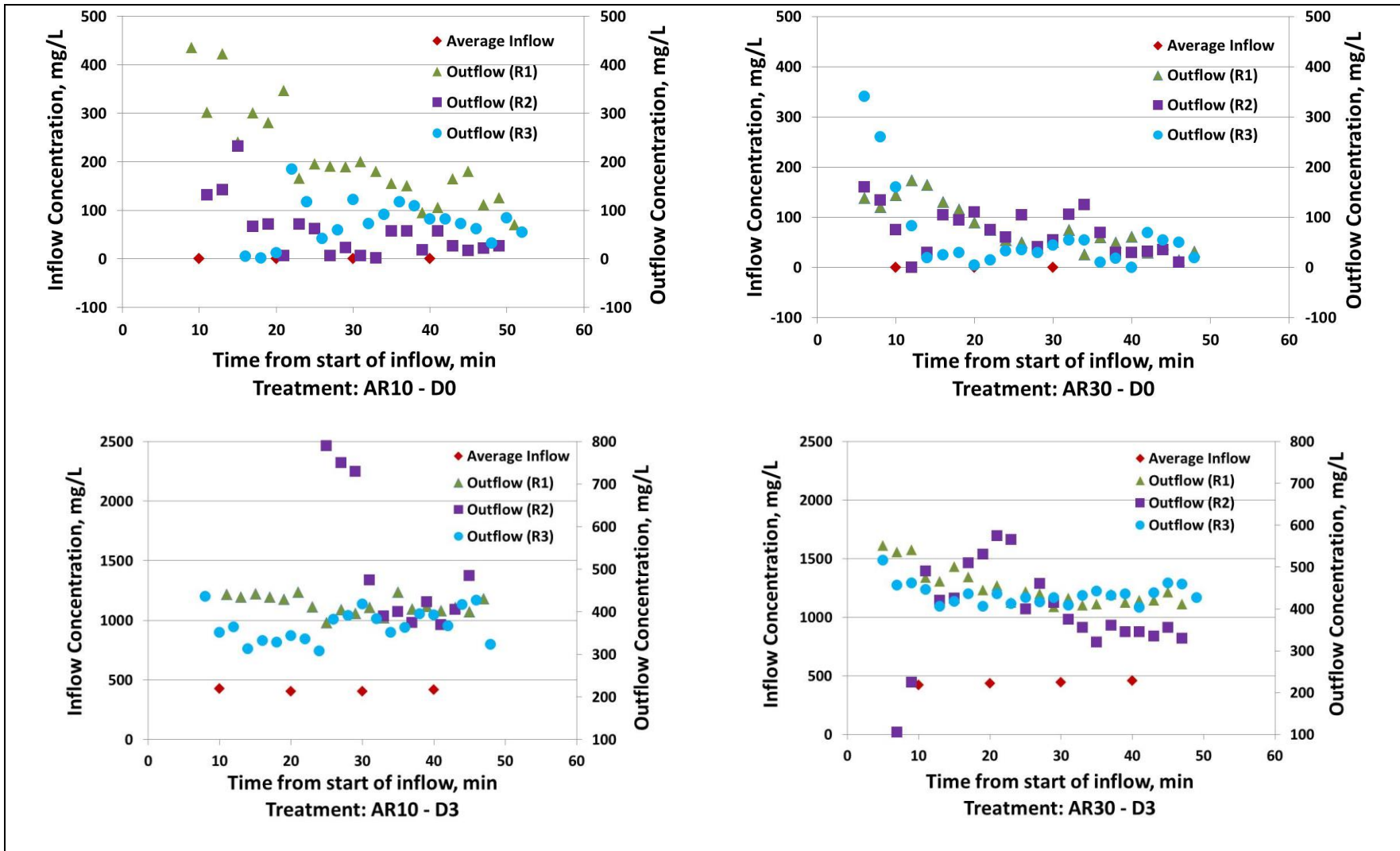


Figure 4.6: Sediment mass concentrations in inflow (average) and in outflow for each replication.

Sediment mass in inflow and outflow was used to calculate sediment mass retention for the four treatments as presented in Table 4.4. For sediment type D3, average sediment mass retention was 55.0% and 38.6% respectively for the AR10 and AR30 strips. These two averages were significantly different at  $\alpha = 0.05$  in the two tailed t-test. Sediment type D3 refers to particles smaller than 2  $\mu\text{m}$  which can easily

Table 4.4: Sediment mass in inflow and outflow from the buffer strips, and percent sediment retained for two area ratios (AR10 and AR30) and two sediment types (D0 and D3).

| Replication #      | Strip # | Strip Area (m <sup>2</sup> ) | Sediment In <sup>1</sup> (kg/ha <sup>2</sup> ) | Sediment Out (kg/ha) | Sediment Retained <sup>3</sup> (%) |
|--------------------|---------|------------------------------|--|----------------------|------------------------------------|
| AR10 - D0 - Rep 1  | 3       | 5.8                          | 0.0  | 115.6                | x                                  |
| AR10 - D0 - Rep 2  | 10      | 5.6                          | 0.0  | 27.1                 | x                                  |
| AR10 - D0 - Rep 3  | 18      | 5.6                          | 0.0  | 38.5                 | x                                  |
| Averages           |         | 5.6                          | 0.0  | 60.4                 | x                                  |
| Standard Deviation |         | 0.1                          | 0.0  | 48.1                 |                                    |
| AR30 - D0 - Rep 1  | 4       | 5.8                          | 0.0  | 138.6                | x                                  |
| AR30 - D0 - Rep 2  | 12      | 5.5                          | 0.0  | 111.3                | x                                  |
| AR30 - D0 - Rep 3  | 15      | 5.6                          | 0.0  | 99.2                 | x                                  |
| Averages           |         | 5.6                          | 0.0  | 116.3                | x                                  |
| Standard Deviation |         | 0.1                          | 0.0  | 20.2                 |                                    |
| AR10 - D3 - Rep 1  | 23      | 5.4                          | 493.0  | 219.1                | 55.6%                              |
| AR10 - D3 - Rep 2  | 7       | 5.8                          | 399.7  | 130.7                | 67.3%                              |
| AR10 - D3 - Rep 3  | 16      | 5.6                          | 461.2  | 259.8                | 43.7%                              |
| Averages           |         | 5.6                          | 451.3  | 203.2                | 55.0% a                            |
| Standard Deviation |         | 0.2                          | 47.5   | 66.0                 |                                    |
| AR30 - D3 - Rep 1  | 22      | 5.4                          | 1512.5   | 891.7                | 41.0%                              |
| AR30 - D3 - Rep 2  | 8       | 5.9                          | 1357.8   | 612.4                | 54.9%                              |
| AR30 - D3 - Rep 3  | 17      | 5.8                          | 1331.0   | 1073.6               | 19.3%                              |
| Averages           |         | 5.7                          | 1400.4   | 859.2                | 38.6% b                            |
| Standard Deviation |         | 0.3                          | 98.0   | 232.3                |                                    |

<sup>1</sup> Sediment mass is determined by multiplying sediment concentration with flow volume. Sediment mass in inflow for area ratio 30:1 is about 3 times the flow for 10:1 due to design of the experiment.

<sup>2</sup> Sediment mass converted to kg/ha over the strip area to account for variations in strip size.

<sup>3</sup> t-test H0: Mean (10:1) = Mean (30:1), no significant difference between the same letters at  $\alpha = 0.05$  in the two-tailed test.

penetrate into the soil surface with infiltration water and/or adhere to grass tillers.

Sediment mass retention, in the case of sediment type D3, does not represent sediment deposition in the buffer strip. Infiltration water is thus carrying clay and smaller-sized particles with it. The sediment mass contained in outflow is a mixture of particles introduced as input and re-entrained particles as shown by the concentration analysis.

The average outflow mass from sediment type D0 was subtracted from the outflow mass for the sediment type D3, for the respective area ratios. For the sediment type D3, the reduced sediment mass was divided by the actual sediment mass output. For the area ratios 10:1 and 30:1, the outflow contained 70.3%  $((203.2 - 60.4) / 203.2)$  and 86.5% of the input sediment mass, respectively. The larger area ratio strips had a higher percentage of the input sediment mass in the outflow (due to greater flow depth) resulting in a lower percentage of clay particles penetrating into the buffer strip soil. Since the particle size analysis samples were destroyed by accident during a facilities move, an evaluation of the particle size analysis results could not be performed.

#### **4.4.4 Sorbed pesticide concentration**

Sediment sorbed pesticide concentrations ( $C_{si}$  and  $C_{sout}$ ) are tabulated in Appendix C, along with the respective dissolved concentrations. These concentrations were determined for all inflow and for combined sediment mass outflow samples. Sediment mass in the outflow samples had to be combined to ensure enough pesticide mass was available for extraction, detection, and quantification. Sorption coefficient (K) values (ratio of sorbed concentration to dissolved concentration) were determined and are tabulated in Appendix C.

There was no sediment in the inflow samples for sediment type D0. As such, there were no sediment sorbed extracts to analyze. Sorbed pesticide concentrations in the outflow for sediment type D0 were zero for all three pesticides. Thus, there was no residual atrazine, chlorpyrifos, and linuron on buffer strip soil to create any complications with data interpretations.

In the case of the sediment type D3 (clay-sized particles), atrazine sorption coefficients for the AR10 treatment averaged 59 (range from 48 – 70) and 54 (ranged from 37 – 97) in inflow and outflow, respectively. The respective averages and ranges for the AR30-D3 treatment were 86 (63 - 132) in inflow and 71 (31 to 104) in outflow. Sorption coefficients for chlorpyrifos for the AR10-D3 treatment averaged in inflow as 340 (ranged from 255 to 559) and in outflow as 502 (ranged from 250 to 819). For AR30-D3 treatment, the respective averages and ranges were 522 (364 to 756) in inflow and 501 (282 to 622) in outflow. For atrazine, the sorption coefficient values were lower in outflow than in inflow. For chlorpyrifos, the sorption coefficient values for AR10 strips were lower in inflow than in outflow, whereas the converse was true for AR30 strips. Sediment sorbed concentrations for both atrazine and chlorpyrifos were also lower for outflow than for inflow for both area ratios for sediment type D3. Re-entrainment of sediment containing no pesticide is the reason why outflow concentrations for atrazine and chlorpyrifos were lower in outflow. Linuron concentrations in sorbed phase were not detected both in inflow and outflow samples for the sediment type D3. Linuron has a higher  $K_{oc}$  value than atrazine. Lack of detection of quantifiable data for sediment sorbed pesticide concentrations indicates that the clay-sized particles consisted of low organic matter content.



#### 4.4.5 Pesticide mass retained

Pesticide mass balance for sediment type D0 was not performed as the three pesticides were not detected in the inflow and outflow samples. The pesticide mass balance, for both dissolved phase and sorbed phase pesticide mass for sediment type D3, is presented in Table 4.5. The AR10 and AR30 strips retained an average of 70.1% and 49.2% total atrazine mass for sediment type D3. This difference in percent retention for atrazine between the two area ratios was significantly different in the two tailed t-test at  $\alpha = 0.05$ . The total sorbed mass for atrazine in inflow was 2.9% of the total input mass, averaged for both AR10 and AR30 strips. It would be expected that this percentage should be relatively high as clay particles have large specific surface area. At the average inflow sediment mass concentration of 425 mg/L, total clay-sized particle mass was not large enough for the percent input mass to be higher. In comparison, sediment type D1 had less than 0.1% atrazine in sorbed phase in inflow at an average sediment mass concentration of 2539 mg/L. In case of sediment type D2, this number was 1.2% for atrazine, with an average sediment mass concentration of 2580 mg/L. To compare pesticide sorption across sediment types, a Sediment Sorption Ratio (SSR) can be determined in terms of percent input sorbed mass per 1000 mg/L sediment mass concentration. The SSR was calculated as 0.04, 0.47, and 6.82 for the sediment types D1, D2, and D3, respectively for atrazine. Clay particles, thus, had the highest percent input sorbed atrazine mass per 1000 mg/L sediment mass concentration. In terms of the sorbed mass retention, the AR10 strips retained 74.7% and the AR30 strips retained 58.5% atrazine for sediment type D3. These two percent retentions were significantly different from each other. The greater flow volume in case of the AR30 strips is the main reason

Table 4.5: Percent retained and dissolved, sorbed, and total pesticide masses in inflow and outflow of the AR10 and AR30 buffer strips for sediment type D3.

| Replication       | Mass             | Atrazine Mass [1] |            |         | Chlorpyrifos Mass |        |         | Linuron Mass |        |         |
|-------------------|------------------|-------------------|------------|---------|-------------------|--------|---------|--------------|--------|---------|
|                   |                  | Dissolved [2]     | Sorbed [2] | Total   | Dissolved         | Sorbed | Total   | Dissolved    | Sorbed | Total   |
| #                 | Inflow / Outflow | g/ha              | g/ha       | g/ha    | g/ha              | g/ha   | g/ha    | g/ha         | g/ha   | g/ha    |
| AR10 - D3 - Rep 1 | Inflow           | 46.8              | 1.2        | 47.9    | 4.9               | 0.623  | 5.5     | 39.3         | -      | 39.3    |
|                   | Outflow          | 14.8              | 0.334      | 15.1    | 0.842             | 0.112  | 0.954   | 11.7         | -      | 11.7    |
|                   | Retained (%)     | 68.3%             | 72.3%      | 68.4%   | 82.7%             | 82.1%  | 82.6%   | 70.1%        | -      | 70.1%   |
| AR10 - D3 - Rep 2 | Inflow           | 47.1              | 1.1        | 48.1    | 4.7               | 0.528  | 5.2     | 33.0         | -      | 33.0    |
|                   | Outflow          | 7.9               | 0.184      | 8.1     | 0.431             | 0.110  | 0.541   | 6.1          | -      | 6.1     |
|                   | Retained (%)     | 83.1%             | 82.7%      | 83.1%   | 90.9%             | 79.1%  | 89.7%   | 81.4%        | -      | 81.4%   |
| AR10 - D3 - Rep 3 | Inflow           | 35.2              | 0.959      | 36.2    | 3.6               | 0.633  | 4.2     | 33.3         | -      | 33.3    |
|                   | Outflow          | 16.0              | 0.298      | 16.2    | 0.836             | 0.219  | 1.1     | 12.5         | -      | 12.5    |
|                   | Retained (%)     | 54.7%             | 68.9%      | 55.1%   | 76.8%             | 65.3%  | 75.0%   | 62.4%        | -      | 62.4%   |
| Average           | In               | 43.0              | 1.1        | 44.1    | 4.4               | 0.595  | 5.0     | 35.2         | -      | 35.2    |
|                   | Out              | 12.9              | 0.272      | 13.2    | 0.703             | 0.147  | 0.850   | 10.1         | -      | 10.1    |
|                   | Retained (%) [3] | 70.0%             | 74.7%      | 70.1% a | 84.0%             | 75.3%  | 83.0% a | 71.2%        | -      | 71.2% a |
| Std. Dev.         | In               | 6.8               | 0.124      | 6.9     | 0.694             | 0.058  | 0.669   | 3.5          | -      | 3.5     |
|                   | Out              | 4.3               | 0.079      | 4.4     | 0.236             | 0.063  | 0.272   | 3.5          | -      | 3.4     |
| AR30 - D3 - Rep 1 | In               | 82.0              | 3.0        | 85.0    | 14.1              | 3.3    | 17.4    | 106.1        | -      | 106.1   |
|                   | Out              | 42.1              | 1.3        | 43.4    | 6.5               | 1.4    | 8.0     | 52.9         | -      | 52.9    |
|                   | Retained (%)     | 48.7%             | 55.7%      | 48.9%   | 53.6%             | 56.3%  | 54.1%   | 50.1%        | -      | 50.1%   |
| AR30 - D3 - Rep 2 | In               | 104.4             | 3.1        | 107.5   | 13.8              | 2.7    | 16.6    | 89.6         | -      | 89.6    |
|                   | Out              | 44.9              | 0.987      | 45.9    | 4.3               | 0.894  | 5.2     | 35.4         | -      | 35.4    |
|                   | Retained (%)     | 57.0%             | 68.1%      | 57.3%   | 69.0%             | 67.2%  | 68.7%   | 60.5%        | -      | 60.5%   |
| AR30 - D3 - Rep 3 | In               | 81.4              | 3.7        | 85.1    | 15.0              | 3.6    | 18.6    | 105.6        | -      | 105.6   |
|                   | Out              | 49.9              | 1.7        | 51.6    | 7.8               | 1.3    | 9.1     | 61.2         | -      | 61.2    |
|                   | Retained (%)     | 38.7%             | 52.6%      | 39.3%   | 48.0%             | 63.1%  | 50.9%   | 42.1%        | -      | 42.1%   |
| Average           | In               | 89.3              | 3.3        | 92.5    | 14.3              | 3.2    | 17.5    | 100.4        | -      | 100.4   |
|                   | Out              | 45.6              | 1.4        | 46.9    | 6.2               | 1.2    | 7.4     | 49.8         | -      | 49.8    |
|                   | Retained (%)     | 48.9%             | 58.5%      | 49.2% b | 56.6%             | 61.9%  | 57.6% a | 50.4%        | -      | 50.4% b |
| Std. Dev.         | In               | 13.1              | 0.350      | 13.0    | 0.630             | 0.424  | 1.0     | 9.4          | -      | 9.4     |
|                   | Out              | 3.9               | 0.377      | 4.2     | 1.8               | 0.282  | 2.0     | 13.2         | -      | 13.2    |

[1] Mass of pesticides is converted to g/ha over the strip area, [2] Dissolved mass refers to pesticide mass retained with infiltration water. Sorbed mass refers to pesticide mass retained with Sediment, [3] Two-tailed t-test with unequal variances with  $H_0(\text{mean AR10}) = H_1(\text{mean AR30})$ ; no significant difference between same letters at  $\alpha = 0.05$ , [4] Standard deviation for inflow and outflow masses.

for the retention to be lower at larger area ratio. As clay-sized particles do not settle out, the process of particle penetration with infiltration water was the key contributing factor for sorbed atrazine retention. In the dissolved phase, average atrazine retention was 70.0% and 48.9% for the AR10 and AR30 buffer strips, respectively. This difference was statistically significant between the two area ratios. As infiltrating water mass is the carrier phase for dissolved pesticides, infiltration is the key factor for retention.

Chlorpyrifos retention for the AR10 and AR30 strips for sediment type D3 averaged 83.0% and 57.6%, respectively. These two averages were not statistically different in the two tailed t-test at  $\alpha = 0.05$ , although, the trend was lower retention at larger area ratio. In the sorbed phase, chlorpyrifos mass was 11.2% and 18.2% of the total input mass for the two area ratios, respectively. Higher sorption of chlorpyrifos than atrazine is mainly due to higher  $K_{oc}$  for chlorpyrifos. The AR10 and AR30 strips retained an average of 75.3% and 61.9% chlorpyrifos for sediment type D3 in the sorbed phase. This difference was significant between the two area ratios. As clay particles are retained mainly by particle penetration, greater infiltration at lower area ratio was the key factor for higher sorbed phase chlorpyrifos retention.

Average linuron retention by the AR10 and AR30 buffer strips for sediment type D3 was 71.2% and 50.4%, respectively. This difference in percent retention for linuron between the two area ratios was significantly different in the two tailed t-test at  $\alpha = 0.05$ . A statistically different infiltration rate between the two area ratios was the main reason for the lower percent retention of linuron at higher area ratio. Linuron was detected in the sorbed phase in some of the D3 sediment samples for both inflow and outflow. The concentrations were too low for quantification. Literature suggests that linuron is sorbed

to organic matter to a greater extent than soil particles. Lack of sediment sorbed linuron mass suggests that the clay fraction was low in large-sized organic particles. All organic particles were fine enough ( $< 0.45 \mu\text{m}$ ) to be included with the dissolved phase linuron concentration determination. During sediment preparation by settling, any floating larger sized organic particles were retained in the particle separation tank (Figure 4.1). Settled sediment and floating particles were left as only the required amount of water containing the desired particles was siphoned.

#### **4.5 Conclusions**

This experiment represents a simulation study where large particles  $> 2 \mu\text{m}$  are not present in the runoff entering the buffer strips. Such can be the case from no-till fields, pastures, and/or alfalfa fields. Absence of larger particles made it easier to interpret the results of clay particles retention by buffer strips. Under these experimental conditions, infiltration water mass retained by AR10 and AR30 buffer strips was 71.1% and 51.4% for sediment type D3 (clay particles), respectively. In comparison, infiltration water mass for the treatment where no sediment was present was 67.9% and 47.0%, respectively for the two area ratios. The difference between the area ratios, for either sediment type, was significant at  $\alpha = 0.05$ . Presence of fine clay particles did not impede infiltration in the buffer strips for sediment type D3 for both area ratios.

In case of the treatment where no sediment was introduced in simulated runoff, re-entrainment of sediment into the runoff was observed. Sources of this re-entrained sediment were the buffer strip soil, previously deposited sediment, and/or erosion at the exit point of the runoff. Sediment concentrations in outflow averaged 113 and 72 mg/L, respectively, for the AR10-D0 and AR30-D0 strips. The AR30 strips are likely to have

higher flow velocities and can potentially re-entrain larger sediment mass compared to the AR10 strips. Lower sediment mass concentrations are likely due to larger flow volume passing through the strips, though the sediment mass re-entrained was higher with higher area ratio.

Average sediment mass retention for clay particles was 55.0% and 38.6% respectively for the AR10 and AR30 strips. These two averages were significantly different at  $\alpha = 0.05$  in the two tailed t-test. This sediment mass is retained by penetration of fine particles into the soil pores with the infiltration water. Sediment mass retention, in the case of sediment type D3, does not represent sediment deposition in the buffer strips. Assuming sediment mass re-entrained in sediment type D3 strips was similar to sediment type D2 strips, the outflow contained 70.3% and 86.5% of the input clay particles for the AR10 and AR30 buffer strips respectively. Flow convergence, more present with the larger area ratio, thus will reduce the retention of clay-sized particles in the buffer strips.

There was a significant difference between the AR10 and AR30 strips for total atrazine mass retained for sediment type D3. Strips retained an average of 70.1% and 49.2% of the total atrazine mass for the smaller and larger area ratios, respectively. This difference is mainly due to difference in total infiltration between the two area ratios.

Chlorpyrifos retention for AR10 and AR30 strips for sediment type D3 averaged 83.0% and 57.6%, respectively. These two averages were not statistically different in the two tailed t-test at  $\alpha = 0.05$ , although, the trend was lower retention at larger area ratio. Lack of significance between the two area ratios indicates that the lower area ration

buffer strips can perform equally well for chlorpyrifos retention under conditions of flow convergence found with the area ratio 30:1 in this experiment.

