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USING INFILTRATION ENHANCEMENT AND SOIL WATER MANAGEMENT TO REDUCE DIAZINON IN RUNOFF[1]

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ABSTRACT: Pesticide runoff from dormant sprayed orchards is a major water quality problem in California's Central Valley. During the past several years, diazinon levels in the Sacramento and San Joaquin Rivers have exceeded water quality criteria for aquatic organisms. Orchard water management, via post-application irrigation, and infiltration enhancement, through the use of a vegetative ground cover, are management practices that are believed to reduce pesticide loading to surface waters. Field experiments were conducted in Davis, California, to measure the effectiveness of these management practices in reducing the toxicity of storm water runoff. Treatments using a vegetative ground cover significantly reduced peak concentrations and cumulative pesticide mass in runoff for first flush experiments compared with bare soil treatments. Post-application irrigation was found to be an effective means of reducing peak concentrations and cumulative mass in runoff from bare soil treatments, but showed no significant effect on vegetated treatments.
(KEY TERMS: nonpoint source pollution; aquatic toxicology; infiltration and soil moisture; storm water management; alternative farming practices; pesticides.)

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INTRODUCTION

Organophosphate pesticides in surface water are a major concern in the Sacramento and San Joaquin River Basins. These pesticides have been implicated in the mortality of important aquatic indicator species (*Ceriodaphnia dubia*) following winter rains in several valley rivers (Kuivila and Foe, 1995; Foe *et al.,* 1998). One of the major organophosphate pesticides used on farms in California's central valley is diazinon. Diazinon is classified as a 'restricted use pesticide' for use by professional pest control operators only. In 1988, the U.S. Environmental Protection Agency (USEPA) canceled registration of diazinon for use on golf courses and sod farms because of die-offs of birds that often congregated in these areas (Extension Toxicology Network, 1996). More recently the USEPA terminated the indoor use of diazinon and began the phase out of outdoor residential and garden uses (USEPA, 2001). The California Department of Fish and Game established the freshwater Final Acute Value and Final Chronic Value at 0.16 mg/l and 0.05 mg/l, respectively for diazinon (Siepmann and Finlayson, 2000). During the past several years, diazinon levels in the Sacramento and San Joaquin Rivers have exceeded these water quality criteria for aquatic organisms (Domagalski and Kuivila, 1993; Kuivila, 1993; Domagalski and Kratzer, 1995; Domagalski *et al.,* 1997; Kratzer, 1999; Schueler, 1999). These findings, coupled with observed declines in many populations of fish and invertebrates in the region (Herbold *et al.,* 1992), have raised concerns about potential impacts of diazinon on aquatic ecosystems in California's central valley.

One of the main sources of diazinon during the winter is dormant spray applications to almond trees and other stone fruit orchards. Total orchard

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applications accounted for approximately 30 to 50 percent of the 0.46 x 10^6 kg of diazinon used in California each year during 1995 to 1999 (University of California, 2003). Dormant sprays are applied between November and January, avoiding spraying close to bloom time due to toxicity to honey bees. Unfortunately, the dormant season coincides with the rainy season in California, allowing the diazinon to sometimes wash off trees and potentially find its way into surface waters. Pesticide monitoring by the Central Valley Regional Water Quality Control Board and the U.S. Geological Survey have found that peak diazinon concentrations in the Sacramento and San Joaquin Rivers occur around the time of greatest precipitation in the months of January and February (Foe, 1995; MacCoy *et al.,* 1995).

It has been shown that conservation tillage can greatly reduce pesticide losses caused by runoff (Wauchope, 1978; Leonard, 1990). Conservation tillage consists of a number of production systems that reduce soil disturbance, including cover cropping, no-till, ridge-till, and strip-till planting systems. These practices can lead to the development of extensive macropore systems, which are capable of rapidly transmitting water through soil (Shipitalo *et al.,* 1990). The improved infiltration increases the runoff lag time, which has been shown to be negatively correlated with pesticide concentrations in runoff (Baker *et al.,* 1982). However, the reduction in pesticide runoff due to improved infiltration could be offset by other mechanisms controlling pesticide transport introduced with conservation tillage. For example, the introduction of pesticides by wash-off from ground cover foliage may have profound impacts on pesticide concentrations in runoff. Depending upon the rate at which the pesticide is released from the plant surface, pesticide concentrations in runoff may not differ from those observed on bare soil treatments, while the total mass of pesticide in runoff may differ due to differences in cumulative runoff volume. Thus, aquatic organisms near field outlets could experience similar toxic effects under conservation and conventional tillage practices, while organisms farther from the point of discharge that experience the effects of blending runoff from several contributing fields may experience significantly different toxic effects under the different management practices.

