EFFECTIVENESS OF VEGETATED BUFFER STRIPS IN REDUCING PESTICIDE TRANSPORT IN SIMULATED RUNOFF

K. Arora, S. K. Mickelson, J. L. Baker

ABSTRACT. Several processes take place within vegetated buffer strips that affect their performance. To better understand these processes, a runoff study was conducted to evaluate vegetated buffer strips performance in reducing atrazine, metolachlor, and chlorpyrifos transport as affected by the drainage area to buffer strip area ratio. The simulated runoff water mixed with pesticide-treated soil was distributed onto six vegetated buffer strips, each 1.52 m wide \times 20.12 m long, located downslope of the inflow distribution tank in a well established vegetated grassed waterway. These strips provided for three replications of two inflow rates designated as "drainage area/buffer strip area ratio treatments" of 15:1 and 30:1. Infiltration for the 15:1 treatment averaged 38.8% of the inflow volume, whereas it averaged 30.4% for the 30:1 treatment. Sediment retention efficiencies averaged 90.1% and 86.8% for the 15:1 and 30:1 treatments, respectively. Concentrations of atrazine and metolachlor associated with sediment outflows from the strips were larger than their respective inflow concentrations, while the results were opposite for chlorpyrifos. Concentrations in runoff water for both atrazine and metolachlor in outflow from the strips were smaller than the inflow concentrations; again, the results were opposite for chlorpyrifos. The 15:1 treatment retained an average of 52.5% of the total input of atrazine, 54.4% of metolachlor, and 83.1% of chlorpyrifos. Corresponding numbers for the 30:1 treatment were 46.8% for atrazine, 48.1% for metolachlor, and 76.9% for chlorpyrifos. Analysis of variance using the randomized block design showed that differences of percent retention of pesticide between treatments were not significant for any of the three pesticides at the 10% significance level. A lack of significant difference indicates either a need for more than three replications and/or larger area ratio treatments to be studied. The results of this study indicate that a 30:1 area ratio buffer strip could perform equally as well as a 15:1 area ratio buffer strip. Thus, less land would be required under buffer strips to get the desired results.

Keywords. Atrazine, Best management practices, Buffer strips, Chlorpyrifos, Filter strips, Herbicide, Insecticide, Metolachlor, Pesticide, Runoff, Simulation, Water quality.

ropland is recognized as an important nonpoint pollution source possibly affecting the water quality of receiving waters. Major water quality concerns have risen in recent years due to the presence of nutrients and various pesticides in surface waters. Research published by various researchers (Hall et al., 1972; Hall, 1974; Wauchope, 1978; Wu, 1980) shows that pesticide losses with runoff typically range from 1% to 5% of the total applied. These losses are particularly dependent on tillage practices, field slope, and timing of application (Baker and Johnson, 1979; Baker and Laflen, 1979; Hall et al., 1983; Shipitalo et al., 1997). Once applied to fields, the fate of pesticides is dependent on many factors, but one of the most important is soil adsorption (Baker and Mickelson, 1994). The degree of interaction between soil and a pesticide can be classified as strongly, moderately, or weakly absorbed to non-adsorbed. For moderately adsorbed pesticides (e.g., atrazine and metolachlor), although concentrations are larger in sediment than in runoff water, generally greater amounts are lost in runoff water because of the relative water and sediment masses lost (Baker and Laflen, 1979). Losses of pesticides from croplands can be large if runoff-producing rainstorms occur shortly after application (Fawcett et al., 1994; Wauchope, 1978). Various in-field and off-site practices for reducing agricultural pesticide transport to receiving waters have been evaluated, and a few others are being evaluated (Baker and Mickelson, 1994). Possible off-site practices involve the use of modified landscape features to control movement of pollutants to water resources. Vegetated buffer strips, wetlands, and terraces are examples of landscape modifications. These practices tend to reduce the movement of agricultural pesticides with runoff water and sediment carriers by reducing chemical concentrations in and/or the masses of the carriers.

Buffer strips in the context of this study are bands of land to which no pesticides have been applied. These strips can either be cropped or have close–grown vegetation planted in them, the latter often being referred to as vegetated or grassed buffer strips (VBS). VBS are located between pollutant sources and the receiving waters and can retain pollutants from runoff by the mechanisms of interception–adsorption, infiltration, and/or by sediment deposition. The main phe-

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nomenon occurring in a VBS is the reduction of flow velocity by the resistance to flowing water caused by the vegetation. VBS have been shown by various researchers such as Young et al. (1980), Magette et al. (1989), and Dillaha et al. (1989) to be effective in reducing off–site transport of sediment, animal waste suspended solids, and nutrients. A review of the literature that follows reveals that limited data exist on different processes occurring within VBS with respect to their net effect on the effectiveness of VBS in reducing off–site transport of agricultural pesticides.

Grassed waterways were evaluated by Asmussen et al. (1977) for reducing off-site transport of 2,4–D through surface runoff. Wet and dry antecedent moisture conditions served as treatments under simulated rainfall in this study. The 24.4 m long grassed waterways with a drainage area to waterway area ratio of 0.25 reduced the suspended sediment concentrations by 98% and 94% for the dry and wet treatments, respectively. Out of the 2.5% and 10.3% of 2,4–D lost under the dry and wet treatments, respectively, the waterway retained about 70% of these amounts irrespective of antecedent soil moisture conditions.

In a study conducted over two consecutive years by Rhode et al. (1980), grassed waterways were evaluated for reduction of off-site movement of trifluralin. Annual trifluralin losses from the treated area over the observation time periods were 0.17% and 0.03% of that applied. Runoff from the treated area was passed through a 24.4 m long grassed waterway with a drainage area to waterway area ratio of 0.25. Average reduction in the amount of trifluralin in runoff was 96% when the waterway was dry and 86% when the waterway was wet. The authors concluded that chemical transport could be significantly reduced by using buffer zones and grassed waterways adjoining treated areas.

