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Foliar and Soil Deposition of Pesticide Sprays in Peanuts and Their Washoff and Runoff under Simulated Worst-Case Rainfall Conditions

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There are few studies that relate the timing and amounts of pesticide washoff from plant foliage during rainfall to runoff losses at the edge of the field. We hypothesized that foliar deposits, if washed onto the soil slowly during rainfall, may then undergo less leaching during the period of infiltration that occurs prior to soil saturation and runoff, thus exhibiting larger runoff losses than pesticides on/in the soil at the beginning of rain. We measured the runoff of ethalfluralin, metolachlor, chlorothalonil, and rhodamine WT dye using simulated rainfall on 450 m^2 mesoplots planted in peanut. Ethalfluralin was applied preplant incorporated, and metolachlor was applied preemergence on bare soil. Chlorothalonil and rhodamine WT were applied to the peanut canopy at maturity. Rainfall was simulated 24 h after each chemical application (in May and July, 1998, and May and August, 1999) using raindrop sprinklers, applying 5.5 $\pm$ 0.5 cm over a 2 h period to create reasonable worst-case conditions; between 3 and 9 mm of runoff was generated. Volume-weighted average concentrations of chemicals in runoff were 7, 104, 163, and 179 ug L^{-1} for ethalfluralin, metolachlor, chlorothalonil, and rhodamine WT, respectively. The total amounts of chemicals lost in the runoff events were 0.04 $\pm$ 0.01, 0.2 $\pm$ 0.1, 0.6 $\pm$ 0.5, and 0.2 $\pm$ 0.1, as percents of amounts applied, respectively. Rhodamine WT formed a vivid red solution on wetting and provided visual clues to the dynamics of chemical washoff/runoff. The washoff from rain-exposed peanut foliage appeared to be complete within a few minutes of the beginning of rainfall, and disappearance of dye from rain-exposed soil surface occurred within the first 10 min of rainfall. However, dye was present in runoff water at near-constant concentrations throughout the 2 h runoff event, indicating that near-constant amounts of chemical remained in the soil extraction zone. These results confirm earlier studies showing that soil incorporation at application significantly reduces runoff losses and that a majority of foliar residues can be washable if rainfall occurs within a few days after application. Runoff losses of foliar-applied pesticides were small relative to washoff amounts but were sensitive to runoff timing relative to washoff.

KEYWORDS: Peanut; *Arachis hypogaea* L.; chlorothalonil (tetrachloroisophthalonitrile); ethalfluralin [*N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine]; metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide]; pesticide runoff; pesticide washoff; rainfall simulation; nonpoint pollution

INTRODUCTION

Pesticide runoff from agricultural fields is the most important source of pesticide contamination of water resources in the continental United States (*1*−*4*). Runoff losses are controlled principally by pesticide use intensity and the time that elapses between application and runoff (*5*−*7*), but a host of other factors are important including site properties (*8*−*11*), foliar vs soil pesticide deposition (*12*), the formulation of the pesticide, and the physical−chemical properties of the active ingredient (*10*, *13*, *14*).

This large number of variables, many interacting, means that many experiments are required to develop a comprehensive understanding and prediction capability for pesticide runoff. For this reason, the convenience and control of using simulated rainfall on small plots makes it an attractive option and an accepted technique for chemical runoff studies. Rainfall simulation allows investigators to readily create the "reasonable worst-case" weather conditions needed for risk assessment (*15*, *16*). "Mesoplot"-scale runoff studies (plot size between 200 and 500

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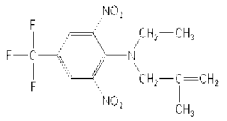
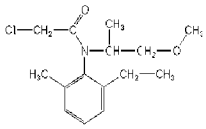
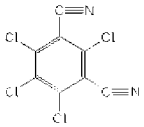
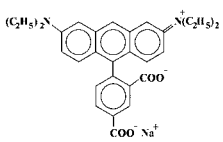
Table 1. Chemicals Applied to Soil and Peanut Plants: Characteristics and Use Patterns

	Ethalfluralin	*Metolachlor*	*Chlorothalonil*	*Rhodamine WT*
	herbicide	herbicide	fungicide	soluble dye
Chemical				
Solubility (mg/L)[a]	0.3	530	0.6	>20%[b]
Vapor Pressure[a]	8.8×10^{-5}	3.13×10^{-5}	0.076 mPa	0[c]
Soil Sorption coefficient[a,d] K_{oc}	4000	200	1380	5000[e]
Application site	Soil Incorporated	Soil surface	Crop canopy	Crop canopy
Appl. rate (kg/ha) (nominal)	0.84	2.2	1.3	2.1