The problem of pesticides entering surface waters in runoff from orchards could be reduced or eliminated by encouraging rainfall to quickly enter the soil. The use of a vegetative ground cover is one management practice that has been shown to enhance rainfall infiltration (Williams, 1966; McVay *et al.,* 1989; Meek *et al.,* 1990; Martens and Frankenburger, 1992; Gulick *et al.,* 1994; Kiesling *et al.,* 1994; Joyce *et al.,* 2002). Irrigating the orchard after pesticides are applied may be another means of transferring pesticides from the soil surface into the soil matrix.

Controlled field experiments were conducted to quantify the effects of ground treatment and soil water management practices on runoff rates (Angermann *et al.,* 2002) and diazinon concentrations in runoff. The purpose of these experiments was to measure the effectiveness of these practices in reducing diazinon concentrations in storm water runoff. Angermann *et al.* (2002) previously reported the results of the hydrologic response patterns of these experiments. The focus of this study is an analysis of the pesticide concentration data collected during these experiments.

MATERIALS AND METHODS

Site Description

Fieldwork was conducted from June to September 2000 in an apricot orchard on the property of the University of California-Davis. The orchard soil was classified as Yolo silt loam (fine-silty, mixed, nonacid, thermic Mollic Xerofluvents) and consisted of approximately 28 percent sand, 47 percent silt, and 25 percent clay from 0 to 0.2 m depth (Table 1). Soil between the tree rows was heavily compacted from repeated operation of farm equipment and had not been tilled in at least five years prior to the study. Prior to the installation of a sprinkler system in the summer of 2000, the orchard was flood irrigated and drained onto an open field. The orchard was surrounded by the nearly flat topography of the Central Valley, and its mean slope was 0.0028 m/m.

Experimental Design

Two ground treatments were investigated: resident vegetation (RV) and bare soil (BS). Resident vegetation was a mixture of annual grasses. Plots were selected where foliage was uniformly dense. The bare soil treatment had no ground vegetation and plots were selected where large areas lacking ground cover occurred within the orchard.

Two types of simulated rainfall/runoff experiments were conducted to investigate the effects of soil and water management practices on pesticide runoff.

1. First and second flush experiments consisted of an initial artificial rainfall (12 hours after pesticide application) followed by a subsequent rainfall (24 hours later). Rainfall applications were terminated

TABLE 1. Grain Size Distribution of Yolo Silt Loam.*

Depth From Surface (cm)	Size Class and Diameter of Particles (mm)							
			Sand					
	Clay < 0.0005	Silt 0.0005 to 0.05	Very Fine 0.05 to 0.1	Fine 0.1 to 0.25	Medium 0.25 to 0.5	Coarse 0.5 to 1.0	Very Coarse 1.0 to 2.0	Gravel > 2.0
0 to 5	24.9	46.4	22.5	5.1	0.7	0.4	0	0
5 to 20	27.1	46.8	14.5	11.3	0.2	0.1	0	0

*Grain size distributions as percentages of total dry weight. Data taken from Andrews (1972).

when peak water discharge was sustained for 10 to 15 minutes.

2. Soak and rinse experiments refer to an initial artificial rainfall (12 hours after pesticide application), which was terminated upon incipient ponding, followed by a subsequent rainfall application (24 hours later) resulting in runoff sustained for 10 to 15 minutes after peak discharge.

The termination of rainfall application after a defined time span of sustained peak water discharge (i.e., 10 minutes of steady runoff) ensured that every response pattern underwent both the full transient stage prior to ponding as well as through the entire rising limb of the hydrograph. For all experiments, the use of a rainfall applicator (shown in Figure 1) provided independence from natural rain events and facilitated consistent replication of experiments in the field. The applicator consisted of two parallel PVC pipe lines 15.5 m length, equipped with 10 brass continuous spray nozzles arranged in a triangular pattern (Angermann *et al.,* 2002).