Results showed sorption for linuron to clay particles to be below the detection limits. This indicates that the clay particle suspension used in the experiment contained low organic matter as linuron sorbs better to organic carbon ( $K_{oc} = 400$ ) than atrazine ( $K_{oc} = 100$ ). Results of linuron retention are estimates as the two unique mass peaks in the chromatograms were added together to obtain the total dissolved concentrations. Readers are advised to interpret results accordingly. The AR10 and AR30 buffer strips for sediment type D3 retained on average, 71.2% and 50.4% of the input dissolved linuron, respectively. This statistically significant difference between the two area ratios was mainly due to significantly different total infiltration. Results indicate that the longer lengths of buffer strips (greater infiltration) will be more effective than shorter length buffer strips in case of linuron.

#### 4.6 References

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## CHAPTER 5. USING VFSSMOD-W TO PREDICT PESTICIDE RETENTION BY BUFFER STRIPS RECEIVING SIMULATED RUNOFF CONTAINING DIFFERENT SIZED SEDIMENT

A paper written for publication as a technical note in the  
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### 5.1 Abstract

VFSSMOD-W, embedded with the empirical linear-additive pesticide mass retention model, was used to predict atrazine, chlorpyrifos, and linuron mass retention by 1.0 m wide x 5.6 m long switchgrass buffer strips. Simulated runoff with fine sand (53 - 250  $\mu\text{m}$ ), fine aggregates (< 53  $\mu\text{m}$ ), and clay-sized particles (< 2  $\mu\text{m}$ ) were considered as three different inflow sediment mass characteristics treatments and compared under the source area to buffer area ratios of 10:1 and 30:1. Saturated hydraulic conductivity ( $K_{\text{sat}}$ ) of the switchgrass soil was the key factor in calibrating the model to the experimental conditions. The calibrated model predicted infiltration mass retention for all three sediment types and the two area ratios with a Root Mean Squared Error (R.M.S.E.) of less than 5, indicating that the model performs well in predicting infiltration under flow convergence conditions. Predicted sediment mass retention was higher than the measured value for five of the six treatments mainly due to the observed re-entrainment of sediment into the outflow. Pesticide mass retained by the switchgrass buffer strips for both area ratios of sediment type D2, fine aggregates, was comparable between the

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measured and predicted values for all three pesticides (average R.M.S.E. < 15), indicating that the model performs well for fine aggregates ( $d_{50} = 15 \mu\text{m}$ ). For clay and smaller-sized particles ( $D_{50} = 1.5 \mu\text{m}$ ), the pesticide mass retention was zero for both area ratios due to the design of the empirical linear-additive model. For fine sands ( $D_{50} = 150 \mu\text{m}$ ), the model predicted significantly higher retention of all three pesticide masses for both area ratios, indicating the model did not perform well for fine sands. Predicted results indicate that the performance of the buffer strips receiving runoff from the farm fields containing large proportions of fine sand or clay-sized particles needs to be further investigated.

## 5.2 Introduction

Agricultural runoff process simulation models allow for data analysis to predict the response of pesticide retention by the buffer strips. Such models, by the design implemented by the modeler, can be either continuous-run or event-based models. Continuous-run models simulate several physical processes sequentially for the time duration specified by the modeler. The time step, upon which the process interactions are calculated, typically depends upon the measured data available for calibration of the model; and can range from a second to a day. Such a process-based model for predicting pesticide retention by the buffer strips, on a continuous basis, does not exist.

An event-based model for predicting pesticide retention by buffer strips has been proposed by Sabbagh et al. (2009). Previously, the pesticide trapping efficiency of the buffer strips has been based on the physical characteristics of buffer strip slope and length in the direction of flow. The proposed model is based on the percent infiltration and percent sediment retention by the buffer strips, a pesticide phase distribution parameter,

and the percent clay content in the runoff entering the buffer strips. The five data sets used in the development of the model had percent clay content values of 21% to 30%, with only one data point with percent clay content of 48%. The model was developed with a condition that the R.M.S.E. between the predicted and measured values of the pesticide mass retention by the buffer strips, using the five different evaluation data sets, should be less than 15%. The buffer strip width-based empirical model predicted a higher R.M.S.E. of 38.7% using the evaluation data sets in comparison to new proposed numerical/empirical model which predicted an R.M.S.E of 14.5% for the same data sets. The authors also proposed a linking procedure for obtaining the percent infiltration and percent sediment mass retentions by the buffer strips from the Vegetative Filter Strip Modeling System, VFSMOD (Muñoz-Carpena et al. 1999, Muñoz-Carpena and Parsons, 2004). The authors concluded that the new numerical/empirical model approach significantly improved the predictability of the pesticide mass retention by the buffer strips over the previously used width-based empirical model.

Poletika et al. (2009) verified the pesticide mass retention predications produced by the newly proposed numerical/empirical approach by Sabbagh et al. (2009) in an experiment conducted on Galva silty clay loam with an average 28.9% clay content and 2.58% organic carbon. Simulated rainfall and simulated runoff experiments under two drainage area to buffer strip area ratios of 15:1 and 30:1 were studied with full buffer strip width and with 10% of the width receiving the simulated runoff. In this experiment, the buffer strip width referred to the dimension of the strip perpendicular to the flow. Use of only 10% of the buffer strip width, thus, represented the concentrated flow in comparison to the use of the full width or uniform flow. Under uniform flow conditions,

the authors reported no significant difference between the 15:1 and 30:1 area ratios. When averaged between the two area ratios, the buffer strips showed 59% infiltration, 88% sediment mass retention, 85% total chlorpyrifos and 62% total atrazine mass retention. In the case of concentrated flow, the performance measures were reduced regardless of the area ratio. When averaged between the two area ratios, the buffer strips showed 16% infiltration, 31% sediment mass retention, 21% total chlorpyrifos and 12% total atrazine mass retention. The authors reported that the un-calibrated VFSSMOD and the empirical model proposed by Sabbagh et al. (2009) were capable of predicting the pesticide mass retention for both of the uniform and concentrated flow experimental conditions and for the two pesticides studied. The authors concluded that due to significant differences between the flow regimes, the uniformity of flow was the key factor for pesticide mass retention in the experiment conducted. This represents a logical conclusion, as on a per unit area basis, the use of 10% of the buffer strip area as concentrated flow path represents equivalent area ratios of 150:1 and 300:1 for the two treatments studied in the experiment.

The model proposed by Sabbagh et al. (2009) is a linear-additive model, with a major advantage that it requires minimal hydrological, soil, and pesticide properties data. In a typical use of this model, the non-equivalent nature of the recurrence intervals of runoff and design storm is ignored. As such, the model can be used with user specified conditions for predicting pesticide retention by the buffer strips under a given set of hydrological and site conditions, and pesticide properties. One major advantage of such a model is that the worst case scenarios of pesticide loss from the source areas can be modeled. Experiments described in Chapters 3 and 4 represent the worst case scenario

where the maximum amount of the pesticide mass applied to the soil particles is lost in the runoff. Use of such a model allows validation of how well the model performs under specific experimental conditions. The objective of the application of this empirical model, to the experiments described in Chapters 3 and 4, is to evaluate how well the model predicts pesticide retention with runoff containing different sized particles, and secondly how well the model predicts the differences in pesticide retention resulting from flow convergence represented by the two different source areas to buffer area ratios.

### 5.3 Empirical Model Application

Sabbagh et al. (2009) developed a linear-additive model consisting of numerically and non-linearly derived terms; and is not a process-based model. This numerical/empirical model is described by equations 5.1, 5.2 and 5.3:

$$\Delta P = 24.79 + 0.54 (\Delta Q) + 0.52 (\Delta E) - 2.42 \ln(F_{ph} + 1) - 0.89 (\%C) \quad (5.1)$$

where  $\Delta P$  = pesticide reduction by buffer strips (%)  
 $\Delta Q$  = runoff volume reduction by the buffer strips (%)  
 $\Delta E$  = reduction in eroded sediment by buffer strips (%)  
 $F_{ph}$  = phase distribution parameter, dimensionless  
 $\%C$  = percent clay in incoming sediment

$$F_{ph} = Q_i / (K_d E_i) \quad (5.2)$$

where  $Q_i$  = volume of water entering the buffer strips (L)  
 $E_i$  = mass of sediment entering the buffer strips (kg)  
 $K_d$  = linear sorption coefficient (L/kg)

$$K_d = K_{oc} f_{oc} \quad (5.3)$$

where  $K_{oc}$  = adsorption coefficient (L/kg)  
 $f_{oc}$  = fractional organic carbon in the soil

Equation 5.1 consists of terms  $\Delta Q$  and  $\Delta E$ , which are derived from the Vegetative Filter Strip Modeling System, VFSSMOD-W (Muñoz-Carpena et al. 1999, Muñoz-Carpena and Parsons, 2004). VFSSMOD is an event-based model, which numerically models flow

through a buffer strip and predicts infiltration and sediment retention. VFSSMOD-W has equations 5.1, 5.2, and 5.3 built into its code and predicts percent pesticide retention.

Several parameter input values are required to obtain the predicted values of infiltration ( $\Delta Q$ ) and sediment retention ( $\Delta E$ ). The procedure, explained by Sabbagh et al. (2009), was used to calculate these parameter values. A buffer strip project in VFSSMOD-W requires input for overland flow, soil properties, buffer vegetation properties, incoming sediment characteristics, storm hyetograph, source area storm runoff, and pesticide properties.

Overland flow input requires the input of buffer length in the direction of flow and the buffer width perpendicular to flow. The buffer strip dimensions in the experiments described in Chapters 3 and 4 were used as input values for these two parameters. A segment roughness and slope of 0.4 and 2.5% were used as inputs, respectively. Default kinematic wave numerical solution parameters, as recommended in the VFSSMOD-W model documentation and user's manual (Muñoz-Carpena and Parsons, 2014), were used in the overland input file.

Infiltration-buffer strip soil properties file required input of vertical saturated hydraulic conductivity which was estimated using the Soil – Plant – Air – Water (SPAW, 2014) model. The SPAW model has a soil water characteristics sub-program built into it which calculates saturated hydraulic conductivity for a given percent sand, percent clay, percent organic matter, and compaction factor. Percent sand and percent clay from Table 3.1 along with a 4% organic matter and a compaction factor of 0.9 were used. A compaction factor of 1.0 is used with normal soils. As the weather prior to the experiment was extremely dry, potential of cracks and dead roots existed in the buffer

strip soil. As such, compaction factor of 0.9 was used to calculate the saturated hydraulic conductivity. The soil water characteristics sub-program of the SPAW model also calculated moisture contents for wilting point, field capacity, and saturation, as percent volume, for the given set of conditions explained above. In the infiltration-buffer strip soil properties file in VFSSMOD-W, field capacity moisture content was used as initial moisture content. This represented the moisture content in the soil at the start of the experiment, twelve hours after the irrigation had been applied to the buffer strips.

One additional parameter required in the infiltration-buffer strip soil properties file for VFSSMOD-W is the average suction at the wetting front. This suction was calculated by using equation 5.4 given by Rawls and Brakensiek (1989) as:

$$H_f = \exp[6.5309 - 7.32561(\Phi) + 0.001583 (C^2) + 3.809479 (\Phi^2) + 0.000344 (S) (C) - 0.049837 (S) (\Phi) + 0.001608 (S^2) (\Phi^2) + 0.001602 (C^2) (\Phi^2) - 0.0000136 (S^2) (C) - 0.003479 (C^2) (\Phi) - 0.000799 (S^2) (\Phi)] \quad (5.4)$$

Where,  $H_f$  is Green-Ampt wetting front suction parameter (cm),  $S$  is percent sand,  $C$  is percent clay, and,  $\Phi$  is porosity of the soil corrected for entrapped air, corrected porosity is 90% of the soil porosity (Fox et al, 2005).

The height of the grass in the vegetation properties file was used as 25.4 cm as the switchgrass was cut to this height prior to the experiment. Grass roughness and bare surface roughness were used as 0.012 and 0.04, respectively. The rainfall hyetograph, inflow storm hydrograph, incoming sediment characteristics, and pesticide properties from the experiments (as described in Chapters 3 and 4) were used as inputs into VFSSMOD-W. Selected input parameters used in VFSSMOD-W are provided in Table 5.1.

As the sediment particle size analysis samples for input and output from buffer strips were accidentally destroyed during the water quality laboratory move to a new building, the values of the parameters listed in Table 5.1 were estimated from analysis performed for Figure 3.2.

Table 5.1: Selected VFSSMOD-W input parameter values used for predicting pesticide retention by buffer strips.

| Parameter  | Sediment Type  |                      |                           |                  |
|--|----------------|----------------------|---------------------------|------------------|
|  | Fine Sand (D1) | Fine Aggregates (D2) | Clay-Sized Particles (D3) | No Sediment (D0) |
| Particle size of sediment entering the strip, $D_{50}$ ( $\mu\text{m}$ )     | 150            | 15                   | 1.5                       | 0                |
| Portion of particles entering the strip with diameter $> 37 \mu\text{m}$ (%) | 100            | 30                   | 0                         | 0                |
| Organic matter content of the sediment (%)                                   | 0.4            | 4                    | 7                         | 0                |
| Clay content in inflow sediment (%)  | 0              | 30                   | 100                       | 0                |

## 5.4 Results and Discussion

### 5.4.1 VFSSMOD-W calibration

The VFSSMOD-W model predicted significantly lower infiltration than the observed infiltration without calibration. Such low infiltration would result in flow volume being higher, thus affecting the sediment transport through the buffer strips. A calibration of VFSSMOD-W was thus performed before it could be used to predict the pesticide retention. This calibration was performed using previously listed parameter values and inflow and outflow hydrographs for each replication of treatments AR10-D0 and AR30-D0. Parameters such as average suction at the wetting front, initial and

saturated moisture content of buffer strip soil, maximum surface storage, strip grass spacing, height, and roughness, and bare surface roughness had minimal impact on percent infiltration water mass. The model was most sensitive to saturated hydraulic conductivity,  $K_{\text{sat}}$  of the buffer strip soil. The value of  $K_{\text{sat}}$  was calibrated using percent infiltration observed for each replication. For the AR10-D0 treatment, the values of  $K_{\text{sat}}$  averaged 9.9 cm/h (9.2, 9.4, and 11.0), whereas for the AR30-D0 treatment, this average was 19.8 cm/h (19.6, 21.9, 17.8), respectively. The calibrated value of  $K_{\text{sat}}$  for the respective area ratio treatments was significantly higher than the  $K_{\text{sat}}$  value obtained from the SPAW model (2.4 cm/h) or from the Web Soil Survey (USDA 2014) (3.2 cm/h). Using the SPAW model to predict texture for the calibrated  $K_{\text{sat}}$ , the texture was calculated as sandy loam (40% sand, 5% clay) for the AR10-D0 treatment and loamy sand (80% sand, 2% clay) for the AR30-D0 treatment. The root density of switchgrass reaches its peak in Central Iowa around early August and then declines (Tufekcioglu et al. 1999). Severe dry weather in the months preceding the experiments conducted in September 2013 could have led to root death and soil cracking resulting in opening of macropores. Bharati et al. (2002) studied soil-water infiltration under crops, pasture and established riparian buffer in Midwestern USA. They reported a 60 min cumulative infiltration of 23 cm in the switchgrass soil in Central Iowa in October months. Bonin et al. (2012) studied soil physical and hydrological properties under three biofuel crops in Ohio and reported an average cumulative infiltration of 69 cm over three hours for switchgrass soil with a constant infiltration rate of 16.8 cm/h. As switchgrass soil has been reported to show high infiltration rates, the calibrated values of  $K_{\text{sat}}$  were, therefore,



used to predict infiltration for the three sediment types and for the two area ratios, respectively.

#### **5.4.2 Infiltration water mass ( $M_x$ )**

The average inflow hydrographs and average rainfall hyetographs for all eight treatments are plotted in Figures 5.1 and 5.2. Hydrographs for the average outflow (averaged for three replications for each treatment) and the outflow predicted by VFSDMOD-W are also plotted in the same figures for the respective treatments. The predicted hydrographs showed a sharp increase in outflow, a very steady increase in outflow after the initial rise, and a very sharp decline in outflow from buffer strips. The predicted outflow hydrographs for all treatments showed a small peak at the initiation of outflow for all treatments. This peak in the rising limb of the hydrographs indicates that equilibrium between the inputs and outputs is reached a few minutes after the start of outflow. The recessional limbs of the predicted outflow hydrographs for all four treatments follow the observed recessional limbs. In a majority of the predicted hydrographs, the outflow started a few minutes earlier and stopped a few minutes later than the observed outflow. Initially, the predicted outflow is higher than the measured outflow, and later in the hydrographs, the predicted outflow is lower. The initial moisture content being lower than the values used in predictions is a possible reason for the outflow to start quicker than the measured outflow. Some of the spread in the measured outflow is due to the average values of the three replications. Overall, the percent infiltration mass predicted by VFSDMOD-W (Table 5.2) was close to the measured value. The Root Mean Square Error (R.M.S.E.) for the AR10 between the measured and predicted percent infiltration was 4.5, whereas it was 2.9 for the AR30 buffer strips. This

means that the calibrated model predicted the percent infiltration water mass fairly well for both area ratios. This indicates that the model can accommodate flow convergence conditions when predicting infiltration water mass.

### 5.4.3 Sediment mass retained

Sediment mass retention was predicted with the calibrated VFSSMOD-W using sediment characteristics listed in Table 5.1. The predicted and measured sediment mass retentions are presented in Table 5.2 for the respective treatments. For sediment types D1 and D2, for both area ratios, the predicted values were higher than the observed values. In the case of the sediment type D1, the model predicted 100% sediment mass retention

Table 5.2: Measured and VFSSMOD-W predicted percent infiltration and sediment mass retention.

| Treatments | Infiltration Water Mass (%) |           | Sediment Mass Retention (%) |           |
|------------|-----------------------------|-----------|-----------------------------|-----------|
|            | Measured                    | Predicted | Measured                    | Predicted |
| AR10 - D0  | 67.9                        | 68.0      | Re-entrained                | 100.0     |
| AR10 - D1  | 71.7                        | 68.0      | 96.4                        | 100.0     |
| AR10 - D2  | 73.6                        | 66.9      | 92.8                        | 99.2      |
| AR10 - D3  | 71.1                        | 67.2      | 55.0                        | 59.0      |
| Average    | 72.1                        | 67.4      |                             |           |
| R.M.S.E.   |                             | 5.0       |                             | 4.8       |
|            |                             |           |                             |           |
| AR30 - D0  | 51.4                        | 51.7      | Re-entrained                | 100.0     |
| AR30 - D1  | 48.9                        | 50.8      | 89.8                        | 100.0     |
| AR30 - D2  | 51.4                        | 52.2      | 90.2                        | 96.2      |
| AR30 - D3  | 48.7                        | 52.1      | 38.6                        | 9.5       |
| Average    | 49.7                        | 51.7      |                             |           |
| R.M.S.E.   |                             | 2.3       |                             | 18.1      |

for both area ratios. It did not predict any sediment re-entrainment, which is why the predicted retention is higher than the measured retention. This is also the likely reason for the predicted results to be higher for sediment type D2 than for the measured results.

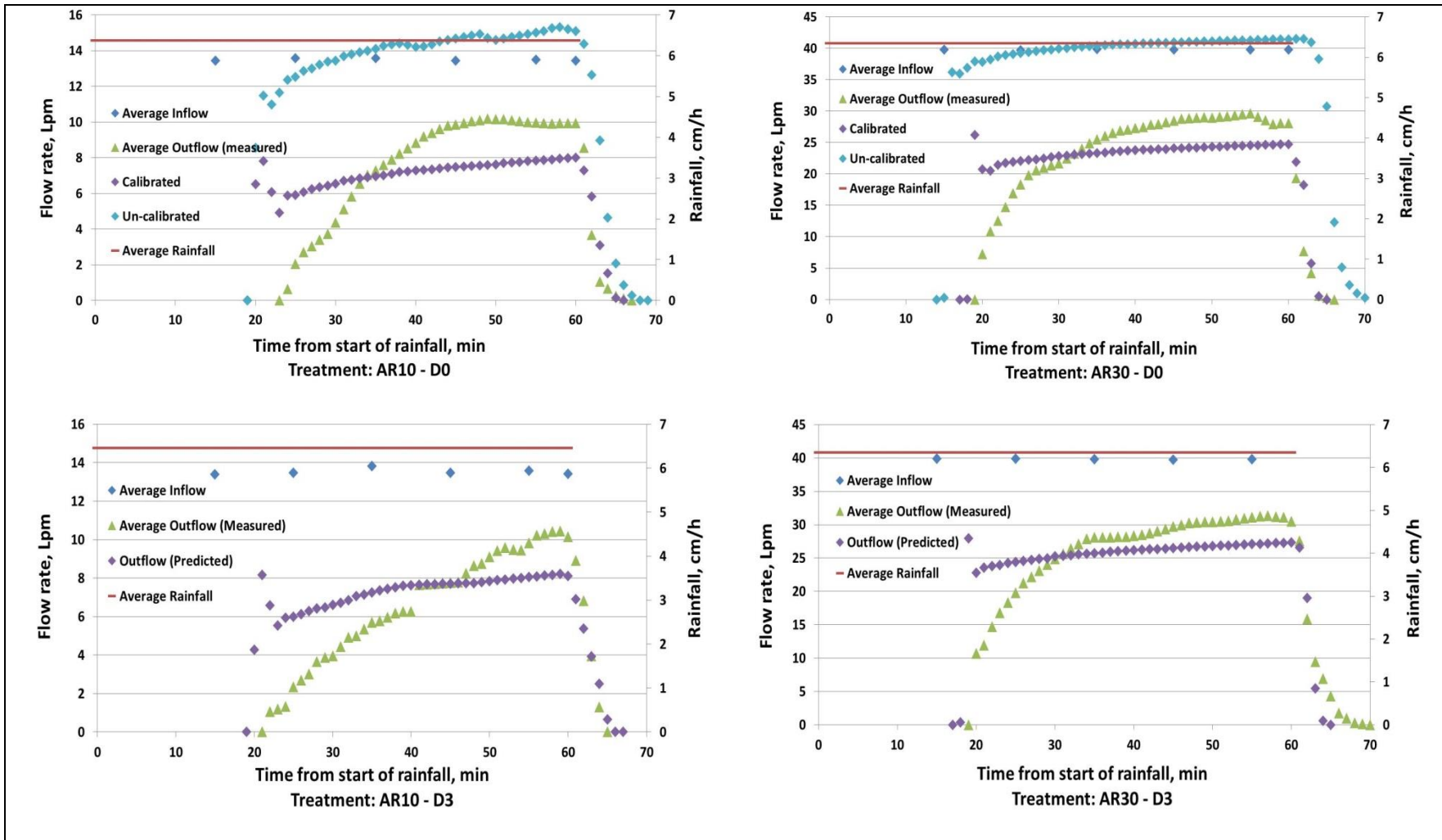


Figure 5.1: Average rainfall and inflow, and average and calibrated outflow for sediment type D0 and D3 treatments.

