

2003

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Abstract

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Keywords

Area ratio, Buffer strip, Chemical transport, Subsurface flow, Surface flow

Disciplines

Agriculture | Bioresource and Agricultural Engineering

Comments

This article is from *Transactions of the ASAE*, 46, no. 3 (2003): 675–684.

Journal Paper No. 19827 of the Iowa Agricultural and Home Economics Experiment Station, Ames, Iowa, Project No. 6548.

PESTICIDE TRANSPORT WITH SURFACE RUNOFF AND SUBSURFACE DRAINAGE THROUGH A VEGETATIVE FILTER STRIP

P. M. Boyd, J. L. Baker, S. K. Mickelson, S. I. Ahmed

ABSTRACT. *Vegetative filter strips (VFS) have become an established best management practice during the last 25 years. This study examined the effectiveness of VFS of brome grass in central Iowa for reducing the mass transport of sediment and pesticides (atrazine, acetochlor, and chlorpyrifos) with surface runoff under natural rainfall conditions. Measurements of pesticide concentrations in water from a single subsurface drain under the plots were also made. Overall results showed that many factors affect pesticide transport, such as rainfall timing and intensity, hydrology, source-to-VFS area ratios, and the adsorption properties of pesticides in VFS inflow. Two primary mechanisms (inflow water infiltration and sediment deposition) had a significant effect on pesticide passage through VFS. Sediment deposition increased with decreased flow volume and velocity, and was considerably higher for the 15:1 area-ratio plots than for the 45:1 plots; this in turn aided in the reduction of transport of pesticides adsorbed to sediment. Reductions in atrazine and acetochlor transport were primarily controlled by the infiltration efficiency of the VFS, as they are moderately adsorbed, and the major portion of these pesticides moved in solution in the surface runoff water phase. Chlorpyrifos was highly adsorbed to the sediment, making sediment deposition in the VFS equally, if not more, important than infiltration for mass removal. The herbicides (atrazine and acetochlor) had low to moderate adsorption characteristics and moved primarily in the runoff water phase. Data collected for the subsurface drainage from the tile line showed that there were measurable concentrations of the moderately adsorbed herbicides in the tile flow at the time surface runoff was taking place; however, concentrations of the more strongly adsorbed chlorpyrifos were below detection. The statistical difference was most prominent in the event with the smallest runoff volume. This showed that at lower flow rates, VFS can effectively reduce runoff, sediment, and pesticide transport from cropland.*

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Due to the world's growing need for food during the last few decades, a certain amount of nonpoint-source pollution from losses of soil, nutrients, and pesticides from intensively managed cropland with surface runoff and subsurface drainage is inevitable. Tillage and other management practices can have a significant effect on the volumes of surface runoff and subsurface drainage. Along with management practices, the transport of sediments, nutrients, and pesticides in surface runoff and subsurface drainage is affected by the intensity and volume of rainfall events (Felsot et al., 1990; Flanagan and Nearing, 2000). Surface runoff can occur when the surface soil becomes saturated or when rainfall intensity exceeds the infiltration capacity of the soil, causing ponding (Harris and Forster, 1996; Lalonde et al., 1998).

VEGETATIVE FILTER STRIPS

Natural vegetation in surface runoff pathways can cause flow resistance, reducing runoff velocities, and therefore help reduce soil, nutrient, and pesticide losses. Vegetative filter strips (VFS) have been recommended as best management practices (BMPs) in controlling nonpoint-source pollution from agricultural lands in the last 25 years (Asmussen et al., 1977; Mickelson and Baker, 1993; Patty et al., 1997). The basic design of a VFS has been an area of low or no-maintenance close-grown vegetation at the end of a field slope, separating the field from a receiving water or waterway. VFS are less expensive than most other soil erosion control structures, and if needed, VFS can be removed and reestablished easily at other positions on the landscape (Robinson et al., 1996). The purpose of most VFS is to control erosion and to reduce soil, nutrient, and pesticide transport in surface runoff. VFS have also been used for controlling losses of nutrients from animal manures (Dillaha et al., 1989; Parsons et al., 1994; Gharabaghi et al., 2000).

For pesticide transport, many researchers have stressed the importance of the first few runoff events after fieldwork and/or application, as these events have been shown to be the ones with the highest pesticide concentrations throughout the growing season. The condition of the VFS for this period of time is critical to its effectiveness for pesticide and sediment retention (Rhode et al., 1981; Arora et al., 1996; Lawrence et al., 1997), with soil moisture, surface porosity, and

Article was submitted for review in September 2002; approved for publication by the Soil & Water of ASAE in February 2003. Journal Paper No. 19827 of the Iowa Agricultural and Home Economics Experiment Station, Ames, Iowa, Project No. 6548.

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vegetation growth and density being factors affecting their effectiveness (Lowrance et al., 1997).

Research has shown that the area ratio, defined as the ratio of the contributing surface runoff area to the VFS area, has a significant effect on the runoff infiltration and sediment, nutrient, and pesticide retention rate of VFS. Arora et al. (1996) determined the effect of two area-ratio treatments (30:1 and 15:1) on VFS retention efficiency for three herbicides (atrazine, metolachlor, and cyanazine) in cropland runoff. They measured reductions from 8% to 100% for the three herbicides, depending to a large degree on rainfall intensities and amounts, and the resultant percentage of surface runoff water that could be infiltrated into the VFS.

INFILTRATION AND VFS LENGTH

The length of VFS, and therefore the area that is necessary to achieve a certain goal, is dependent on local conditions. VFS have been effective in enhancing infiltration and reducing runoff, and sometimes reducing pesticide concentrations in inflow through adsorption to in-place soil and plant residue. Concentrations are also reduced by dilution with rain that falls on the VFS during flood-through. Using 4.6 and 9.1 m long VFS, Mickelson and Baker (1993) found average reductions in surface runoff volumes/inflow by infiltration of 36% and 54%, respectively (infiltration = inflow + rainfall - outflow). In another study under similar conditions, infiltration was found to be the most important pesticide removal mechanism associated with the VFS studied (Misra et al., 1996). The length of the VFS also greatly affects sediment reduction (Barfield et al., 1998). Dillaha et al. (1989) found on average that doubling the vegetative filter length from 4.6 to 9.1 m resulted in a reduction of sediment transport of an additional 15%, with the 9.1 m long VFS removing an average of 84% of incoming runoff sediment. However, Robinson et al. (1996) found insignificant additional sediment removal beyond 9.1 m in VFS due to soil texture and aggregate size.