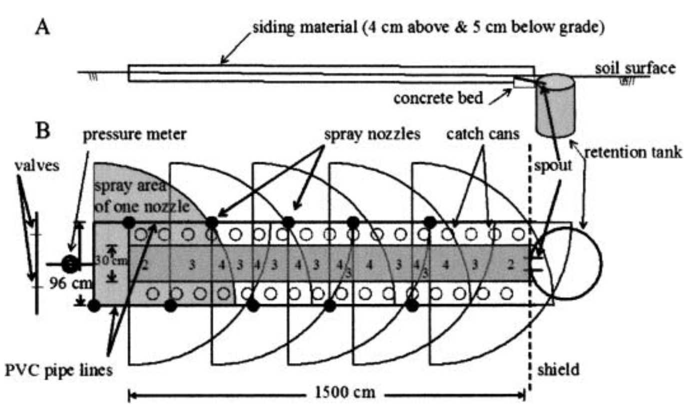

Figure 1. (A) Side View of a Plot Retention Tank System; (B) Schematic of Rainfall Simulator and Its Position in Relation to Runoff Plot and Retention Tank (not to scale). Numbers indicate how many spray areas overlap.

The above experiments were conducted on both initially "dry" (a relative measure) and wetted soil conditions with three replications each. Wetted conditions were established by applying rain for one hour at a rate of 4.3 cm/hr prior to experiments. The entire experiment yielded a total of 48 rain applications (four experiments on two initial soil moisture conditions with two ground treatments, replicated three times) on 24 plots.

Field Measurements

Prior to each experiment soil core samples were taken at a depth of 10 cm using a cylindrical sampler (6.8 cm by 3.5 cm). Bulk density (ρ_b) and soil water content (θ) were measured by weighing samples after collection, drying them in an oven for 24 hours at 105°C, and reweighing the dried samples (Goldhamer and Snyder, 1989). Porosity (φ) was calculated from the bulk density measurements using the relationship $\rho_b = \rho_m - \rho_m \varphi$, where ρ_m is the mineral density and was assumed to be 2.65 g/cm^3. The degree of saturation (S) was calculated using the relationship $S = \theta/\varphi$.

Simulated rainfall was applied to enclosed plots (Figure 1). Water only entered the plots by precipitation and only exited the plots by infiltration and as runoff into 200 liter stainless steel retention tanks, installed at the downstream end of the plots. Plots were 15 m long by 0.3 m wide and were enclosed with metal flowerbed siding material fitted tightly into grooves cut into the ground with a lawn edger. Plots were oriented parallel to the tree rows and at the downstream end of each plot a stainless steel spout was fitted into a bed of concrete so that the risk of sample contamination due to contact between concrete and runoff was minimized. Discharge rates were determined by recording bottle fill times as water exited the plot.

Twelve hours prior to the first rainfall application, Diazinon 4E (Gowan Company, Yuma, Arizona) was spray applied to the enclosed runoff plots at a rate of 2.3 liters of active ingredient per hectare. The pesticide mixture was prepared once prior to the initial rainfall/runoff experiment and kept refrigerated for the duration of all experiments. No adjuvants were included in the mixture. The sprayer consisted of a hand pumped pressurized canister and a hand held spraying unit. The sprayer was pressurized by hand pumping prior to application of diazinon to each runoff plot. The spray nozzle was held 50 cm above the ground surface, such that the spray covered the width of runoff plots. Uniformity of application rates was determined by consistent walking rates (100 cm/sec) along the length of the runoff plot. Two petri dishes were placed within each application area to collect spray samples from which the application rate of pesticide was confirmed. It was assumed that the application rate was equal to the average of the measured concentrations. During each runoff event several water samples (four to eight per runoff event) were collected and analyzed for diazinon concentrations. Cumulative diazinon mass in runoff was calculated by multiplying the total volume of runoff by diazinon concentration in cumulative runoff measured at the end of the experiment.

Chemical Analysis

Diazinon in runoff samples was extracted by Solid Phase Extraction and quantified by gas chromatographic analysis. Extraction columns (Varian, part no. 12102028) packed with C18 sorbent were conditioned using three column volumes (3mL) each of ethyl acetate, methanol, and water. The total volume of runoff sample, 100 ml, then was applied to the column. The column then was washed with three column volumes of distilled deionized water. Finally, 2 by 2 ml of ethyl acetate was passed through the column to elute the diazinon adsorbed on the column matrix. This ethyl acetate solution was brought to a 5 ml volume and used for gas chromatographic analysis.