Hall et al. (1983) evaluated oat buffer strips along with application methodology for retention of atrazine losses. A 6 m long oat strip placed at the bottom of 16 m long source area was observed for 11 erosion events (drainage area to buffer strip area ratio of 2.7:1). The oat buffer strip reduced runoff inflow and sediment mass by 66% and 76%, respectively, when compared with a plot area without an oat buffer strip. This oat strip reduced atrazine losses by 91% when the application rate of atrazine was 2.2 kg/ha on the drainage area. The retention was 65% for the higher atrazine application rate of 4.5 kg/ha. Atrazine losses were reduced by 91% and 87% for these two application rates when pre-plant incorporation with the oat buffer strip treatment was compared with pre-emergent application without an oat buffer strip. The authors concluded that use of an oat buffer strip under a conventional tillage system could significantly reduce herbicide losses to receiving streams.

Mickelson et al. (2003) evaluated 4.6 and 9.1 m long buffer strips for controlling herbicide transport using simulated rainfall. Rainfall with an intensity of 66 mm/h was simulated over the filter strip area. Ten minutes after the start of simulated rainfall, inflow representing a runoff of 2.5 cm/h with an atrazine concentration of 1 mg/L, either with or without sediment, was added to the buffer strips. The 4.6 m long buffer strips (drainage area to buffer strip area ratio of 10:1) reduced sediment load by 71%, whereas the 9.1 m long buffer strips (drainage area to buffer area ratio of 5:1) reduced it by 87%. The difference in sediment load reduction between the two buffer strip lengths was significant, with the first few meters of the buffer strips trapped the majority of the

sediment. The two buffer strip lengths reduced atrazine loss by 31% and 80%, respectively; these reductions were significantly different. The difference in atrazine losses between runoff with and without sediment was not significant. Outflow concentrations of atrazine, both for runoff with and without sediment, did not show any specific trends over the duration of simulation.

Hoffman et al. (1995) evaluated the use of contour strip cropping to reduce atrazine loads in runoff. The study was conducted on nine 0.63 ha watersheds, 45×140 m, to compare the effectiveness of contour strip cropping in reducing off-site transport of herbicides. Three conventionally tilled field corn cropping systems, with grass filter strips, with wheat filter strips, and with no filter strips, were evaluated. The three herbicides (atrazine at 2.24 kg/ha, metolachlor at 2.8 kg/ha, and cyanazine at 4.48 kg/ha) were applied pre-emergence to each corn crop. Filter strip length of 9.0 m (drainage area to filter strip area ratio of 4:1) was evaluated under the two cropping systems of grass and wheat filter strips. Contour filter strips reduced the cropped area and thus total herbicide application by 20% within each watershed. Observations made during natural rainfall events in 1993 and 1994 indicated an average reduction of 46% and 80% in atrazine and metolachlor amounts, respectively, when runoff leaving the watersheds after passing through filter strips was compared to runoff from watersheds with no filters. Due to large time periods between the date of application and rainfall events, cyanazine concentrations were below detection limits. The authors concluded that herbicide transport could be significantly reduced by using filter strips in conjunction with strip cropping.

Misra et al. (1996) conducted a rainfall simulation study to determine buffer strip effectiveness in reducing herbicide transport. Simulated rainfall with an intensity of 63.5 mm/h was applied, using a 15.2 m diameter rotating overhead boom simulator (Swanson, 1965), to vegetated buffer strip plots 1.5 m wide by 12.2 m long. Two area ratio treatments of 15:1 and 30:1 were evaluated in this study. Fifteen minutes into the rainfall simulation, inflow with nominal concentrations of 0.1 mg/L and 1.0 mg/L treatments of atrazine, metolachlor, and cyanazine was added to the strips. Three inflow samples were collected, each being a composite of three subsamples taken over a 5 min flow duration. Outflow from the strips was sampled at 5-min intervals. The authors reported a load reduction of 40.5% for atrazine, 39.2% for metolachlor, and 38.4% for cyanazine for the 15:1 treatment. For the 30:1 treatment, the corresponding herbicide load reductions were 37.0%, 34.6%, and 34.0%, respectively. These load reductions were not significantly different in spite of the fact that lower area ratio buffer strips had larger load reductions than higher area ratio buffer strips for each of the three herbicides. Load reductions for 1.0 mg/L nominal inflow concentrations were 48.6%, 44.3%, and 44.5% for atrazine, metolachlor, and cyanazine. These reductions were 28.8%, 29.4%, and 27.8% for 0.1 mg/L nominal inflow concentrations for the three herbicides, respectively. These differences between load reductions for the two different nominal inflow concentrations were significant. The authors determined with the help of a bromide tracer that infiltration within the vegetative strips was the key factor for herbicide load reduction. This rainfall simulation study did not introduce any sediment into the buffer strips, as might occur in a natural runoff event. Additionally, rainfall was simulated simultaneously with

flow passing through the buffer strips, except for the first 15 min when there was no inflow. As such, results of this study represent a combined effect of infiltration, adsorption, and rainfall dilution processes on the buffer strip effective-ness.