[a] Ref *40*. [b] Rhodamine WT was packaged as a 20% w/w aqueous solution. [c] Assume salt has zero vapor pressure. [d] Soil organic carbon sorption coefficient. [e] Reported values range from about 1000 to 30 000 (*48*).

m^2) are being submitted to the U.S. Environmental Protection Agency by pesticide registrants as part of an environmental exposure assessment, and a few studies have been published (*17*−*19*). "Microplot"-scale runoff studies, on plots of a few square meters, have also been successfully used to study many process variables and appear to give similar results to larger scale studies—at least for soil-applied chemicals (*5*, *15*, *16*, *19*).

Runoff studies of pesticides applied to soils generally indicate that pesticides are entrained in runoff water by a mixing/extraction process (*6*, *20*) in which, typically, a few percent or less of pesticides present within a few millimeters of the surface of the soil are removed (see below). The runoff of pesticides applied on crop or weed plants has been less investigated; most studies report losses similar to soil-applied pesticides although a few cases of losses of 10% or more have been observed (*6*, *7*). Two recent studies on microplots under severe conditions exhibited high losses: Potter et al. (*21*) obtained 15% losses of two cotton (*Gossypium hirsutum*) defoliants, thidiazuron and tribufos, and Reddy et al. (*12*) generated a 23% loss of imazaquin from smooth pigweed (*Amaranthus hybridus* L.).

These examples of large runoff losses of foliar pesticide residues are not surprising if "washoff" studies, direct measurements of the removal of pesticides from foliage surfaces by rain, are considered. Washoff studies generally indicate that a large fraction of pesticide deposits on foliage—sometimes approaching 100% with highly soluble pesticides—can be removed by rain (*22*−*29*). If rainfall occurs within hours of pesticide application, even highly insoluble pesticides can be removed. However, washoff fractions rapidly decrease in time after application, and foliar residues also dissipate rapidly; runoff losses reflect this (*6*, *7*, *30*). Overall, there is a contrast between the large loss fractions observed in washoff studies and the small (with a few exceptions) runoff losses typically observed for foliar residues. The exceptions may involve either the severity of the conditions or perhaps the small scale of the plots used (*16*).

Potter et al. (*21*), in the experiment where 15% of two slightly soluble defoliants were lost in runoff, reported only 4% loss of a much more soluble (and leachable) defoliant, dimethipin. They and others (*31*) suggest that there may be a timing effect within rainfall/runoff events: relatively soluble chemicals that wash off foliage quickly may reach the soil surface before runoff has begun, i.e., when all rainfall is infiltrating, and be leached downward into the soil and thus made less available for runoff. Poorly soluble chemicals with slower washoff may have a larger fraction of the washoff chemical reach the soil surface after soil saturation has occurred and runoff has begun, and thus, more will be transported to the field edge.

Clearly, studies are needed where both washoff and runoff of the same pesticide application are characterized. To our knowledge, only one such study has been published; Reddy and Locke (*12*), in the severe conditions microplot study cited above in which 23% imazaquin losses were observed, found in a separate experiment that 33−88% of imazaquin could be washed off foliage. We have conducted a mesoplot-scale experiment in peanut in which the runoff of typical soil-applied and foliar-applied pesticides and a soluble dye are compared under nearly identical rainfall amounts and intensities. We also measured the washoff of the foliar-applied chemicals.

MATERIALS AND METHODS

The chemicals applied and their properties are listed in **Table 1**. Chlorothalonil is a broad-spectrum fungicide commonly used in peanut production for the control of foliar diseases. It is applied 4−7 times throughout the growing season at biweekly intervals. Chlorothalonil persistence has been measured on peanut foliage (*32*) and in soil under peanut cropping practices (*33*). Ethalfluralin, applied preplant incorporated, and metolachlor, surface applied after planting, are commonly used peanut herbicides. Rhodamine WT (hereafter referred to as rhodamine) is a tracer dye that serves as a convenient, easily quantified, and highly visible proxy for a water soluble pesticide (*34*). Its wide range for reported soil sorptivity (**Table 1**) is likely a function of clay content; we expected its K_d to be at the lower end in the sandy soil in our experiments.