PESTICIDE TRANSPORT

The chemical and physical properties of pesticides used also contribute greatly to their runoff characteristics, primarily their solubilities and their partitioning between the soil sediment and water phases. The major pathways of losses for each may be different, and the degree to which a pesticide is adsorbed to soil sediment depends to a large extent on its properties (Marshall et al., 1996). Reductions in sediment concentrations in surface runoff have little effect on total pesticide losses if the pesticide is very weakly adsorbed to the soil particles (Baker and Johnson, 1979). Wauchope (1978) noted that in general only pesticides with solubilities greater than 10 mg L⁻¹ are likely to be lost primarily in solution in the runoff water phase. Conversely, slightly soluble and/or strongly adsorbed pesticides move mainly with the sediment, but as sediment usually makes up a fairly small fraction of surface runoff (usually less than 1% by mass), and is filtered from leaching water before it reaches subsurface drains, lower overall losses for these pesticides have been observed (Jones et al., 1995).

SUBSURFACE DRAINAGE

While it has been shown that infiltration is the major driving force in sediment and pesticide reduction in surface

runoff (Correll et al., 1996), the infiltrate has been rarely looked at as a source of pesticide contamination concern. The presence of macropores in the soil profile is very important in determining the potential contamination from subsurface drainage for a surface runoff event (Harris and Forster, 1996). Lowrance et al. (1997) collected groundwater samples below a VFS of common bermudagrass (*Cynodon dactylon* L. Pers.) to a depth of 200 cm, and found that average atrazine concentrations were reduced from 1.29 to 0.14 µg L⁻¹ in wells going from 0 to 68 m from the edge of the source area, showing that pesticide movement from surface runoff in a VFS to shallow groundwater was possible.

There has been little reported evidence of any benefits to using VFS for reducing pesticide movement in subsurface drainage water (Harris and Forster, 1996). This could be due to the rapid movement from the VFS surface to subsurface drains, making the residence time in the VFS very small. Recent research by Harris et al. (1996) has shown a 25% reduction in loss of isoproturon by restricting infiltration until soil saturation occurred in the VFS.

OBJECTIVES

Past research on the site of the study reported here has shown that infiltration of surface runoff water was the most important herbicide removal mechanism associated with the VFS (Arora et al., 1996; Misra et al., 1996). This knowledge raises additional concerns about the fate of infiltrated runoff water. As this water moves through the soil profile, movement to groundwater or subsurface drainage tiles is possible. Although it is not a common practice, a subsurface drainage tile below a VFS could aid in determining if movement of pesticides with water to the tile line could be detected, and if detected, if the extent of this movement creates a groundwater or tile drainage concern (this case existed at the study site).

To more fully investigate the impacts of VFS use on overall pesticide transport, this study incorporated different pesticides and area ratios at an established research site. Increased flow rates entering the VFS at even higher area ratios than used in previous studies were used to determine the maximum loading rate while still having some runoff control under natural rainfall conditions. The overall goal of the study was to evaluate the effectiveness of VFS for reduction of sediment and pesticide concentrations and transport in surface runoff and subsurface drainage under natural rainfall conditions. The specific objectives were to:

- Determine to what extent VFS infiltration and sediment deposition can reduce sediment, atrazine, acetochlor, and chlorpyrifos transport from treated cropland with area ratios of 15:1 and 45:1.
- Establish if there should be concern for concentrations and transport of pesticides in surface runoff that infiltrates into a VFS and is possibly released with subsurface drainage.

METHODS AND MATERIALS

The study was conducted at Iowa State University's Swine Nutrition Facility, near Ames, Iowa. The field layout of the site is shown in figure 1. The field source area of 0.58 ha (1.41 ac) consisted of mainly Canisteo silty clay loam and had an average slope of 3.5%. The site has been in continuous

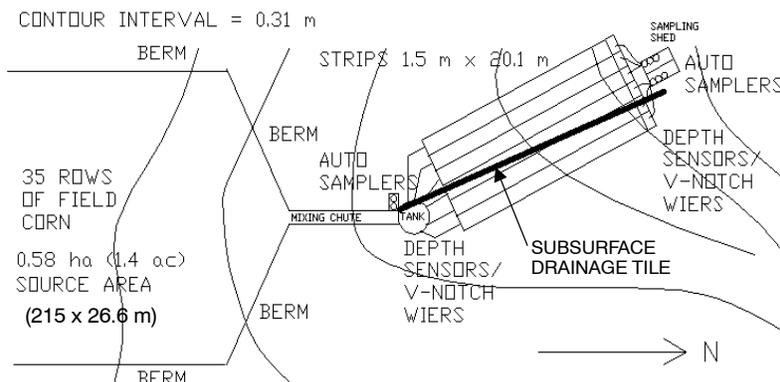


Figure 1. Schematic of VFS study site in Boone County, Iowa.

Table 1. Pesticide application summary for 1999.

Pesticide	Common Name	Application Rate (kg ha ⁻¹) A.I.	Application Date
Atrazine	AAtrex (4L)	1.68	19 May 1999
Acetochlor	Harness Plus (4L)	1.96	19 May 1999
Chlorpyrifos	Lorsban (15G)	1.22	19 May 1999

acetochlor) were applied as a broadcast spray with 187 L ha⁻¹ (20 gal ac⁻¹) water and surfactant; the insecticide (chlorpyrifos) was banded over the row in granular form using insecticide hoppers on the planter. After pesticide application at planting, each interrow was tracked over by the planter tractor to facilitate sufficient runoff for the study.

The source area began at the top of a hill and was bermed on each side and at the downslope end to direct all surface runoff towards an opening in the berm at the lowest point of the field. Matched to the opening, a wooden chute 1.22 m wide × 0.41 m deep × 12.2 m long channeled the runoff into a partially buried, 3.05 m diameter by 0.76 m deep circular galvanized steel collection and distribution tank (fig. 2). This tank allowed for measurement of flow rates, sampling for inflow sediment and pesticide concentrations, and provided a system for distribution of surface runoff into individual VFS. The tank was separated into two halves by a hanging screen. The screen kept debris and other field trash away from the sampling inlets and outflow weirs. It also served the purpose of buffering turbulence in the runoff water, making a smoother surface at the outflow weirs and decreasing the variability of flows into the VFS. Six V-notch weirs were mounted on the perimeter of the tank opposite the inflow chute. Each weir was machined from 0.32 cm thick stainless steel to handle a maximum flow depth of 25.4 cm.