Lowrance et al. (1997) evaluated the transport of the herbicides atrazine and alachlor in a managed riparian forest buffer system. This system consisted of a grassed buffer strip right next to the field, a managed pine forest downslope from the grassed buffer strip, and a narrow hardwood forest with an overall drainage area to buffer system area ratio of 2:1. During the three years of observations, atrazine and alachlor concentrations averaged 34.1 and 9.1 μ g/L at the field edge, respectively. These concentrations were observed to be $1 \,\mu g/L$ or less in the runoff that passed through the riparian forest buffer system. The authors concluded that the reduction in concentration was greatest per meter of flow length in the grassed buffer strip adjacent to the field. The authors attributed infiltration and adsorption to plant/organic matter within the buffer system as the key processes affecting the herbicide concentrations. However, it was not possible to determine the net effect of each process on herbicide concentrations due to the setup of the study. The authors also reported that negligible transport of the two herbicides occurred through the buffer system in shallow groundwater.

Paterson and Schnoor (1992) published a study evaluating the fate of atrazine and alachlor in a riparian zone field site. In this study, the authors applied the herbicides directly to a streamside area on three different plots: a corn plot, a bare soil plot, and a plot of deep-rooted poplar trees (*Populus* spp.). The authors found that plant uptake by vegetation was an important process affecting the fate of the two herbicides when compared with the bare soil plot. In this study, the authors did not address transport of the lost herbicides from experimental plots into and through vegetative buffer strips and/or a riparian zone.

Arora et al. (1996) evaluated vegetative buffer strips for herbicide retention under natural rainfall conditions. The experimental design consisted of six equal-size buffer strips with drainage area to buffer area ratios of 15:1 and 30:1. Three herbicides (atrazine, metolachlor, and cyanazine) were applied to the source drainage area for each of the two years of study. Retention by the vegetative buffer strips ranged from 11% to 100% for atrazine, 16% to 100% for metolachlor, and 8% to 100% for cyanazine. The authors also reported that runoff leaving the buffer strips had lower concentrations than the runoff entering the buffer strips for all three herbicides. Herbicide retention through sediment trapping by buffer strips was about 5% of the total retention. The key process for herbicide retention was found to be infiltration. The difference between herbicide retention for the two treatments of 15:1 and 30:1 area ratios was not significant (α = 0.10). As a part of this study, the authors presented a mathematical analysis to quantify herbicide concentration change with respect to adsorption to organic/plant matter, dilution due to rainfall, and infiltration processes occurring within the VBS. The authors calculated an array of concentration reduction factors ranging from impermeable surface to fully pervious surface for both source area and buffer area. Concentrations reduction factors when applied to inflow concentrations showed higher outflow concentrations than observed. The authors concluded through their analysis that herbicide adsorption to plant and organic matter within

VBS was responsible for additional concentration reduction. However, due to the setup of the study, the net effect each of the adsorption to organic/plant matter, dilution due to rainfall, and infiltration processes occurring within the VBS could not be determined.

The literature suggests that buffer strips can play a significant role in moderating the impacts of nonpoint–source pollution occurring due to agricultural pesticides. However, most studies conducted to date have evaluated small drainage area to buffer area ratios, generally 1:1 to 5:1, with 30:1 being the highest. A small area ratio (e.g., 5:1) means that for every five units of crop land, one unit of buffer area would be required to achieve the reported contaminant reductions. Information on larger drainage area to buffer strip area ratios is limited, but such information is much needed during planning stages to decide how much land is adequate to provide the needed pesticide load reduction. Additionally, limited literature exists on the net effect of the processes occurring within the VBS on pesticide retention efficiency.

The overall objective of this project was to determine the retention efficiency of the VBS for pesticides of different adsorption properties without dilution from rainfall. This study also evaluated the effect of relatively large drainage area to buffer strip area ratio on pesticide retention efficiency.

METHODS AND MATERIALS

Figure 1 shows the setup of the experimental area used for evaluating VBS in reducing pesticide transport. The pesticides used in this study were two herbicides, atrazine (AAtrex) and metolachlor (Dual), and an insecticide, chlorpyrifos (Lorsban), and are listed in table 1. The VBS were established at the Swine Nutrition Farm of Iowa State University in the spring of 1993. More details on establishment of the site are presented in another study (Arora et al., 1996).

In this study, runoff from a field was simulated as input to the buffer strip system in July 1995. About 53,000 L of water were stored at the site for this runoff simulation. Prior to runoff simulation, the VBS area was wetted with about 25 mm of simulated rainfall applied in 30 min using a sprinkler system. This was done to achieve a replicable antecedent moisture condition in the VBS area, as might occur in a large natural rainfall event just prior to the initiation of runoff. However, no rainfall was added to the buffer area during runoff simulation. Again, this was done to avoid the complicating effect of dilution of flow through the buffer strips.

Water to simulate runoff was pumped into an 800 L metal tank placed at the upper end of the mixing chute, close to the source area (fig. 1). The water was pumped at a variable rate (first increasing and then decreasing) to generate a hydrograph of runoff comparable to one that might occur from a cropped field. Flows into buffer strips were measured downstream of the mixing chute and are explained later. Total water pumped into the tank was equivalent to a runoff event of 10.7 mm. Along with water, soil was also added to the tank to generate runoff with sediment. This soil had all three pesticides (atrazine, metolachlor, and chlorpyrifos) applied to it in an amount resulting in a nominal concentration of 100 mg of each pesticide per kg of soil. This concentration represents a similar concentration in the top



Figure 1. Field setup for the vegetative buffer strips runoff simulation study, 1995.