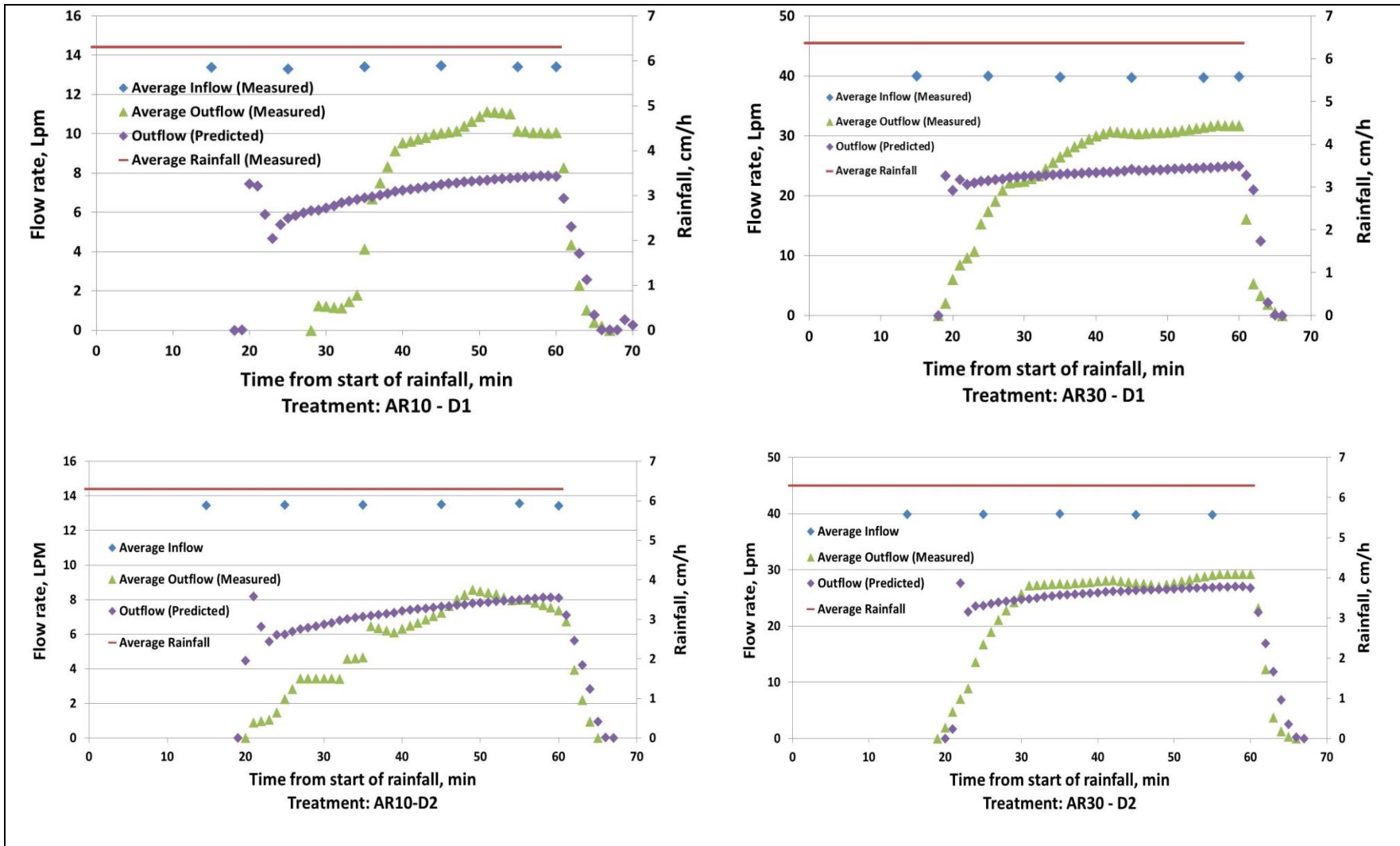


Figure 5.2: Average rainfall and inflow, and average and calibrated outflow for sediment type D1 and D2 treatments.

The predicted sediment mass retentions for sediment type D3 showed different results. For the treatment AR10, the predicted value was higher, whereas it was lower for the AR30 treatment, when compared with the measured values. The likely reason for the AR30 predicted value being lower is a greater influence of flow convergence in the model calculations than for the observed values. Consequently, the R.M.S.E. values for AR10 were lower than the AR30 treatments (Table 5.2). This indicates that the predictive effect of flow convergence on clay-sized particles ( $< 2 \mu\text{m}$ ) for sediment mass retention when using VFSSMOD-W needs to be further investigated.

#### 5.4.4 Pesticide mass retained

Using the predicted infiltration water mass and sediment mass retained from Table 5.2, the percent pesticide retention was calculated using equation 5.1, 5.2, and 5.3. The percent pesticide retention was obtained directly from the water quality output file of VFSSMOD-W, as these equations are built into VFSSMOD-W. The total predicted and measured mass retentions, for the three pesticides, are presented in Table 5.3. Sabbagh et

Table 5.3: Measured and VFSSMOD-W predicted percent atrazine, chlorpyrifos, and linuron mass retention.

| Treatments | Atrazine Retention |            | Chlorpyrifos Retention |            | Linuron Retention |            |
|------------|--------------------|------------|------------------------|------------|-------------------|------------|
|            | Measured           | Predicted  | Measured               | Predicted  | Measured          | Predicted  |
| AR10 - D1  | 73.0               | 96.8       | 87.2                   | 100.0      | 80.5              | 100.0      |
| AR10 - D2  | 71.5               | 74.6       | 87.4                   | 77.9       | 75.5              | 77.9       |
| AR10 - D3  | 70.1               | 0.0        | 83.0                   | 0.0        | 71.2              | 0.0        |
| R.M.S.E.   |                    | 42.8(17.0) |                        | 48.8(11.3) |                   | 42.6(13.9) |
|            |                    |            |                        |            |                   |            |
| AR30 - D1  | 52.5               | 87.5       | 79.5                   | 90.8       | 53.9              | 97.3       |
| AR30 - D2  | 53.7               | 65.5       | 71.3                   | 83.4       | 57.5              | 68.4       |
| AR30 - D3  | 49.2               | 0.0        | 57.6                   | 0.0        | 50.4              | 0.0        |
| R.M.S.E.   |                    | 35.5(26.1) |                        | 34.6(11.7) |                   | 38.9(31.6) |

al. (2009) noted that the five studies used to develop equation 5.1 and the five studies used to validate the model only had a percent clay range of 12% to 48%. The model assumes that the source area and buffer area soil are same, and also assumes that the inflow into buffer strips contains same percent clay as the source area soil. The model did not predict any pesticide retention (for sediment type D3) for both area ratios when the clay content of the inflow sediment was 100%. Model modifications need to be considered when the percent clay content of the inflow sediment is 100%. For sediment type D1, the model predicted nearly 100% pesticide mass retention for AR10 strips, and over 85% pesticide retention for AR30 strips. For both area ratios, the model predicted pesticide retention for all three pesticides was higher than the measured retention in the case of sediment type D1. For sediment type D2, the model predicted and the measured values for the three pesticide retentions for both area ratios were within the R.M.S.E tolerance value of 15% set by Sabbagh et al. (2009). The R.M.S.E. value for the AR10-D2 strips, across the three pesticides, was 5.9 and the corresponding number was 11.6 for the AR30-D2 strips. This indicates that the model works well when predicting pesticide retention for sediment with  $d_{50}$  of 15  $\mu\text{m}$  (sediment type D2). When comparing between the AR10 and AR30 strips for all three sediment types, the R.M.S.E pesticide retention was higher for the AR10 strips than for the AR30 strips. This is mainly due to the prediction of zero pesticide retention for sediment type D3. Excluding the numbers for sediment type D3, the R.M.S.E (values in parenthesis in Table 5.3) was lower for AR10 strips for all three pesticides than for AR30 strips. This indicates that uncertainty in the predicted pesticide mass retention is increased with increased area ratio.

## 5.5 Conclusions

VFSMOD-W was used to compare the predicted pesticide mass retention for the three pesticides, two area ratios, and the three sediment types with the measured retentions as described in Chapters 3 and 4. The empirical pesticide mass retention model embedded into VFSMOD-W does not differentiate different sediment sizes in the inflow to the buffer strips, but only contains a percent clay term. The purpose of such a comparison, thus, was to measure how well the model predicted pesticide retention under specific sediment sizes and different flow convergence conditions.

The model calibration results indicate that saturated hydraulic conductivity ( $K_{sat}$ ) can be greatly influence the percent infiltration by VFSMOD. After calibration, the model predicted infiltration water mass for all three sediment types and area ratios fairly well (R.M.S.E. < 5). This indicates that the model can handle the flow convergence conditions adequately for all three sediment types studied.

Re-entrainment of sediment from the buffer strip soil or pre-deposited sediment or from the exit of outflow occurs. This re-entrainment is the likely reason for the VFSMOD-W predicting sediment mass retentions to be higher than the measured values for AR10 and AR30 buffer strips for D1 and D2 sediment types. For the AR30-D3 treatment, the model predicted lower sediment mass retention than observed values, likely due to the effects of flow convergence. These flow convergence effects on model predictions need to be further investigated.

The empirical linear-additive model embedded within VFSMOD-W predicted that the buffer strips will not retain any of the three pesticides mass when the inflow sediment contains 100% clay or smaller sized particles (sediment type D3). Under any field

application, any time the sum of the first four terms in the empirical model is less than the percent clay term, the model will predict zero pesticide mass retention. As such, revisions to the model need to be considered to predict pesticide mass retention with greater accuracy.

The calibrated VFSSMOD-W model predicted pesticide mass retention for all three pesticides for fine aggregates (sediment type D2,  $D_{50} = 15 \mu\text{m}$ ) very close to the measured values in the experiments for both area ratios. This means that the model is well-suited for predicting pesticide mass retention under conditions of flow convergence when the inflow sediment size ranges between  $2 \mu\text{m}$  to  $53 \mu\text{m}$ .

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## CHAPTER 6. GENERAL CONCLUSIONS

### 6.1 General Discussion

Buffer strips can take different shapes under different USDA-NRCS conservation practices such as riparian buffers, filter strips, grassed waterways, shelterbelts, windbreaks, living snow fences, contour grass strips, cross-wind trap strips, shallow water areas for wildlife, field borders, alley cropping, herbaceous wind barriers, and vegetative barriers. The intent of the design upon which the buffer strips are based is to reduce the transport of runoff, sediment, nutrients, pesticides, pathogens, and other potential contaminants from source areas (agricultural fields) to the receiving water bodies. Different applications of the buffer strips are subject to different site conditions in terms of crop rotations, tillage, and residue cover; and source area to buffer area ratios. These conditions can influence the sediment composition of the runoff leaving the source areas and the runoff transmission through the buffer strips.

The experiments conducted as a part of this research represent situations where fine sand is either present or absent from runoff or the runoff consists only of clay or smaller sized particles. Under typical applications of the buffer strips, this represents the upstream and downstream parts of buffer strips where one specific sediment type can be absent in the runoff. In case of fine sand particle (53 - 250  $\mu\text{m}$ ), the buffer strips were able to retain majority of the pesticide mass sorbed with sediment as majority of the sand particles were trapped by sedimentation in the upstream end of the buffer strip under both area ratios. Due to low organic matter content of the sand particle, the sorbed pesticide mass was low. Fine aggregates, on the other hand, had higher organic matter content.

The results for pesticide retention were, however, similar between the two sediment types for the respective area ratios for the three pesticides studied. For clay or smaller-sized particles ( $< 2 \mu\text{m}$ ), particle penetration into the buffer strip soils with the infiltrating water was the key process for retention of sediment sorbed pesticide. The Sediment Sorption Ratios (SSR) calculated for atrazine showed that clay-sized particles had largest percent pesticide mass per 1000 mg/L sediment mass concentration, followed by fine aggregated, and then by the fine sand particles. Total pesticide mass retained with clay-sized particles was significantly lower than the fine sand and fine aggregate sediment type for the lower area ratio.

Flow convergence in terms of deeper flow depth in the case of the larger area ratio of 30:1 in comparison with 10:1, showed significant difference for atrazine due to significantly different infiltration. This is mainly due the low sorption coefficient for atrazine. Linuron data followed a similar trend as no quantifiable mass was detected sorbed to the sediment. Linuron has a higher sorption coefficient, however, in these experiments; linuron behavior was similar to atrazine. Chlorpyrifos data showed no significant difference between the area ratios, however, the trend was lower retention at higher area ratios.

The calibrated VFSSMOD-W, embedded with the empirical linear-additive model, predicted pesticide mass retention in the case of fine aggregates very well. In the case of fine sand, the model predicted significantly higher pesticide reduction. In the case of clay-sized particles, the model predicted no pesticide retention. These differences mainly exist due to the design of the model. In practical applications of buffer strips, the likelihood of runoff containing only fine sand is rare. The runoff can contain

significantly high concentrations of clay particles under no-till tillage systems and low slope topography with good residue cover. Modifications to this empirical linear-additive model should be considered to more accurately predict pesticide mass retention when runoff consists of higher concentrations of clay or fine sand.

## **6.2 Recommendations for Future Research**

Sieving of ground soil to obtain specific particle sizes is a time consuming process. Less time consuming methods for particle separation need to be developed which can produce particles from the source areas under consideration. These methods need to consider the magnitude of field scale studies as a large mass of precisely separated particles is needed in such studies. Such methods can be very helpful in the evaluation of several different agricultural practices on a field scale in relation to the nutrients, pesticides, and pathogens.

Very limited data exists on the transport of pesticides through the buffer strips with sorption coefficient over 150. Studies need to be considered with different pesticides with sorption coefficient higher than 150 to improve the pesticide retention predicting ability of the available models. Re-entrainment of sediment into the flow exiting the buffer strips needs to be further evaluated. This can help answer questions on changes in the outflow pesticide concentrations as reported in different studies.

Most of the data extracted from the studies reviewed by Arora et al. (2010) represent buffer strips established on loamy/silty soils. Sandy soils can have higher infiltration rates just based on the soil texture. Clayey soils on the other hand can have cracks or large macro pores developed through them due to insect/earthworm populations

or due to the root mass decay, thus increasing the infiltration rates. Future work should consider different soil textures outside of the 10% to 30% clay range.

One of the major recommendations for future work with buffer strip studies is to perform mass balance analysis by considering inflow, rainfall, and outflow from each strip individually. Experimental designs, where the analysis of data considering outflow from non-buffered plots as input for buffered plots is performed, are not appropriate and can lead to impractical results. In such experimental designs, errors are introduced in analysis due to variability in non-buffered plots (due to micro topography and/or soil type difference) and can lead to outflow from non-buffered plots being lower in mass than the outflow from the buffered plots. Secondly, rainfall over the buffer area should be considered as input in the mass balance, especially when the rain occurs during the flow transmission through the buffer strip. Such experimental designs do not accurately represent field conditions as rainfall volume is part of infiltration.

Arora et al. (2010) summarized the natural rainfall/runoff studies showing the temporal pattern of hydrologic conditions and their impact on pesticide retention. This event by event variability is bound to happen in field conditions. Best and worst runoff events should not be considered as performance indicators as they only represent either extreme. At the same time, it is practically impossible to evaluate all combinations of site factors, hydrologic factors, and pesticide properties on field scale basis. The empirical models developed to date have limited applicability. Therefore, a process-based model that can analyze these combinations for pesticide mass retention needs to be developed and validated. Studies performed to date can, however, serve the purpose of validating the model. Validation of such a process-based model will, however, require

additional studies to be undertaken, as several of the past studies have used very small test plots and area ratios. In addition, several studies have not considered a complete mass balance considering all inputs and outputs, providing impractical data sets that cannot be used for model validation. Several existing buffer strip models such as Agricultural Policy/Environmental eXtender (APEX), Riparian Ecosystem Management Model (REMM), Pesticide Root Zone Model (PRZM), Soil Water Assessment Tool (SWAT), VFSSMOD-W (Vegetative Filter Strip Modeling System), Iowa State University Vegetative Infiltration Basin/Vegetative Treatment Area Model (ISU-VIB/VTA), Water Erosion Prediction Project (WEPP), and others can serve as platforms for such a process-based pesticide mass retention model.

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## APPENDIX A. FIELD OBSERVATIONS AND EXPERIMENTAL FLOW DATA

Appendix A1: Field observations and experimental flow data for buffer strips replication  
AR10 – D1 – R1.

| Replication                                    | Run                 | Strip                    | Irrigation                                |               |
|--|---------------------|--------------------------|---|---------------|
| #  | #                   | #                        | Amount (L)                                | Duration (hr) |
| AR10 - D1 - Rep 1                              | 3                   | 2                        | 2,432                                     | 4.0           |
| Simulated Rainfall Start Time:                 |                     |                          | 12:12 PM                                  |               |
| Simulated Rainfall Stop Time:                  |                     |                          | 1:12 PM                                   |               |
| Sediment Mix Start Time:                       |                     |                          | 11:57 AM                                  |               |
| Total Sediment Used (kg):                      |                     |                          | 2.08                                      |               |
| Simulated Runoff Start Time:                   |                     |                          | 12:27 PM                                  |               |
| Simulated Runoff Stop Time:                    |                     |                          | 1:12 PM                                   |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data ----- |   |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time               | Corrected Flow Rate                       | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                    | Lpm                                       | °F            |
| 12:27  | 13.21               | 12:45                    | Outflow started                           |               |
| 12:37  | 13.29               | 12:47                    | 0.93                                      | 80.9          |
| 12:47  | 13.40               | 12:51                    | 7.08                                      | 80.5          |
| 12:57  | 13.32               | 12:56                    | 8.72                                      | 80.3          |
| 13:07  | 13.29               | 1:00                     | 8.92                                      | 80.3          |
| 13:12  | 13.29               | 1:04                     | 9.18                                      | 80.1          |
|  |                     | 1:11                     | 9.08                                      | 80.1          |
|  |                     | 1:12                     | 2.42                                      | 80.0          |
|  |                     | 1:13                     | 2.42                                      | 80.0          |
|  |                     | 1:14                     | Outflow stopped                           |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |                          |   |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                   | 4 (mm)                                    | 5 (mm)        |
| 63   | 55                  | 55                       | 66  | 66            |
| 6 (mm)   | 7 (mm)              |                          | External Rain Gauges (Outside Strip Area) |               |
| 66   | -                   |                          | 1 (mm)                                    | 2 (mm)        |
| Average Rainfall (mm) = 62                     |                     |                          | 0   | 0             |



Appendix A2: Field observations and experimental flow data for buffer strips replication  
AR10 – D1 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D1 - Rep 2                              | 14                  | 24  | 2,846               | 5.0           |
| Simulated Rainfall Start Time:                 |                     |   | 12:35 PM            |               |
| Simulated Rainfall Stop Time:                  |                     |   | 1:35 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 12:20 PM            |               |
| Total Sediment Used (kg):                      |                     |   | 2.08                |               |
| Simulated Runoff Start Time:                   |                     |   | 12:50 PM            |               |
| Simulated Runoff Stop Time:                    |                     |   | 1:35 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 12:50  | 13.44               | 13:03                                     | Outflow started     |               |
| 13:00  | 13.29               | 13:04                                     | 3.74                | 64.6          |
| 13:10  | 13.40               | 13:07                                     | 3.38                | 64.5          |
| 13:20  | 13.32               | 13:11                                     | 7.34                | 64.5          |
| 13:30  | 13.44               | 13:15                                     | 10.52               | 64.5          |
| 13:35  | 13.40               | 13:18                                     | 5.78                | 64.4          |
|  |                     | 13:22                                     | 10.05               | 64.3          |
|  |                     | 13:26                                     | 10.90               | 64.3          |
|  |                     | 13:29                                     | 10.90               | 64.3          |
|  |                     | 13:32                                     | 10.51               | 64.3          |
|  |                     | 13:35                                     | 10.51               | 64.3          |
|  |                     | 13:36                                     | 12.84               | 64.2          |
|  |                     | 13:37                                     | 5.79                | 64.2          |
|  |                     | 13:38                                     | 1.93                | 64.2          |
|  |                     | 13:41                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 76   | 76                  | 76  | 64                  | 51            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 50   | 50                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     |   | 0                   | 0             |

Appendix A3: Field observations and experimental flow data for buffer strips replication  
AR10 – D1 – R3.

| Replication   | Run                 | Strip                                     | Irrigation          |               |
|---|---------------------|---|---------------------|---------------|
| #   | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D1 -Rep 3  | 19                  | 19  | 2,861               | 4.5           |
| Simulated Rainfall Start Time:  |                     |   | 11:30 AM            |               |
| Simulated Rainfall Stop Time:   |                     |   | 12:45 PM            |               |
| Sediment Mix Start Time:  |                     |   | 11:15 AM            |               |
| Total Sediment Used (kg):   |                     |   | 2.01                |               |
| Simulated Runoff Start Time:  |                     |   | 11:45 AM            | See note      |
| Simulated Runoff Stop Time:   |                     |   | 12:45 PM            | below         |
| ----- Inflow Data -----   |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time  | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm   | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 11:45   | 13.51               | 12:19                                     | Outflow started     |               |
| 11:55   | 13.29               | 12:21                                     | 10.23               | 72.0          |
| 12:00   | 13.59               | 12:24                                     | 10.59               | 69.1          |
| 12:15   | 13.74               | 12:30                                     | 11.28               | 66.9          |
| 12:25   | 13.51               | 12:36                                     | 11.96               | 67.2          |
| 12:35   | 13.29               | 12:40                                     | 10.55               | 67.7          |
| 12:45   | 13.25               | 12:45                                     | 10.55               | 67.7          |
|   |                     | 12:46                                     | 4.90                | 67.6          |
|   |                     | 12:48                                     | 4.90                | 67.6          |
|   |                     | 12:50                                     | 1.15                | 67.7          |
|   |                     | 12:52                                     | Outflow stopped     |               |
| Note: Simulator broke at 12 Noon, everything stopped, simulator, fixed and everything restarted at 12:15 PM |                     |   |                     |               |
| Rain Gauges on the Strip Area (up to 7 gauges)  |                     |   |                     |               |
| 1 (mm)  | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 58  | 64                  | 64  | 64                  | 76            |
| 6 (mm)  | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 56  | 64                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 64  |                     |   | 0                   | 0             |