For this study, two different field-to-VFS area ratios (15:1 and 45:1) were used. These area ratios were used based on the effectiveness of different ratios in past research (Arora et al., 1996). For the 15:1 and 45:1 area ratios, the weir angles were 30.0° and 78.3°, respectively. Each weir was placed at exactly the same elevation to ensure that the calculated flow rates into each VFS (with the same V-notch weir) and the ratio of flows for the two area-ratio treatments remained constant. Below the weirs of the distribution tank, galvanized steel channels directed runoff to the entrance of each VFS. Figure 2 shows the layout of the distribution tank, from the runoff inflow chute to the channels to the VFS, and the area ratio of each plot. The two flow ratios were replicated three times, requiring a total of six plots. Plot treatment was assigned using a randomized block design.

The VFS were established in 1993 in existing waterway vegetation. Each strip measures 20.1 m long × 1.5 m wide (30.1 m²), the six strips sharing their lengthwise borders. Each of the VFS was separated by steel borders 0.30 m high and driven about 0.08 m into the soil. The VFS were at an offset angle to the source area only to ensure that all six VFS had a consistent slope of approximately 2%. The vegetative

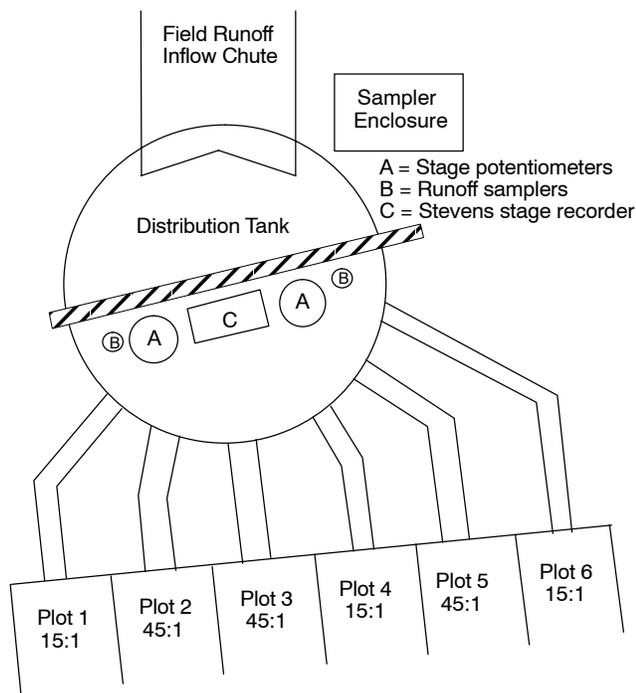


Figure 2. Runoff inflow chute, distribution tank, and channels to VFS plots.

corn since the inception of the VFS research at this location in 1993. The field was tandem disked in the fall of 1998 and again in the spring of 1999 prior to planting and pesticide application. The source area was planted with field corn in 1999; 35 rows, 215 m long, were planted on a 0.76 m row spacing at an average population of 69,200 seeds ha⁻¹ (28,000 seeds ac⁻¹), with the rows parallel to the slope of the source area.

Table 1 summarizes the application of pesticides to the source area. Atrazine, acetochlor, and chlorpyrifos were applied at the time of planting. The herbicides (atrazine and

cover in the VFS plot area had remained unchanged over the past 10 years. The composition of the VFS was 81% bromegrass (*Bromus inermis*), 12% bluegrass (*Poa pratensis*), 5% bluegrass (*Festuca arundinacea*), and the remaining 2% comprised varying species. Tiller population was measured to be 8.82 M tillers ha⁻¹.

Flow through the entire VFS monitoring system was driven by gravity. Runoff exiting the downstream end of the VFS was collected in individual tanks below each plot. The tanks measured 1.52 m wide × 0.76 m long × 0.61 m deep. Each of these tanks contained the same sampling, flow measurement, and stage recording equipment as the distribution tank, including a weir corresponding to the distribution tank weir. Runoff exiting the weirs on the outflow tanks was directed to one of two excavated ditches that returned the runoff to the waterway.

A subsurface drainage tile was discovered during the installation of the research facility in 1993 (see fig. 1). The tile had a 10.2 cm inside diameter and was laid in 30.5 cm sections. In 1993, the tile was capped at the upslope end, where the runoff inflow chute dumps into the distribution tank, stopping all tile flow from the source area. The tile continues downslope, passing under VFS plots 3 and 4, and exits the plot area below the ditch that drains VFS plots 1, 2, and 3. Because the tile was capped near the distribution tank, only surface water infiltrating through the VFS can enter the tile. In the spring of 1997, a tile sampling tube was inserted into the tile line 1.8 m downslope from the outflow tanks for VFS plots 3 and 4.

DATA COLLECTION INSTRUMENTATION

To determine pesticide and sediment concentrations in the runoff water before and after moving through the VFS, samples were collected at the distribution tank and in each of the outflow tanks as a function of time. These samples were collected with ISCO 3700 portable water samplers. Each sampler used a Teflon-coated 0.95 cm diameter suction hose with a weighted pickup head and a debris screen. Each sampler was set to activate automatically when runoff began by the use of magnetic liquid-level switches.

The sampling program for surface runoff through the VFS was as follows: at the time of activation, and following in 2 min intervals, each sampler would purge the collection line, collect a 100 mL sample in a clean glass collection jar, and then purge the line again. Three samples were collected in each bottle, giving a 6 min composite per bottle. Each sampler contained 24 bottles, giving a total possible collection time of 144 min, sufficient for most storm events. When these samples were collected from the field, they were further composited into 12 min samples by transferring pairs into 900 mL glass bottles and refrigerated at 4°C until laboratory extraction and analysis. After each runoff event, runoff remaining in the tanks was pumped out and the tanks cleaned in preparation for the next event.

The water-sampling program for the tile sampler was designed to collect an entire set of samples before shutting off. The liquid-level switch was located in VFS plot 1, so tile sampling started when surface runoff reached the plot 1 outflow tank. Due to the retardation of flow between the surface runoff and subsurface runoff, a longer sampling period was used. A 300 mL sample was taken from the tile line every 15 min, and only one sample was contained in each bottle. With 24 bottles available, total sampling time was

345 min. These samples were also composited in pairs to give 30 min samples for pesticide analysis.

Flow stage measurements were made at the same locations as the water samples were taken. Two stage recorders were installed in the distribution tank and one in each of the outflow tanks. Measurements were made using Maurey Model M1326-12 linear potentiometers with a 30.5 cm usable stroke length. Each potentiometer was outfitted with a 7.6 cm thick × 20.3 cm diameter float. With no water in each tank, the float rested on a crossbar in its enclosure at near the maximum stroke. PVC irrigation pipes (25.4 cm diameter) with HDPE (high-density polyethylene) plastic bucket covers provided watertight enclosures for the potentiometers. These enclosures were rigidly mounted to each tank, ensuring no movement of the potentiometer that could affect depth readings. All eight potentiometer outputs were connected to a Campbell Scientific CR-10 datalogger through a Campbell AM416 relay multiplexer, which allowed for all eight values to be recorded almost simultaneously. Each potentiometer was calibrated individually, and a very high correlation between calibrations allowed for a single calibration value to be used for all potentiometers.