Table 1. Nan	nes, half lives, an	d sorption coefficient	s for the three	pesticides studied. ^[a]

		Field	Sorption	Partitioning
Trade		Half Life	Coefficient	Coefficient ^[a]
Name	Chemical Name	(days)	$K_{oc} (mL/g)$	$K = K_{oc} \times F_{oc}$
AAtrex	2-chloro-4-ethylamino-6-isopropylamino-S-triazine	60	100	3
Dual	$2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) \ acetamide$	90	200	6
Lorsban, Dursban	O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate	30	6070	182
	Trade Name AAtrex Dual Lorsban, Dursban	Trade NameChemical NameAAtrex2-chloro-4-ethylamino-6-isopropylamino-S-triazineDual2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamideLorsban, Dursban0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)-phosphorothioate	Trade NameField Half Life (days)AAtrex2-chloro-4-ethylamino-6-isopropylamino-S-triazine60Dual2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide90Lorsban, Dursban0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)-phosphorothioate30	Trade NameField Half LieSorption Coefficient Koc (mL/g)AAtrex2-chloro-4-ethylamino-6-isopropylamino-S-triazine60100Dual2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyl) acetamide90200Lorsban, Dursban0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)-phosphorothioate306070

^[a] Source: Hornsby et al., 1996, pp. 6–16, 50, 70, 146.

^[b] K values are calculated for 3% average fractional organic carbon content of soil (F_{oc}).

2 cm of soil one day after surface pesticide application. The application or spraying of pesticides was carried out on dried and sieved soil (1050 kg) one day prior to simulation. The pesticide-treated soil was added to the tank placed at the top end of the chute at a rate of 46 kg/min for the first 4 min, 31 kg/min for the next 6 min, and 23 kg/min for the remaining time for a total of 48 min. This was done to simulate similar sediment concentrations in runoff, as would be expected in a natural rainfall event. This simulated event represents the case of having greater loss from the treated fields in comparison with an event occurring several days after application, as reported by Baker and Mickelson (1994). These pesticides might be expected to persist for 30 days or more (table 1), but this simulation represents a case in which maximum amounts would be present in the field for potential loss with runoff.

Actual sediment concentrations over time were measured downstream from the mixing chute and are discussed later. The sediment–water–pesticide mixture was thoroughly stirred in the tank by addition of water at high velocity and by use of a 380 L/min recirculating pump. Runoff water mixed with soil overflowing from the tank was conveyed by the mixing chute (1.22 m wide) to a round metal inflow distribution tank, 3.05 m in diameter and 0.76 m in depth. This mixing chute had a 10 cm high obstruction placed at the outflow end, which helped to create storage in the mixing chute. The storage in the first tank, in the chute, and in the inflow distribution tank was assumed to provide roughly the same amount of time for the pesticides to equilibrate in the water/soil mixture as would happen in runoff from a field.

The inflow distribution tank at the downstream end of the mixing chute provided a point for sampling and a mechanism for distributing the runoff onto the buffer strips. Distribution of runoff was achieved using six 25.4 cm deep V–notch weirs along the periphery of the tank, all positioned at the same elevation. Three of the V–notches had a 30.0° weir angle, and the other three had a 56.8° weir angle. These two weir angles provided for two different flow rates, which differed by a factor of two for any depth of flow over the weirs. The volume of water flowing over the 30.0° notch is given by the following equation (Brakensiek et al., 1979, pp. 78–83):

$$Q = 0.373 * H^{2.5}$$
(1)

where

Q = flow over the notch (m^3/s)

H = head of water above the notch base (m).

For the 56.8° notch angle, the coefficient in the above equation is 0.746. As such, these weirs provided for two inflow rates designated as "drainage area/buffer strip area ratio treatments" of 15:1 and 30:1. Equal elevation placement of these weirs allowed an average single head value to be used for calculating the rate of runoff flowing onto the strips at any point during the runoff simulation. Elevations were measured at two points in the inflow distribution tank and then averaged. The total flow volume was calculated by integrating the flow rates over time. The weirs were calibrated in 1993 and 1994 as a part of an earlier study (Arora et al., 1996). During calibration, water was discharged through each weir for a total of 2 min. Water exiting from the weir was collected and measured for a 30 s time interval, accompanied with head of water (H) measurements every 10 s. This process was repeated three times for each weir. The percent error between the measured flow rates and flow rates calculated using equation 1 was less than 1%.

Six vegetated buffer strips, each 1.52 m wide \times 20.12 m long, were located downslope of the inflow distribution tank in an established vegetated grassed waterway on Clarion loam soil with an average 3% organic matter content. Each strip was equal in area (30.58 m^2); however, three strips received flow based on the 15:1 area ratio, and the other three strips received flow based on the 30:1 area ratio. These strips were isolated from one another by 0.25 m high metal borders driven 0.10 m into the ground. The strip vegetation was 81% brome grass (Bromus inermis), 12% blue grass (Poa pratensis), 5% fescue (Festuca arundinacea), and 2% other. The average tiller population was determined to be 8.82 M tillers/ha. Type of tiller species and population was determined by randomly tossing a 0.09 m² metallic ring at six different locations along the length of the VBS. Tiller species were then counted for each of the six locations within each of the six strips, resulting in 36 sets of numbers. These numbers were averaged and then scaled on a per hectare basis to determine average tiller population and percentage composition of each species.

Outflow from the downstream end of the buffer strips was collected in tanks (1.52 m wide \times 0.61 m deep \times 0.76 m long), as shown in figure 1. Identical V–notch weirs, as on the upstream side, were used to measure outflow from the buffer strips. The complete setup was such that it provided for free flow of runoff water without any ponding at the upstream or downstream ends of the buffer areas. Automatic samplers (model 3700 portable sampler, ISCO Environmental Systems, Lincoln, Neb.) were used to sample the effluent and influent for determining sediment and pesticide concentrations.