Appendix A4: Field observations and experimental flow data for buffer strips replication  
AR30 – D1 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D1 -Rep 1                               | 5                   | 5   | 6,391                    | 10.0          |
| Simulated Rainfall Start Time:                 |                     |   | 2:24 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 3:24 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | 2:09 PM                  |               |
| Total Sediment Used (kg):                      |                     |   | 5.26                     |               |
| Simulated Runoff Start Time:                   |                     |   | 2:39 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 3:24 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 14:39  | 39.82               | 14:43                                     | Outflow started          |               |
| 14:49  | 39.78               | 14:44                                     | 5.95                     | 75.7          |
| 14:59  | 39.78               | 14:46                                     | 8.92                     | 75.3          |
| 15:09  | 39.63               | 14:51                                     | 16.94                    | 75.1          |
| 15:19  | 39.56               | 14:54                                     | 17.95                    | 74.8          |
| 15:24  | 39.56               | 14:58                                     | 22.74                    | 74.8          |
|  |                     | 15:04                                     | 28.79                    | 74.5          |
|  |                     | 15:10                                     | 33.56                    | 74.5          |
|  |                     | 15:16                                     | 33.56                    | 74.5          |
|  |                     | 15:21                                     | 36.53                    | 74.6          |
|  |                     | 15:24                                     | 36.53                    | 74.6          |
|  |                     | 15:25                                     | 23.10                    | 74.5          |
|  |                     | 15:27                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 53   | 56                  | 61  | 76                       | -             |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 66   | 69                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A5: Field observations and experimental flow data for buffer strips replication  
AR30 – D1 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR30 - D1 -Rep 2                               | 7                   | 9   | 4,277               | 7.0           |
| Simulated Rainfall Start Time:                 |                     |   | 2:32 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 3:32 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 2:17 PM             |               |
| Total Sediment Used (kg):                      |                     |   | 5.35                |               |
| Simulated Runoff Start Time:                   |                     |   | 2:47 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 3:32 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 2:47   | 39.86               | 14:55                                     | Outflow started     |               |
| 14:57  | 39.63               | 14:56                                     | 10.18               | 70.6          |
| 15:07  | 39.71               | 15:00                                     | 22.27               | 70.6          |
| 15:17  | 39.78               | 15:04                                     | 20.58               | 70.1          |
| 15:27  | 39.94               | 15:09                                     | 29.21               | 70.1          |
| 15:32  | 39.94               | 15:14                                     | 33.78               | 69.8          |
|  |                     | 15:18                                     | 32.07               | 69.8          |
|  |                     | 15:24                                     | 30.48               | 69.8          |
|  |                     | 15:30                                     | 30.48               | 69.8          |
|  |                     | 15:32                                     | 30.48               | 69.7          |
|  |                     | 15:33                                     | 3.21                | 69.7          |
|  |                     | 15:34                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 69   | 64                  | 64  | 58                  | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 61   | 64                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     |   | 0                   | 0             |

Appendix A6: Field observations and experimental flow data for buffer strips replication  
AR30 – D1 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D1 -Rep 3                               | 18                  | 14  | 2,668                    | 4.5           |
| Simulated Rainfall Start Time:                 |                     |   | 4:35 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 5:35 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | 4:20 PM                  |               |
| Total Sediment Used (kg):                      |                     |   | 5.35                     |               |
| Simulated Runoff Start Time:                   |                     |   | 4:50 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 5:35 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 16:50  | 40.39               | 16:53                                     | Outflow started          |               |
| 17:00  | 40.54               | 16:54                                     | 6.19                     | 70.1          |
| 17:10  | 39.86               | 16:56                                     | 18.02                    | 69.5          |
| 17:20  | 39.63               | 17:00                                     | 25.27                    | 69.5          |
| 17:30  | 39.71               | 17:04                                     | 27.43                    | 69.4          |
| 17:35  | 39.94               | 17:09                                     | 30.06                    | 69.4          |
|  |                     | 17:15                                     | 29.32                    | 69.4          |
|  |                     | 17:21                                     | 27.48                    | 69.3          |
|  |                     | 17:26                                     | 27.48                    | 69.3          |
|  |                     | 17:30                                     | 28.13                    | 69.3          |
|  |                     | 17:35                                     | 28.17                    | 69.3          |
|  |                     | 17:38                                     | 9.84                     | 69.3          |
|  |                     | 17:40                                     | 1.54                     | 69.3          |
|  |                     | 17:41                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 51   | 64                  | 94  | 64                       | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | 51                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A7: Field observations and experimental flow data for buffer strips replication  
AR10 – D2 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D2 -Rep 1                               | 6                   | 6   | 7,386               | 11.0          |
| Simulated Rainfall Start Time:                 |                     |   | 4:20 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 5:20 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 4:05 PM             |               |
| Total Sediment Used (kg):                      |                     |   | 2.09                |               |
| Simulated Runoff Start Time:                   |                     |   | 4:35 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 5:20 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 16:35  | 13.29               | 16:42                                     | Outflow started     |               |
| 16:49  | 13.67               | 16:44                                     | 0.94                | 74.8          |
| 16:55  | 13.36               | 16:47                                     | 6.99                | 74.0          |
| 17:00  | 13.40               | 16:50                                     | 7.68                | 73.8          |
| 17:05  | 13.40               | 16:55                                     | 8.52                | 73.6          |
| 17:10  | 13.59               | 17:00                                     | 9.13                | 73.6          |
| 17:15  | 13.67               | 17:05                                     | 9.06                | 73.5          |
| 17:20  | 13.67               | 17:10                                     | 8.47                | 73.5          |
|  |                     | 17:15                                     | 8.47                | 73.5          |
|  |                     | 17:20                                     | 8.62                | 73.5          |
|  |                     | 17:22                                     | 0.78                | 73.5          |
|  |                     | 17:25                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 53   | 58                  | 58  | 66                  | 76            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 64   | -                   |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     |   | 0                   | 0             |

Appendix A8: Field observations and experimental flow data for buffer strips replication  
AR10 – D2 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D2 -Rep 2                               | 9                   | 11  | 2,652               | 4.5           |
| Simulated Rainfall Start Time:                 |                     |   | 1:25 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 2:25 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 1:10 PM             |               |
| Total Sediment Used (kg):                      |                     |   | 2.03                |               |
| Simulated Runoff Start Time:                   |                     |   | 1:40 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 2:25 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 13:40  | 13.51               | 13:45                                     | Outflow started     |               |
| 13:50  | 13.29               | 13:46                                     | 2.64                | 63.8          |
| 14:00  | 13.59               | 13:50                                     | 3.77                | 63.8          |
| 14:10  | 13.48               | 13:58                                     | 5.52                | 63.5          |
| 14:20  | 13.51               | 14:04                                     | 5.49                | 63.5          |
| 14:25  | 13.29               | 14:10                                     | 6.00                | 63.1          |
|  |                     | 14:14                                     | 9.27                | 63.0          |
|  |                     | 14:17                                     | 4.90                | 62.9          |
|  |                     | 14:22                                     | 4.90                | 62.9          |
|  |                     | 14:25                                     | 4.90                | 62.9          |
|  |                     | 14:26                                     | 7.68                | 62.9          |
|  |                     | 14:28                                     | 2.72                | 62.9          |
|  |                     | 14:29                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 64   | 71                  | 64  | 64                  | 69            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 61   | 58                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                   | 0             |

Appendix A9: Field observations and experimental flow data for buffer strips replication  
AR10 – D2 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D2 - Rep 3                              | 17                  | 13  | 3,181               | 9.5           |
| Simulated Rainfall Start Time:                 |                     |   | 2:40 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 3:40 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 2:25 PM             |               |
| Total Sediment Used (kg):                      |                     |   | 2.08                |               |
| Simulated Runoff Start Time:                   |                     |   | 2:55 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 3:40 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 14:55  | 13.59               | 15:14                                     | Outflow started     |               |
| 15:05  | 13.67               | 15:16                                     | 5.28                | 70.6          |
| 15:15  | 13.51               | 15:19                                     | 3.78                | 70.6          |
| 15:25  | 13.67               | 15:23                                     | 5.62                | 70.1          |
| 15:35  | 13.48               | 15:27                                     | 7.75                | 69.7          |
| 15:40  | 13.29               | 15:30                                     | 8.37                | 69.7          |
|  |                     | 15:34                                     | 7.75                | 69.7          |
|  |                     | 15:36                                     | 8.66                | 69.7          |
|  |                     | 15:38                                     | 8.66                | 69.5          |
|  |                     | 15:40                                     | 8.66                | 69.5          |
|  |                     | 15:41                                     | 7.84                | 69.5          |
|  |                     | 15:43                                     | 3.85                | 69.5          |
|  |                     | 15:45                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 64   | 69                  | 61  | 58                  | 56            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 64   | 64                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 62                     |                     |   | 0                   | 0             |



Appendix A10: Field observations and experimental flow data for buffer strips replication AR30 – D2 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D2 -Rep 1                               | 4                   | 1   | 3,284                    | 5.5           |
| Simulated Rainfall Start Time:                 |                     |   | 3:04 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 4:04 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | 2:49 PM                  |               |
| Total Sediment Used (kg):                      |                     |   | 5.12                     |               |
| Simulated Runoff Start Time:                   |                     |   | 3:19 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 4:04 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 15:19  | 39.78               | 15:27                                     | Outflow started          |               |
| 15:29  | 40.09               | 15:28                                     | 8.16                     | 79.8          |
| 15:39  | 40.54               | 15:31                                     | 19.32                    | 79.7          |
| 15:49  | 40.24               | 15:35                                     | 28.37                    | 79.7          |
| 15:59  | 39.82               | 15:41                                     | 28.31                    | 79.6          |
| 16:04  | 39.82               | 15:46                                     | 26.97                    | 79.6          |
|  |                     | 15:51                                     | 28.08                    | 79.6          |
|  |                     | 15:56                                     | 26.84                    | 79.5          |
|  |                     | 16:01                                     | 26.39                    | 79.5          |
|  |                     | 16:04                                     | 26.39                    | 79.5          |
|  |                     | 16:07                                     | 2.44                     | 79.5          |
|  |                     | 16:09                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 53   | 58                  | 64  | 64                       | 66            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 69   | 66                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     |   | 0                        | 0             |

Appendix A11: Field observations and experimental flow data for buffer strips replication AR30 – D2 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D2 -Rep 2                               | 13                  | 21  | 2,439                    | 4.0           |
| Simulated Rainfall Start Time:                 |                     |   | 10:25 AM                 |               |
| Simulated Rainfall Stop Time:                  |                     |   | 11:25 AM                 |               |
| Sediment Mix Start Time:                       |                     |   | 10:10 AM                 |               |
| Total Sediment Used (kg):                      |                     |   | 5.25                     |               |
| Simulated Runoff Start Time:                   |                     |   | 10:40 AM                 |               |
| Simulated Runoff Stop Time:                    |                     |   | 11:25 AM                 |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 10:40  | 39.78               | 10:44                                     | Outflow started          |               |
| 10:50  | 39.82               | 10:45                                     | 5.96                     | 65.3          |
| 11:00  | 39.75               | 10:47                                     | 12.01                    | 65.3          |
| 11:10  | 39.63               | 10:50                                     | 18.57                    | 65.3          |
| 11:20  | 39.78               | 10:53                                     | 24.81                    | 65.2          |
| 11:25  | 39.78               | 10:56                                     | 29.02                    | 65.1          |
|  |                     | 11:01                                     | 26.71                    | 65.0          |
|  |                     | 11:07                                     | 29.07                    | 65.0          |
|  |                     | 11:13                                     | 29.07                    | 65.0          |
|  |                     | 11:18                                     | 31.01                    | 65.0          |
|  |                     | 11:21                                     | 30.72                    | 65.0          |
|  |                     | 11:25                                     | 30.72                    | 65.0          |
|  |                     | 11:26                                     | 29.18                    | 65.0          |
|  |                     | 11:27                                     | 12.33                    | 65.0          |
|  |                     | 11:28                                     | 2.15                     | 65.0          |
|  |                     | 11:30                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 58   | 64                  | 64  | 69                       | 56            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 71   | 64                  | 1 (mm)                                    | 2 (mm)                   |               |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A12: Field observations and experimental flow data for buffer strips replication AR30 – D2 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D2 -Rep 3                               | 20                  | 20  | 2,792                    | 4.5           |
| Simulated Rainfall Start Time:                 |                     |   | 1:45 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 2:45 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | 1:30 PM                  |               |
| Total Sediment Used (kg):                      |                     |   | 5.25                     |               |
| Simulated Runoff Start Time:                   |                     |   | 2:00 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 2:45 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 14:00  | 40.01               | 14:05                                     | Outflow started          |               |
| 14:10  | 39.82               | 14:06                                     | 5.39                     | 69.6          |
| 14:20  | 39.52               | 14:10                                     | 19.88                    | 68.4          |
| 14:30  | 39.63               | 14:16                                     | 24.18                    | 68.4          |
| 14:40  | 39.67               | 14:20                                     | 27.08                    | 68.9          |
| 14:45  | 39.67               | 14:27                                     | 28.64                    | 68.5          |
|  |                     | 14:33                                     | 24.22                    | 68.5          |
|  |                     | 14:39                                     | 30.65                    | 68.6          |
|  |                     | 14:41                                     | 30.65                    | 68.5          |
|  |                     | 14:45                                     | 30.65                    | 68.6          |
|  |                     | 14:46                                     | 22.11                    | 68.6          |
|  |                     | 14:48                                     | 6.52                     | 68.6          |
|  |                     | 14:50                                     | 0.95                     | 68.6          |
|  |                     | 14:52                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | 69                  | 64  | 69                       | 56            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 69   | 51                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     |   | 0                        | 0             |

Appendix A13: Field observations and experimental flow data for buffer strips replication AR10 – D3 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D3 -Rep 1                               | 12                  | 23  | 1,847               | 3.0           |
| Simulated Rainfall Start Time:                 |                     |   | 2:01 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 3:01 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 1:49 PM             |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay      |               |
| Simulated Runoff Start Time:                   |                     |   | 2:16 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 3:01 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 14:16  | 13.51               | 14:25                                     | Outflow started     |               |
| 14:26  | 13.48               | 14:26                                     | 2.61                | 63.5          |
| 14:36  | 13.85               | 14:28                                     | 3.71                | 63.5          |
| 14:46  | 13.48               | 14:31                                     | 4.53                | 63.1          |
| 14:56  | 13.55               | 14:34                                     | 6.95                | 63.1          |
| 15:01  | 13.55               | 14:37                                     | 8.57                | 63.0          |
|  |                     | 14:40                                     | 9.22                | 63.0          |
|  |                     | 14:42                                     | 7.81                | 62.8          |
|  |                     | 14:47                                     | 7.81                | 62.8          |
|  |                     | 14:50                                     | 8.14                | 62.8          |
|  |                     | 14:53                                     | 9.23                | 62.7          |
|  |                     | 14:56                                     | 8.42                | 62.7          |
|  |                     | 15:00                                     | 8.95                | 62.7          |
|  |                     | 15:01                                     | 8.95                | 62.7          |
|  |                     | 15:02                                     | 6.85                | 62.7          |
|  |                     | 15:03                                     | 5.50                | 62.7          |
|  |                     | 15:04                                     | 2.47                | 62.7          |
|  |                     | 15:05                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 71   | 64                  | 64  | -                   | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 64   | 64                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 65                     |                     |   | 0                   | 0             |

Appendix A14: Field observations and experimental flow data for buffer strips replication AR10 – D3 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR10 - D3 - Rep 2                              | 16                  | 7   | 3,571                    | 6.0           |
| Simulated Rainfall Start Time:                 |                     |   | 1:25 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 2:25 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | 1:10 PM                  |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay           |               |
| Simulated Runoff Start Time:                   |                     |   | 1:40 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 2:25 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 13:40  | 13.55               | 14:05                                     | Outflow started          |               |
| 13:50  | 13.63               | 14:06                                     | 4.08                     | 71.4          |
| 14:00  | 14.20               | 14:11                                     | 5.38                     | 71.1          |
| 14:10  | 13.51               | 14:14                                     | 7.52                     | 70.6          |
| 14:20  | 13.82               | 14:19                                     | 8.25                     | 70.6          |
| 14:25  | 13.29               | 14:22                                     | 10.09                    | 70.6          |
|  |                     | 14:25                                     | 10.09                    | 70.6          |
|  |                     | 14:26                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | 81                  | 64  | 51                       | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | -                   |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A15: Field observations and experimental flow data for buffer strips replication AR10 – D3 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D3 -Rep 3                               | 22                  | 16  | 1,671               | 3.0           |
| Simulated Rainfall Start Time:                 |                     |   | 1:40 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 2:40 PM             |               |
| Sediment Mix Start Time:                       |                     |   | 1:25 PM             |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay      |               |
| Simulated Runoff Start Time:                   |                     |   | 1:55 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 2:40 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 13:55  | 13.14               | 14:01                                     | Outflow started     |               |
| 14:05  | 13.29               | 14:02                                     | 3.14                | 69.4          |
| 14:15  | 13.40               | 14:08                                     | 6.84                | 69.0          |
| 14:25  | 13.40               | 14:15                                     | 8.51                | 69.6          |
| 14:35  | 13.40               | 14:20                                     | 9.55                | 69.6          |
| 14:40  | 13.40               | 14:28                                     | 10.28               | 69.6          |
|  |                     | 14:33                                     | 11.54               | 69.6          |
|  |                     | 14:39                                     | 12.32               | 69.6          |
|  |                     | 14:40                                     | 12.32               | 69.6          |
|  |                     | 14:42                                     | 10.43               | 69.6          |
|  |                     | 14:44                                     | 3.86                | 69.6          |
|  |                     | 14:48                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 64   | 64                  | 64  | 58                  | 76            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 64   | -                   |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 65                     |                     |   | 0                   | 0             |

Appendix A16: Field observations and experimental flow data for buffer strips replication AR30 – D3 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D3 -Rep 1                               | 11                  | 22  | 3,196                    | 5.5           |
| Simulated Rainfall Start Time:                 |                     |   | 11:45 AM                 |               |
| Simulated Rainfall Stop Time:                  |                     |   | 12:45 PM                 |               |
| Sediment Mix Start Time:                       |                     |   | 11:30 AM                 |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay           |               |
| Simulated Runoff Start Time:                   |                     |   | 12:00 PM                 |               |
| Simulated Runoff Stop Time:                    |                     |   | 12:45 PM                 |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 12:00  | 40.01               | 12:03                                     | Outflow started          |               |
| 12:10  | 40.01               | 12:05                                     | 10.57                    | 62.9          |
| 12:20  | 39.86               | 12:08                                     | 15.17                    | 62.9          |
| 12:30  | 39.75               | 12:14                                     | 21.46                    | 62.5          |
| 12:40  | 39.63               | 12:19                                     | 27.57                    | 62.5          |
| 12:45  | 39.63               | 12:24                                     | 27.10                    | 62.5          |
|  |                     | 12:29                                     | 28.31                    | 62.4          |
|  |                     | 12:33                                     | 29.74                    | 62.4          |
|  |                     | 12:36                                     | 29.74                    | 62.4          |
|  |                     | 12:41                                     | 32.00                    | 62.3          |
|  |                     | 12:45                                     | 32.00                    | 62.3          |
|  |                     | 12:46                                     | 25.34                    | 62.4          |
|  |                     | 12:47                                     | 4.54                     | 62.4          |
|  |                     | 12:49                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 69   | 69                  | 64  | 64                       | 53            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | -                   |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A17: Field observations and experimental flow data for buffer strips replication AR30 – D3 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D3 - Rep 2                              | 15                  | 8   | 3,937                    | 11.0          |
| Simulated Rainfall Start Time:                 |                     |   | 10:15 AM                 |               |
| Simulated Rainfall Stop Time:                  |                     |   | 11:15 AM                 |               |
| Sediment Mix Start Time:                       |                     |   | 10:00 AM                 |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay           |               |
| Simulated Runoff Start Time:                   |                     |   | 10:30 AM                 |               |
| Simulated Runoff Stop Time:                    |                     |   | 11:15 AM                 |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 10:30  | 39.78               | 10:35                                     | Outflow started          |               |
| 10:40  | 39.86               | 10:37                                     | 4.62                     | 60.1          |
| 10:50  | 39.63               | 10:41                                     | 15.23                    | 59.6          |
| 11:00  | 39.71               | 10:45                                     | 19.45                    | 59.6          |
| 11:10  | 40.20               | 10:50                                     | 22.77                    | 59.8          |
| 11:15  | 40.20               | 10:57                                     | 23.42                    | 59.8          |
|  |                     | 11:02                                     | 25.94                    | 59.6          |
|  |                     | 11:07                                     | 25.93                    | 59.6          |
|  |                     | 11:11                                     | 25.93                    | 59.5          |
|  |                     | 11:14                                     | 27.05                    | 59.5          |
|  |                     | 11:15                                     | 27.05                    | 59.6          |
|  |                     | 11:16                                     | 24.87                    | 59.6          |
|  |                     | 11:17                                     | 10.57                    | 59.5          |
|  |                     | 11:18                                     | 1.77                     | 59.5          |
|  |                     | 11:19                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | -                   | -   | -                        | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | -                   | 1 (mm)                                    | 2 (mm)                   |               |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |



Appendix A18: Field observations and experimental flow data for buffer strips replication AR30 – D3 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D3 -Rep 3                               | 21                  | 17  | 3,414                    | 5.5           |
| Simulated Rainfall Start Time:                 |                     |   | 10:40 AM                 |               |
| Simulated Rainfall Stop Time:                  |                     |   | 11:40 AM                 |               |
| Sediment Mix Start Time:                       |                     |   | 10:25 AM                 |               |
| Total Sediment Used (kg):                      |                     |   | Pre-Mixed Clay           |               |
| Simulated Runoff Start Time:                   |                     |   | 10:55 AM                 |               |
| Simulated Runoff Stop Time:                    |                     |   | 11:40 AM                 |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 10:55  | 40.01               | 10:58                                     | Outflow started          |               |
| 11:05  | 39.78               | 11:00                                     | 21.43                    | 65.5          |
| 11:15  | 40.05               | 11:03                                     | 28.03                    | 65.5          |
| 11:25  | 39.90               | 11:09                                     | 32.28                    | 65.5          |
| 11:35  | 39.63               | 11:14                                     | 33.98                    | 65.5          |
| 11:40  | 39.63               | 11:20                                     | 34.42                    | 65.5          |
|  |                     | 11:25                                     | 35.61                    | 65.4          |
|  |                     | 11:32                                     | 35.77                    | 65.5          |
|  |                     | 11:37                                     | 35.77                    | 65.5          |
|  |                     | 11:39                                     | 34.27                    | 65.5          |
|  |                     | 11:40                                     | 32.52                    | 65.5          |
|  |                     | 11:42                                     | 20.81                    | 65.5          |
|  |                     | 11:44                                     | 5.26                     | 65.5          |
|  |                     | 11:46                                     | 0.89                     | 65.5          |
|  |                     | 11:48                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | -                   | 76  | 64                       | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | 51                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A19: Field observations and experimental flow data for buffer strips replication AR10 – D0 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR10 - D0 -Rep 1                               | 2                   | 3   | 4,129                    | 7.0           |
| Simulated Rainfall Start Time:                 |                     |   | 1:47 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 2:47 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | x                        |               |
| Total Sediment Used:                           |                     |   | None                     |               |
| Simulated Runoff Start Time:                   |                     |   | 2:02 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 2:47 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 14:02  | 13.36               | 14:09                                     | Outflow started          |               |
| 14:14  | 13.55               | 14:11                                     | 1.93                     | 82.6          |
| 14:24  | 13.29               | 14:13                                     | 4.50                     | 82.4          |
| 14:34  | 13.17               | 14:16                                     | 5.62                     | 82.4          |
| 14:44  | 13.32               | 14:20                                     | 8.91                     | 82.3          |
| 14:47  | 13.32               | 14:27                                     | 9.46                     | 82.4          |
|  |                     | 14:34                                     | 9.63                     | 82.3          |
|  |                     | 14:40                                     | 9.34                     | 82.3          |
|  |                     | 14:47                                     | 9.34                     | 82.2          |
|  |                     | 14:48                                     | 7.06                     | 82.2          |
|  |                     | 14:52                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | 61                  | 53  | 76                       | 76            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 53   | -                   |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

Appendix A20: Field observations and experimental flow data for buffer strips replication AR10 – D0 – R2.

| Replication                                    | Run                 | Strip                                     | Irrigation          |               |
|--|---------------------|---|---------------------|---------------|
| #  | #                   | #   | Amount (L)          | Duration (hr) |
| AR10 - D0 -Rep 2                               | 8                   | 10  | 4,080               | 6.5           |
| Simulated Rainfall Start Time:                 |                     |   | 4:00 PM             |               |
| Simulated Rainfall Stop Time:                  |                     |   | 5:00 PM             |               |
| Sediment Mix Start Time:                       |                     |   | x                   |               |
| Total Sediment Used:                           |                     |   | None                |               |
| Simulated Runoff Start Time:                   |                     |   | 4:15 PM             |               |
| Simulated Runoff Stop Time:                    |                     |   | 5:00 PM             |               |
| ----- Inflow Data -----                        |                     | ----- Outflow Data -----                  |                     |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                 | °F            |
| 16:15  | 13.29               | 16:24                                     | Outflow started     |               |
| 16:25  | 13.40               | 16:25                                     | 2.98                | 69.8          |
| 16:35  | 13.59               | 16:29                                     | 5.58                | 69.8          |
| 16:39  | 13.67               | 16:35                                     | 7.15                | 69.7          |
| 16:45  | 13.40               | 16:41                                     | 9.98                | 69.6          |
| 16:50  | 13.29               | 16:45                                     | 10.33               | 69.6          |
| 17:00  | 13.29               | 16:49                                     | 11.13               | 69.5          |
|  |                     | 16:51                                     | 11.11               | 69.6          |
|  |                     | 16:57                                     | 10.29               | 69.5          |
|  |                     | 17:00                                     | 10.29               | 69.5          |
|  |                     | 17:01                                     | 8.98                | 69.5          |
|  |                     | 17:02                                     | 4.61                | 69.4          |
|  |                     | 17:05                                     | Outflow stopped     |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                     |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)              | 5 (mm)        |
| 69   | 69                  | 58  | 64                  | 64            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                     |               |
| 64   | 64                  |   | 1 (mm)              | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                   | 0             |

Appendix A21: Field observations and experimental flow data for buffer strips replication AR10 – D0 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR10 - D0 -Rep 3                               | 24                  | 18  | 2,453                    | 4.0           |
| Simulated Rainfall Start Time:                 |                     |   | 4:00 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 5:00 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | x                        |               |
| Total Sediment Used:                           |                     |   | None                     |               |
| Simulated Runoff Start Time:                   |                     |   | 4:15 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 5:00 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 16:15  | 13.67               | 16:29                                     | Outflow started          |               |
| 16:25  | 13.85               | 16:30                                     | 0.82                     | 73.6          |
| 16:35  | 13.74               | 16:34                                     | 5.25                     | 73.4          |
| 16:45  | 13.89               | 16:40                                     | 7.55                     | 72.6          |
| 16:55  | 13.67               | 16:44                                     | 9.61                     | 71.9          |
| 17:00  | 13.67               | 16:49                                     | 9.86                     | 71.9          |
|  |                     | 16:54                                     | 9.94                     | 71.9          |
|  |                     | 16:58                                     | 10.15                    | 71.9          |
|  |                     | 17:00                                     | 10.15                    | 71.9          |
|  |                     | 17:01                                     | 9.65                     | 71.9          |
|  |                     | 17:03                                     | 3.16                     | 71.9          |
|  |                     | 17:05                                     | 0.79                     | 71.9          |
|  |                     | 17:07                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 53   | 71                  | 64  | 56                       | 58            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 69   | 71                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 63                     |                     | 63  | 0                        | 0             |

Appendix A22: Field observations and experimental flow data for buffer strips replication AR30 – D0 – R1.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D0 -Rep 1                               | 1                   | 4   | 4,281                    | 7.0           |
| Simulated Rainfall Start Time:                 |                     |   | 11:05 AM                 |               |
| Simulated Rainfall Stop Time:                  |                     |   | 12:05 PM                 |               |
| Sediment Mix Start Time:                       |                     |   | x                        |               |
| Total Sediment Used:                           |                     |   | None                     |               |
| Simulated Runoff Start Time:                   |                     |   | 11:20 AM                 |               |
| Simulated Runoff Stop Time:                    |                     |   | 12:05 PM                 |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 11:20  | 39.56               | 11:24                                     | Outflow started          |               |
| 11:22  | 39.60               | 11:25                                     | 12.02                    | 80.1          |
| 11:30  | 39.52               | 11:27                                     | 16.06                    | 80            |
| 11:44  | 39.41               | 11:29                                     | 21.99                    | 79.9          |
| 11:49  | 39.71               | 11:34                                     | 23.78                    | 79.8          |
| 11:52  | 39.41               | 11:41                                     | 25.40                    | 79.6          |
| 12:00  | 39.71               | 11:47                                     | 29.33                    | 79.6          |
| 12:05  | Stop                | 11:55                                     | 26.36                    | 79.7          |
|  |                     | 12:05                                     | 26.36                    | 79.7          |
|  |                     | 12:06                                     | 9.68                     | 79.7          |
|  |                     | 12:07                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 79   | 64                  | 56  | 64                       | 61            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| -  | -                   |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 65                     |                     |   | 0                        | 0             |

Appendix A23: Field observations and experimental flow data for buffer strips replication AR30 – D0 – R2.

| Replication  | Run                 | Strip                                     | Irrigation               |                |
|--|---------------------|---|--------------------------|----------------|
| #  | #                   | #   | Amount (L)               | Duration (hr)  |
| AR30 - D0 -Rep 2   | 10                  | 12  | 3,856                    | 6.0            |
| Simulated Rainfall Start Time:   |                     |   | 5:05 PM                  | See note below |
| Simulated Rainfall Stop Time:  |                     |   | 6:05 PM                  |                |
| Sediment Mix Start Time:   |                     |   | x                        |                |
| Total Sediment Used:   |                     |   | None                     |                |
| Simulated Runoff Start Time:   |                     |   | 5:20 PM                  |                |
| Simulated Runoff Stop Time:  |                     |   | 6:05 PM                  |                |
| ----- Inflow Data -----  |                     |   | ----- Outflow Data ----- |                |
| Clock Time   | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp     |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F             |
| 17:20  | 39.82               | 17:24                                     | Outflow started          |                |
| 17:30  | 39.86               | 17:26                                     | 7.01                     | 63.4           |
| 17:40  | 39.90               | 17:29                                     | 10.59                    | 63.1           |
| 17:50  | 39.82               | 17:32                                     | 15.20                    | 63.1           |
| 18:00  | 39.71               | 17:35                                     | 16.07                    | 63.1           |
| 18:05  | 39.78               | 17:39                                     | 22.05                    | 63.0           |
|  |                     | 17:43                                     | 25.54                    | 63.0           |
| Note: Rainfall simulator initial startup at 4:40 PM, broke after 10 seconds, everything stopped, simulator fixed, and run re-started at 5:05 PM. |                     | 17:48                                     | 26.37                    | 63.0           |
|  |                     | 17:54                                     | 31.01                    | 63.0           |
|  |                     | 18:00                                     | 32.66                    | 63.0           |
|  |                     | 18:03                                     | 27.56                    | 62.9           |
|  |                     | 18:05                                     | 28.02                    | 62.9           |
|  |                     | 18:06                                     | 21.78                    | 62.9           |
|  |                     | 18:07                                     | Outflow stopped          |                |
| Rain Gauges on the Strip Area (up to 7 gauges)   |                     |   |                          |                |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)         |
| 69   | 71                  | 64  | 64                       | 53             |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |                |
| 58   | 64                  |   | 1 (mm)                   | 2 (mm)         |
| Average Rainfall (mm) = 63   |                     |   | 0                        | 0              |

Appendix A24: Field observations and experimental flow data for buffer strips replication AR30 – D0 – R3.

| Replication                                    | Run                 | Strip                                     | Irrigation               |               |
|--|---------------------|---|--------------------------|---------------|
| #  | #                   | #   | Amount (L)               | Duration (hr) |
| AR30 - D0 -Rep 3                               | 23                  | 15  | 2,400                    | 4.0           |
| Simulated Rainfall Start Time:                 |                     |   | 2:15 PM                  |               |
| Simulated Rainfall Stop Time:                  |                     |   | 3:15 PM                  |               |
| Sediment Mix Start Time:                       |                     |   | x                        |               |
| Total Sediment Used:                           |                     |   | None                     |               |
| Simulated Runoff Start Time:                   |                     |   | 2:30 PM                  |               |
| Simulated Runoff Stop Time:                    |                     |   | 3:15 PM                  |               |
| ----- Inflow Data -----                        |                     |   | ----- Outflow Data ----- |               |
| Clock Time                                     | Corrected Flow Rate | Clock Time                                | Corrected Flow Rate      | Water Temp    |
| hh:mm  | Lpm                 | hh:mm                                     | Lpm                      | °F            |
| 14:30  | 40.01               | 14:34                                     | Outflow started          |               |
| 14:40  | 39.82               | 14:35                                     | 6.20                     | 72.1          |
| 14:50  | 39.78               | 14:37                                     | 13.27                    | 72.1          |
| 15:00  | 39.71               | 14:41                                     | 23.01                    | 72.0          |
| 15:10  | 40.01               | 14:46                                     | 25.49                    | 71.7          |
| 15:15  | 39.78               | 14:51                                     | 29.05                    | 71.7          |
|  |                     | 14:56                                     | 27.62                    | 71.7          |
|  |                     | 15:01                                     | 29.70                    | 71.7          |
|  |                     | 15:05                                     | 29.14                    | 71.7          |
|  |                     | 15:10                                     | 29.86                    | 71.7          |
|  |                     | 15:14                                     | 29.99                    | 71.7          |
|  |                     | 15:15                                     | 29.92                    | 71.7          |
|  |                     | 15:17                                     | 23.18                    | 71.7          |
|  |                     | 15:19                                     | 1.70                     | 71.7          |
|  |                     | 15:20                                     | Outflow stopped          |               |
| Rain Gauges on the Strip Area (up to 7 gauges) |                     |   |                          |               |
| 1 (mm)   | 2 (mm)              | 3 (mm)                                    | 4 (mm)                   | 5 (mm)        |
| 64   | 71                  | 56  | 64                       | 69            |
| 6 (mm)   | 7 (mm)              | External Rain Gauges (Outside Strip Area) |                          |               |
| 64   | 58                  |   | 1 (mm)                   | 2 (mm)        |
| Average Rainfall (mm) = 64                     |                     |   | 0                        | 0             |

**APPENDIX B. SEDIMENT MASS AND DISSOLVED  
PESTICIDE CONCENTRATIONS**

Sediment mass concentrations and dissolved phase pesticide concentrations in inflow (in) and outflow (out) from the buffer strips. n. d. is not detected, d. b.q.l. is detected but below quantitation limit. Sampling time for inflow is from start of inflow and for outflow is from start of outflow. Sediment mass concentrations for all samples are corrected for total solids concentration in the rainfall sample for the respective treatment.

| Treatment and Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D1 - R1            | In - 1A     | 10   | 2552                                  | 21                            | 3            | 34      |
| AR10 - D1 - R1            | In - 2A     | 20   | 2498                                  | 19                            | 3            | 31      |
| AR10 - D1 - R1            | In - 3A     | 30   | 2591                                  | 18                            | 2            | 35      |
| AR10 - D1 - R1            | In - 4A     | 40   | 2497                                  | 18                            | 2            | 36      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D1 - R1            | Out 1       | 2    | 405                                   | 5                             | 1            | 5       |
| AR10 - D1 - R1            | Out 2       | 4    | 340                                   |                               |              |         |
| AR10 - D1 - R1            | Out 3       | 6    | 255                                   | 8                             | 1            | 10      |
| AR10 - D1 - R1            | Out 4       | 8    | 305                                   |                               |              |         |
| AR10 - D1 - R1            | Out 5       | 10   | 240                                   |                               |              |         |
| AR10 - D1 - R1            | Out 6       | 12   | 230                                   | 9                             | 1            | 12      |
| AR10 - D1 - R1            | Out 7       | 14   | 300                                   |                               |              |         |
| AR10 - D1 - R1            | Out 8       | 16   | 250                                   |                               |              |         |
| AR10 - D1 - R1            | Out 9       | 18   | 220                                   | 13                            | 1            | 19      |
| AR10 - D1 - R1            | Out 10      | 20   | 190                                   |                               |              |         |
| AR10 - D1 - R1            | Out 11      | 22   | 135                                   |                               |              |         |
| AR10 - D1 - R1            | Out 12      | 24   | 165                                   | 12                            | 1            | 19      |
| AR10 - D1 - R1            | Out 13      | 26   | 25                                    |                               |              |         |
| AR10 - D1 - R1            | Out 14      | 28   | 135                                   | 13                            | 1            | 18      |
| AR10 - D1 - R1            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D1 - R2            | In - 1A     | 10   | 2500                                  | 20                            | 2            | 33      |
| AR10 - D1 - R2            | In - 2A     | 20   | 2555                                  | 20                            | 2            | 33      |
| AR10 - D1 - R2            | In - 3A     | 30   | 2580                                  | 21                            | 1            | 33      |
| AR10 - D1 - R2            | In - 4A     | 40   | 2563                                  | 23                            | 2            | 38      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D1 - R2            | Out 1       | 2    | 100                                   | 7                             | d, b.q.l.    | 7       |
| AR10 - D1 - R2            | Out 2       | 4    | 60                                    |                               |              |         |



| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D1 - R2            | Out 3       | 6    | 110                                   | 9                             | d, b.q.l.    | 10      |
| AR10 - D1 - R2            | Out 4       | 8    | 137                                   |                               |              |         |
| AR10 - D1 - R2            | Out 5       | 10   | 175                                   |                               |              |         |
| AR10 - D1 - R2            | Out 6       | 12   | 141                                   | 9                             | d, b.q.l.    | 11      |
| AR10 - D1 - R2            | Out 7       | 14   | 95                                    |                               |              |         |
| AR10 - D1 - R2            | Out 8       | 16   | 110                                   |                               |              |         |
| AR10 - D1 - R2            | Out 9       | 18   | 160                                   | 13                            | d, b.q.l.    | 16      |
| AR10 - D1 - R2            | Out 10      | 20   | 100                                   |                               |              |         |
| AR10 - D1 - R2            | Out 11      | 22   | 160                                   |                               |              |         |
| AR10 - D1 - R2            | Out 12      | 24   | 160                                   | 14                            | d, b.q.l.    | 18      |
| AR10 - D1 - R2            | Out 13      | 26   | 185                                   |                               |              |         |
| AR10 - D1 - R2            | Out 14      | 28   | 135                                   |                               |              |         |
| AR10 - D1 - R2            | Out 15      | 30   | 125                                   | 13                            | 1            | 18      |
| AR10 - D1 - R2            | Out 16      | 32   | 140                                   |                               |              |         |
| AR10 - D1 - R2            | Out 17      | 34   | 105                                   |                               |              |         |
| AR10 - D1 - R2            | Out 18      | 36   | 132                                   | 15                            | 1            | 20      |
| AR10 - D1 - R2            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D1 - R3            | In - 1A     | 10   | 2527                                  | 22                            | 2            | 27      |
| AR10 - D1 - R3            | In - 2A     | 20   | 2461                                  | 21                            | 2            | 28      |
| AR10 - D1 - R3            | In - 3A     | 30   | 2445                                  | 22                            | 2            | 31      |
| AR10 - D1 - R3            | In - 4A     | 40   | 2475                                  | 21                            | 2            | 29      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D1 - R3            | Out 1       | 2    | 295                                   | 7                             | d, b.q.l.    | 5       |
| AR10 - D1 - R3            | Out 2       | 4    | 293                                   |                               |              |         |
| AR10 - D1 - R3            | Out 3       | 6    | 285                                   | 9                             | 1            | 8       |
| AR10 - D1 - R3            | Out 4       | 8    | 278                                   |                               |              |         |
| AR10 - D1 - R3            | Out 5       | 10   | 308                                   |                               |              |         |
| AR10 - D1 - R3            | Out 6       | 12   | 270                                   | 10                            | 1            | 9       |
| AR10 - D1 - R3            | Out 7       | 14   | 240                                   |                               |              |         |
| AR10 - D1 - R3            | Out 8       | 16   | 280                                   |                               |              |         |
| AR10 - D1 - R3            | Out 9       | 18   | 268                                   | 13                            | 1            | 11      |
| AR10 - D1 - R3            | Out 10      | 20   | 265                                   |                               |              |         |
| AR10 - D1 - R3            | Out 11      | 22   | 273                                   |                               |              |         |
| AR10 - D1 - R3            | Out 12      | 24   | 300                                   | 15                            | 1            | 13      |
| AR10 - D1 - R3            | Out 13      | 26   | 215                                   |                               |              |         |
| AR10 - D1 - R3            | Out 14      | 28   | 225                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D1 - R3            | Out 15      | 30   | 208                                   | 14                            | 1            | 12      |
| AR10 - D1 - R3            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
| AR30 - D1 - R1            | In - 1A     | 10   | 2595                                  | 28                            | 4            | 37      |
| AR30 - D1 - R1            | In - 2A     | 20   | 2675                                  | 28                            | 3            | 38      |
| AR30 - D1 - R1            | In - 3A     | 30   | 2527                                  | 25                            | 3            | 33      |
| AR30 - D1 - R1            | In - 4A     | 40   | 2457                                  | 23                            | 3            | 32      |
| AR30 - D1 - R1            | Out 1       | 2    | 565                                   | 18                            | 1            | 18      |
| AR30 - D1 - R1            | Out 2       | 4    | 565                                   |                               |              |         |
| AR30 - D1 - R1            | Out 3       | 6    | 452                                   | 19                            | 1            | 23      |
| AR30 - D1 - R1            | Out 4       | 8    | 460                                   |                               |              |         |
| AR30 - D1 - R1            | Out 5       | 10   | 458                                   |                               |              |         |
| AR30 - D1 - R1            | Out 6       | 12   | 460                                   | 20                            | 1            | 27      |
| AR30 - D1 - R1            | Out 7       | 14   | 488                                   |                               |              |         |
| AR30 - D1 - R1            | Out 8       | 16   | 450                                   |                               |              |         |
| AR30 - D1 - R1            | Out 9       | 18   | 365                                   | 19                            | 1            | 31      |
| AR30 - D1 - R1            | Out 10      | 20   | 355                                   |                               |              |         |
| AR30 - D1 - R1            | Out 11      | 22   | 365                                   |                               |              |         |
| AR30 - D1 - R1            | Out 12      | 24   | 325                                   | 18                            | 2            | 33      |
| AR30 - D1 - R1            | Out 13      | 26   | 285                                   |                               |              |         |
| AR30 - D1 - R1            | Out 14      | 28   | 355                                   |                               |              |         |
| AR30 - D1 - R1            | Out 15      | 30   | 395                                   |                               |              |         |
| AR30 - D1 - R1            | Out 16      | 32   | 280                                   | 21                            | 1            | 27      |
| AR30 - D1 - R1            | Out 17      | 34   | 330                                   |                               |              |         |
| AR30 - D1 - R1            | Out 18      | 36   | 325                                   |                               |              |         |
| AR30 - D1 - R1            | Out 19      | 38   | 295                                   |                               |              |         |
| AR30 - D1 - R1            | Out 20      | 40   | 315                                   | 24                            | 1            | 32      |
| AR30 - D1 - R1            | Out 21      | 42   | 275                                   |                               |              |         |
| AR30 - D1 - R1            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
| AR30 - D1 - R2            | In - 1A     | 10   | 2359                                  | 27                            | 4            | 38      |
| AR30 - D1 - R2            | In - 2A     | 20   | 2568                                  | 30                            | 4            | 39      |
| AR30 - D1 - R2            | In - 3A     | 30   | 2623                                  | 27                            | 3            | 37      |
| AR30 - D1 - R2            | In - 4A     | 40   | 2515                                  | 27                            | 3            | 38      |
| AR30 - D1 - R2            | Out 1       | 2    | 280                                   | 21                            | 1            | 24      |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D1 - R2            | Out 2       | 4    | 325                                   |                               |              |         |
| AR30 - D1 - R2            | Out 3       | 6    | 275                                   | 19                            | 1            | 21      |
| AR30 - D1 - R2            | Out 4       | 8    | 265                                   |                               |              |         |
| AR30 - D1 - R2            | Out 5       | 10   | 310                                   |                               |              |         |
| AR30 - D1 - R2            | Out 6       | 12   | 240                                   | 19                            | 1            | 23      |
| AR30 - D1 - R2            | Out 7       | 14   | 250                                   |                               |              |         |
| AR30 - D1 - R2            | Out 8       | 16   | 241                                   |                               |              |         |
| AR30 - D1 - R2            | Out 9       | 18   | 270                                   | 20                            | 1            | 24      |
| AR30 - D1 - R2            | Out 10      | 20   | 250                                   |                               |              |         |
| AR30 - D1 - R2            | Out 11      | 22   | 245                                   |                               |              |         |
| AR30 - D1 - R2            | Out 12      | 24   | 245                                   | 23                            | 1            | 27      |
| AR30 - D1 - R2            | Out 13      | 26   | 180                                   |                               |              |         |
| AR30 - D1 - R2            | Out 14      | 28   | 205                                   |                               |              |         |
| AR30 - D1 - R2            | Out 15      | 30   | 175                                   |                               |              |         |
| AR30 - D1 - R2            | Out 16      | 32   | 191                                   | 24                            | 1            | 29      |
| AR30 - D1 - R2            | Out 17      | 34   | 205                                   |                               |              |         |
| AR30 - D1 - R2            | Out 18      | 36   | 200                                   |                               |              |         |
| AR30 - D1 - R2            | Out 19      | 38   | 191                                   | 22                            | 1            | 26      |
| AR30 - D1 - R2            | Rainfall    |      | 0                                     | d, b,q,l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D1 - R3            | In - 1A     | 10   | 2655                                  | 26                            | 2            | 31      |
| AR30 - D1 - R3            | In - 2A     | 20   | 2493                                  | 27                            | 2            | 37      |
| AR30 - D1 - R3            | In - 3A     | 30   | 2538                                  | 26                            | 2            | 36      |
| AR30 - D1 - R3            | In - 4A     | 40   | 2585                                  | 27                            | 2            | 29      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D1 - R3            | Out 1       | 2    | 463                                   | 19                            | 1            | 20      |
| AR30 - D1 - R3            | Out 2       | 4    | 560                                   |                               |              |         |
| AR30 - D1 - R3            | Out 3       | 6    | 550                                   | 18                            | 1            | 16      |
| AR30 - D1 - R3            | Out 4       | 8    | 619                                   |                               |              |         |
| AR30 - D1 - R3            | Out 5       | 10   | 917                                   |                               |              |         |
| AR30 - D1 - R3            | Out 6       | 12   | 680                                   | 19                            | 1            | 22      |
| AR30 - D1 - R3            | Out 7       | 14   | 615                                   |                               |              |         |
| AR30 - D1 - R3            | Out 8       | 16   | 720                                   |                               |              |         |
| AR30 - D1 - R3            | Out 9       | 18   | 599                                   | 23                            | 1            | 27      |
| AR30 - D1 - R3            | Out 10      | 20   | 705                                   |                               |              |         |
| AR30 - D1 - R3            | Out 11      | 22   | 669                                   |                               |              |         |
| AR30 - D1 - R3            | Out 12      | 24   | 492                                   | 19                            | 1            | 26      |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D1 - R3            | Out 13      | 26   | 587                                   |                               |              |         |
| AR30 - D1 - R3            | Out 14      | 28   | 950                                   |                               |              |         |
| AR30 - D1 - R3            | Out 15      | 30   | 528                                   |                               |              |         |
| AR30 - D1 - R3            | Out 16      | 32   | 796                                   | 20                            | 1            | 29      |
| AR30 - D1 - R3            | Out 17      | 34   | 528                                   |                               |              |         |
| AR30 - D1 - R3            | Out 18      | 36   | 649                                   |                               |              |         |
| AR30 - D1 - R3            | Out 19      | 38   | 485                                   |                               |              |         |
| AR30 - D1 - R3            | Out 20      | 40   | 478                                   | 20                            | 1            | 28      |
| AR30 - D1 - R3            | Out 21      | 42   | 689                                   |                               |              |         |
| AR30 - D1 - R3            | Out 22      | 44   | 695                                   |                               |              |         |
| AR30 - D1 - R3            | Out 23      | 46   | 545                                   | 18                            | 1            | 27      |
| AR30 - D1 - R3            | Rainfall    |      | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D2 - R1            | In - 1A     | 10   | 2653                                  | 35                            | 5            | 34      |
| AR10 - D2 - R1            | In - 2A     | 20   | 2518                                  | 32                            | 4            | 33      |
| AR10 - D2 - R1            | In - 3A     | 30   | 2535                                  | 33                            | 4            | 32      |
| AR10 - D2 - R1            | In - 4A     | 40   | 2515                                  | 39                            | 4            | 35      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D2 - R1            | Out 1       | 2    | 403                                   | 15                            | 1            | 10      |
| AR10 - D2 - R1            | Out 2       | 4    | 423                                   |                               |              |         |
| AR10 - D2 - R1            | Out 3       | 6    | 378                                   | 21                            | 1            | 17      |
| AR10 - D2 - R1            | Out 4       | 8    | 358                                   |                               |              |         |
| AR10 - D2 - R1            | Out 5       | 10   | 317                                   |                               |              |         |
| AR10 - D2 - R1            | Out 6       | 12   | 403                                   | 22                            | 2            | 20      |
| AR10 - D2 - R1            | Out 7       | 14   | 361                                   |                               |              |         |
| AR10 - D2 - R1            | Out 8       | 16   | 373                                   |                               |              |         |
| AR10 - D2 - R1            | Out 9       | 18   | 303                                   | 22                            | 2            | 19      |
| AR10 - D2 - R1            | Out 10      | 20   | 368                                   |                               |              |         |
| AR10 - D2 - R1            | Out 11      | 22   | 351                                   |                               |              |         |
| AR10 - D2 - R1            | Out 12      | 24   | 288                                   | 27                            | 2            | 23      |
| AR10 - D2 - R1            | Out 13      | 26   | 563                                   |                               |              |         |
| AR10 - D2 - R1            | Out 14      | 28   | 528                                   |                               |              |         |
| AR10 - D2 - R1            | Out 15      | 30   | 500                                   | 24                            | 2            | 20      |
| AR10 - D2 - R1            | Out 16      | 32   | 393                                   |                               |              |         |
| AR10 - D2 - R1            | Out 17      | 34   | 353                                   |                               |              |         |
| AR10 - D2 - R1            | Out 18      | 36   | 428                                   | 23                            | 2            | 21      |
| AR10 - D2 - R1            | Out 19      | 38   | 418                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D2 - R1            | Out 20      | 40   | 448                                   | 24                            | 2            | 23      |
| AR10 - D2 - R1            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
| AR10 - D2 - R2            | In - 1A     | 10   | 2575                                  | 35                            | 4            | 29      |
| AR10 - D2 - R2            | In - 2A     | 20   | 2608                                  | 35                            | 3            | 30      |
| AR10 - D2 - R2            | In - 3A     | 30   | 2550                                  | 36                            | 3            | 31      |
| AR10 - D2 - R2            | In - 4A     | 40   | 2655                                  | 34                            | 3            | 29      |
| AR10 - D2 - R2            | Out 1       | 2    | 1011                                  | 15                            | d, b.q.l.    | 10      |
| AR10 - D2 - R2            | Out 2       | 4    | 910                                   |                               |              |         |
| AR10 - D2 - R2            | Out 3       | 6    | 1076                                  | 18                            | d, b.q.l.    | 11      |
| AR10 - D2 - R2            | Out 4       | 8    | 1080                                  |                               |              |         |
| AR10 - D2 - R2            | Out 5       | 10   | 1045                                  |                               |              |         |
| AR10 - D2 - R2            | Out 6       | 12   | 1015                                  | 24                            | 1            | 17      |
| AR10 - D2 - R2            | Out 7       | 14   | 1051                                  |                               |              |         |
| AR10 - D2 - R2            | Out 8       | 16   | 1045                                  |                               |              |         |
| AR10 - D2 - R2            | Out 9       | 18   | 982                                   | 23                            | 1            | 17      |
| AR10 - D2 - R2            | Out 10      | 20   | 982                                   |                               |              |         |
| AR10 - D2 - R2            | Out 11      | 22   | 1076                                  |                               |              |         |
| AR10 - D2 - R2            | Out 12      | 24   | 1070                                  | 26                            | 1            | 19      |
| AR10 - D2 - R2            | Out 13      | 26   | 645                                   |                               |              |         |
| AR10 - D2 - R2            | Out 14      | 28   | 465                                   |                               |              |         |
| AR10 - D2 - R2            | Out 15      | 30   | 430                                   |                               |              |         |
| AR10 - D2 - R2            | Out 16      | 32   | 495                                   | 23                            | 1            | 19      |
| AR10 - D2 - R2            | Out 17      | 34   | 325                                   |                               |              |         |
| AR10 - D2 - R2            | Out 18      | 36   | 325                                   |                               |              |         |
| AR10 - D2 - R2            | Out 19      | 38   | 375                                   |                               |              |         |
| AR10 - D2 - R2            | Out 20      | 40   | 255                                   | 24                            | 1            | 21      |
| AR10 - D2 - R2            | Out 21      | 42   | 220                                   |                               |              |         |
| AR10 - D2 - R2            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D2 - R3            | In - 1A     | 10   | 2644                                  | 30                            | 3            | 35      |
| AR10 - D2 - R3            | In - 2A     | 20   | 2594                                  | 27                            | 3            | 34      |
| AR10 - D2 - R3            | In - 3A     | 30   | 2603                                  | 33                            | 2            | 35      |
| AR10 - D2 - R3            | In - 4A     | 40   | 2651                                  | 25                            | 3            | 28      |
| AR10 - D2 - R3            | Out 1       | 2    | 454                                   | 12                            | d, b.q.l.    | 9       |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D2 - R3            | Out 2       | 4    | 434                                   |                               |              |         |
| AR10 - D2 - R3            | Out 3       | 6    | 386                                   | 14                            | d, b.q.l.    | 11      |
| AR10 - D2 - R3            | Out 4       | 8    | 349                                   |                               |              |         |
| AR10 - D2 - R3            | Out 5       | 10   | 334                                   |                               |              |         |
| AR10 - D2 - R3            | Out 6       | 12   | 229                                   | 20                            | 1            | 20      |
| AR10 - D2 - R3            | Out 7       | 14   | 219                                   |                               |              |         |
| AR10 - D2 - R3            | Out 8       | 16   | 223                                   |                               |              |         |
| AR10 - D2 - R3            | Out 9       | 18   | 239                                   | 25                            | 1            | 21      |
| AR10 - D2 - R3            | Out 10      | 20   | 194                                   |                               |              |         |
| AR10 - D2 - R3            | Out 11      | 22   | 149                                   |                               |              |         |
| AR10 - D2 - R3            | Out 12      | 24   | 114                                   | 22                            | 1            | 19      |
| AR10 - D2 - R3            | Out 13      | 26   | 193                                   |                               |              |         |
| AR10 - D2 - R3            | Out 14      | 28   | 183                                   | 23                            | 1            | 21      |
| AR10 - D2 - R3            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R1            | In - 1A     | 10   | 2513                                  | 26                            | 5            | 28      |
| AR30 - D2 - R1            | In - 2A     | 20   | 2580                                  | 27                            | 4            | 29      |
| AR30 - D2 - R1            | In - 3A     | 30   | 2650                                  | 29                            | 5            | 31      |
| AR30 - D2 - R1            | In - 4A     | 40   | 2615                                  | 30                            | 4            | 33      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R1            | Out 1       | 2    | 387                                   | 19                            | 1            | 15      |
| AR30 - D2 - R1            | Out 2       | 4    | 667                                   |                               |              |         |
| AR30 - D2 - R1            | Out 3       | 6    | 512                                   | 22                            | 2            | 21      |
| AR30 - D2 - R1            | Out 4       | 8    | 457                                   |                               |              |         |
| AR30 - D2 - R1            | Out 5       | 10   | 432                                   |                               |              |         |
| AR30 - D2 - R1            | Out 6       | 12   | 417                                   | 23                            | 3            | 21      |
| AR30 - D2 - R1            | Out 7       | 14   | 417                                   |                               |              |         |
| AR30 - D2 - R1            | Out 8       | 16   | 432                                   |                               |              |         |
| AR30 - D2 - R1            | Out 9       | 18   | 417                                   | 25                            | 3            | 24      |
| AR30 - D2 - R1            | Out 10      | 20   | 461                                   |                               |              |         |
| AR30 - D2 - R1            | Out 11      | 22   | 442                                   |                               |              |         |
| AR30 - D2 - R1            | Out 12      | 24   | 514                                   | 26                            | 4            | 26      |
| AR30 - D2 - R1            | Out 13      | 26   | 397                                   |                               |              |         |
| AR30 - D2 - R1            | Out 14      | 28   | 502                                   |                               |              |         |
| AR30 - D2 - R1            | Out 15      | 30   | 474                                   |                               |              |         |
| AR30 - D2 - R1            | Out 16      | 32   | 538                                   | 26                            | 3            | 26      |
| AR30 - D2 - R1            | Out 17      | 34   | 567                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D2 - R1            | Out 18      | 36   | 497                                   |                               |              |         |
| AR30 - D2 - R1            | Out 19      | 38   | 652                                   |                               |              |         |
| AR30 - D2 - R1            | Out 20      | 40   | 642                                   | 29                            | 3            | 30      |
| AR30 - D2 - R1            | Out 21      | 42   | 442                                   |                               |              |         |
| AR30 - D2 - R1            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R2            | In - 1A     | 10   | 2544                                  | 30                            | 5            | 31      |
| AR30 - D2 - R2            | In - 2A     | 20   | 2603                                  | 30                            | 4            | 30      |
| AR30 - D2 - R2            | In - 3A     | 30   | 2543                                  | 29                            | 4            | 29      |
| AR30 - D2 - R2            | In - 4A     | 40   | 2538                                  | 27                            | 3            | 29      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R2            | Out 1       | 2    | 340                                   | 21                            | 1            | 17      |
| AR30 - D2 - R2            | Out 2       | 4    | 360                                   |                               |              |         |
| AR30 - D2 - R2            | Out 3       | 6    | 360                                   | 24                            | 2            | 21      |
| AR30 - D2 - R2            | Out 4       | 8    | 425                                   |                               |              |         |
| AR30 - D2 - R2            | Out 5       | 10   | 410                                   |                               |              |         |
| AR30 - D2 - R2            | Out 6       | 12   | 385                                   | 25                            | 3            | 22      |
| AR30 - D2 - R2            | Out 7       | 14   | 373                                   |                               |              |         |
| AR30 - D2 - R2            | Out 8       | 16   | 385                                   |                               |              |         |
| AR30 - D2 - R2            | Out 9       | 18   | 415                                   | 23                            | 3            | 22      |
| AR30 - D2 - R2            | Out 10      | 20   | 415                                   |                               |              |         |
| AR30 - D2 - R2            | Out 11      | 22   | 425                                   |                               |              |         |
| AR30 - D2 - R2            | Out 12      | 24   | 445                                   | 21                            | 3            | 21      |
| AR30 - D2 - R2            | Out 13      | 26   | 435                                   |                               |              |         |
| AR30 - D2 - R2            | Out 14      | 28   | 455                                   |                               |              |         |
| AR30 - D2 - R2            | Out 15      | 30   | 485                                   | 21                            | 2            | 20      |
| AR30 - D2 - R2            | Out 16      | 32   | 467                                   |                               |              |         |
| AR30 - D2 - R2            | Out 17      | 34   | 490                                   |                               |              |         |
| AR30 - D2 - R2            | Out 18      | 36   | 465                                   |                               |              |         |
| AR30 - D2 - R2            | Out 19      | 38   | 495                                   | 18                            | 1            | 24      |
| AR30 - D2 - R2            | Out 20      | 40   | 490                                   |                               |              |         |
| AR30 - D2 - R2            | Out 21      | 42   | 448                                   |                               |              |         |
| AR30 - D2 - R2            | Out 22      | 44   | 315                                   | 20                            | 1            | 25      |
| AR30 - D2 - R2            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R3            | In - 1A     | 10   | 2565                                  | 35                            | 5            | 31      |
| AR30 - D2 - R3            | In - 2A     | 20   | 2528                                  | 33                            | 5            | 26      |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D2 - R3            | In - 3A     | 30   | 2573                                  | 35                            | 4            | 24      |
| AR30 - D2 - R3            | In - 4A     | 40   | 2568                                  | 37                            | 4            | 26      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D2 - R3            | Out 1       | 2    | 365                                   | 22                            | 1            | 8       |
| AR30 - D2 - R3            | Out 2       | 4    | 322                                   |                               |              |         |
| AR30 - D2 - R3            | Out 3       | 6    | 317                                   | 26                            | 2            | 19      |
| AR30 - D2 - R3            | Out 4       | 8    | 347                                   |                               |              |         |
| AR30 - D2 - R3            | Out 5       | 10   | 345                                   |                               |              |         |
| AR30 - D2 - R3            | Out 6       | 12   | 350                                   | 27                            | 3            | 17      |
| AR30 - D2 - R3            | Out 7       | 14   | 351                                   |                               |              |         |
| AR30 - D2 - R3            | Out 8       | 16   | 370                                   |                               |              |         |
| AR30 - D2 - R3            | Out 9       | 18   | 371                                   | 28                            | 3            | 16      |
| AR30 - D2 - R3            | Out 10      | 20   | 360                                   |                               |              |         |
| AR30 - D2 - R3            | Out 11      | 22   | 380                                   |                               |              |         |
| AR30 - D2 - R3            | Out 12      | 24   | 386                                   | 28                            | 3            | 18      |
| AR30 - D2 - R3            | Out 13      | 26   | 322                                   |                               |              |         |
| AR30 - D2 - R3            | Out 14      | 28   | 355                                   |                               |              |         |
| AR30 - D2 - R3            | Out 15      | 30   | 366                                   |                               |              |         |
| AR30 - D2 - R3            | Out 16      | 32   | 405                                   | 28                            | 4            | 17      |
| AR30 - D2 - R3            | Out 17      | 34   | 420                                   |                               |              |         |
| AR30 - D2 - R3            | Out 18      | 36   | 476                                   |                               |              |         |
| AR30 - D2 - R3            | Out 19      | 38   | 475                                   |                               |              |         |
| AR30 - D2 - R3            | Out 20      | 40   | 487                                   | 24                            | 3            | 20      |
| AR30 - D2 - R3            | Out 21      | 42   | 366                                   |                               |              |         |
| AR30 - D2 - R3            | Out 22      | 44   | 280                                   | 30                            | 4            | 19      |
| AR30 - D2 - R3            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D3 - R1            | In - 1A     | 10   | 448                                   | 43                            | 5            | 37      |
| AR10 - D3 - R1            | In - 2A     | 20   | 437                                   | 45                            | 5            | 39      |
| AR10 - D3 - R1            | In - 3A     | 30   | 426                                   | 42                            | 5            | 36      |
| AR10 - D3 - R1            | In - 4A     | 40   | 438                                   | 37                            | 3            | 30      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D3 - R1            | Out 1       | 2    | 441                                   | 29                            | 1            | 23      |
| AR10 - D3 - R1            | Out 2       | 4    | 435                                   |                               |              |         |
| AR10 - D3 - R1            | Out 3       | 6    | 443                                   | 32                            | 1            | 25      |
| AR10 - D3 - R1            | Out 4       | 8    | 435                                   |                               |              |         |
| AR10 - D3 - R1            | Out 5       | 10   | 430                                   |                               |              |         |



| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D3 - R1            | Out 6       | 12   | 446                                   | 18                            | 2            | 17      |
| AR10 - D3 - R1            | Out 7       | 14   | 411                                   |                               |              |         |
| AR10 - D3 - R1            | Out 8       | 16   | 375                                   |                               |              |         |
| AR10 - D3 - R1            | Out 9       | 18   | 405                                   | 28                            | 2            | 22      |
| AR10 - D3 - R1            | Out 10      | 20   | 397                                   |                               |              |         |
| AR10 - D3 - R1            | Out 11      | 22   | 410                                   |                               |              |         |
| AR10 - D3 - R1            | Out 12      | 24   | 387                                   | 29                            | 2            | 23      |
| AR10 - D3 - R1            | Out 13      | 26   | 446                                   |                               |              |         |
| AR10 - D3 - R1            | Out 14      | 28   | 407                                   |                               |              |         |
| AR10 - D3 - R1            | Out 15      | 30   | 413                                   | 30                            | 2            | 23      |
| AR10 - D3 - R1            | Out 16      | 32   | 403                                   |                               |              |         |
| AR10 - D3 - R1            | Out 17      | 34   | 410                                   |                               |              |         |
| AR10 - D3 - R1            | Out 18      | 36   | 400                                   |                               |              |         |
| AR10 - D3 - R1            | Out 19      | 38   | 431                                   | 33                            | 1            | 25      |
| AR10 - D3 - R1            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D3 - R2            | In - 1A     | 10   | 394                                   | 40                            | 5            | 28      |
| AR10 - D3 - R2            | In - 2A     | 20   | 350                                   | 42                            | 5            | 29      |
| AR10 - D3 - R2            | In - 3A     | 30   | 390                                   | 46                            | 4            | 33      |
| AR10 - D3 - R2            | In - 4A     | 40   | 370                                   | 47                            | 4            | 33      |
|                           |             |      |                                       |                               |              |         |
| AR10 - D3 - R2            | Out 1       | 2    | 790                                   | 30                            | 1            | 27      |
| AR10 - D3 - R2            | Out 2       | 4    | 750                                   |                               |              |         |
| AR10 - D3 - R2            | Out 3       | 6    | 730                                   | 32                            | 2            | 23      |
| AR10 - D3 - R2            | Out 4       | 8    | 475                                   |                               |              |         |
| AR10 - D3 - R2            | Out 5       | 10   | 390                                   |                               |              |         |
| AR10 - D3 - R2            | Out 6       | 12   | 400                                   | 28                            | 2            | 24      |
| AR10 - D3 - R2            | Out 7       | 14   | 375                                   |                               |              |         |
| AR10 - D3 - R2            | Out 8       | 16   | 423                                   |                               |              |         |
| AR10 - D3 - R2            | Out 9       | 18   | 370                                   | 28                            | 2            | 19      |
| AR10 - D3 - R2            | Out 10      | 20   | 405                                   | 27                            | 1            | 20      |
| AR10 - D3 - R2            | Out 11      | 22   | 485                                   | 26                            | 1            | 21      |
| AR10 - D3 - R2            | Rainfall    |      | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10 - D3 - R3            | In - 1A     | 10   | 435                                   | 31                            | 4            | 31      |
| AR10 - D3 - R3            | In - 2A     | 20   | 424                                   | 33                            | 3            | 32      |
| AR10 - D3 - R3            | In - 3A     | 30   | 396                                   | 34                            | 4            | 31      |

