

Movement of Simazine in Runoff Water from Citrus Orchard Row Middles as Affected by Mechanical Incorporation

J. Troiano* and C. Garretson

Environmental Monitoring and Pest Management Branch
California Department of Pesticide Regulation
830 K Street, Room 200
Sacramento, CA., 95814-3510

*Corresponding author (jtroiano@cdpr.ca.gov)

ABSTRACT

In California, pre-emergence herbicide residues have been measured in runoff water from citrus orchards that resulted from winter rainfall. This study measured the effect of rainfall on the redistribution of herbicides within a citrus orchard and the effect that shallow mechanical incorporation had on residue movement. Simulated rainfall treatments were applied to plots within a citrus orchard where simazine was applied only to row middles. Simazine movement in runoff water was compared between middles that were either undisturbed, the normal orchard practice, or subject to shallow mechanical incorporation. In undisturbed middles, simazine concentration in runoff water collected from the first of two simulated rain events averaged 0.87 mg L^{-1} ; simazine concentration in runoff water from a second event applied 1 week later averaged 0.40 mg L^{-1} . Shallow mechanical incorporation of row middles decreased runoff water volume from the first simulated rain event by approximately 50% with simazine concentration decreased to 0.14 mg L^{-1} ; runoff water volume was unaffected at the second rainfall event but simazine concentration remained low at 0.07 mg L^{-1} . Total simazine mass removed from both events, which also accounts for mass recovered in furrow soil, was estimated at 13.1% of the amount applied to row middles in undisturbed plots compared to only 2.1% in mechanically disturbed middles. We conclude that ambient rainfall is unreliable for incorporation of pre-emergence herbicides into orchard soil with low infiltration, and that shallow mechanical incorporation should be tested under commercial citrus growing conditions.

Abbreviations: ELISA, enzyme-linked immunosorbent assay; TMB, tetramethylbenzidine.

Published in J. Environ. Qual. 27:488-4494 (1998).

Movement of pesticide residues in runoff water is a well-documented source for contamination of surface water (Glotfelty, et. al., 1984; Leonard, 1990; Thurman, et. al., 1991). In California, movement of pesticide residues in runoff water also has been identified as a potential source for ground water contamination (Braun and Hawkins, 1991, Simmons and Leyva, 1994). Residues of the pre-emergent herbicides bromacil, diuron, and simazine have been detected in well water sampled in Tulare County, California (Maes, et. al., 1992). These detections were determined to originate from non-point source application of these herbicides to citrus. Although leaching was originally suspected, subsequent evidence linked contamination to movement of residues in orchard runoff water that was directed into drainage wells (Roux, et. al., 1991; Troiano, et. al., 1997). Drainage wells had been installed to relieve flooding caused in part by hardpan soils that have low water infiltration rates. These shallow wells rapidly move runoff water past the hardpan layer into deeper, more permeable subsoil strata. Sampling of winter rain runoff water in citrus growing areas of Tulare County, California confirmed the presence of bromacil, diuron, and simazine residues at concentrations ranging from 0.2 to 1.0 mg L⁻¹ where pesticide applications had been made 1 to 2-1/2 months prior to sample collection (Braun and Hawkins, 1991).

Pre-emergence herbicides are usually broadcast onto the soil surface, but they require further incorporation into the soil matrix to be effective (Ashton et. al., 1989). Incorporation by rainfall is a recommended method for many pre-emergence herbicides so they are often applied prior to the wet winter season in California. Although rainfall may be effective in moving residue into the matrix of soils with high permeability, it is a poor choice for incorporation into soils where runoff is produced due either to low infiltration rates (Heathman et. al., 1985) or to sloping landscapes (Buttle, 1990). Incorporation by mechanical methods has been shown to be effective in reducing pesticide loss from soils that have high runoff potential (Buttle, 1990) or that have been mechanically compacted (Baker and Laflen, 1979). For this current study, runoff from a citrus orchard was generated by application of simulated rainfall. Water and soil samples were obtained: 1) to document the movement and distribution of pre-emergent herbicide residues from citrus orchard row middles to furrows caused by runoff water; and 2) to measure the effect of a shallow mechanical soil incorporation on the redistribution of the herbicide residues within the orchard floor.

MATERIALS AND METHODS

The study site was a 25 year old citrus grove, on a 5.5 m x 6.1 m tree spacing, located on the farm at the California State University, Fresno campus. An experimental unit was the area bounded by 4 trees (Fig. 1). Tree row refers to the area between furrows where trees are located and row middle denotes the area between furrows where trees were not located. The soil is classified as a Hanford sandy loam (coarse-loamy, mixed, nonacid, thermic, Typic Xerorthent; USDA-SCS, 1971). Texture analysis of six randomly selected soil samples taken down to 153 mm indicated sand content of 73±1.5%, silt content of 19±1.5%, and clay content of 8±0.6% (Bouyoucos, G.J. 1962). Organic carbon content in these samples was low at 0.4%±0.1 (California Fertilizer Association, 1980). The average bulk density of the surface 63.5 mm of soil from twelve randomly collected samples from row middles was 1.71±0.12 Mg m⁻³ and from furrows was 1.28±0.09 Mg m⁻³ (Blake and Hartge, 1986). The infiltration rate of undisturbed soil averaged from six random samples taken from the row middle was 0.0024 mm s⁻¹, as measured with a single ring infiltrometer (Haise

et. al., 1956). The high measured bulk density and slow infiltration rate of soil in the row middles supported field observations of compaction, a common condition in orchards where soil is kept barren due to use of herbicides and is subjected to vehicular traffic (Stephenson and Schuster, 1942; Meek et. al., 1992). Also, this soil is described in the USDA-SCS survey as having a moderately rapid permeability but it is prone to compaction by wheeled vehicles, which significantly slows the infiltration of surface water (USDA-SCS, 1971).