To accurately measure rainfall before and during each rainfall event, a Davis Instruments tipping bucket rain gauge was installed in 1997. Within the data storage time limit of the datalogger, the stage and rainfall data were downloaded to a laptop PC within 16 h of an event using Campbell Scientific PC208 data collection software through an RS-232 serial port.

SAMPLE PROCESSING AND ANALYSIS

Total solid concentrations were measured using a gravimetric oven-drying method (Standard Methods, 2540B). Duplicate 20 mL aliquots of a well-mixed sample were weighed and oven dried at 105°C for 24 h. Concentrations were redetermined if the duplicate values varied by more than 5%.

For pesticide analyses, a subsample of approximately 200 g was taken from each well-mixed sample, placed in a 250 mL round flat-bottom flask, and extracted with a weighed (~20 g) 23 mL volume of toluene on an orbital shaker for 1 h at 250 rpm. This extracted the pesticides in the total (sediment plus water) sample. Excluding the subsurface drainage samples, which had little or no sediment in them, analyses of sediment for pesticides in every other sample for each event (e.g., 1, 3, 5...) were performed to calculate concentrations in the water and sediment phases for each pesticide for all the samples. After removal of the subsamples for total pesticide extraction, the remainders of the samples in which sediment was to be analyzed were allowed to settle in the cooler (4°C) for several days. Much of the clear liquid was decanted into a clean beaker, and the bottom 100 mL of liquid was used to stir and transfer sediment to a Teflon centrifuge bottle. Additional clear liquid was used to wash and transfer the remaining sediment to the centrifuge bottle. This subsample was centrifuged at 3300 rpm for 20 min using an IEC M84 centrifuge. The water fraction was discarded, and the "wet" sediment fraction was weighed and then extracted with a weighed (~5 g) 6 mL volume of toluene on an orbital shaker for 1 h at 250 rpm; six 1.5 mm diameter glass beads were added to enhance mixing through loosening of the sediment from the bottle bottom and sidewalls. The amount of sediment extracted (and the amount of water in the wet

sediment) was determined by oven drying the extracted sample at 105°C for 24 h. The ratio of pesticide concentration in sediment to that in water was used to calculate concentrations in sediment and water for samples 2, 4, 6..., for which only a total concentration value was obtained.

The toluene extracts were analyzed for pesticides using a Tracor 540 gas chromatograph (GC) equipped with a Ni-63 ECD detector and a Tracor 774 autosampler. The GC conditions were: J&W DB-5 capillary column (30 m length × 0.25 mm i.d. × 20 µm film thickness) with the inlet temperature at 250°C and the detector temperature at 350°C; hydrogen at 4 mL min⁻¹ as the carrier gas and argon, containing 5% methane, at 30 mL min⁻¹ as the make-up detector gas; split and septum purge hydrogen gas flows were 30 and 10 mL min⁻¹, respectively. The GC was operated in the splitless mode using 1 µL injections. The column temperature was 75°C for 0.75 min following injection, ramped at 40°C min⁻¹ to 185°C, and maintained for 8 min at this temperature. The split vent was opened at 0.70 min after injection.

Calibration of the GC-ECD was with nine standards spanning the concentration range from 30 to 13000 ng mL⁻¹ for the herbicides (acetochlor and atrazine) and from 7 ng mL⁻¹ to 3000 ng mL⁻¹ for the insecticide chlorpyrifos. The retention times were approximately 6.25 min for atrazine, 8.25 min for acetochlor, and 10.1 min for chlorpyrifos. Duplicate injections were performed on each calibration standard and sample extract. The detection limits were 20 µg L⁻¹ for atrazine, 3 µg L⁻¹ for acetochlor, and 0.1 µg L⁻¹ for chlorpyrifos. Microsoft Excel was used for data processing by entering peak area data from the integrator into the spreadsheet. Calibration curves of peak area versus concentration were prepared for each of the pesticides each time a set of standards and extracts was analyzed. Trend lines were fitted to the calibration data and used to calculate the concentrations of atrazine, acetochlor, and chlorpyrifos in the water and sediment fractions of the original samples. The concentrations of the pesticides in the water or sediment fraction were calculated by dividing the pesticide concentration in the toluene extract by the ratio of the water (or sediment) weight to the toluene weight used in the extraction.

PESTICIDE CONCENTRATION CALCULATIONS

Using the sample concentration of each pesticide in the water and sediment phases, an adsorption coefficient was calculated. The coefficient (K_d) represents the ratio of the concentration of pesticide in the sediment phase to the concentration in the water phase. Using the K_d value and the total concentration of each sample, the concentrations in each phase were calculated using the following equations:

$$K_d = C_s / C_w \quad (1)$$

$$C_T X_T = C_w X_w + C_s X_s \quad (2)$$

where

- K_d = soil/water partitioning coefficient
- C_s = pesticide concentration in sediment (µg L⁻¹)
- C_w = pesticide concentration in water (µg L⁻¹)
- C_T = pesticide concentration total (µg L⁻¹)
- X_T = total mass fraction of water and sediment (µg)

X_w = mass fraction of water (µg)

X_s = mass fraction of sediment (µg).

The sediment concentrations in the samples were low enough to not significantly change the total unit mass of the samples from that of pure water. This allowed X_T to equal X_w and the second equation to be simplified to:

$$C_T = C_w + C_s X_s \quad (3)$$

Substituting one equation into the other allowed solving for both the concentration in the water and in the sediment phase.

RESULTS AND DISCUSSION

HYDROLOGY

Table 2 summarizes the rainfall events causing runoff in the 1999 crop season. The complete profile of event E3 on 9 June 1999 will be discussed in detail. Event E3 had the largest cumulative rainfall and moderate rainfall intensity, accumulating 29.4 mm of rainfall in approximately 110 min. This long duration allowed for saturation of the soil surface in the source area, causing the highest flow rate and yielding the largest total volume of runoff.

Figures 3 and 4 show hydrographs of average inflow and outflow rates during event E3 for the 15:1 and 45:1 area-ratio plots, respectively. The shaded box plotted on the outflow hydrograph represents the volume of the outflow tank to the bottom of the V-notch weir (0.28 m³), which was included as VFS outflow. The volume stored in the distribution tank was not considered in total runoff volume calculations, as runoff remaining in the tank did not move through the VFS.