Aliquots of 1 ml were injected in the gas chromatograph (Hewlett Packard, model 5890 series II Plus). Diazinon was analyzed using a DB-210 column (J&W Scientific; 30 m by 0.53 mm, 1 mm film thickness) and a Nitrogen Phosphorus Detector. A single extraction was performed on each water sample, and each extract was analyzed twice each by gas chromatography. The amount of pesticide present was calculated by comparing measurements against analytical standards purchased from Chem Service: diazinon (99 percent) and parathion (99.5 percent). A set of analytical standards was run on the chromatograph with every set of extraction samples. The analytical standards encompass a range beginning below the limit of detection. The chromatograph response was linear over the range of the standards and the concentration of pesticide in the samples was calculated by interpolation. Percent recoveries were determined by analyzing laboratory water spiked with analytical standards. The range for diazinon was 1, 5, 10, 50, 100, 500, 1,000, and 5,000 mg/l with a constant 100 mg/l parathion in standards and sample extracts. The diazinon spikes showed an 84.8 percent + 10.1 percent recovery (n = 33). The detection limit for diazinon was 0.29 mg/l. This is derived from a 5 mg/l detection limit on the chromatograph, a 20 times concentration during sample preparation and an 85 percent recovery.

Statistical Analysis

Differences in peak pesticide concentrations and cumulative pesticide mass in runoff were determined using SAS (SAS Institute Inc., 1999). An analysis of covariance (ANCOVA) was performed, because true replication did not exist in this study due to variations in soil physical properties and measured precipitation and pesticide application rates. Thus, soil water content, slope, precipitation rate, and pesticide application rate were selected as concomitant variables. The ANCOVA also permitted interaction effects between treatment (RV or BS), flush (first, second, or rinse) and concomitant variables. Interaction effects were accepted when F-tests showed significance ($p \leq 0.05$). Prior to running the ANCOVA, a Box-Cox transformation ($Y' = Y^{\lambda}$) was applied to the dependent variables (Y) to correct for skewness of the distribution of error terms, unequal error variances, and nonlinearity of the regression function. The assumption of normality of residuals was tested using the Shapiro-Wilk test, which can be viewed as being based approximately on the coefficient of correlation between the ordered residuals and their expected values under normality (Neter *et al.,* 1996). Tukey's honest significant difference test was used for comparison of means.

RESULTS AND DISCUSSION

Since the criterion for terminating the experiment was a defined period of sustained peak discharge rather than a specified time interval, a direct comparison of runoff events is less meaningful than if all precipitation events were of equal duration and intensity. Clearly, runoff events conducted with shorter precipitation durations would have continued to have water and pesticide run off the orchard if rainfall had not been terminated. Thus, the measured cumulative runoff and pesticide mass were underestimated for the shorter rainfall events. It follows that a statistical analysis would be invalid if it indicated significantly lower total pesticide load in runoff from experiments with shortened rainfall. However, a comparison of the underestimated values is relevant if their magnitudes are nearly the same or greater than those of the longer events. This would suggest that there are treatment effects that result in enhanced pesticide runoff from experiments with shortened rainfall durations.

Experimental Data

Angermann *et al.* (2002) performed an analysis of variance (ANOVA) and multiple analysis of covariance of the hydrologic response patterns of the runoff experiments. Due to large variance within treatments, these analyses showed no significant difference in lag time between BS and RV. However, their analyses considered wetted and dry soil experiments as separate statistical populations. Considerable overlap in measured degree of soil saturation suggests that these experiments can be pooled for evaluation of treatment effects on hydrologic response. These data were aggregated and an ANOVA of runoff lag time and total event duration was performed to reveal experiments that tended to underestimate cumulative pesticide mass in runoff.

Average runoff lag times are shown in Figure 2. The presence of a vegetative cover increased the infiltration capacity such that average runoff lag time of all RV experiments was longer than on BS. While RV had longer average lag times than BS for first and second flush experiments, ANOVA showed significant ($p < 0.05$) differences between treatments for first flush experiments only. The lack of significant differences between treatments for second flush and rinse experiments supports the finding of Angermann *et al.* (2002) that differences in runoff patterns decrease under elevated soil water conditions.

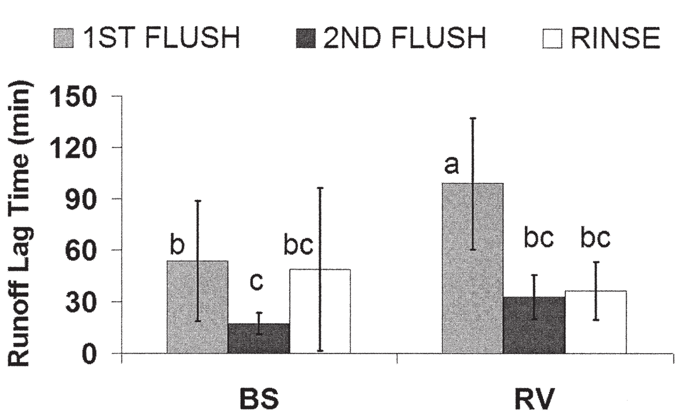

Figure 2. Average Runoff Lag Time. Columns with the same letter are not significantly different ($p < 0.05$).