The study was a repeated measures design where the effect of shallow mechanical incorporation of soil in the row middles on simazine runoff was measured after application of two simulated rain applications, applied 1 week apart. Simazine (2-chloro-4, 6-bis (ethylamino)-s-triazine), a pre-emergence herbicide, was applied to twelve plots randomly selected throughout the orchard. Simazine was applied only to the row middles; during application the furrows were covered with plastic tarp. The row middles of six randomly selected plots were mechanically disrupted immediately after simazine application. Soil was disturbed to approximately a 76 mm depth with a right angle tined rototiller pulled down the row middle with a tractor.

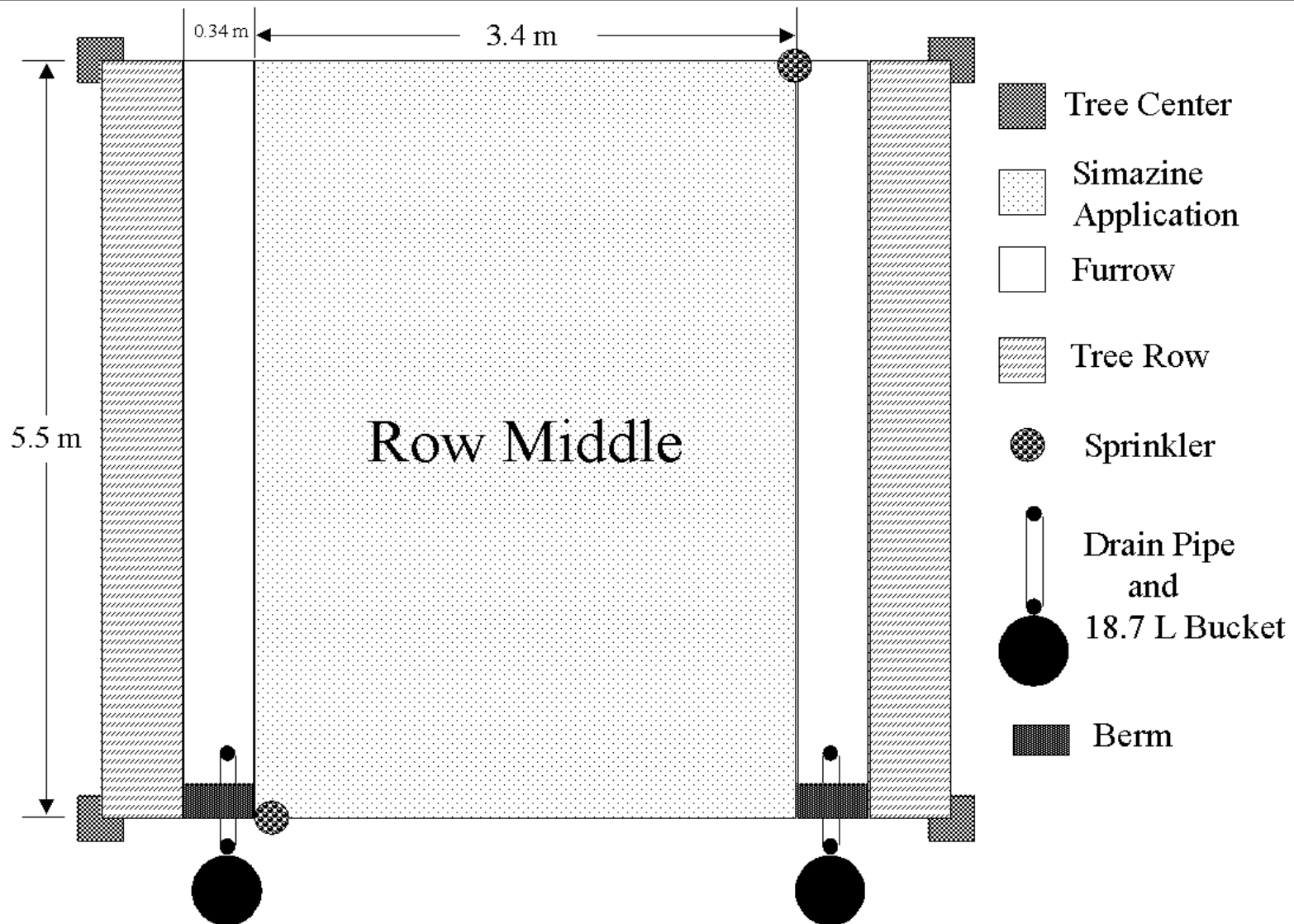
Runoff water was then generated by application of simulated rainfall. Since a small north-to-south change in elevation was engineered into the furrow-irrigated system, water was collected on the south end of each plot by constructing a berm over a PVC pipe placed into the furrows. Runoff water collected from the middles was directed through the PVC pipe into 18.7 L plastic buckets situated in pits excavated into the furrow (Fig. 1). Wire mesh was placed over the collection end of the pipe to screen out large objects such as leaves. The mass of simazine moved from the row middle by the event was determined by analyzing runoff water samples and soil sampled from the furrows. Simazine analysis of shallow soil samples from row middles was used in determining total recovery. Each plot received a second application of simulated rain 1 week later, which was the basis for the repeated measures effect. Treatments were randomly applied and they commenced on 22 August 1995 with 3 plots processed daily.

Glyphosate [isopropylamine salt of N-(phosphono-methyl)glycine], which is a contact herbicide, was applied two weeks prior to the study to eradicate weed growth. Each row middle was lightly leveled with a shovel and garden cultivating rake prior to treatment application, a procedure that did not disturb the continuity of the surface soil. Foliage from the four trees bordering each plot was trimmed to remove interference from limbs that extended into the plot over the irrigation furrows or row middles.

Simazine and Water Application

Twenty-four hours prior to herbicide application, each plot received a 5.5 mm sprinkler pre-irrigation to reduce variability in initial soil moisture across the plots. Simazine applications were made through a handheld spray boom with four nozzles spaced 0.48 m apart and using a CO₂ gas-pressurized (27.6 kPa) backpack sprayer. The nozzles were 8002 VS Driftguard Flat TeeJet spray nozzles (Spraying Systems Co., Wheaton, IL) with 50 mesh screens. The boom was held

Figure 1. Plot schematic depicting the dimensions of treated row middles and runoff collection sites in furrows. Furrows were covered with plastic during simazine application.



approximately 0.48 m above the ground, and the walking speed was approximately 3.2 km hr⁻¹.