Field Experiments. The location and practices employed (except for rhodamine) are typical of the peanut production region in the southeastern U.S. coastal plain. Experiments were conducted on different field sites in 1998 and 1999 at the Ponder Research Farm, a unit of the University of Georgia Coastal Plain Experiment Station, near Tifton, GA (latitude, 31° 30′; longitude, 83° 33′). Field operations are summarized in **Table 2**. The soil at both sites was a Tifton loamy sand (Plinthic Kandiudult) having 88% sand, 10% silt, 2% clay, and 0.4% organic matter in 1998 and 84% sand, 10% silt, 6% clay, and 0.3% organic matter in 1999. The sites had 2.8 ± 0.5% slope (average

Table 2. Field Operations Summary, 1998 and 1999, Tifton, GA

date	operation
1998	
18 May	ethalfluralin applied 0.8 kg/ha PPI to peanuts; peanuts planted
19 May	metolachlor applied 2.2 kg/ha PRE
20 May	rainfall simulation; plot A in a.m., plot B in p.m.
5 June, 19 June, 3 July, 19 August	maintenance fungicide applications
21 July	chlorothalonil applied 1.3 kg/ha and rhodamine dye applied 6.6 kg/ha in a.m.; plot A rainfall simulation in p.m.
22 July	plot B rainfall simulation in a.m.
1999	
17 May	ethalfluralin applied 0.8 kg/ha PPI to peanut; peanuts planted
18 May	metolachlor applied 2.2 kg/ha PRE
18 May	rainfall simulation; plot A in a.m., plot B in p.m.
3 June, 16 June, 1 July, 19 July, 17 August, 30 August	maintenance fungicide applications
5 Aug	chlorothalonil applied 1.3 kg/ha and rhodamine dye applied 6.6 kg/ha in a.m.
5 Aug	plot A rainfall simulation in a.m.
6 Aug	plot B rainfall simulation in p.m.

of eight measurements down the sides of the four plots) with rows oriented downslope to facilitate runoff. The plots were 14.6 m (16 rows) wide and 30.5 m long (0.0445 ha), with Georgia Green peanut seeded in rows 91 cm apart. Ethalfluralin was applied at 0.8 kg ai/ha preplant incorporated with a sprayer mounted on a two-row power tiller tilling 7.6 cm deep. Phorate was applied in-furrow for early season insect control but was not measured in the runoff. Immediately after the seeds were planted, metolachlor was applied broadcast on the soil surface at 2.2 kg ai/ha with a tractor-mounted boom sprayer. Both sprayers were calibrated to deliver 234 L/ha at 207 kPa, using flat fan tips (Turbo TeeJet spray tips TT11003VP, Spraying Systems Co., Wheaton, IL). Chlorothalonil was applied broadcast over the peanut canopy at 1.3 kg ai/ha for foliar disease control at biweekly intervals beginning 30 days after peanut emergence. Chlorothalonil was applied with a boom sprayer calibrated at 187 L/ha at 414 kPa using hollow cone spray tips. Each year, after the fourth chlorothalonil application, the spray deposit was allowed to dry for 1 h, and then, a solution of rhodamine [2 L of 19.5% w/w dye solution (Keystone Corp., Chicago, IL), specific gravity 1.13 g/mL, in 38 L of water] was applied broadcast over the peanut canopy using the same sprayer as the chlorothalonil, giving a 2.1 kg/ha nominal application rate. The rainfall was simulated 24 h later.

The application rates for metolachlor, chlorothalonil, and rhodamine were quantified by evenly distributing 16−20 9.8 cm diameter glass Petri dishes in the plots and collecting them immediately after application and transporting them to a freezer. The Petri dishes were rinsed with methanol, and the rinsates were analyzed. The dishes were placed on the soil surface to collect metolachlor spray; for chlorothalonil and rhodamine, the dishes were placed above the canopy and at soil level under the canopy, to determine the fractions depositing on peanut foliage and soil. Ethalfluralin sprays were not sampled because they were soil incorporated in the same operation as spraying.