| Treatment<br>And<br>Replication | Sample<br>I.D. | Time | Corrected<br>Sediment Mass<br>Concentration | Dissolved Phase Concentration |              |         |
|---------------------------------|----------------|------|---|-------------------------------|--------------|---------|
|                                 |                |      |   | Atrazine                      | Chlorpyrifos | Linuron |
| #                               | #              | min  | mg/L  | µg/L                          | µg/L         | µg/L    |
| AR10 - D3 - R3                  | In - 4A        | 40   | 446   | 33                            | 3            | 30      |
| AR10 - D3 - R3                  | Out 1          | 2    | 557   | 13                            | d, b.q.l.    | 10      |
| AR10 - D3 - R3                  | Out 2          | 4    | 437   |                               |              |         |
| AR10 - D3 - R3                  | Out 3          | 6    | 352   | 19                            | 1            | 16      |
| AR10 - D3 - R3                  | Out 4          | 8    | 365   |                               |              |         |
| AR10 - D3 - R3                  | Out 5          | 10   | 313   |                               |              |         |
| AR10 - D3 - R3                  | Out 6          | 12   | 332   | 22                            | 1            | 15      |
| AR10 - D3 - R3                  | Out 7          | 14   | 328   |                               |              |         |
| AR10 - D3 - R3                  | Out 8          | 16   | 343   |                               |              |         |
| AR10 - D3 - R3                  | Out 9          | 18   | 337   | 24                            | 1            | 19      |
| AR10 - D3 - R3                  | Out 10         | 20   | 308   |                               |              |         |
| AR10 - D3 - R3                  | Out 11         | 22   | 382   |                               |              |         |
| AR10 - D3 - R3                  | Out 12         | 24   | 391   | 23                            | 1            | 19      |
| AR10 - D3 - R3                  | Out 13         | 26   | 418   |                               |              |         |
| AR10 - D3 - R3                  | Out 14         | 28   | 383   |                               |              |         |
| AR10 - D3 - R3                  | Out 15         | 30   | 352   | 25                            | 1            | 21      |
| AR10 - D3 - R3                  | Out 16         | 32   | 363   |                               |              |         |
| AR10 - D3 - R3                  | Out 17         | 34   | 395   |                               |              |         |
| AR10 - D3 - R3                  | Out 18         | 36   | 393   | 23                            | 1            | 15      |
| AR10 - D3 - R3                  | Out 19         | 38   | 367   |                               |              |         |
| AR10 - D3 - R3                  | Out 20         | 40   | 417   |                               |              |         |
| AR10 - D3 - R3                  | Out 21         | 42   | 427   | 24                            | 1            | 23      |
| AR10 - D3 - R3                  | Out 22         | 44   | 323   |                               |              |         |
| AR10 - D3 - R3                  | Rainfall       |      | 0   | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D3 - R1                  | In - 1A        | 10   | 431   | 27                            | 4            | 28      |
| AR30 - D3 - R1                  | In - 2A        | 20   | 440   | 26                            | 4            | 30      |
| AR30 - D3 - R1                  | In - 3A        | 30   | 441   | 23                            | 4            | 34      |
| AR30 - D3 - R1                  | In - 4A        | 40   | 485   | 23                            | 5            | 34      |
| AR30 - D3 - R1                  | Out 1          | 2    | 551   | 20                            | 1            | 16      |
| AR30 - D3 - R1                  | Out 2          | 4    | 535   |                               |              |         |
| AR30 - D3 - R1                  | Out 3          | 6    | 541   | 21                            | 3            | 21      |
| AR30 - D3 - R1                  | Out 4          | 8    | 475   |                               |              |         |
| AR30 - D3 - R1                  | Out 5          | 10   | 465   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D3 - R1            | Out 6       | 12   | 500                                   | 22                            | 3            | 24      |
| AR30 - D3 - R1            | Out 7       | 14   | 476                                   |                               |              |         |
| AR30 - D3 - R1            | Out 8       | 16   | 445                                   |                               |              |         |
| AR30 - D3 - R1            | Out 9       | 18   | 455                                   | 19                            | 3            | 24      |
| AR30 - D3 - R1            | Out 10      | 20   | 415                                   |                               |              |         |
| AR30 - D3 - R1            | Out 11      | 22   | 441                                   |                               |              |         |
| AR30 - D3 - R1            | Out 12      | 24   | 436                                   | 19                            | 4            | 25      |
| AR30 - D3 - R1            | Out 13      | 26   | 405                                   |                               |              |         |
| AR30 - D3 - R1            | Out 14      | 28   | 425                                   |                               |              |         |
| AR30 - D3 - R1            | Out 15      | 30   | 408                                   | 21                            | 3            | 27      |
| AR30 - D3 - R1            | Out 16      | 32   | 411                                   |                               |              |         |
| AR30 - D3 - R1            | Out 17      | 34   | 435                                   |                               |              |         |
| AR30 - D3 - R1            | Out 18      | 36   | 415                                   | 21                            | 3            | 30      |
| AR30 - D3 - R1            | Out 19      | 38   | 420                                   |                               |              |         |
| AR30 - D3 - R1            | Out 20      | 40   | 420                                   |                               |              |         |
| AR30 - D3 - R1            | Out 21      | 42   | 440                                   | 22                            | 3            | 29      |
| AR30 - D3 - R1            | Out 22      | 44   | 411                                   |                               |              |         |
| AR30 - D3 - R1            | Rainfall    |      | 0                                     | n.d.                          | n. d.        | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D3 - R2            | In - 1A     | 10   | 423                                   | 33                            | 3            | 26      |
| AR30 - D3 - R2            | In - 2A     | 20   | 447                                   | 34                            | 5            | 30      |
| AR30 - D3 - R2            | In - 3A     | 30   | 456                                   | 35                            | 5            | 29      |
| AR30 - D3 - R2            | In - 4A     | 40   | 450                                   | 35                            | 5            | 31      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D3 - R2            | Out 1       | 2    | 105                                   | 26                            | 1            | 16      |
| AR30 - D3 - R2            | Out 2       | 4    | 225                                   |                               |              |         |
| AR30 - D3 - R2            | Out 3       | 6    | 490                                   | 26                            | 1            | 19      |
| AR30 - D3 - R2            | Out 4       | 8    | 420                                   |                               |              |         |
| AR30 - D3 - R2            | Out 5       | 10   | 425                                   |                               |              |         |
| AR30 - D3 - R2            | Out 6       | 12   | 510                                   | 28                            | 2            | 21      |
| AR30 - D3 - R2            | Out 7       | 14   | 530                                   |                               |              |         |
| AR30 - D3 - R2            | Out 8       | 16   | 575                                   |                               |              |         |
| AR30 - D3 - R2            | Out 9       | 18   | 565                                   | 33                            | 3            | 25      |
| AR30 - D3 - R2            | Out 10      | 20   | 400                                   |                               |              |         |
| AR30 - D3 - R2            | Out 11      | 22   | 460                                   |                               |              |         |
| AR30 - D3 - R2            | Out 12      | 24   | 415                                   | 29                            | 3            | 22      |
| AR30 - D3 - R2            | Out 13      | 26   | 375                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D3 - R2            | Out 14      | 28   | 355                                   |                               |              |         |
| AR30 - D3 - R2            | Out 15      | 30   | 320                                   | 30                            | 3            | 25      |
| AR30 - D3 - R2            | Out 16      | 32   | 360                                   |                               |              |         |
| AR30 - D3 - R2            | Out 17      | 34   | 345                                   |                               |              |         |
| AR30 - D3 - R2            | Out 18      | 36   | 345                                   | 32                            | 3            | 26      |
| AR30 - D3 - R2            | Out 19      | 38   | 335                                   |                               |              |         |
| AR30 - D3 - R2            | Out 20      | 40   | 355                                   |                               |              |         |
| AR30 - D3 - R2            | Out 21      | 42   | 330                                   | 25                            | 3            | 22      |
| AR30 - D3 - R2            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D3 - R3            | In - 1A     | 10   | 412                                   | 25                            | 4            | 28      |
| AR30 - D3 - R3            | In - 2A     | 20   | 422                                   | 27                            | 5            | 36      |
| AR30 - D3 - R3            | In - 3A     | 30   | 435                                   | 25                            | 5            | 32      |
| AR30 - D3 - R3            | In - 4A     | 40   | 440                                   | 28                            | 5            | 38      |
|                           |             |      |                                       |                               |              |         |
| AR30 - D3 - R3            | Out 1       | 2    | 516                                   | 19                            | 1            | 19      |
| AR30 - D3 - R3            | Out 2       | 4    | 456                                   |                               |              |         |
| AR30 - D3 - R3            | Out 3       | 6    | 461                                   | 22                            | 2            | 21      |
| AR30 - D3 - R3            | Out 4       | 8    | 446                                   |                               |              |         |
| AR30 - D3 - R3            | Out 5       | 10   | 406                                   |                               |              |         |
| AR30 - D3 - R3            | Out 6       | 12   | 418                                   | 18                            | 4            | 20      |
| AR30 - D3 - R3            | Out 7       | 14   | 436                                   |                               |              |         |
| AR30 - D3 - R3            | Out 8       | 16   | 406                                   |                               |              |         |
| AR30 - D3 - R3            | Out 9       | 18   | 436                                   | 18                            | 3            | 25      |
| AR30 - D3 - R3            | Out 10      | 20   | 413                                   |                               |              |         |
| AR30 - D3 - R3            | Out 11      | 22   | 426                                   |                               |              |         |
| AR30 - D3 - R3            | Out 12      | 24   | 416                                   | 23                            | 3            | 28      |
| AR30 - D3 - R3            | Out 13      | 26   | 426                                   |                               |              |         |
| AR30 - D3 - R3            | Out 14      | 28   | 408                                   |                               |              |         |
| AR30 - D3 - R3            | Out 15      | 30   | 431                                   | 20                            | 4            | 23      |
| AR30 - D3 - R3            | Out 16      | 32   | 443                                   |                               |              |         |
| AR30 - D3 - R3            | Out 17      | 34   | 431                                   |                               |              |         |
| AR30 - D3 - R3            | Out 18      | 36   | 436                                   | 19                            | 3            | 25      |
| AR30 - D3 - R3            | Out 19      | 38   | 403                                   |                               |              |         |
| AR30 - D3 - R3            | Out 20      | 40   | 438                                   |                               |              |         |
| AR30 - D3 - R3            | Out 21      | 42   | 461                                   |                               |              |         |
| AR30 - D3 - R3            | Out 22      | 44   | 459                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D3 - R3            | Out 23      | 46   | 426                                   | 22                            | 4            | 31      |
| AR30 - D3 - R3            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | In - 1A     | 10   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | In - 2A     | 20   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | In - 3A     | 30   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | In - 4A     | 40   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 1       | 2    | 435                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 2       | 4    | 301                                   |                               |              |         |
| AR10 - D0 - R1            | Out 3       | 6    | 423                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 4       | 8    | 241                                   |                               |              |         |
| AR10 - D0 - R1            | Out 5       | 10   | 300                                   |                               |              |         |
| AR10 - D0 - R1            | Out 6       | 12   | 280                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 7       | 14   | 347                                   |                               |              |         |
| AR10 - D0 - R1            | Out 8       | 16   | 165                                   |                               |              |         |
| AR10 - D0 - R1            | Out 9       | 18   | 195                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 10      | 20   | 190                                   |                               |              |         |
| AR10 - D0 - R1            | Out 11      | 22   | 190                                   |                               |              |         |
| AR10 - D0 - R1            | Out 12      | 24   | 200                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 13      | 26   | 180                                   |                               |              |         |
| AR10 - D0 - R1            | Out 14      | 28   | 155                                   |                               |              |         |
| AR10 - D0 - R1            | Out 15      | 30   | 150                                   |                               |              |         |
| AR10 - D0 - R1            | Out 16      | 32   | 95                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 17      | 34   | 106                                   |                               |              |         |
| AR10 - D0 - R1            | Out 18      | 36   | 165                                   |                               |              |         |
| AR10 - D0 - R1            | Out 19      | 38   | 180                                   |                               |              |         |
| AR10 - D0 - R1            | Out 20      | 40   | 111                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R1            | Out 21      | 42   | 126                                   |                               |              |         |
| AR10 - D0 - R1            | Out 22      | 44   | 70                                    |                               |              |         |
| AR10 - D0 - R1            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR10 - D0 - R2            | In - 1A     | 10   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | In - 2A     | 20   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | In - 3A     | 30   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | In - 4A     | 40   | 0                                     | n.d.                          | n.d.         | n. d.   |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10 - D0 - R2            | Out 1       | 2    | 131                                   | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 2       | 4    | 141                                   |                               |              |         |
| AR10 - D0 - R2            | Out 3       | 6    | 231                                   | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 4       | 8    | 66                                    |                               |              |         |
| AR10 - D0 - R2            | Out 5       | 10   | 71                                    |                               |              |         |
| AR10 - D0 - R2            | Out 6       | 12   | 6                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 7       | 14   | 71                                    |                               |              |         |
| AR10 - D0 - R2            | Out 8       | 16   | 61                                    |                               |              |         |
| AR10 - D0 - R2            | Out 9       | 18   | 6                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 10      | 20   | 23                                    |                               |              |         |
| AR10 - D0 - R2            | Out 11      | 22   | 6                                     |                               |              |         |
| AR10 - D0 - R2            | Out 12      | 24   | 1                                     | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 13      | 26   | 56                                    |                               |              |         |
| AR10 - D0 - R2            | Out 14      | 28   | 56                                    |                               |              |         |
| AR10 - D0 - R2            | Out 15      | 30   | 18                                    | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 16      | 32   | 56                                    |                               |              |         |
| AR10 - D0 - R2            | Out 17      | 34   | 26                                    | n.d.                          | n.d.         | n. d.   |
| AR10 - D0 - R2            | Out 18      | 36   | 16                                    |                               |              |         |
| AR10 - D0 - R2            | Out 19      | 38   | 21                                    |                               |              |         |
| AR10 - D0 - R2            | Out 20      | 40   | 26                                    |                               |              |         |
| AR10 - D0 - R2            | Rainfall    |      | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10- D0 - R3             | In - 1A     | 10   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | In - 2A     | 20   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | In - 3A     | 30   | 2                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | In - 4A     | 40   | 3                                     | d, b,q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR10- D0 - R3             | Out 1       | 2    | 12                                    | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 2       | 4    | 184                                   |                               |              |         |
| AR10- D0 - R3             | Out 3       | 6    | 117                                   | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 4       | 8    | 42                                    |                               |              |         |
| AR10- D0 - R3             | Out 5       | 10   | 60                                    |                               |              |         |
| AR10- D0 - R3             | Out 6       | 12   | 122                                   | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 7       | 14   | 72                                    |                               |              |         |
| AR10- D0 - R3             | Out 8       | 16   | 92                                    |                               |              |         |
| AR10- D0 - R3             | Out 9       | 18   | 117                                   | d, b,q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 10      | 20   | 109                                   |                               |              |         |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR10- D0 - R3             | Out 11      | 22   | 82                                    |                               |              |         |
| AR10- D0 - R3             | Out 12      | 24   | 82                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 13      | 26   | 72                                    |                               |              |         |
| AR10- D0 - R3             | Out 14      | 28   | 62                                    |                               |              |         |
| AR10- D0 - R3             | Out 15      | 30   | 32                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Out 16      | 32   | 85                                    |                               |              |         |
| AR10- D0 - R3             | Out 17      | 34   | 55                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR10- D0 - R3             | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D0 - R1            | In - 1A     | 10   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | In - 2A     | 20   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | In - 3A     | 30   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | In - 4A     | 40   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D0 - R1            | Out 1       | 2    | 139                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 2       | 4    | 121                                   |                               |              |         |
| AR30 - D0 - R1            | Out 3       | 6    | 145                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 4       | 8    | 175                                   |                               |              |         |
| AR30 - D0 - R1            | Out 5       | 10   | 165                                   |                               |              |         |
| AR30 - D0 - R1            | Out 6       | 12   | 131                                   | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 7       | 14   | 116                                   |                               |              |         |
| AR30 - D0 - R1            | Out 8       | 16   | 90                                    |                               |              |         |
| AR30 - D0 - R1            | Out 9       | 18   | 75                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 10      | 20   | 55                                    |                               |              |         |
| AR30 - D0 - R1            | Out 11      | 22   | 50                                    |                               |              |         |
| AR30 - D0 - R1            | Out 12      | 24   | 40                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 13      | 26   | 52                                    |                               |              |         |
| AR30 - D0 - R1            | Out 14      | 28   | 75                                    |                               |              |         |
| AR30 - D0 - R1            | Out 15      | 30   | 27                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 16      | 32   | 60                                    |                               |              |         |
| AR30 - D0 - R1            | Out 17      | 34   | 50                                    |                               |              |         |
| AR30 - D0 - R1            | Out 18      | 36   | 62                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Out 19      | 38   | 30                                    |                               |              |         |
| AR30 - D0 - R1            | Out 20      | 40   | 47                                    |                               |              |         |
| AR30 - D0 - R1            | Out 21      | 42   | 15                                    |                               |              |         |
| AR30 - D0 - R1            | Out 22      | 44   | 32                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R1            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |

| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D0 - R2            | In - 1A     | 10   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | In - 2A     | 20   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | In - 3A     | 30   | 0                                     | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | In - 4A     | 40   | 0                                     | n.d.                          | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D0 - R2            | Out 1       | 2    | 160                                   | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 2       | 4    | 134                                   |                               |              |         |
| AR30 - D0 - R2            | Out 3       | 6    | 75                                    | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 4       | 8    | 0                                     |                               |              |         |
| AR30 - D0 - R2            | Out 5       | 10   | 30                                    |                               |              |         |
| AR30 - D0 - R2            | Out 6       | 12   | 105                                   | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 7       | 14   | 95                                    |                               |              |         |
| AR30 - D0 - R2            | Out 8       | 16   | 110                                   |                               |              |         |
| AR30 - D0 - R2            | Out 9       | 18   | 75                                    | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 10      | 20   | 60                                    |                               |              |         |
| AR30 - D0 - R2            | Out 11      | 22   | 105                                   |                               |              |         |
| AR30 - D0 - R2            | Out 12      | 24   | 42                                    | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 13      | 26   | 55                                    |                               |              |         |
| AR30 - D0 - R2            | Out 14      | 28   | 106                                   |                               |              |         |
| AR30 - D0 - R2            | Out 15      | 30   | 125                                   | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 16      | 32   | 70                                    |                               |              |         |
| AR30 - D0 - R2            | Out 17      | 34   | 30                                    |                               |              |         |
| AR30 - D0 - R2            | Out 18      | 36   | 30                                    | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Out 19      | 38   | 32                                    |                               |              |         |
| AR30 - D0 - R2            | Out 20      | 40   | 35                                    |                               |              |         |
| AR30 - D0 - R2            | Out 21      | 42   | 10                                    | n.d.                          | n.d.         | n. d.   |
| AR30 - D0 - R2            | Rainfall    |      | 0                                     | n.d.                          | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D0 - R3            | In - 1A     | 10   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | In - 2A     | 20   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | In - 3A     | 30   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | In - 4A     | 40   | 0                                     | d, b,q.l.                     | n.d.         | n. d.   |
|                           |             |      |                                       |                               |              |         |
| AR30 - D0 - R3            | Out 1       | 2    | 342                                   | d, b,q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 2       | 4    | 260                                   |                               |              |         |
| AR30 - D0 - R3            | Out 3       | 6    | 160                                   | d, b,q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 4       | 8    | 83                                    |                               |              |         |



| Treatment And Replication | Sample I.D. | Time | Corrected Sediment Mass Concentration | Dissolved Phase Concentration |              |         |
|---------------------------|-------------|------|---------------------------------------|-------------------------------|--------------|---------|
|                           |             |      |                                       | Atrazine                      | Chlorpyrifos | Linuron |
| #                         | #           | min  | mg/L                                  | µg/L                          | µg/L         | µg/L    |
| AR30 - D0 - R3            | Out 5       | 10   | 20                                    |                               |              |         |
| AR30 - D0 - R3            | Out 6       | 12   | 25                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 7       | 14   | 30                                    |                               |              |         |
| AR30 - D0 - R3            | Out 8       | 16   | 5                                     |                               |              |         |
| AR30 - D0 - R3            | Out 9       | 18   | 15                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 10      | 20   | 33                                    |                               |              |         |
| AR30 - D0 - R3            | Out 11      | 22   | 35                                    |                               |              |         |
| AR30 - D0 - R3            | Out 12      | 24   | 30                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 13      | 26   | 45                                    |                               |              |         |
| AR30 - D0 - R3            | Out 14      | 28   | 55                                    |                               |              |         |
| AR30 - D0 - R3            | Out 15      | 30   | 55                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 16      | 32   | 10                                    |                               |              |         |
| AR30 - D0 - R3            | Out 17      | 34   | 18                                    |                               |              |         |
| AR30 - D0 - R3            | Out 18      | 36   | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 19      | 38   | 70                                    |                               |              |         |
| AR30 - D0 - R3            | Out 20      | 40   | 55                                    |                               |              |         |
| AR30 - D0 - R3            | Out 21      | 42   | 50                                    | d, b.q.l.                     | n.d.         | n. d.   |
| AR30 - D0 - R3            | Out 22      | 44   | 20                                    |                               |              |         |
| AR30 - D0 - R3            | Rainfall    |      | 0                                     | d, b.q.l.                     | n.d.         | n. d.   |

**APPENDIX C. SORBED PESTICIDE CONCENTRATIONS FOR  
COMBINED SAMPLES**

Sorbed pesticide concentrations and sorption coefficients for atrazine and chlorpyrifos for combined inflow and outflow samples from buffer strips.