Simazine was applied at a rate of 2.2 kg ha⁻¹ of wettable powder with 90% active ingredient resulting in a theoretical deposition of 3.4 g of simazine per plot. Deposition samples were taken to measure actual application by placing three 0.47 L jars, 76 mm diameter x 70 mm height, in the row middles. Each jar contained 50 g of air-dried, sieved, simazine-free soil. Deposition values averaged 4.12± 0.33 g in undisturbed plots and 3.82± 0.67 g in mechanically disturbed treatments. Since these values were not significantly different at P=0.05, the average value, 3.97 was used in calculating percent recovery per plot.

Simulated rain was applied through two Rainbird impact sprinklers (Model 2045PJ Maxi-Bird, Rainbird National Sales, San Diego, CA) situated 1.8 m above the soil surface. The sprinklers were operated under constant pressure, and were placed on diagonally opposite corners of each plot with the sprinkler heads adjusted to turn in a 90° arc (Fig. 1). The average rate of water deposition onto plots was measured at 22 mm hr⁻¹ using catchcans with a Distribution Uniformity of 75%. The amount of water applied to each plot was measured with a meter and set at 540 L, resulting in events that were approximately 90 minutes in duration and that delivered approximately 32 mm of water.

Water and Soil Sampling

Prior to herbicide application, six soil cores, each 51 mm in depth and 12.5 mm in diameter, were composited in each plot and analyzed to evaluate background concentration of simazine. Simazine was not detected in 9 of the 12 plots at a minimum reporting limit of 15 µ Kg⁻¹ while levels of 17, 18, and 19 µ g Kg⁻¹ were measured in 3 plots. The detected levels were three orders of magnitude less than at application and were considered negligible.

Runoff water was collected in sequential samples, each 15.1 L in volume. Paired sequential water samples from the two furrows were pooled into a large container and during agitation, subsamples were collected in 1-L amber glass bottles. These subsamples were further split into unfiltered and filtered samples. Samples were filtered through a 1.0 µm filter to remove sediment. Sediment mass was determined gravimetrically after oven-drying tared filters at 105 °C.

Soil was sampled after application of simulated rain and after water had drained from the plot. For row middles, three composite samples were obtained from each plot representing the north, center, and south portions of the middles. Each sample was a composite of 5 subsamples taken across an east-west transect at each position. Each subsample was 51 mm deep and 12.5 mm in diameter. The same sampling procedure was used for furrows.

Chemical Analysis

Concentration of simazine in water and soil samples was determined through enzyme-linked immunosorbent assay (ELISA). The ELISA methodology has previously been described and results from similar soils have been show to be equivalent to results obtained with gas chromatography (Goh et. al., 1991; Goh et. al., 1993). Water samples were analyzed directly. For

soil, 25 g samples were extracted in a mixture of 10 mL methanol and 15 mL deionized water which was shaken on an orbital shaker for 10 minutes at 200 rpm. The extract was decanted and saved and the extraction repeated. The combined extracts were filtered through 0.2 μm nylon acrodisc. Prior to ELISA the filtrates were diluted ten-fold to reduce the methanol content to less than 4%. The double-antibody, haptenated enzyme, competitive inhibition ELISA assay was run according to Format II of Schneider and Hammock (1992). Microtiter plates were coated with 100 μL per well of affinity-purified goat anti-mouse antibody (Boehringer Mannheim, Indianapolis, IN) diluted 1:2,000 in 0.5 M carbonate buffer (pH 9.6), sealed with an acetate plate sealer (Dynatech, Chantilly, VA) and incubated overnight at 4 °C. After washing 5 times with PBSTA (0.2 M phosphate buffer with 0.8% NaCl, 0.05% Tween 20, 0.02% NaN_3 , pH 7.5), the plates were tapped dry and coated with 100 μL per well of hybridoma culture fluid with monoclonal mouse anti-atrazine antibodies (AM7B2.1;1:3,000 in PBSTA). The plates were sealed and incubated overnight at 4 °C or for 4 hours at room temperature. Fifty μL of standard or sample were added into each well followed with 50 μL of enzyme tracer (horseradish peroxidase-simazine hapten conjugate) and incubated for 15 minutes at room temperature. Plates were washed 5 times to remove unbound immunoreactives. Color development was obtained by adding 100 μL of substrate buffer per well. The substrate buffer consisted of 200 μL of chromogen tetramethylbenzidine (TMB) (6 mg TMB in 1 mL of dimethyl sulfoxide) and 50 μL of 1% H_2O_2 in 12.5 ml of 0.1 M sodium acetate buffer (pH 5.5). After 25 minutes, the color was stopped by adding 50 μL of 4N H_2SO_4 and the absorbance measured at 450-650 nm.

Method validation was conducted on soil and water matrices that were determined to have no detectable level of simazine. The validation consisted of spiking each medium with 5 replicates at 3 spike levels. Overall mean recoveries were $101 \pm 12.7\%$ for water and $105 \pm 13.6\%$ for soil. These data were used for continuing quality control to set upper and lower control limits, which was the mean $\pm 2x$ standard deviation. For quality control, a matrix blank and duplicate matrix spikes were analyzed with each extraction set. Simazine was never detected in matrix blanks. Percent recovery for spikes was within control limits with an average of 5% percent difference between duplicates for both matrices. Minimum reporting limits were $0.5 \mu\text{g L}^{-1}$ for water and $15 \mu\text{g Kg}^{-1}$ for soil.