A comparison of total event duration revealed that statistical significance followed a pattern similar to that seen for runoff lag time, with RV having significantly ($p < 0.05$) longer periods of rainfall/runoff than BS only for the first flush experiments (Figure 3). This suggests that cumulative pesticide mass in runoff was underestimated for first flush BS experiments. Shorter first flush events on BS also suggest that second flush BS experiments may have overestimated total pesticide load. This bias will be considered when interpreting any differences in pesticide runoff between BS and RV second flush experiments. Similarity in total event duration suggests that neither treatment had a tendency to underestimate total pesticide mass in runoff for the rinse experiments.

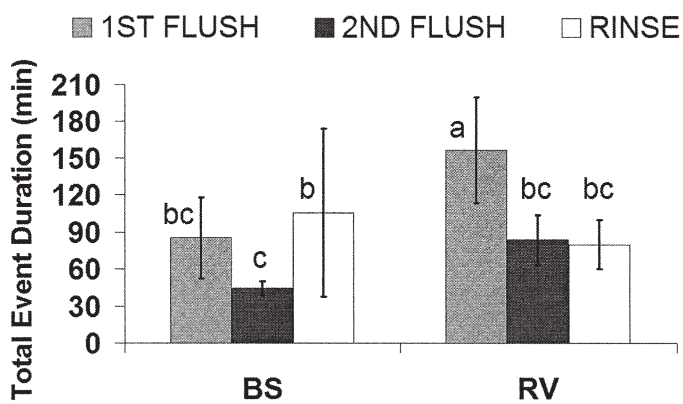

Figure 3. Average Rainfall/Runoff Event Duration. Columns with the same letter are not significantly different ($p < 0.05$).

Regression Analysis

In preparation for regression analysis, peak pesticide concentrations and cumulative pesticide mass data from the wetted and dry soil experiments were pooled. Since the initial soil moisture was expected to have a significant effect on runoff behavior, degree of saturation was considered as a covariate and the combined experiments gave six replications. The maximum likelihood estimate of λ with the Box-Cox transformation was 0.5 for both peak pesticide concentration and total pesticide load. These transformations resulted in Shapiro-Wilk W-statistics above 0.95 for both ANCOVA runs, indicating that residuals were normally distributed, and the regression model was appropriate.

The ANCOVA indicated that degree of saturation was the only concomitant variable that had a significant effect on peak pesticide concentrations and total pesticide load. Slope, precipitation rate, and pesticide application rate showed no effect on either dependent variable. The near zero slope was most likely rejected as a covariate because it was not consistent within the orchard. Variation in the response of pesticide runoff to precipitation rate and diazinon application rate likely resulted in the rejection of these variables as covariates.

Average peak concentrations for the three flushes within each treatment are shown in Figure 4. Highest peak concentrations were expected with first flushes, when the greatest amount of pesticide was available for transport. The peak concentrations of second flush and rinse experiments were expected to be similar, because each had a prior rainfall application that removed some portion of the pesticide initially applied to the enclosed plots. The clearest difference within a single treatment was found with BS, with highest concentrations observed during the first flush and significantly lower ($p \leq 0.05$) peak concentrations during the second flush and rinse. Second flush and rinse BS experiments had similar peak concentrations, despite longer average run times of the initial wetting event on rinse, 56 minutes, than the first flush average run time (31 minutes). Lack of statistical significance is likely due to large variance in the concentrations of the second flush experiment. First flush experiments within RV had significantly higher ($p \leq 0.05$) peak concentrations than second flush experiments. RV rinse experiments had intermediate peak concentrations. Large variance in peak concentrations with the rinse experiment explains the lack of statistical significance between the first flush and rinse in RV.

flush experiments, with BS having higher average peak concentrations than RV. Higher peak concentrations from first flush BS experiments can be partly explained by the shorter lag times noted above. Despite the likely overestimation of diazinon concentrations in runoff from second flush BS experiments, no differences in peak concentrations were observed between treatments for second flushes. This lack of significance between treatments suggests that the increased total infiltration opportunity time (i.e., total run time of the first flush plus runoff lag time of the second flush) on RV may be offset by other mechanisms controlling the transfer of pesticide into runoff (e.g., foliar wash off and diffusive and turbulent transfer of dissolved pesticides from soil pores to the runoff stream). This is the subject of the authors' ongoing modeling research.