Table 3 lists the details of infiltration and runoff for each of the plots used in calculating the overall water budget. Volumes for rainfall and runoff were converted to equivalent

Table 2. Runoff events for the 1999 crop season.

Event	Date	Cumulative Rainfall (mm)	Days after Application
E1	21 May 1999	15.5	2
E2	4 June 1999	12.4	16
E3	9 June 1999	29.4	21
E4	10 June 1999	10.9	22
E5	23 June 1999	21.3	35

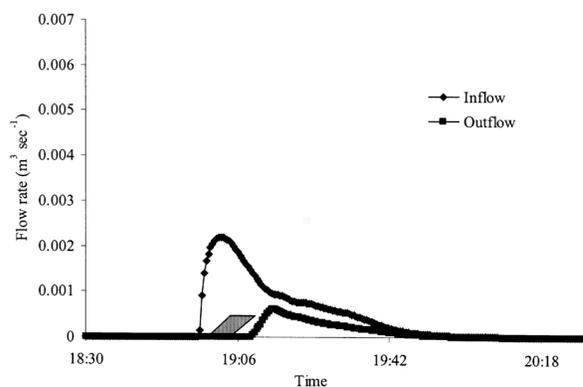


Figure 3. Hydrographs of average inflow and outflow of 15:1 area-ratio plots for event E3. The shaded box represents the volume of the outflow tank to the bottom of the V-notch weir.

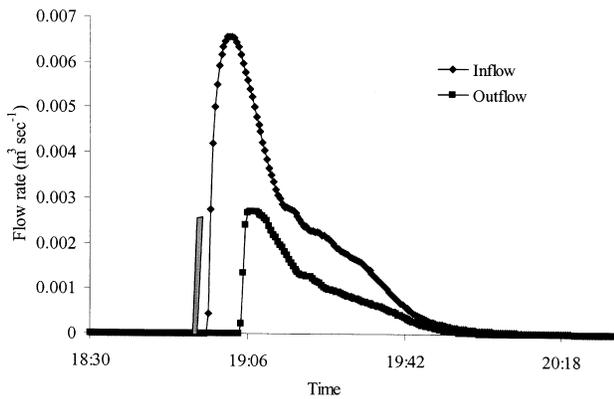


Figure 4. Hydrographs of average inflow and outflow of 45:1 area-ratio plots for event E3. The shaded box represents the volume of the outflow tank to the bottom of the V-notch weir.

depth in millimeters across one VFS plot. The inflow value was the sum of all time-integrated flow rates as the runoff passed through the distribution tank. This value varied slightly from the 45:1 to the 15:1 plots and as compared to the recorded rainfall totals in table 2. The reason was to incorporate rainfall that fell onto the metal channels that directed runoff from the distribution tank to the VFS; rainfall collected in these channels passed through the VFS. In addition, the depth of rainfall collected by the surface area of the outflow tanks was added. Therefore, the sum of the rainfall depth and inflow values became the total inflow value. The outflow value was only the runoff that passed out of the outflow tank weir. This value was added to the outflow tank volume, which resulted in the total outflow value. Table 3 shows that inflow for the 45:1 plots was three times higher than for the 15:1 plots; adding in rainfall, the ratio drops to 2.5. For outflow, this ratio was over 3.5 because approximately 10% more of the runoff plus rainfall in the VFS infiltrated in the 15:1 plots. The percentage of average infiltration amount was higher for the 15:1 plots than for the 45:1 plots; however, it was not significantly ($\alpha = 0.05$) different.

Table 4 gives the water budget summaries averaged over infiltrations for the 1999 runoff events. For the results in table 4, infiltration was calculated under two different assumptions: first, that all rainfall that fell on the VFS can be considered inflow, making the total inflow the sum of runoff inflow and rainfall, as discussed above; and second, only the runoff inflow was used as total inflow. While the former

Table 3. Infiltration^[a] and flow volumes for individual plots for event E3.

Strip	Area Ratio	Inflow (mm)	Inflow+Rain (mm) ^[b]	Outflow (mm)	Infiltration (%)
1	15:1	91.0	122.7	32.8	73.3
4	15:1	91.0	122.7	22.2	81.9
6	15:1	91.0	122.7	37.0	69.8
Average		91.0	122.7	30.6	75.0 a ^[c]
2	45:1	273.0	304.7	133.9	56.1
3	45:1	273.0	304.7	83.2	72.7
5	45:1	273.0	304.7	No data	No data
Average		273.0	304.7	108.3	64.5 a

^[a] Infiltration was calculated as the percentage of inflow plus rainfall that was not measured in the outflow tanks and therefore remained in the VFS.

^[b] Includes rain on the metal channels and outflow tanks (equaled to 2.3 mm).

^[c] Means followed by the same letter are not significantly different at $\alpha = 0.05$; t-test H_0 : mean(15:1) = mean(45:1).

assumption is considered a more realistic indicator of the actual water budget of a plot, the latter assumption shows the significance of rainfall volume in the total budget. Infiltration values were reduced due to the reduced total inflow when not considering rainfall. This reduction was very prevalent in events E1 and E4, where runoff values were small, magnifying the effect that rainfall had on the total water budget. In event E1, the depth of rainfall exceeded the depth of runoff in the VFS and reduced infiltration by nearly 15% when rainfall was not considered as inflow.

Statistical analysis of infiltration percentages showed that only event E2 had significantly different % infiltration between area ratios (table 4). The small volume and short duration of event E2 prevented any of the 15:1 plots from having outflow. At lower flow rates and durations, the 15:1 plots were much more effective at allowing runoff to infiltrate. As runoff volumes and durations increased, the difference in % infiltration between the area ratios decreased. This could be expected if the infiltration rates (cm h^{-1}) were similar for all plots. With successive events, the difference between the area-ratio plots became smaller to the point where events E4 and E5 had infiltration rates that were the opposite of what would be expected. Statistical analysis could not be performed on the last two events because only one sampler had a complete set of samples for one of the treatments. Overall, the 1999 data established an excellent set of similar events for evaluating pesticide transport through VFS.

Table 4. Average water budget summaries for 1999 runoff events.