One depth sensor and one ISCO sampler were used at the downstream end of each buffer strip to measure runoff depth and to sample the outflow. Depth sensors (styrofoam floats connected to slide resistors) gave outputs in mV, which were recorded by a datalogger (CR–10, Campbell Scientific, Logan, Utah). The datalogger scanned all the sensors every 20 s and recorded the instantaneous voltages. These voltages were later converted to head values (H) by multiplying with a conversion factor. The sensors, the datalogger, and the samplers were powered by 12 V batteries.

During a runoff event, each sampler took 300 mL samples every 2 min for both inflow and outflow. Twenty–four 350 mL glass bottles, placed in the sampler, provided for a total sampling period of 48 min. Samplers started sampling inflow as soon as the water began to flow over the weirs of the distribution tank at the inflow end of the strips. Outflow sampling was started as soon as outflow completely submerged the sampler intake, just before it began to flow over the weirs. Three samples were composited into a 1 L glass jar to obtain a sample representative of a 6 min time interval. These samples were refrigerated immediately at 4°C for extraction and analysis for sediment and pesticide concentrations at a later time. Sediment concentrations were determined by using a gravimetric oven-drying method. Duplicate subsamples of stirred samples were weighed and oven dried at 105°C for 24 h. Dried samples were then weighed, and the resulting subsample concentrations were analyzed for percent difference. Subsamples having more than 5% difference in calculated concentrations were reanalyzed.

Pesticide concentrations in the sample water were determined using gas-liquid chromatography. Refrigerated samples were stirred and shaken to obtain a uniform subsample. To obtain water free of sediment, subsamples were filtered through 5 μ pore filter paper (medium porosity, slow flow rate). A known weight of this filtered water subsample was extracted with a known volume of toluene by shaking it on an orbital shaker for 50 min. The water-toluene mixture was then allowed to separate for 30 min, and the separated toluene was decanted into glass test tubes. Fifty milliliters of the filtered water subsample were extracted with 50 mL of toluene.

To extract pesticides from sediment, a known amount of runoff sample was centrifuged, and the water was decanted. A known volume of toluene was then added to the wet centrifuged sediment. Glass beads were added to the sediment-toluene mixture to lift the sediment into suspension in the toluene. The centrifuge bottle was then rotated for 1 h in a horizontal orientation and then for 1 h in a vertical orientation. The toluene from the stirred mixture was decanted into test tubes. The remaining mixture was oven dried to obtain the dry weight of the sediment.

Two microliters of water and sediment extract were injected into a Tracor 540 gas–liquid chromatograph using split–less injection mode to determine the pesticide concentrations. This chromatograph was equipped with an electron capture detector and a 774 Tracor autosampler. The flow velocity for the hydrogen carrier gas was 25 cm/s, and the flow rate for the makeup gas (5% argon and methane) was 40 mL/min. The column oven, inlet, and detector temperatures were held constant at 160°C, 250°C, and 350°C, respectively. Pesticides were separated using a 0.25 mm diameter \times 30 m long capillary column (DB–5, 0.25 µm film; J&W Scientific). Data acquisition was performed using a Spectra–Physics 4270 integrator and a Fisher Recordall 5000 strip–chart recorder.

Infiltration occurring on the buffer strip was determined by an inflow-outflow mass balance. Cumulative instantaneous volumes from these rate-time series were multiplied by the time intervals to obtain the total amounts of inflow and outflow. Total infiltration was then determined by subtracting total outflow from total inflow. The mass of runoff water remaining in the inflow distribution tank at the end of a storm event was not included in the mass balance because it never passed through the VBS area. However, the runoff water remaining in the outflow collection tanks for each buffer strip was included in the mass balance since it was a part of inflow passing through the buffer strip. The following equation was thus developed and used in calculating total infiltration:

$$M_{inflt} = M_{inflow} - M_{outflow} - M_{outflow, tank}$$
(2)

where

M _{inflt}	= mass of water infiltrating in the buffer strip
	(mm)
M _{inflow}	= mass of water entering the buffer strip (mm)

as measured through the weirs

M_{outflow} = mass of water leaving the buffer strip (mm) as measured through the weir

 $M_{outflow, tank}$ = mass of water left in the outflow tank (mm).

Adsorption coefficients (K, equal to pesticide concentration in sediment divided by its concentration in water) were determined for inflow and outflow samples for the three pesticides. However, K values resulting from sediment-adsorbed concentrations of samples with less than 0.5 g total sediment (after oven drying) were not used due to analytical limitations. The remaining K values were averaged for both inflow and outflow for the three pesticides. Using this average K value, the overall pesticide concentration of the sample mix, the pesticide concentration in solution, and the concentration as adsorbed to sediment were calculated for the samples for which insufficient total sediment was available for analysis. Hydrographs for flow into the six buffer strips were divided into four parts. These four parts were the rising limb (first 6 min of flow), the equilibrium period (next 12 min of flow), the recessional limb (next 18 min of flow), and the asymptotic period (remaining duration of inflow). Comparisons were made for these four parts of the hydrograph between the inflow and outflow. A flow differential rate curve was developed by subtracting outflow from inflow on a real-time basis. Percent pesticide retention values were analyzed for significant differences among area ratios and between pesticides using a randomized block design (Cochran and Cox, 1992).

RESULTS

This study represents a natural rainfall event in which rainfall has stopped by the time runoff from the field enters the buffer strip. This implies that there is no effect of dilution due to rainfall on flow through the buffer strip. There was a small amount of rainwater adhering to the tillers within the buffer strip due to sprinkler rain. This amount is considered to be negligible in comparison to inflow volume when considering any dilution effect.