Statistical Analysis

A repeated measures analysis of variance was used to measure the main effect of shallow mechanical incorporation over the two simulated rain applications. When there are only two levels of time, the analysis is similar to a split-plot Analysis of Variance (Milliken and Johnson, 1984). Here, mechanical incorporation was the main effect and the simulated rain treatments (time) was the sub plot effect. Since the interaction term was significant in nearly every test, further analyses were conducted within each simulated rain event. These were essentially t-tests for the effect of mechanical incorporation on the volume of runoff water, the simazine concentration in runoff water and soil samples, and the mass of simazine calculated for water and soil samples. The volume of soil used in mass balance for furrows was estimated as 0.34 m (width) x 5.5 m (length) x 0.051 m (depth) and for row middles was 3.4 m (width) x 5.5 m (length) x 0.051 m (soil sample depth). Mass of soil was determined by multiplying the volume by 1.71 Mg m^{-3} for row middles and by 1.28 Mg m^{-3} for furrows, the bulk density values determined from sampling.

RESULTS

Characterization of water runoff

For the first simulated rainfall event, the average volume of runoff water collected from plots with undisturbed row middles was 37.8% of the total amount of water applied per plot (Table 1). Shallow mechanical incorporation of the row middles significantly decreased runoff volume to 18.7% of total water applied. Since mechanical incorporation caused greater soil roughness, the decrease in runoff was due to an increase in the amount of water infiltrated into the soil.

The average volume of runoff water measured from undisturbed plots during the second simulated rainfall was 31.3% of total water applied which was similar to the amount measured for the first rainfall event (Table 1). In contrast to the first simulated rainfall, shallow mechanical incorporation in the row middles did not affect the volume of runoff water which was estimated at 41.1% of total applied water. These data indicate that reduction in volume of runoff water from shallow mechanical incorporation was limited to only the first application of simulated rain.

Simazine Movement in Runoff Water

For the first simulated rainfall event, simazine concentration in runoff water from undisturbed plots was greatest at the first volumetric sampling interval with a gradual decrease in subsequent samples (Fig. 2A). The estimated mass of simazine recovered in runoff samples was 4.5% of the application (Table 1). Shallow mechanical incorporation affected the pattern of simazine runoff with simazine concentration an order of magnitude lower in the first volumetric sample, compared to undisturbed plots, and with concentrations consistently near 0.1 mg L^{-1} in all samples (Fig. 2A). Decreases in both the volume and simazine concentration of runoff water resulted in a ten-fold reduction of simazine mass recovered in runoff water from the shallow mechanical incorporation treatment to only 0.4% of the application.

Runoff water samples were filtered to determine the partitioning of simazine mass between dissolved and sorbed phases. In both treatments, the major portion of simazine residue was dissolved in water rather than sorbed onto sediment with 78.2% and 71.4% of simazine mass recovered in filtered water samples from undisturbed and shallow mechanical incorporation treatment, respectively (Table 1). The patterns observed in simazine concentration and the effects of treatments were similar between filtered and unfiltered samples (Figs. 2A and 3A).

Although simazine concentration in runoff water samples for the second simulated rainfall event was less than at the first rainfall event, simazine concentration was still decreased by the shallow mechanical incorporation treatment (Fig. 2B). The estimated recovery of simazine mass in runoff water was 1.6% of the application in undisturbed plots compared to 0.4% in the shallow mechanical incorporation treatment.

Table 1. Mass balance for runoff water, sediment, and simazine mass in water and soil compared between normal citrus orchard undisturbed row middles and shallow mechanical incorporation of middles exposed to two simulated rain events.