Cumulative pesticide mass in runoff is shown for the three flushes within each treatment in Figure 5. The pattern of statistical significance was similar to that shown in Figure 4 for peak pesticide concentrations. First flush experiments on both BS and RV had significantly higher ($p < 0.05$) total pesticide runoff than second flush experiments. The average total difference between flushes was less pronounced for RV than BS. This is partly due to longer runoff lag times observed for RV first flush experiments. Total diazinon runoff from second flush BS was significantly higher than the rinse experiment, which may be explained by the longer initial rainfall application of the rinse experiment noted above.

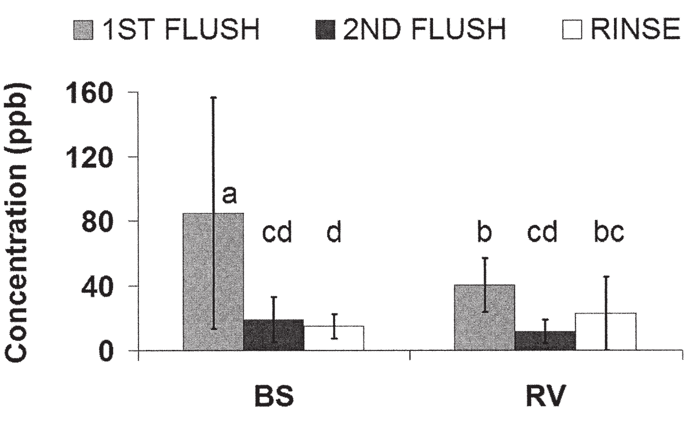

Figure 4. Average Peak Diazinon Concentrations in Runoff. Columns with the same letter are not significantly different ($p < 0.05$).

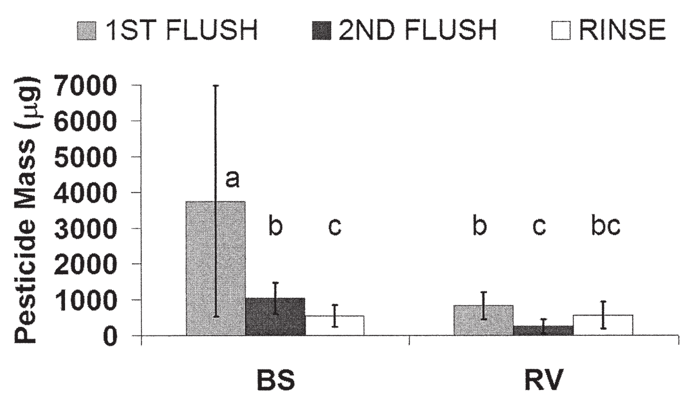

Figure 5. Average Total Mass of Diazinon in Cumulative Runoff. Columns with the same letter are not significantly different ($p < 0.05$).

Vegetative ground cover appeared to affect peak pesticide concentrations in runoff. Intertreatment comparisons of like flushes showed significant differences ($p \leq 0.05$) between treatments only for first

Significant reductions ($p < 0.05$) in total pesticide runoff due to the use of a vegetative cover were only shown for the first flush experiment. Not surprisingly, the longer opportunity times for pesticide infiltration on all RV experiments and BS second flush and rinse experiments resulted in less cumulative pesticide mass in orchard runoff. The longer infiltration opportunity times also tended to obscure treatment effects.

CONCLUSIONS

The use of a vegetative ground cover significantly reduced peak concentrations and cumulative pesticide mass in runoff for first flush rainfall/runoff events. Differences between treatments for first flush events were partially due to increased runoff lag times where a ground cover was present. Similarity in runoff response under elevated soil water conditions resulted in similar pesticide runoff from BS and RV for subsequent flushes. Lack of significant differences between treatments for second flush and rinse experiments indicated that foliar wash off might also be a controlling mechanism in pesticide runoff.

Irrigating orchards after pesticide application was effective in this study for reducing pesticide runoff on fields where there was no vegetative cover. Despite shortening the runoff lag time for a subsequent event, a wetting event prior to rinse experiments effectively removed the highly mobile applied pesticide from the soil surface.

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