Table 2 shows the mass balance for inflow and infiltration averaged over three replications for the two area ratio treatments. Inflow volume was 15.8 cm into the 15:1 treatment and 31.5 cm into the 30:1 treatment. These inflow volumes were the same for all three replications of the two area ratio buffer strips due to the setup of the inflow distribution system. Mean outflow volume was 9.7 cm for the 15:1 treatment, and 21.9 cm for the 30:1 treatment. The total inflow and total outflow volume values were converted to depth over the buffer strip area. Mean percent infiltration calculated through mass balance was 38.8% (range of 27% to 50%) and 30.4% (range of 22% to 40%) for the 15:1 and 30:1 treatments, respectively. However, these percent infiltrations were not significantly different at $\alpha = 0.10$. Assuming similar infiltration rates for all buffer strips for both treatments, the greater percentage infiltration occurring on the 15:1 treatment versus the 30:1 treatment can be accounted for in part by less input depth.

Figure 2 shows the inflow rates and average outflow rates over time for the two treatments. Infiltration on the buffer strips was determined by the difference of the two areas under the curves (inflow and outflow curves) for the respective treatments. The average time difference between flow to enter buffer strips and appear as outflow at the downstream end was 13.3 and 14.0 min for the 15:1 and 30:1 treatments, respectively. Inflow hydrographs were divided into four hydrologic periods, as shown in figure 2: "A" refers to the end of the rising limb, "B" refers to the end of an equilibrium period, and "C" refers to the end of the recessional limb and the start of an asymptotic period to the end of the hydrograph. For the rising limb (first 6 min of inflow hydrographs), there was no volume of water leaving the buffer strips. As there was no rainfall being added and mass conservation must apply, this means that all inflow during the rising limb was traveling and infiltrating along the flow length of the buffer strips. The time difference between the start of inflow and the start of outflow represented in part the travel time from the inlet to outlet points of the buffer strips, as infiltration was occurring simultaneously.

The flow differential rate curve, for the difference between inflow and average outflow (fig. 3), followed the inflow hydrographs. Outflow from the buffer strips started about 6 min into the equilibrium period of the inflow hydrograph. As such, the flow differential rate curve began to drop. As the inflow hydrographs entered the recessional limb, average outflow was still steady. However, about 32 min into inflow hydrograph, average outflow from the buffer strips exceeded inflow. As such, the flow differential rate dropped to zero and then became negative (fig. 3). During the recessional limb of the inflow hydrographs, average outflow was still greater than inflow. Outflow

Attribute	Units	Buffer Strip ^[a] and Mean Value							
		15:1 Area Ratio				30:1 Area Ratio			
		1	4	6	Mean	2	3	5	Mean
Flow ^[b]									
Inflow	cm	15.8	15.8	15.8	15.8	31.5	31.5	31.5	31.5
Outflow	cm	9.7	11.5	7.8	9.7	22.6	18.8	24.3	21.9
Infiltration	%	38.6	27.2	50.6	38.8 a[c]	28.2	40.3	22.8	30.4 a
Sediment ^[d]									
Inflow	kg/ha	6476.3	6476.3	6476.3	6476.3	12952.5	12952.5	12952.5	12952.5
Outflow	kg/ha	650.7	927.2	350.3	642.7	1965.8	909.5	2273.0	1761.1
Retention	%	90.0	85.7	94.6	90.1 b[c]	84.8	93.0	82.5	86.8 b

Table 2. Inflow, outflow, infiltration, sediment mass input, output, and percent retention for the six buffer strips.

[a] Buffer strips for both area ratio treatments are of the same area (30.6 m²).

[b] Flow converted into cm of depth over strip area; inflow of 30:1 treatment is twice (2×) that of 15:1 treatment due to setup of project.

[c] t-test H0: mean(15:1) = mean(30:1), no significant difference between the same letters at $\alpha = 0.10$.

[d] Sediment mass converted to kg/ha over strip area; sediment mass input of 30:1 treatment is twice (2×) that of 15:1 treatment due to setup of project.



Figure 2. Inflow rates and average outflow rates for the two treatments. Inflow hydrograph cutoff marks: A = end of rising limb, B = end of equilibrium period, and C = end of recessional period and start of asymptotic period.



Figure 3. Flow differential rates (difference between inflow and outflow on real-time scale) for the two treatments.

continued even though inflow became relatively small and eventually zero. This outflow was a result of depletion of temporary storage created within the buffer strips. The flow differential rate during the recessional limb of the inflow hydrograph stayed negative and gradually became zero. Total area under the flow differential rate curve represented total infiltration taking place within the buffer strips. However, instantaneous flow differential values did not represent infiltration, as infiltration was occurring as a function of both time and place within the buffer strips.

Figure 4 shows average sediment concentrations for the mean inflows and outflows from the buffer strips. Note that the average outflow concentrations were moved back in time for all concentrations to be viewed on the same time scale. Buffer strips reduced average outflow sediment concentrations by more than 60% (60% to 80%) relative to inflow concentrations, although these reductions were not significantly different ($\alpha = 0.10$) between the two area ratio treatments. Thus, reduced sediment concentrations, combined with the effect of infiltration, resulted in high sediment retention efficiencies for both the 15:1 and 30:1 treatments. As shown in table 2, these sediment retention efficiencies averaged 90% and 87% for the 15:1 and 30:1 treatments, respectively. Average sediment retention was less for the 30:1 treatment when compared with the 15:1 treatment. However, the difference between the sediment retention for the two treatments was not statistically significant ($\alpha = 0.10$). Increased flow volume over the same area and same time period would increase flow velocity, thereby increasing the



Figure 4. Average sediment concentrations for inflow and the outflow for the two treatments (outflow concentration time scales are offset to match with inflow concentration time scale).