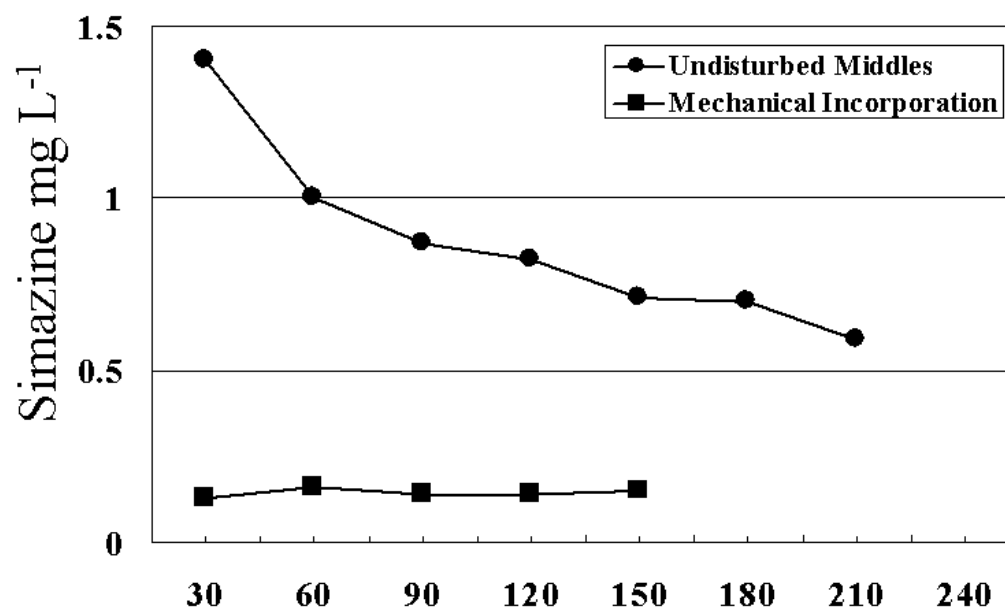
Sample date and Variable	Mechanical Incorporation Treatment		T-Test Significance Level
	No Soil Disruption	Mechanical Disruption	
	Mean \pm SD	Mean \pm SD	
<u>Simazine Deposition per Plot (mg/plot)</u>	4120.00 \pm 330.00	3820.00 \pm 670.00	0.35
<u>First Simulated Rain Event[†]</u>			
<u>Runoff Water - Unfiltered Samples</u>			
Simazine Concentration (mg/L)	0.87 \pm 0.18	0.14 \pm 0.05	0.001
Water Volume (L/plot)	204.00 \pm 20.00	101.00 \pm 60.00	0.003
Simazine Mass (mg/plot)	179.00 \pm 40.00	14.00 \pm 10.00	0.001
<u>Runoff Water - Filtered Samples</u>			
Simazine Concentration (mg/L)	0.69 \pm 0.09	0.10 \pm 0.02	0.001
Water Volume (L/plot)	204.00 \pm 20.00	101.00 \pm 60.00	0.003
Simazine Mass (mg/plot)	140.00 \pm 25.00	10.00 \pm 7.00	0.001
<u>Sediment in Runoff</u>			
Mass per Volume (g/L)	0.81 \pm 0.30	2.61 \pm 0.94	0.001
Total Mass (g/plot)	164.00 \pm 59.00	229.00 \pm 116.00	0.25
Simazine Concentration (mg/kg)	311.00 \pm 223.00	21.00 \pm 29.00	0.01
Simazine Mass (mg/plot)	44.00 \pm 29.00	3.90 \pm 4.70	0.007
<u>Soil - Furrow</u>			
Simazine Concentration (mg/kg)	0.53 \pm 0.21	0.09 \pm 0.01	0.001
Simazine Mass (mg/plot)	115.00 \pm 46.00	20.00 \pm 3.00	0.001
<u>Soil - Row Middles</u>			
Simazine Concentration (mg/kg)	1.83 \pm 0.40	1.32 \pm 0.51	0.082
Simazine Mass (mg/plot)	2661.00 \pm 580.00	1920.00 \pm 737.00	0.082
<u>Total Simazine recovered (mg/plot)[‡]</u>	2954 \pm 560	1954 \pm 738	0.022
<u>2nd Simulated Rain Event</u>			
<u>Runoff Water - Unfiltered Samples</u>			
Simazine Concentration (mg/L)	0.40 \pm 0.10	0.07 \pm 0.06	0.001
Water Volume (L/plot)	169.00 \pm 55.00	222.00 \pm 50.00	0.11
Simazine Mass (mg)	65.00 \pm 19.00	14.00 \pm 9.00	0.001
<u>Runoff Water - Filtered Samples</u>			
Simazine Concentration (mg/L)	0.28 \pm 0.14	0.04 \pm 0.02	0.002
Water Amount (L/plot)	169.00 \pm 55.00	222.00 \pm 50.00	0.11
Simazine Mass (mg/plot)	44.00 \pm 19.00	9.00 \pm 4.00	0.001
<u>Sediment in Runoff</u>			
Mass per Volume (g/L)	0.84 \pm 0.34	1.47 \pm 0.14	0.002
Total Mass (g/plot)	134.00 \pm 43.00	328.00 \pm 95.00	0.001
Simazine Concentration (mg/kg)	179.00 \pm 177.00	20.00 \pm 22.00	0.055
Simazine Mass (mg/plot)	21.00 \pm 15.00	5.30 \pm 5.50	0.034
<u>Soil - Furrow</u>			
Simazine Concentration (mg/kg)	0.75 \pm 0.66	0.17 \pm 0.13	0.061
Simazine Mass (mg/plot)	163.00 \pm 144.00	36.00 \pm 29.00	0.061
<u>Soil - Row Middles</u>			
Simazine Concentration (mg/kg)	1.84 \pm 0.66	1.40 \pm 0.67	0.28
Simazine Mass (mg/plot)	2670.00 \pm 956.00	2034.00 \pm 970.00	0.28
<u>Total Simazine recovered (mg/plot)[‡]</u>	2897 \pm 1030	2084 \pm 985	0.18

[†] Simulated rain applied at a rate of 2.2 cm/hr for 1.5 hours totalling 3.2 cm.

[‡] Total mass determined from amount recovered per plot in unfiltered runoff water, and furrow and row middle soil.

Figure 2. Concentration of simazine in unfiltered runoff water from citrus orchard row middles that were undisturbed or subject to shallow mechanical incorporation.