Rainfall was simulated with raindrop irrigation sprinkler heads raised 1.8 m above the soil surface in two rows at the long edges of the plots. The simulator is described by Coody and Lawrence (*35*) and Sumner et al. (*36*). The nozzles produce droplet sizes and impact energies similar to a typical southeastern U.S. thunderstorm. The simulated rainfall events were nominally 50 mm during a 2 h period, a storm that has a probability of once per year in this region. For six of the eight simulations, two rows of 15 or 16 catch cups (waxed beverage cups with an opening diameter of 9.2 cm) were placed at the upper and lower ends of the plots perpendicular to the lines of simulator nozzles. Rainfall was simulated 24 h after pesticide applications and immediately after the rhodamine application had dried, in May and July, 1998, and May and August, 1999; see **Table 2**. Rainfall events were replicated twice each year, one plot being done in the morning and one in the afternoon of the same day.

Mesoplot wheeltracks were drained into a ditch lined with polyethylene film, which was connected to an ASTM Large 600 trapezoidal flume (Plasti-Fab Inc., Tualatin, OR). Flows were measured with a bubbler stage recorder (model 3220, ISCO Inc., Lincoln, NB) with manual stage observations at 10 min intervals as backup; for three of the eight plot events (event 1, 1998 plot B, and event 2, 1999, plots A and B), visual stage observations were used due to recorder operator failure. Samples of runoff water were collected every 10 min by holding a container in the flume nappe.

Foliar Washoff. On the day that chlorothalonil and rhodamine were applied to the peanut plants, 20 plant tops were clipped after spraying from an area outside the runoff plots, and 20 tops were clipped in the rainfall area after simulation. The plants were stored in plastic bags in a freezer until analysis, thawed, and rinsed in a pail containing 4 L of water, and the water was analyzed.

Sample Analysis. Runoff samples from the second 1998 event were dried to determine total solids content; amounts were typically less than 0.5 g/L. On the basis of the K_{oc} of rhodamine (**Table 1**), we estimated that less than 1% of rhodamine would be in the sediment phase of runoff, and rhodamine analyses were made by direct injection of settled and filtered runoff and washoff water samples into a Perkin-Elmer 410 high-performance liquid chromatography (HPLC) pump and helium degassing system and Hewlett-Packard 1043A fluorescence deector; excitation and emission wavelengths were 228 and 574 nm, respectively. Ethalfluralin, metolachlor, and chlorothalonil were extracted from unfiltered runoff and washoff water samples in separatory funnels using dichloromethane. The extracts were dried with anhydrous sodium sulfate, several drops of a 5% v/v mineral oil in acetone solution was added, and the extract was evaporated in a rotary evaporator at 50 °C under vacuum until just dry. The flask was then rinsed with 3 mL of methanol, and the methanol was evaporated; then, another 3 mL of methanol was added and this mixture was stored in an autosampler vial in a freezer until analysis. Metolachlor in the extracts was analyzed by HPLC (same HPLC with Perkin-Elmer UV diode array detector and 3.3 cm × 0.46 cm Perkin-Elmer C18, 5 μm column), ethalfluralin, and chlorothalonil by Varian 3600 GC using a DB-5 30 m × 0.25 mm column and a nitrogen specific (TSD) detector. Recoveries of 10−100 ppb standard additions to unfiltered runoff water were 98 ± 11% for ethalfluralin, 117 ± 9% for chlorothalonil, and 88 ± 8% metolachlor. No corrections for recoveries were made.

Calculations and Data Analysis. Runoff stage data were converted to flows using the flume rating equation (*37*):

$$Q = 0.00651 \times H^{2.58}$$

where Q is flow (L s^{-1}) and H is stage height (cm). Flows were then multiplied by the time segment that the flow measurement represented and then corrected for background flow due to simulated rainfall in the flume and collection trough. Similarly, chemical concentrations (mg L^{-1}) were multiplied by the volume of runoff represented by the samples taken for analysis (typically 10 min of runoff) and the results were summed to give total loads (masses) of chemicals transported in each runoff event. Load and concentration means and variances for chemicals (four observations each) were compared using standard F tests at the 5% level of significance using Excel (Microsoft Corp.) statistical functions.

RESULTS AND DISCUSSION

Some technical difficulties occurred. The peanut canopy was so full at the time of the 1999 summer rain that rain catch cups could not be used, and we used the nominal depth value of 5.0 cm in the calculations. One of four rhodamine runoff analytical data sets (plot B, 1998) was lost.