	E1		E2		E3		E4		E5	
	45:1	15:1	45:1	15:1	45:1	15:1	45:1	15:1	45:1	15:1
Area ratio	45:1	15:1	45:1	15:1	45:1	15:1	45:1	15:1	45:1	15:1
Inflow (mm)	41.2	13.7	121.9	40.6	273.3	91.0	57.1	19.0	190.6	63.5
Outflow (mm)	13.5	0.2	34.1	0.0	99.1	21.4	5.7	2.3	81.6	30.4
Outflow tank volume (mm)	9.2	3.1	9.2	0.0	9.2	9.2	9.2	9.2	9.2	9.2
Rainfall depth (mm)	16.7	16.7	13.4	13.4	31.7	31.7	11.8	11.8	23.0	23.0
Total in (mm)	57.9	30.4	135.3	54.0	305.0	122.7	68.9	30.8	213.6	86.5
Total out (mm)	22.7	3.3	43.4	0.0	108.3	30.6	14.9	11.5	90.9	39.6
Infiltration										
% with rainfall	60.8 a ^[a]	89.2 a	67.9 a	100.0 b	64.5 a	75.0 a	78.3 ^[b]	62.5 ^[b]	57.5 ^[b]	54.2 ^[b]
% runoff only	44.9 a	76.2 a	64.4 a	100.0 b	60.4 a	66.3 a	73.8 ^[b]	39.3 ^[b]	52.3 ^[b]	37.6 ^[b]

^[a] Means followed by the same letter are not significantly different at $\alpha = 0.05$.

^[b] A t-test was not run due to lack of sufficient replications to produce reliable mean.

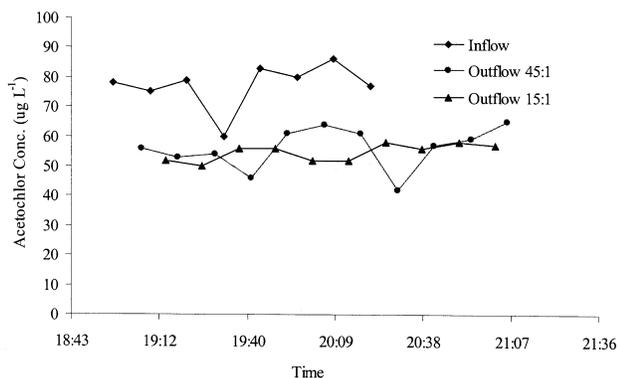


Figure 5. Average acetochlor runoff concentrations in the water phase for event E3.

PESTICIDE CONCENTRATIONS

Figure 5 shows the average concentrations of acetochlor in the water phase of inflow and outflow for event E3. For this event, as with all events, concentrations of all pesticides in the water phase were higher in the inflow than in the outflow. Concentrations in the outflow for 45:1 plots were slightly higher than those for the 15:1 plots. The total volume of inflow passing through the 45:1 plots was three times higher than in the 15:1 plots; therefore, equal volumes of rainfall on each of the plots would have a greater dilution effect on the 15:1 plots, resulting in lower concentrations in outflow from these plots.

The rainfall timing and volume directly affected the runoff dilution process. Events in which rainfall continued throughout the duration of the runoff were affected to a larger extent than those in which rainfall had essentially stopped by the time runoff began. During event E2 (data not shown), rainfall causing runoff occurred very quickly and had for the most part subsided by the time runoff started. Because of this, the inflow concentrations in the water phase of each pesticide were not noticeably different than the outflow concentrations in either the 45:1 or 15:1 plots. However, inflow concentrations of atrazine varied from 170 to 190 $\mu\text{g L}^{-1}$, and outflow concentrations were in the 160 to 185 $\mu\text{g L}^{-1}$ range.

While dilution affected the pesticide concentrations in the water phase, it had no observable effect on pesticide concentrations in the sediment phase. Figure 6 shows the concentrations of acetochlor in the sediment phase for event E3. As the runoff passed through the VFS, runoff velocity was reduced, allowing sediment deposition, with larger and/or more dense sediment particles to be preferentially deposited in the VFS. This would cause a reduction in the mean particle diameter of sediment in the outflow. The smaller particles have a greater specific area for pesticide adsorption and generally higher organic matter content than larger particles. Therefore, the concentrations of pesticides in these smaller particles were higher, and when the larger particles were removed, the overall pesticide concentrations in sediment increased. However, in the case of event E3, the 45:1 plots had a slightly higher mean concentration than the 15:1 plots. It would be expected that with a larger decrease in runoff velocity and a larger percentage sediment deposition in the 15:1 plots, pesticide concentrations in the sediment would be higher in the 15:1 plots. While the expected trend was not evident in event E3, it was generally the case in the other events (data not shown) for all pesticides. Enrichment within

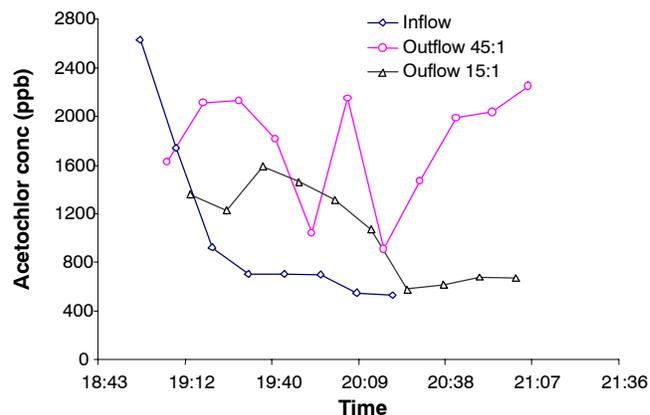


Figure 6. Average acetochlor runoff concentrations in the sediment phase for event E3.

Table 5. Average inflow K_d values for 1999 runoff events.

Event	Atrazine	Acetochlor	Chlorpyrifos
E1	10.3	11.5	1620
E2	23.6	22.6	3780
E3	54.3	15.7	986
E4	28.5	24.3	1560
E5 ^[a]	50.0	131.0	1200

[a] E5 atrazine and chlorpyrifos values estimated; some samples were below the detection level.

the sediment phase is a commonly seen process, resulting in an overall mass reduction of pesticides being transported within the sediment, being less than the reduction in sediment transport. The level to which this happens can be determined by the affinity of each pesticide to adhere to finer/less dense sediment particles.

PESTICIDE PARTITIONING

The extent to which each pesticide will move with a given phase (sediment and water) can be indicated by the K_d value. The K_d value is defined as the partitioning coefficient between phases for a chemical. For each sample, a K_d value was calculated using the total concentration and the concentration in the sediment phase. Table 5 summarizes the average K_d value for each of the pesticides in field runoff for each event. The effect of the sediment enrichment has no effect on the concentration of pesticides in the water phase, as the pesticide is believed to already be at near equilibrium in its distribution between sediment and water, but the K_d will change due to the increased pesticide concentration in the sediment. The K_d increased notably between events E1 and E2. Event E1 was only two days after pesticide application. The 14 days that elapsed between the first two runoff events could have allowed for increased adsorption of pesticide to soil/sediment, attributed to the ability of a pesticide to bind stronger adsorption sites with time.