A. First Simulated Rainfall



B. Second Simulated Rainfall

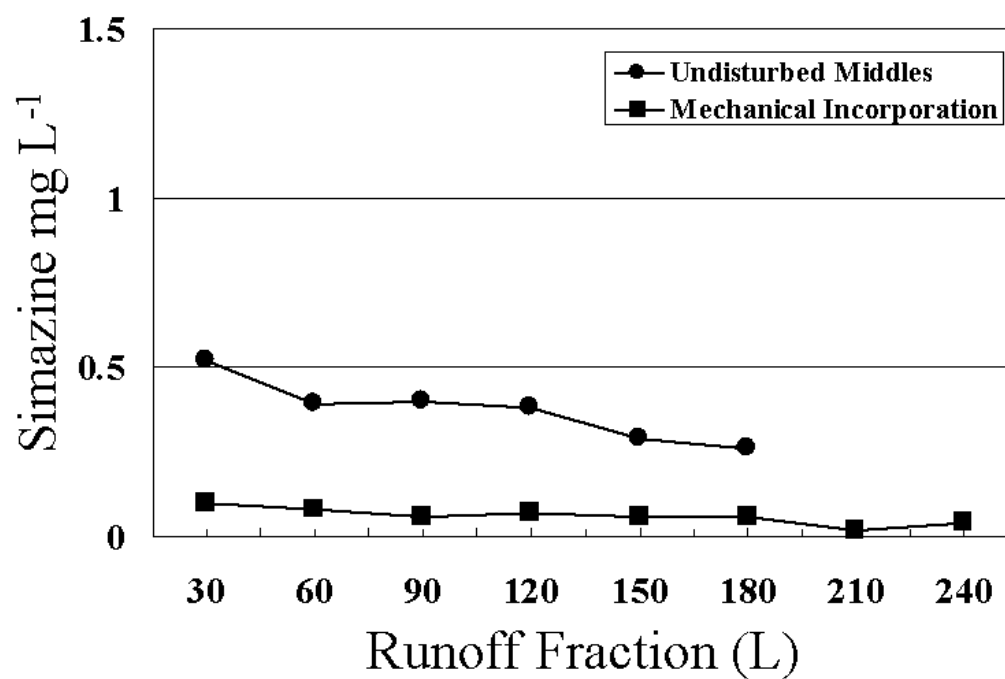
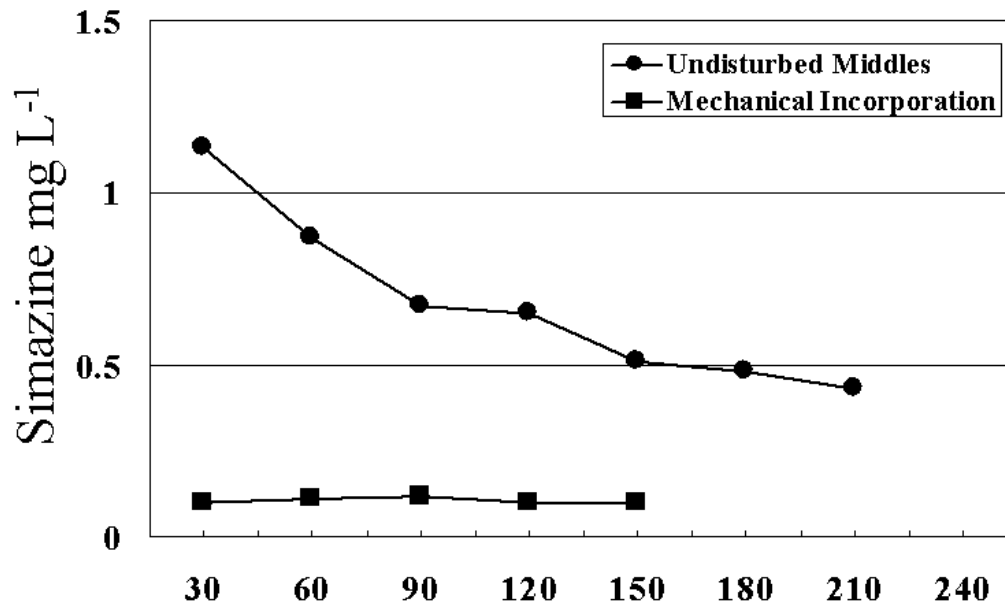
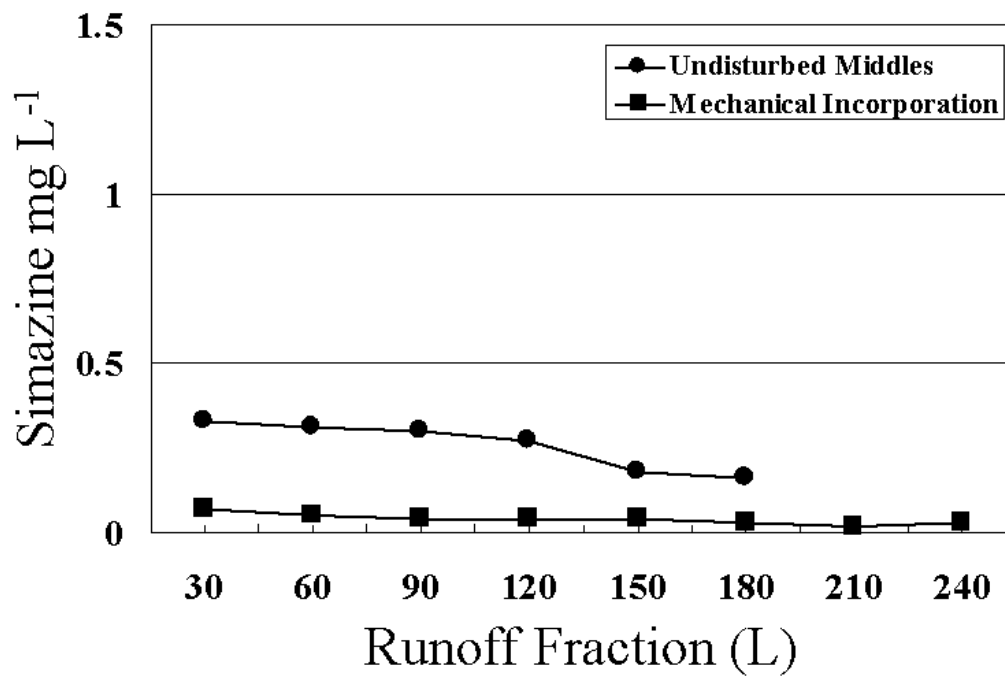


Figure 3. Concentration of simazine in filtered runoff water from citrus orchard row middles that were undisturbed or subject to shallow mechanical incorporation.

A. First Simulated Rainfall



B. Second Simulated Rainfall



Temporal patterns and treatment effects for simazine concentration in filtered water samples for the second simulated rain event were similar to those measured for unfiltered water samples (Figs. 2B and 3B). One exception was that the overall portion of simazine recovered in filtered runoff water samples was apparently less at 67.7% and 64.3% of unfiltered values in undisturbed and mechanically incorporated plots, respectively (Table 1). Although the majority of residue was still in a dissolved phase, slightly more was partitioned onto sediment.

Simazine mass distribution

Simazine residue was measured in soil sampled from the furrows after the first simulated rainfall (Table 1). Since simazine had not been applied to furrows and pretreatment samples indicated negligible background levels, the residues must have been deposited by runoff water that infiltrated into furrow soil during the runoff event. For undisturbed plots, the mass of simazine recovered from furrow soil was estimated at 2.9% of the application. Simazine concentration in furrow soil sampled from the shallow mechanical incorporation treatment was significantly less than in undisturbed plots with an estimated recovery at 0.5% of the application. Combining the simazine mass recovered in runoff water and in furrow soil samples resulted in an estimate of 7.4% of the application moved from row middles of undisturbed plots compared to only 0.9% for the shallow mechanical incorporation treatment.

Simazine concentration in furrow soil increased after the second simulated rainfall, increasing the estimated mass of simazine in the top 51 mm of soil to 4.1% of the application in undisturbed row middles and to 0.9% in mechanically disturbed row middles. Combining simazine mass recovered in runoff water from the first and second rain event with simazine mass recovered in furrow soil at the second rain event resulted in an estimate of 13.1% of the application moved from row middles of undisturbed plots compared to only 2.1% for shallow mechanical incorporation treatment.