Visual Observations with Rhodamine. Rhodamine forms a vivid, ruby red solution in water, allowing visual observation of the dynamics of washoff and runoff. When applied to the

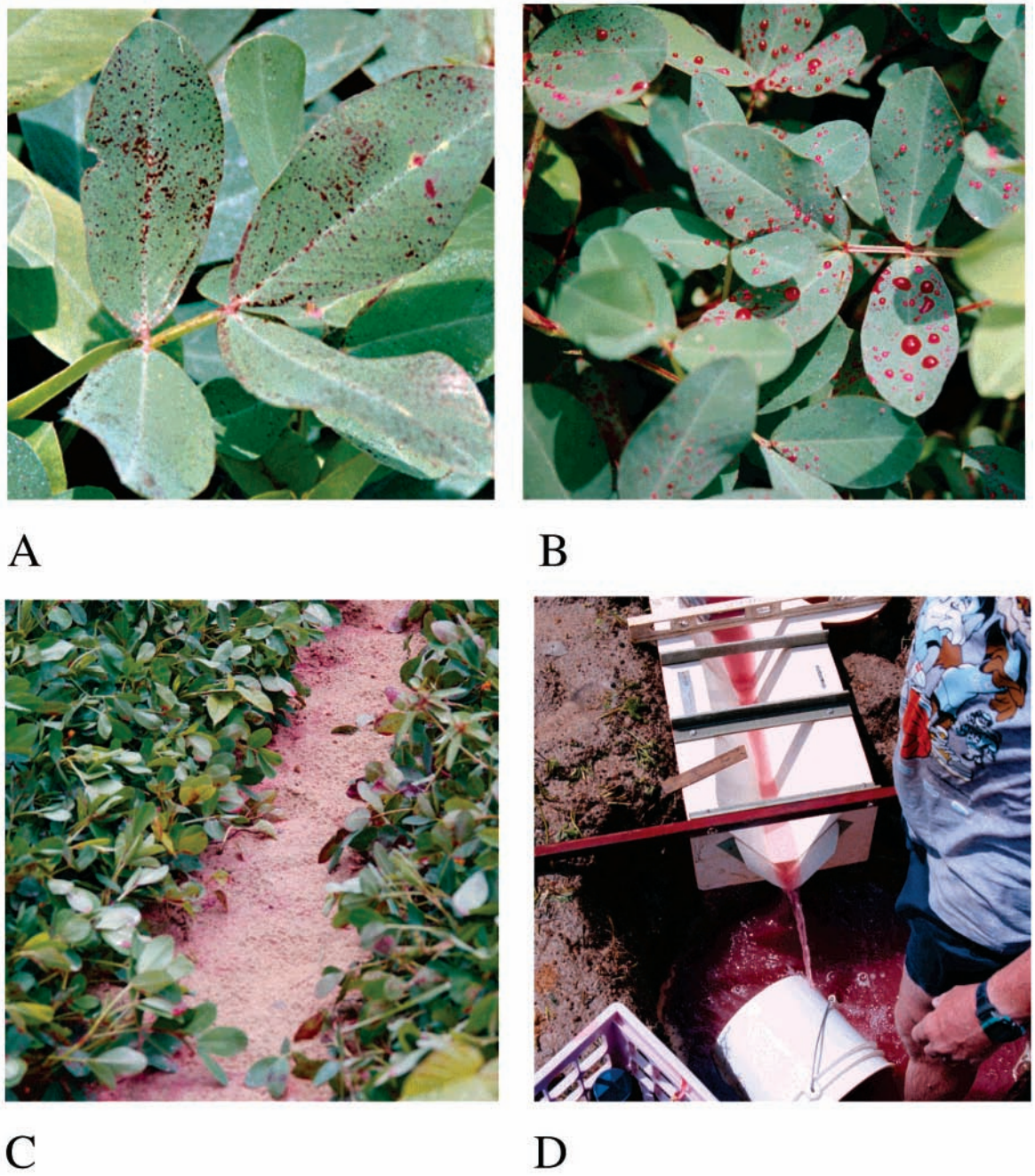


Figure 1. Visual observations with rhodamine WT dye. (**A**) Spray droplets after drying on peanut foliage. (**B**) Early raindrops colored by dissolving rhodamine WT. (**C**) Exposed soil between peanut rows, approximately 10 min after the start of rain; note the deeper dye color on the soil near plants in areas protected from rain D. (**D**) Rhodamine WT color in runoff water, observed throughout runoff event.

peanut canopy, rhodamine spray droplets dried within a few minutes to form small dark crystalline deposits (**Figure 1A**). When rainfall began, the rhodamine was instantly dissolved into water, coloring the first raindrops, which adhered to foliar surfaces (**Figure 1B**). On the basis of visual observation, this colored water was completely washed off the foliage within the first 10 min of rainfall. Similarly, the soil surface exposed to rhodamine spray immediately formed a reddish hue when first wetted with rain. This color disappeared within about 10 min, depending on the exposure to rainfall (**Figure 1C**). Thus, foliar and soil spray deposits of rhodamine appeared to be quickly washed into the soil and leached downward prior to the beginning of runoff.