Figure 5. Average atrazine concentrations in solution and as adsorbed to sediment for two area ratio buffer strip treatments (outflow concentration time scales are offset to match with inflow concentration time scale).

turbulent energy to keep sediment in suspension and allowing less time for sediment settling, and thus less sediment trapping in the 30:1 area ratio buffer strip. Research studies by Young et al. (1980), Magette et al. (1989), Dillaha et al. (1989), and Mickelson et al. (2003) each show that the first few meters of the buffer strip length retain 50% or more of the sediment mass. This can explain to some extent the non–significant differences between the sediment retentions for the two treatments.

Figure 5 shows average atrazine concentrations (both as adsorbed to sediment and in solution with water) for inflow to and outflow from the buffer strips as a function of time. Again, outflow concentrations were moved back in time to match the timing for the inflow values so both concentrations can be viewed on same time scale. Flow-weighted sediment adsorbed concentrations for atrazine averaged over the whole event are given in table 3. These event-averaged concentrations were 18.2, 60.4, and 49.4 mg/kg for inflow, the 15:1 treatment outflow, and the 30:1 treatment outflow, respectively. As is evident from figure 5 and table 3, these event-average concentrations were 2.7 to 3.3 times larger in outflow than in inflow for both treatments. Larger and thus heavier sediment particles and/or aggregates are expected to be trapped in the buffer strips, and sediment in outflow is expected to have a larger percentage of finer particles than sediment in inflow. Greater adsorbed pesticide concentrations are expected in outflow, as the finer sediment particles have greater specific surface area. Particle size distribution analysis could not be performed, as the amount of sediment in the samples was just enough to determine sediment concentrations and as-adsorbed pesticide concentrations.

Metolachlor showed similar trends when compared with atrazine for adsorbed pesticide concentrations (table 3). However, the opposite was true for chlorpyrifos (fig. 6 and table 3). Event–averaged sediment–adsorbed concentrations for chlorpyrifos were larger in inflow than in outflow for both treatments. The event–averaged values were 103.3, 83.9, and 93.9 mg/kg for inflow, the 15:1 treatment outflow, and the 30:1 treatment outflow, respectively, as shown in table 3. Most of the sediment settling in the strip is expected to be the larger and heavier particles (sand and silt). Although it is hard to explain, lower sediment–adsorbed concentrations of chlorpyrifos in outflow from the strips seemingly indicates that it is adsorbed to a greater degree on larger and/or heavier particles.



Figure 6. Average chlorpyrifos concentrations in solution and as adsorbed to sediment for two area ratio buffer strip treatments (outflow concentration time scales are offset to match with inflow concentration time scale).

				Atrazine		Atrazine		Metolachlor		Chlorpyrifos	
Attribute	Phase	Flow	Units	15:1	30:1	15:1	30:1	15:1	30:1		
Concentration	As adsorbed (Cs) ^[d]	Inflow ^[a]	mg/kg	18.2		23.3		103.3			
		Outflow ^[b]	mg/kg	60.4 a ^[c]	49.4 a	65.3 b	50.4 b	83.9 c	93.9 c		
				(7.6) ^[e]	(9.8)	(5.9)	(13.2)	(4.1)	(18.4)		
-	In solution (Cw) ^[f]	Inflow ^[a]	mg/L	0.820		0.961		0.076			
		Outflow	mg/L	0.651 d	0.645 d	0.740 e	0.749 e	0.082 f	0.093 f		
				(0.080)	(0.110)	(0.049)	(0.199)	(0.008)	(0.016)		
Pesticide Mass ^[g]	With sediment	Inflow ^[h]	g/ha	117.9	235.8	151.0	301.9	669.2	1338.4		
		Outflow	g/ha	38.8	84.8	41.9	86.4	53.9	161.2		
				(13.6) ^[e]	(47.6)	(15.9)	(21.5)	(25.8)	(54.8)		
-	With water	Inflow ^[h]	g/ha	1291.6	2583.2	1514.0	3027.9	119.4	238.8		
		Outflow	g/ha	630.9	1414.0	717.0	1641.3	79.0	203.2		
				(47.6)	(412.0)	(104.5)	(199.9)	(22.9)	(25.3)		

Table 3. Flow-weighted average pesticide concentrations as adsorbed with sediment and in solution, and pesticide mass for inflow and for outflow for both the area ratio treatments.

[a] Inflow concentrations are the same for both area ratio treatments due to setup of project.

^[b] Refer to text for explanation of why atrazine and metolachlor Cs values are greater in outflow.

[c] t-test H0: mean(15:1) = mean(30:1); no significant difference between same letters at $\alpha = 0.10$.

^[d] Cs = concentration in sediment.

[e] Standard deviations in parentheses.

[f] Cw = concentration in solution.

[g] Masses converted to g/ha over strip area.

[h] Input masses of 30:1 treatment are twice (2×) those of 15:1 treatment due to setup of project.

In solution, flow-weighted concentrations for atrazine averaged over the entire runoff are also listed in table 3. These event-averaged values were 0.82, 0.65, and 0.64 mg/L for inflow, the 15:1 treatment outflow, and the 30:1 treatment outflow, respectively. The event-averaged outflow concentrations were 21% smaller than the inflow concentrations. Similar results were observed for metolachlor, as shown in table 3. No rainfall was applied on the strips during inflow/outflow, and therefore there was no dilution effect. However, adsorption to in-place soil and dead/living organic matter could possibly account for the reduction in outflow concentrations. Average flow-weighted, in-solution concentrations for the insecticide chlorpyrifos were 0.076 mg/L, 0.082 mg/L, and 0.093 mg/L for inflow, the 15:1 treatment, and the 30:1 treatment, respectively (table 3). Opposite from the herbicide trends, chlorpyrifos event-averaged in-solution concentrations in outflow for the 15:1 and 30:1 treatments were greater than the inflow concentrations.