The total mass of simazine recovered from all media was estimated as a combination of results from the post-runoff soil samples taken from row middles and furrows after the second rainfall event and the combined mass recovered from runoff water sampled from both simulated rain events. Individual t-tests within each simulated rainfall event are indicated in Table 1. However, the incorporation x simulated rainfall interaction term in the repeated measures ANOVA for total mass recovered was not significant so it may be inappropriate to decompose this analysis into separate t-tests. In the full ANOVA, the main effect for soil treatment indicated a trend ($P=0.06$) for greater mass recovered in the undisturbed plots. Using the values calculated for total mass of simazine recovered after the second rainfall as a guide, 73% of the simazine application was accounted for in undisturbed plots as compared to only 52.5% in plots with shallow mechanical incorporation. Since the depth of incorporation was approximately 76 mm, the lower mass recovered in the mechanical incorporation treatment could be due to a combination of incorporation or leaching of residue below the 51 mm depth of soil sampled.

Sediment Movement

Shallow mechanical incorporation increased sediment concentration in runoff water from both simulated rain events; the average sediment concentration increased in the first event from 0.8 g L^{-1} to 2.6 g L^{-1} in undisturbed and shallow mechanical incorporation treatments, respectively, and in the second event from 0.8 g L^{-1} to 1.5 g L^{-1} in undisturbed and shallow mechanical incorporation treatments, respectively (Table 1). At the first simulated rain event, the increase in sediment concentration was offset by the decrease in runoff volume so total soil mass removed was not significantly different from that measured in undisturbed plots. Lack of an effect on runoff water volume at the second simulated rain event resulted in a greater estimate of soil mass removed from row middles of the shallow mechanical incorporation treatment.

Although the sediment concentration was greater in mechanically disturbed plots, the estimated concentration of simazine on sediment was greatly reduced from $311 \text{ mg simazine kg}^{-1} \text{ soil}$ to $21 \text{ mg simazine kg}^{-1} \text{ soil}$ for undisturbed and mechanical incorporation treatments respectively, for the first simulated rain event and from $179 \text{ mg simazine kg}^{-1} \text{ soil}$ to $20 \text{ mg simazine kg}^{-1} \text{ soil}$ for undisturbed and mechanical incorporation treatments respectively, for the second simulated rain event. It is interesting to note that the simazine concentration varied between simulated rain events in undisturbed plots but remained relatively constant and low in mechanically disturbed plots.

DISCUSSION AND CONCLUSIONS

The architecture of the citrus orchard used in this study was typical of commercial groves in the Southern San Joaquin Valley of California. Many commercial groves are situated on soils that have low water infiltration rates, resulting in a high potential for runoff during the winter rainy season (Troiano et. al., 1997). This study illustrated that herbicides applied to orchard row middles with compacted soils are a significant source of residues in runoff water generated from rain events.

Furthermore, the range of simazine concentration in runoff water from undisturbed plots was similar to concentrations measured in runoff water sampled from commercial citrus orchards (Braun and Hawkins, 1991). Even though the percentage of residue that runs off may not be a large fraction of the application, concentrations of herbicide residue in runoff water between 0.1 and 1.0 mg L^{-1} are 3 to 4 orders of magnitude greater than those commonly detected in ground water (Maes et al., 1992). The use of drainage wells for disposal of runoff water, containing residues at these levels, into the subsoil represents a significant source of ground water contamination. Mechanical incorporation is an effective method to decrease runoff volume, pesticide concentration, and consequently offsite movement of environmental contaminants (Baker and Laflen 1979). Currently, there is resistance to use of mechanical incorporation in citrus because of perceived deleterious effects on root health. The depth of incorporation in this study was shallow, down to 76 mm, but it was sufficient to disrupt the compacted surface soil layer, allowing greater infiltration of water and greatly reducing the movement of simazine.

Although a mechanistic explanation for the observed effects was beyond the scope of this study, lower concentration of simazine measured on sediment in runoff water from mechanical incorporated plots indicated less mass transfer between soil and water due to decreased

concentration of simazine in surface soil. Pesticide concentration in runoff has been shown to be correlated with pesticide concentrations in shallow surface soil samples (Leonard, 1990). The effect of shallow incorporation on reducing simazine concentration was probably caused through a combination of soil mixing during incorporation and subsequent redistribution of residue in water that infiltrated into the soil. Qualitatively, we observed a greater time period between initiation of the first simulated rain event and eventual generation of runoff water in the shallow mechanical incorporation treatment, indicating greater retention of water during the early phase of the rain event. The lack of a treatment effect on runoff volume during the second simulated rain treatment applied 1 week later is particularly interesting because it indicates reformation of a restrictive surface soil layer. Yet runoff of simazine was still greatly reduced in the mechanical incorporation treatment due to lower surface soil concentration of simazine as evidenced by the low concentration of simazine on sediment. One potential drawback to mechanical incorporation is the increase in sediment concentration caused by disturbing the soil. Although further field study is needed to determine the significance of sediment effects, sediment concentration values below 5 g L⁻¹ have been considered as relatively low sediment loading values (Leonard, 1990). Average sediment concentrations in our study were below this value.

In conclusion, runoff water generated from compacted orchard soil is a source for offsite movement of herbicide residues applied to row middles. Although ambient rainfall is a recommended method for soil incorporation of pre-emergence herbicides, use of this method on compacted orchard soils that have low infiltration rates could result in high concentrations of residues in runoff water. The prevailing management practices in citrus orchards, which is to keep row middles bare with herbicide treatment, increases the potential for compaction of soil already subject to vehicular traffic. Shallow mechanical incorporation of the row middle temporarily alleviates the compaction and reduces the volume of water runoff as well as herbicide concentration in runoff. Although this study indicated that shallow mechanical incorporation could be an alternative method of incorporation that mitigates offsite movement of herbicide residues, implementation and effectiveness should be studied under commercial citrus growing conditions.