| Treatment   | Sample      | Atrazine Concentration      |                            | Atrazine Sorption | Chlorpyrifos Concentration  |                            | Chlorpyrifos Sorption |
|-------------|-------------|-----------------------------|----------------------------|-------------------|-----------------------------|----------------------------|-----------------------|
|             |             | Sorbed                      | Dissolved                  | Coefficient       | Sorbed                      | Dissolved                  | Coefficient           |
| Replication | I.D.        | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)          | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)              |
| AR10-D1-R1  | In 1A + 1B  | 25                          | 21                         | 1                 | 91                          | 3                          | 32                    |
| AR10-D1-R1  | In 2A + 2B  | 23                          | 19                         | 1                 | 98                          | 3                          | 30                    |
| AR10-D1-R1  | In 3A + 3B  | 17                          | 18                         | 1                 | 106                         | 2                          | 43                    |
| AR10-D1-R1  | In 4A + 4B  | 21                          | 18                         | 1                 | 89                          | 2                          | 47                    |
| AR10-D1-R1  | Out 1 - 4   | 16                          | 7                          | 2                 | 40                          | 1                          | 39                    |
| AR10-D1-R1  | Out 5 - 8   | 27                          | 10                         | 3                 | 107                         | 1                          | 105                   |
| AR10-D1-R1  | Out 9 - 14  | 30                          | 13                         | 2                 | 74                          | 1                          | 71                    |
|             |             |                             |                            |                   |                             |                            |                       |
| AR10-D1-R2  | In 1A + 1B  | 25                          | 20                         | 1                 | 67                          | 2                          | 40                    |
| AR10-D1-R2  | In 2A + 2B  | 24                          | 20                         | 1                 | 55                          | 2                          | 30                    |
| AR10-D1-R2  | In 3A + 3B  | 20                          | 21                         | 1                 | 28                          | 1                          | 20                    |
| AR10-D1-R2  | In 4A + 4B  | 20                          | 23                         | 1                 | 40                          | 2                          | 26                    |
| AR10-D1-R2  | Out 1 - 6   | 28                          | 9                          | 3                 | 32                          | d, b.q.l.                  | -                     |
| AR10-D1-R2  | Out 13 - 18 | 19                          | 14                         | 1                 | 38                          | d, b.q.l.                  | -                     |
| AR10-D1-R2  | Out 7 - 12  | 25                          | 12                         | 2                 | 46                          | 1                          | 47                    |
|             |             |                             |                            |                   |                             |                            |                       |
| AR10-D1-R3  | In 1A + 1B  | 16                          | 22                         | 1                 | 25                          | 2                          | 13                    |
| AR10-D1-R3  | In 2A + 2B  | 28                          | 21                         | 1                 | 24                          | 2                          | 11                    |
| AR10-D1-R3  | In 3A + 3B  | 23                          | 22                         | 1                 | 33                          | 2                          | 16                    |
| AR10-D1-R3  | In 4A + 4B  | 25                          | 21                         | 1                 | 29                          | 2                          | 13                    |
| AR10-D1-R3  | Out 1 - 6   | 18                          | 9                          | 2                 | 18                          | 1                          | 18                    |
| AR10-D1-R3  | Out 12 - 15 | 38                          | 14                         | 3                 | 34                          | 1                          | 34                    |
| AR10-D1-R3  | Out 7 - 11  | 23                          | 12                         | 2                 | 20                          | 1                          | 19                    |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D1-R1  | In 1A + 1B  | 16                          | 28                         | 1                 | 38                          | 4                          | 11                    |
| AR30-D1-R1  | In 2A + 2B  | 16                          | 28                         | 1                 | 43                          | 3                          | 13                    |
| AR30-D1-R1  | In 3A + 3B  | 18                          | 25                         | 1                 | 38                          | 3                          | 12                    |
| AR30-D1-R1  | In 4A + 4B  | 16                          | 23                         | 1                 | 44                          | 3                          | 14                    |
| AR30-D1-R1  | Out 1 - 4   | 11                          | 19                         | 1                 | 16                          | 1                          | 13                    |
| AR30-D1-R1  | Out 15 - 21 | 8                           | 22                         | 0                 | 13                          | 1                          | 10                    |
| AR30-D1-R1  | Out 5 - 8   | 9                           | 19                         | 0                 | 18                          | 1                          | 15                    |
| AR30-D1-R1  | Out 9 - 14  | 11                          | 19                         | 1                 | 18                          | 2                          | 10                    |

| Treatment   | Sample      | Atrazine Concentration      |                            | Atrazine Sorption | Chlorpyrifos Concentration  |                            | Chlorpyrifos Sorption |
|-------------|-------------|-----------------------------|----------------------------|-------------------|-----------------------------|----------------------------|-----------------------|
|             |             | Sorbed                      | Dissolved                  | Coefficient       | Sorbed                      | Dissolved                  | Coefficient           |
| Replication | I.D.        | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)          | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)              |
| AR30-D1-R2  | In 1A + 1B  | 18                          | 27                         | 1                 | 35                          | 4                          | 10                    |
| AR30-D1-R2  | In 2A + 2B  | 15                          | 30                         | 1                 | 33                          | 4                          | 9                     |
| AR30-D1-R2  | In 3A + 3B  | 17                          | 27                         | 1                 | 39                          | 3                          | 13                    |
| AR30-D1-R2  | In 4A + 4B  | 15                          | 27                         | 1                 | 40                          | 3                          | 16                    |
| AR30-D1-R2  | Out 1 - 6   | 10                          | 20                         | 0                 | 21                          | 1                          | 20                    |
| AR30-D1-R2  | Out 13 - 19 | 17                          | 23                         | 1                 | 23                          | 1                          | 22                    |
| AR30-D1-R2  | Out 7 - 12  | 9                           | 20                         | 0                 | 26                          | 1                          | 25                    |
| AR30-D1-R3  | In 1A + 1B  | 20                          | 26                         | 1                 | 39                          | 2                          | 16                    |
| AR30-D1-R3  | In 2A + 2B  | 21                          | 27                         | 1                 | 40                          | 2                          | 17                    |
| AR30-D1-R3  | In 3A + 3B  | 14                          | 26                         | 1                 | 48                          | 2                          | 21                    |
| AR30-D1-R3  | In 4A + 4B  | 17                          | 27                         | 1                 | 36                          | 2                          | 14                    |
| AR30-D1-R3  | Out 1 - 4   | 2                           | 18                         | 0                 | 18                          | 1                          | 18                    |
| AR30-D1-R3  | Out 13 - 16 | 3                           | 20                         | 0                 | 12                          | 1                          | 12                    |
| AR30-D1-R3  | Out 17 - 20 | 5                           | 20                         | 0                 | 15                          | 1                          | 14                    |
| AR30-D1-R3  | Out 21 - 23 | 8                           | 19                         | 0                 | 22                          | 1                          | 21                    |
| AR30-D1-R3  | Out 5 - 8   | 1                           | 20                         | 0                 | 12                          | 1                          | 12                    |
| AR30-D1-R3  | Out 9 - 12  | 6                           | 21                         | 0                 | 15                          | 1                          | 15                    |
| AR10-D2-R1  | In 1A + 1B  | 210                         | 35                         | 6                 | 605                         | 5                          | 126                   |
| AR10-D2-R1  | In 2A + 2B  | 290                         | 32                         | 9                 | 639                         | 4                          | 157                   |
| AR10-D2-R1  | In 3A + 3B  | 225                         | 33                         | 7                 | 587                         | 4                          | 163                   |
| AR10-D2-R1  | In 4A + 4B  | 221                         | 39                         | 6                 | 566                         | 4                          | 133                   |
| AR10-D2-R1  | Out 1 - 4   | 764                         | 19                         | 41                | 485                         | 1                          | 398                   |
| AR10-D2-R1  | Out 10 - 14 | 300                         | 25                         | 12                | 693                         | 2                          | 317                   |
| AR10-D2-R1  | Out 15 - 20 | 249                         | 24                         | 11                | 285                         | 2                          | 138                   |
| AR10-D2-R1  | Out 5 - 9   | 315                         | 22                         | 14                | 1508                        | 2                          | 754                   |
| AR10-D2-R2  | In 1A + 1B  | 216                         | 35                         | 6                 | 655                         | 4                          | 165                   |
| AR10-D2-R2  | In 2A + 2B  | 206                         | 35                         | 6                 | 735                         | 3                          | 222                   |
| AR10-D2-R2  | In 3A + 3B  | 102                         | 36                         | 3                 | 699                         | 3                          | 209                   |
| AR10-D2-R2  | In 4A + 4B  | 191                         | 34                         | 6                 | 714                         | 3                          | 272                   |
| AR10-D2-R2  | Out 1 - 3   | 188                         | 17                         | 11                | 234                         | d, b.q.l.                  | -                     |
| AR10-D2-R2  | Out 10 - 13 | 315                         | 25                         | 13                | 188                         | 1                          | 188                   |
| AR10-D2-R2  | Out 14 - 17 | 382                         | 23                         | 16                | 953                         | 1                          | 953                   |
| AR10-D2-R2  | Out 18 - 21 | 461                         | 24                         | 19                | 609                         | 1                          | 609                   |

| Treatment   | Sample      | Atrazine Concentration      |                            | Atrazine Sorption | Chlorpyrifos Concentration  |                            | Chlorpyrifos Sorption |
|-------------|-------------|-----------------------------|----------------------------|-------------------|-----------------------------|----------------------------|-----------------------|
|             |             | Sorbed                      | Dissolved                  | Coefficient       | Sorbed                      | Dissolved                  | Coefficient           |
| Replication | I.D.        | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)          | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)              |
| AR10-D2-R2  | Out 4 - 6   | 204                         | 21                         | 10                | 232                         | 1                          | 411                   |
| AR10-D2-R2  | Out 7 - 9   | 208                         | 23                         | 9                 | 253                         | 1                          | 264                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR10-D2-R3  | In 1A + 1B  | 98                          | 30                         | 3                 | 627                         | 3                          | 250                   |
| AR10-D2-R3  | In 2A + 2B  | 116                         | 27                         | 4                 | 693                         | 3                          | 220                   |
| AR10-D2-R3  | In 3A + 3B  | 106                         | 33                         | 3                 | 685                         | 2                          | 286                   |
| AR10-D2-R3  | In 4A + 4B  | 108                         | 25                         | 4                 | 559                         | 3                          | 197                   |
| AR10-D2-R3  | Out 1 - 4   | 413                         | 14                         | 30                | 486                         | d, b.q.l.                  | -                     |
| AR10-D2-R3  | Out 10 - 14 | 786                         | 23                         | 34                | 607                         | 1                          | 599                   |
| AR10-D2-R3  | Out 5 - 9   | 513                         | 21                         | 24                | 645                         | 1                          | 626                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D2-R1  | In 1A + 1B  | 104                         | 26                         | 4                 | 522                         | 5                          | 109                   |
| AR30-D2-R1  | In 2A + 2B  | 112                         | 27                         | 4                 | 590                         | 4                          | 139                   |
| AR30-D2-R1  | In 3A + 3B  | 110                         | 29                         | 4                 | 628                         | 5                          | 123                   |
| AR30-D2-R1  | In 4A + 4B  | 117                         | 30                         | 4                 | 609                         | 4                          | 141                   |
| AR30-D2-R1  | Out 1 - 5   | 307                         | 21                         | 14                | 360                         | 2                          | 176                   |
| AR30-D2-R1  | Out 11 - 15 | 313                         | 26                         | 12                | 864                         | 4                          | 243                   |
| AR30-D2-R1  | Out 16 - 21 | 218                         | 28                         | 8                 | 872                         | 3                          | 257                   |
| AR30-D2-R1  | Out 6 - 10  | 357                         | 24                         | 15                | 618                         | 3                          | 192                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D2-R2  | In 1A + 1B  | 103                         | 30                         | 3                 | 607                         | 5                          | 110                   |
| AR30-D2-R2  | In 2A + 2B  | 88                          | 30                         | 3                 | 568                         | 4                          | 130                   |
| AR30-D2-R2  | In 3A + 3B  | 120                         | 29                         | 4                 | 566                         | 4                          | 146                   |
| AR30-D2-R2  | In 4A + 4B  | 136                         | 27                         | 5                 | 617                         | 3                          | 212                   |
| AR30-D2-R2  | Out 1 - 5   | 344                         | 23                         | 15                | 258                         | 2                          | 153                   |
| AR30-D2-R2  | Out 11 - 14 | 428                         | 22                         | 20                | 495                         | 3                          | 194                   |
| AR30-D2-R2  | Out 15 - 18 | 396                         | 20                         | 19                | 464                         | 2                          | 248                   |
| AR30-D2-R2  | Out 19 - 22 | 452                         | 19                         | 24                | 263                         | 1                          | 278                   |
| AR30-D2-R2  | Out 6 - 10  | 287                         | 24                         | 12                | 704                         | 3                          | 268                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D2-R3  | In 1A + 1B  | 116                         | 35                         | 3                 | 646                         | 5                          | 138                   |
| AR30-D2-R3  | In 2A + 2B  | 101                         | 33                         | 3                 | 652                         | 5                          | 136                   |
| AR30-D2-R3  | In 3A + 3B  | 100                         | 35                         | 3                 | 734                         | 4                          | 189                   |
| AR30-D2-R3  | In 4A + 4B  | 114                         | 37                         | 3                 | 703                         | 4                          | 161                   |
| AR30-D2-R3  | Out 1 - 4   | 730                         | 24                         | 30                | 265                         | 2                          | 155                   |
| AR30-D2-R3  | Out 13 - 16 | 639                         | 28                         | 23                | 750                         | 4                          | 214                   |
| AR30-D2-R3  | Out 17 - 19 | 641                         | 27                         | 24                | 498                         | 3                          | 146                   |

| Treatment   | Sample      | Atrazine Concentration                |   | Atrazine Sorption       | Chlorpyrifos Concentration            |   | Chlorpyrifos Sorption   |
|-------------|-------------|---------------------------------------|---|-------------------------|---------------------------------------|---|-------------------------|
|             |             | Sorbed<br>( $\mu\text{g}/\text{kg}$ ) | Dissolved<br>( $\mu\text{g}/\text{L}$ ) | Coefficient<br>K (L/kg) | Sorbed<br>( $\mu\text{g}/\text{kg}$ ) | Dissolved<br>( $\mu\text{g}/\text{L}$ ) | Coefficient<br>K (L/kg) |
| Replication | I.D.        | ( $\mu\text{g}/\text{kg}$ )           | ( $\mu\text{g}/\text{L}$ )              | K (L/kg)                | ( $\mu\text{g}/\text{kg}$ )           | ( $\mu\text{g}/\text{L}$ )              | K (L/kg)                |
| AR30-D2-R3  | Out 20 - 22 | 671                                   | 27                                      | 25                      | 1115                                  | 4                                       | 317                     |
| AR30-D2-R3  | Out 5 - 8   | 639                                   | 27                                      | 24                      | 420                                   | 3                                       | 158                     |
| AR30-D2-R3  | Out 9 - 12  | 529                                   | 28                                      | 19                      | 373                                   | 3                                       | 122                     |
|             |             |                                       |   |                         |                                       |   |                         |
| AR10-D3-R1  | In 1A + 1B  | 2088                                  | 43                                      | 48                      | 1286                                  | 5                                       | 257                     |
| AR10-D3-R1  | In 2A + 2B  | 2875                                  | 45                                      | 64                      | 1259                                  | 5                                       | 255                     |
| AR10-D3-R1  | In 3A + 3B  | 2443                                  | 42                                      | 58                      | 1288                                  | 5                                       | 258                     |
| AR10-D3-R1  | In 4A + 4B  | 2398                                  | 37                                      | 64                      | 1237                                  | 3                                       | 413                     |
| AR10-D3-R1  | Out 1 - 4   | 1103                                  | 30                                      | 37                      | 346                                   | 1                                       | 309                     |
| AR10-D3-R1  | Out 13 - 16 | 1765                                  | 30                                      | 59                      | 529                                   | 2                                       | 294                     |
| AR10-D3-R1  | Out 17 - 19 | 2632                                  | 32                                      | 83                      | 795                                   | 2                                       | 520                     |
| AR10-D3-R1  | Out 5 - 8   | 892                                   | 22                                      | 41                      | 383                                   | 2                                       | 250                     |
| AR10-D3-R1  | Out 9 - 12  | 1279                                  | 29                                      | 44                      | 485                                   | 2                                       | 301                     |
|             |             |                                       |   |                         |                                       |   |                         |
| AR10-D3-R2  | In 1A + 1B  | 2088                                  | 40                                      | 52                      | 1216                                  | 5                                       | 251                     |
| AR10-D3-R2  | In 2A + 2B  | 2875                                  | 42                                      | 69                      | 1439                                  | 5                                       | 299                     |
| AR10-D3-R2  | In 3A + 3B  | 2443                                  | 46                                      | 53                      | 1279                                  | 4                                       | 286                     |
| AR10-D3-R2  | In 4A + 4B  | 2398                                  | 47                                      | 51                      | 1349                                  | 4                                       | 349                     |
| AR10-D3-R2  | Out 1 - 3   | 1103                                  | 31                                      | 35                      | 638                                   | 2                                       | 413                     |
| AR10-D3-R2  | Out 4 - 7   | 1765                                  | 29                                      | 60                      | 944                                   | 2                                       | 546                     |
| AR10-D3-R2  | Out 8 - 11  | 2632                                  | 27                                      | 97                      | 889                                   | 1                                       | 616                     |
|             |             |                                       |   |                         |                                       |   |                         |
| AR10-D3-R3  | In 1A + 1B  | 1903                                  | 31                                      | 62                      | 1739                                  | 4                                       | 466                     |
| AR10-D3-R3  | In 2A + 2B  | 1648                                  | 33                                      | 50                      | 1555                                  | 3                                       | 559                     |
| AR10-D3-R3  | In 3A + 3B  | 2357                                  | 34                                      | 70                      | 1258                                  | 4                                       | 346                     |
| AR10-D3-R3  | In 4A + 4B  | 2302                                  | 33                                      | 70                      | 1088                                  | 3                                       | 337                     |
| AR10-D3-R3  | Out 1 - 4   | 634                                   | 17                                      | 37                      | 622                                   | 1                                       | 620                     |
| AR10-D3-R3  | Out 10 - 14 | 1041                                  | 23                                      | 44                      | 801                                   | 1                                       | 621                     |
| AR10-D3-R3  | Out 15 - 18 | 1068                                  | 24                                      | 44                      | 845                                   | 1                                       | 665                     |
| AR10-D3-R3  | Out 19 - 22 | 1629                                  | 24                                      | 69                      | 1038                                  | 1                                       | 819                     |
| AR10-D3-R3  | Out 5 - 9   | 1161                                  | 22                                      | 52                      | 820                                   | 1                                       | 673                     |
|             |             |                                       |   |                         |                                       |   |                         |
|             |             |                                       |   |                         |                                       |   |                         |
| AR30-D3-R1  | In 1A + 1B  | 2202                                  | 27                                      | 82                      | 2355                                  | 4                                       | 661                     |
| AR30-D3-R1  | In 2A + 2B  | 2118                                  | 26                                      | 82                      | 2197                                  | 4                                       | 547                     |
| AR30-D3-R1  | In 3A + 3B  | 1802                                  | 23                                      | 77                      | 2149                                  | 4                                       | 478                     |
| AR30-D3-R1  | In 4A + 4B  | 1962                                  | 23                                      | 85                      | 2034                                  | 5                                       | 440                     |

| Treatment   | Sample      | Atrazine Concentration      |                            | Atrazine Sorption | Chlorpyrifos Concentration  |                            | Chlorpyrifos Sorption |
|-------------|-------------|-----------------------------|----------------------------|-------------------|-----------------------------|----------------------------|-----------------------|
|             |             | Sorbed                      | Dissolved                  | Coefficient       | Sorbed                      | Dissolved                  | Coefficient           |
| Replication | I.D.        | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)          | ( $\mu\text{g}/\text{kg}$ ) | ( $\mu\text{g}/\text{L}$ ) | K (L/kg)              |
| AR30-D3-R1  | Out 1 - 4   | 1520                        | 21                         | 74                | 1268                        | 2                          | 606                   |
| AR30-D3-R1  | Out 13 - 16 | 1983                        | 20                         | 97                | 1960                        | 3                          | 597                   |
| AR30-D3-R1  | Out 17 - 22 | 1124                        | 22                         | 52                | 1239                        | 3                          | 380                   |
| AR30-D3-R1  | Out 5 - 8   | 1258                        | 21                         | 59                | 1755                        | 3                          | 536                   |
| AR30-D3-R1  | Out 9 - 12  | 1772                        | 19                         | 92                | 1774                        | 4                          | 505                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D3-R2  | In 1A + 1B  | 2163                        | 33                         | 66                | 2250                        | 3                          | 665                   |
| AR30-D3-R2  | In 2A + 2B  | 2554                        | 34                         | 74                | 1828                        | 5                          | 395                   |
| AR30-D3-R2  | In 3A + 3B  | 2215                        | 35                         | 64                | 1991                        | 5                          | 364                   |
| AR30-D3-R2  | In 4A + 4B  | 2206                        | 35                         | 63                | 1986                        | 5                          | 431                   |
| AR30-D3-R2  | Out 1 - 5   | 1959                        | 26                         | 75                | 914                         | 1                          | 721                   |
| AR30-D3-R2  | Out 10 - 13 | 1717                        | 30                         | 57                | 1739                        | 3                          | 531                   |
| AR30-D3-R2  | Out 14 - 17 | 1715                        | 30                         | 57                | 1184                        | 3                          | 370                   |
| AR30-D3-R2  | Out 18 - 21 | 2052                        | 29                         | 71                | 1942                        | 3                          | 622                   |
| AR30-D3-R2  | Out 6 - 9   | 949                         | 30                         | 31                | 1284                        | 2                          | 550                   |
|             |             |                             |                            |                   |                             |                            |                       |
| AR30-D3-R3  | In 1A + 1B  | 3277                        | 25                         | 132               | 2746                        | 4                          | 756                   |
| AR30-D3-R3  | In 2A + 2B  | 3072                        | 27                         | 115               | 2505                        | 5                          | 468                   |
| AR30-D3-R3  | In 3A + 3B  | 2423                        | 25                         | 98                | 2699                        | 5                          | 519                   |
| AR30-D3-R3  | In 4A + 4B  | 2455                        | 28                         | 88                | 2727                        | 5                          | 539                   |
| AR30-D3-R3  | Out 1 - 4   | 1267                        | 21                         | 61                | 1355                        | 2                          | 691                   |
| AR30-D3-R3  | Out 13 - 16 | 2132                        | 21                         | 104               | 985                         | 3                          | 282                   |
| AR30-D3-R3  | Out 17 - 20 | 1625                        | 19                         | 85                | 985                         | 3                          | 306                   |
| AR30-D3-R3  | Out 21 - 23 | 1372                        | 21                         | 64                | 1615                        | 3                          | 471                   |
| AR30-D3-R3  | Out 5 - 8   | 1128                        | 19                         | 60                | 1264                        | 4                          | 356                   |
| AR30-D3-R3  | Out 9 - 12  | 1905                        | 20                         | 94                | 1450                        | 3                          | 485                   |