The K_d values categorize each pesticide by its adsorption affinity. Atrazine and acetochlor are considered moderately adsorbed pesticides, while chlorpyrifos is highly adsorbed. These adsorption values indicate that with chlorpyrifos, sediment transport would figure significantly into pesticide mass movement.

Figure 7 shows moderately adsorbed acetochlor mass movement with sediment and water phases for inflow and outflow for the 45:1 plots of event E3. This figure shows that

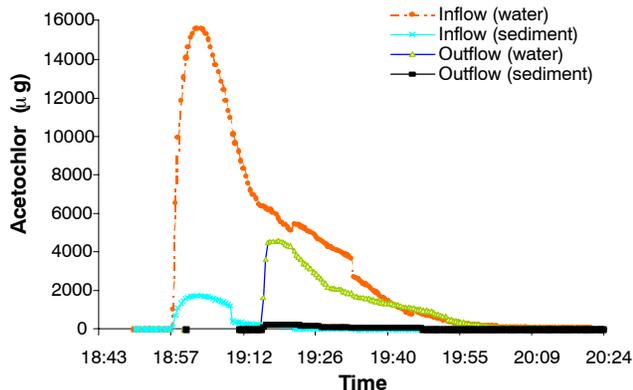


Figure 7. Acetochlor mass in inflow and outflow in water and sediment phases (45:1 area ratio) for event E3.

very little of the total acetochlor mass was transported with the sediment. The reduction in sediment concentration and infiltration resulted in a reduction in pesticide mass within each phase, with the majority still associated with the water phase. The trend of atrazine mass movement with sediment and water was similar to acetochlor movement because of the similarities in partitioning properties of these two pesticides.

Moderately adsorbed acetochlor was compared with highly adsorbed chlorpyrifos, as shown in figure 8. The partitioning of chlorpyrifos more evenly distributes the pesticide mass between the sediment and water phases, with the greater fraction contained in the sediment. After passing through the VFS, sediment deposition and runoff water infiltration reduced the total mass flow to almost equal between the two phases. In this example, sediment deposition had a greater effect on mass outflow than did infiltration. These trends were also found in the other runoff events. The K_d for acetochlor was similar to that of atrazine, and acetochlor transport mimicked that of atrazine. These trends indicate that pesticide in the water phase was the primary transport mechanism for atrazine and acetochlor, and

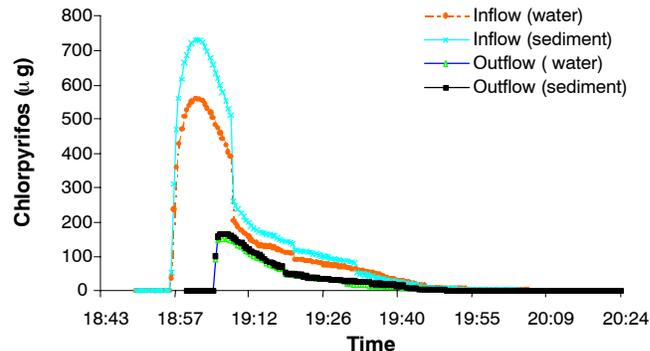


Figure 8. Chlorpyrifos mass in inflow and outflow in water and sediment phases (45:1 area ratio) for event E3.

chlorpyrifos was transported almost equally between the water and sediment phases.

PESTICIDE MASS REDUCTION

The total mass of each pesticide entering and exiting the VFS was determined for each event. Table 6 summarizes all total masses for each sampler for event E3. There were noticeable differences in retention percentage between the replications of each treatment. Even though the inflow was the same, the outflow volumes varied greatly, resulting in the variations in total mass outflow of each pesticide.

For both area ratios, the percentage of pesticide removed from the sediment phase was greater than from the water phase (table 6). However, a considerably greater mass of atrazine and acetochlor was removed from the water phase than from the sediment phase. Only in the case of chlorpyrifos was a greater total mass removed from the sediment phase.

For event E2, the absence of outflow on the 15:1 plots created a statistically significant difference between the treatments for all pesticides except acetochlor in the water phase. In events E1 and E3, the mass removal of acetochlor

Table 6. Total mass summaries for event E3.

	Atrazine		Acetochlor		Chlorpyrifos		
	Total Mass Sediment (mg)	Total Mass in Water (µg)	Total Mass in Sediment (µg)	Total Mass in Water (µg)	Total Mass in Sediment (µg)	Total Mass in Water (µg)	Total Mass in Sediment (µg)
45:1 area ratio							
S7 45:1	19230704	594748	57425	638788	45357	16967	24186
S8 45:1	19770469	552624	51533	650645	40965	17517	22174
S2 45:1	5621897	308292	2782	217867	13222	5223	5481
S3 45:1	3124915	146515	8102	118295	3607	4304	4703
Inflow avg.	19500587	573686	54479	644717	43161	17242	23180
Outflow avg.	4373406	227404	5442	168081	8414	4763	5092
Avg. % reduction	77.6 a ^[a]	60.4 a	90.0 a	73.9 a	80.5 a	72.4 a	78.0 a
15:1 area ratio							
S7 15:1	6404511	198072	19124	212739	15106	5651	8055
S8 15:1	6584272	184043	17162	216688	13643	5834	7385
S1 15:1	524184	42111	5056	40093	503	900	252
S4 15:1	320694	21227	1215	17003	293	699	256
S6 15:1	856864	52578	4221	47945	1813	1272	872
Inflow avg.	6494392	191058	18144	214714	14374	5742	7720
Outflow avg.	567247	38639	3497	35014	869	957	460
Avg. % reduction	91.3 a	79.8 a	80.7 a	83.7 a	94.0 a	83.3 a	94.0 b

^[a] Means followed by the same letters are not significantly different at $\alpha = 0.05$; t-test H_0 : $\text{mean}(15:1) = \text{mean}(45:1)$. Statistical comparison made in each vertical column.

Table 7. Mean dissolved solid concentrations for the 1999 events.

Runoff Event	Event Date	Mean Dissolved Solids Concentration (mg kg ⁻¹)	
		Surface Flow	Tile Line Flow
E1	21 May 1999	350	390
E2	4 June 1999	230	390
E3	9 June 1999	160	390
E4	10 June 1999	150	390
E5	23 June 1999	125	390

and chlorpyrifos in the sediment phase was statistically different at $\alpha = 0.05$. Overall, these statistical results show that the effect of the area ratio was most prevalent in pesticide transport within the sediment phase.