ACKNOWLEDGMENTS

The project would not have been possible without the assistance of Alfredo DaSilva, Sanjay Witharana, and Bart Haycraft who participated in sampling and Jean Hsu who conducted the ELISA analyses on the samples.

REFERENCES

- Ashton, F.M., A.S. Crafts, and H.S. Agamalian. 1989. Chemical Control Methods. p. 115-170. *In* E.A. Kurtz (ed.) *Principals of Weed Control in California*. California Weed Conference, Thompson Publications, Fresno, CA.
- Baker, J.L., and J.M. Laflen. 1979. Runoff losses of surface-applied herbicides as affected by wheel tracks and incorporation. *J. Environ. Qual.*, 8:602-607.

- Blake, G.R., and Hartge, K.H. 1986. Bulk Density. p. 363-375. *In* A. Klute (ed.) *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods-Agronomy Monograph no. 9* (2nd Edition), American Agronomy Society-Soil Science Society of America, Madison, WI.
- Bouyoucos, G.J. 1962. Hydrometer method improved for making particle size analyses of soils. *Agron. J.* 54:464-465.
- Braun, A.L., and L.S. Hawkins. 1991. Presence of bromacil, diuron, and simazine in surface water runoff from agricultural fields and non-crop sites in Tulare County. PM 91-1. California. Environmental Monitoring and Pest Management Branch, California Department of Pesticide Regulation, 1020 N Street, Room 161, Sacramento, CA., 95814.
- Buttle, J.M. 1990. Metolachlor transport in surface runoff. *J. Environ. Qual.* 19:531-538
- California Fertilizer Association. 1980. Method S:18-Organic matter (O.M.)-dichromate reduction. p. S:18.0. *In* R.S. Rauschkolb and J. Quick (eds.) *Soil Testing Procedures for California*, California Fert. Assoc., Soil Improvement Comm. Publ., Sacramento, CA.
- Glotfelty, D.E., A.W. Taylor, A.R. Isensee, J. Jersey, and S. Glenn. 1984. Atrazine and simazine movement to Wye river estuary. *J. Environ. Qual.* 13:115-121.
- Goh, K.S., Hernandez J., Powell S.J., Garretson C., Troiano J., Rany M., and Greene C.D. 1991. Enzyme immunoassay for the determination of atrazine residues in soil. *Bull. Environ., Contam. Toxicol.* 46:30-36.
- Goh, K.S., D.J. Weaver, J. Hsu, S.J. Richman, D. Tran, and T.A. Barry. 1993. ELISA regulatory application: compliance monitoring of simazine and atrazine in California soils. *Bull. Environ. Cont. Toxicol.* 51:333-340.
- Haise, H.R., W.W. Donnan, J.T. Phelan, L.F. Lawhan, and D.G. Shockley. 1956. The use of cylinder infiltrometers to determine the intake characteristics of irrigated soil. USDA-ARS and USDA-SCS, ARS 41-7. U.S. Gov. Print. Office, Washington, DC.
- Heathman, G.C., L.R. Ahuja, and O.R. Lehman. 1985. The transfer of soil surface-applied chemicals to runoff. *Trans. ASAE.* 28:1909-1915.
- Leonard, R.A. 1990. Movement of pesticides into surface waters. *In* H.H. Cheng (ed.) *Pesticides in the soil environment: Processes, impacts, and modeling.* p. 303-348. *Soil Sci. Soc. Amer. Book Series No. 2.* Soil Sci. Soc. Amer., Inc, Madison, WI.
- Maes, C.M., M. Pepple, J. Troiano, D. Weaver, W. Kimaru, and SWRCB Staff. 1992. Sampling for pesticide residues in California well water: 1992 well inventory data base, cumulative report 1986-1992. EH 93-02. Environmental Monitoring and Pest Management Branch, California Department of Pesticide Regulation, 1020 N Street, Room 161,

- Sacramento, CA., 95814.
- Meek, B.D., E.R. Rechel, L.M. Carter, and W.R. DeTar. 1992. Bulk density of a sandy loam: traffic, tillage, and irrigation-method effects. *Soil Sci. Soc. Am. J.* 56:562-565.
- Milliken, G.A., and D.E. Johnson. 1984. *Analysis of Messy Data Volume 1: Designed Experiments*. Van Nostrand Reinhold, New York, N.Y.,
- Roux, P.H., R.L. Hall, and R.H. Ross Jr. 1991. Small-scale retrospective ground water monitoring study for simazine in different hydrogeological settings. *Ground Water Monitor. Rev.* XI:173-181.
- Schneider P., and Hammock B.D. 1992. Influence of the ELISA format and the hapten-enzyme conjugate on the sensitivity of an immunoassay for s-triazine herbicides using monoclonal antibodies. *J. Ag. Food Chem.* 40:525-530.
- Simmons, S.E., and J.J. Leyva. 1994. Presence of soil-applied herbicides in three rights-of-way infiltration basins in San Joaquin County. EH 94-01. California. Environmental Monitoring and Pest Management Branch, California Department of Pesticide Regulation, 1020 N Street, Sacramento, CA., 95814.
- Stephenson, R.E., and C.E. Schuster. 1942. Soil properties of tilled orchards compared with untilled areas. *Soil Sci.*, 54:325-332.
- Thurman, E.M., D.A. Goolsby, M.T. Meyer, and D.W. Kolpin. 1991. Herbicides in surface waters of the midwestern United States: the effects of the spring flush. *Environ. Sci. Technol.* 25:1794-1796.
- Troiano, J., C. Nordmark, T. Barry, and B. Johnson. 1997. Profiling areas of ground water contamination by pesticides in California: Phase II - evaluation and modification of a statistical model. *Environ. Monit. Assess.* 45:301-318.
- USDA-SCS. 1971. *Soil survey: Easter Fresno area, California*. USDA in cooperation with California Agric. Exp. St. Superintendent of Documents, U.S. Gov. Print. Office, Washington, DC.