Adsorption coefficients (K, ratio of as-adsorbed concentration to in-solution concentration) for atrazine, metolachlor, and chlorpyrifos for inflow into buffer strips were 22, 24, and 1359, respectively. The adsorption coefficients for the three pesticides, for the 15:1 area ratio treatment average outflow from the buffer strips, were 93, 88, and 1023, respectively. The corresponding numbers for the 30:1 area ratio treatments were 77, 67, and 1010, respectively. When compared with the partitioning coefficients, as listed in table 1, adsorption coefficients for atrazine were 7 times greater in inflow and 25 to 31 times greater in outflow for the two treatments. Similarly, adsorption coefficients for metolachlor were 4 times greater in inflow and 11 to 14 times greater in outflow. Chlorpyrifos adsorption coefficient magnitudes showed a decline from inflow values to outflow values, being 7 times greater in inflow and only 5 to 6 times greater in outflow, in comparison with the K values listed in table 1. Partitioning coefficients as listed in table 1 show how a pesticide would partition between soil and water in a field where it is applied. Larger values of K observed in inflow indicate large proportions of fractional organic carbon in sediment to which the pesticide would be adsorbed. Organic carbon particles are lighter than sediment and are expected to be lost relatively easily in runoff, thereby resulting in larger adsorption coefficient values. These organic carbon particles and fine sediment particles are not expected to settle out in buffer strips. The increase in adsorption coefficient values in outflow for atrazine and metolachlor indicates a greater degree of adsorption of these pesticides to organic carbon particles and fine sediment. A decrease in adsorption coefficient values for chlorpyrifos in outflow indicates a greater degree of adsorption of this insecticide to larger sediment particles, which are likely to settle out in buffer strips.

Table 3 shows the total masses of the three pesticides in inflow and outflows for both the treatments. Buffer strips with the 15:1 treatment retained about 52.5% of the total input (sum of both in–solution mass and as–adsorbed to sediment mass) for atrazine, while the 30:1 treatment retained 46.8%. Corresponding numbers for the two treatments were 54.4% and 48.1% for metolachlor, and 83.1% and 76.9% for chlorpyrifos. For chlorpyrifos, being strongly adsorbed, the percent retention with sediment was much greater than with water. About 5% of the total atrazine and metolachlor retained was through sediment retention; in

comparison, chlorpyrifos retention with sediment was about 75%.

Analysis of variance, using the randomized block design, showed that differences between the two treatments were not significant for any of the three pesticides ($\alpha = 0.10$). Despite this lack of statistical significance, the trend of lower buffer strip retention of pesticides at higher area ratios for all three pesticides was what would be expected based on the potential effects of the processes of infiltration, adsorption, and sediment deposition (Baker and Mickelson, 1994; Misra et al., 1996; Arora et al., 1996). Surface storage can possibly play a role in newly established buffer strips. A well established six–year old buffer strip area was used in this study. All depressions, crevices, etc., were expected to have been filled, and therefore surface storage effects were deemed insufficient to cause any change in reported numbers.

There was no significant difference ($\alpha = 0.10$) between atrazine and metolachlor retention, but retention of chlorpyrifos was significantly greater ($\alpha = 0.10$) than that of the other two pesticides for both treatments. For both atrazine and metolachlor, most of the retention was the result of infiltration alone, as most of the mass was retained by infiltration (table 3). However, higher sediment retention in the strips resulted in higher chlorpyrifos retention. Thus, due to higher sediment retention efficiency, VBS were found to be more effective in retaining strongly adsorbed pesticides. As explained earlier, comparable studies have found that the first few meters of the buffer strip length retain 50% or more sediment mass. This means that retention of strongly adsorbed pesticides will follow the sediment retention trends. As no significant difference ($\alpha = 0.10$) between the two treatments was obtained, a 30:1 area ratio buffer strip will be more practical in fields that are receiving strongly adsorbed pesticide applications.

SUMMARY AND CONCLUSIONS

- The runoff simulation performed in this study represented the case in which runoff from the source area enters the buffer strip after the rain has stopped and thus eliminated rainfall dilution as a complication in interpreting the data. Under this condition, the buffer strips retained 49.7% of atrazine, 51.2% of metolachlor, and 80.0% of chlorpyrifos, averaged for both the 15:1 and 30:1 treatments.
- Differences between the two treatments were not found to be significant ($\alpha = 0.10$) for the three pesticides, indicating that similar retention processes of infiltration and sediment deposition were taking place in the buffer strips; however, the non-significant trend was lower retention at the higher area ratio.
- No significant difference was found between the retention percentages for atrazine and metolachlor; however, retention of chlorpyrifos in the buffer strips was significantly greater than that of both atrazine and metolachlor for both treatments.
- For atrazine and metolachlor, most of the retention was through infiltration of runoff, while deposition of sediment contributed to most of the chlorpyrifos retention in the buffer strips. Storage effects were considered to be negligible due to the buffer strip area being a well

established grassed waterway and due to wetting of the buffer strip area prior to runoff simulation.

- Higher sediment retention in the buffer strips (about 88% averaged over both area ratio treatments) contributed to higher retention of chlorpyrifos; thus, buffer strips were found to be more effective in retaining this more strongly adsorbed pesticide of the three pesticides considered in this study.
- A flow differential (difference between inflow and average outflow) rate curve initially followed the inflow hydrographs, then declined and became negative, and became zero towards the end of simulation. The area under the flow differential rate curve represented the total infiltration occurring within the buffer strips. However, instantaneous flow differential values were not equal to infiltration due to the temporary storage occurring within the buffer strips.

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