For events E4 and E5, hydrology affected the pesticide removal percentages of the area-ratio plots. Event E4 was a fairly low-volume and low-intensity event. The removal percentages were very high for all constituents, but there was not a perceptible difference in removal percentages between the treatments. Event E5 was of higher intensity and duration. Due to the longer event E5, the removal percentages were lower than in event E4, but the difference in removal percentages between treatments was again not noticeable. A t-test could not be performed because of limited replications of reliable data for these two events.

SEDIMENT TRANSPORT AND REMOVAL

The dissolved solids samples showed a distinct trend of concentration that decreased through the season. Table 7 shows the mean dissolved solids concentrations for the sample from each event. Due to the distinct differences in concentrations for each event, the corresponding dissolved solids concentration was subtracted from the total solids concentration to represent the concentration of pesticide-carrying sediment. Sediment concentrations were highest at the beginning to the midpoint of each event, corresponding with the times of highest flow velocities. Figure 9 shows sediment concentrations with respect to time for event E3.

In the tile line samples, sediment concentrations were found to be almost all dissolved solids. Statistical analysis of sediment reduction in each event only showed difference between the two treatments at $\alpha = 0.05$ in event E2, due to the very low volume and flow velocity of runoff. Dissolved sediment concentrations in the tile line did not change significantly throughout the season; the value 390 mg kg⁻¹ was used for calculations for all events. The high sediment concentration for the first tile line sample was most likely due to sediment deposited in the tile line from prior events and from initial macropore flow of runoff to the tile line at the beginning of each event. After the first sample, sediment in the tile line samples was imperceptible to the naked eye, and sediment concentrations in those samples did not exceed 150 mg kg⁻¹.

Sediment reduction played a large part of pesticide removal, as the majority of pesticide mass reductions that were statistically different between treatments were in the sediment phase. Sediment may have also been a factor in the reduced infiltration capacity of the VFS plots throughout the crop season. Deposition of sediments in the plots may have filled possible macropores and reduced the soil permeability at the soil surface.

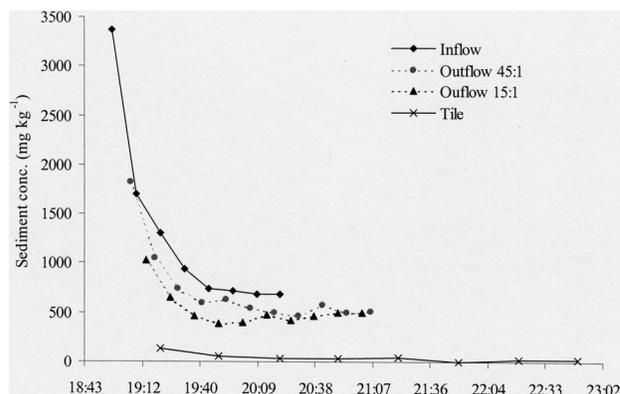


Figure 9. Sediment concentrations for event E3.

TILE LINE PESTICIDE MOVEMENT

Tile line samples were taken for all events except event E4, when sampler malfunction resulted in no sample collection. Partitioning between sediment and water phases could not be determined due to the very low sediment concentrations. Figure 10 shows the maximum acetochlor concentration of the surface inflow and the maximum concentration found in the tile samples for each event. Atrazine concentrations dropped below the detection limit of the gas chromatograph after a number of events. Chlorpyrifos was below the detect limit for every tile sample collected (data not shown). This could be attributed to its high adsorption to soil sediment, as discussed earlier. Acetochlor, having similar transport characteristics to atrazine, could be used to describe the movement of both herbicides. The reporting of acetochlor data was selected because of a lower detection limit using gas chromatography, giving a larger set of reliable data to draw conclusions.

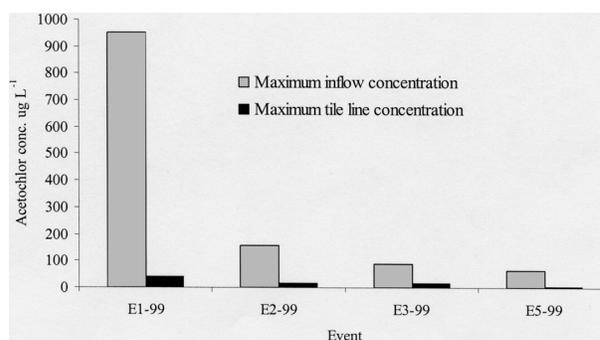


Figure 10. Maximum acetochlor concentrations in surface inflow and tile samples for various rainfall events.

CONCLUSIONS

Overall results of the study showed that many factors affect the pesticide transport, such as rainfall timing and intensity, hydrology, area ratios, and the types of pesticides in VFS inflow. The following key conclusions were drawn from the study:

- Two primary mechanisms, infiltration and adsorption of pesticide to sediment, had a very large effect on pesticide fate with passage through VFS. Sediment retention rate also played an important role in pesticide reduction in outflow and decreased with increased flow volume and velocity.

- The 45:1 plots increased the volume of outflow in all cases. For the latter events, the percentage of runoff volume retained was not significantly less than that of the 15:1 plots.
- Sediment reduction was considerably higher in the 15:1 plots than in the 45:1 plots, and this in turn aided in the reduction of transport of pesticides adsorbed to sediment.
- Atrazine and acetochlor fate were primarily controlled by infiltration efficiency of VFS, as the major portion of these pesticides moved within the water phase. Chlorpyrifos was highly adsorbed to the sediment, making sediment reduction through the VFS equally, if not more, important than infiltration for mass removal.
- Data collected from the tile line showed that there were measurable concentrations for the moderately adsorbed herbicides (acetochlor) in the tile flow at the time surface runoff was taking place. Subsurface movement only appeared to be a concern for this herbicide, as the highly adsorbed pesticide (chlorpyrifos) was below a measurable detection level due to the near absence of sediment in the tile flow.
- A statistical difference was noted between the two area-ratio treatments for at least one constituent of each of the three events. The statistical difference was most prominent in the event with the smallest runoff volume. This showed that at lower flow rates, VFS can effectively reduce runoff, sediment, and pesticide transport from cropland. As flow rate and total volume increase, VFS can easily become saturated and result in a significant drop in removal efficiency.

Past research at this study site failed to show a consistent significant difference between 15:1 and 30:1 area-ratio plots (Arora et al., 1996). The difference shown in VFS plots in this research between 15:1 and 45:1 area ratios indicates that somewhere between the area ratios of 30:1 and 45:1 would be the maximum area ratio that could be used in the area without losing VFS effectiveness at this location.

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