It would be expected that as the rhodamine leached downward into the soil that concentrations available for runoff would decline as the chemical moved below the extraction zone. However, runoff water remained pink in color throughout the event (**Figure 1D**), and approximately steady state chemical losses for both chlorothalonil and rhodamine were apparent in the runoff sample analytical data throughout the event except at the end (**Figure 2**). We hypothesize that both washoff and leaching rates varied spatially within the plot: foliage and soil would be subjected to varying amounts of rain impact depending on their protection by higher foliage. This may have spread out the times of appearance of chemical at the edge of the plot as described by Leonard (*6*) and obscured the exponential decrease of chemical concentration in time usually observed in microplots.

Measured Rainfall and Runoff. Average catch cup data at positions across the transect for the six measured events are

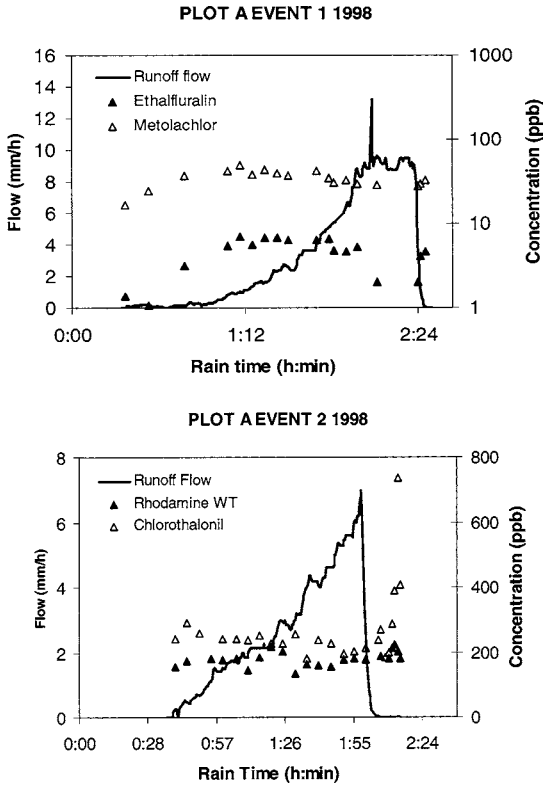


Figure 2. Hydrographs and chemical concentrations in typical first and second events (plot A, 1998). Note the scale differences in the concentrations and the surge in the chlorothalonil concentration after rainfall ceased.

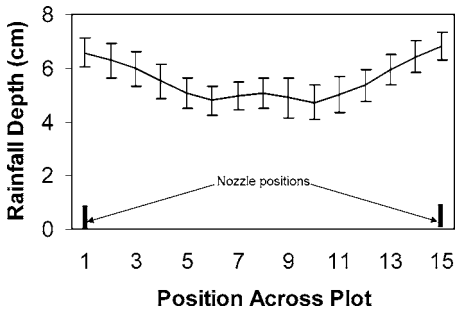


Figure 3. Rainfall depth as measured by catch cups; average of transects 1/4 and 3/4 the distance up the plot slope for six of eight events. The canopy prevented cup placement in 1999.

shown in **Figure 3**. These confirm the intensity pattern observed by Sumner et al. (*36*), in which intensity maxima occur near the sprinklers. Averages for upper and lower transects were not significantly different at the 5% level within plots, generally agreeing within 0.5 cm or less. The average rainfall for all events was 5.5 ± 0.5 cm, ranging from 5.0 to 6.4 with no significant differences ($P < 0.05$) between season, year, or plot averages (**Table 3**).

Runoff varied from 5 to 15% of rainfall and was correlated between replicate plots ($r = 0.88$), reflecting sensitivity to antecedent moisture and crop cover. There were no significant differences between runoff averages by plot, year, or presence of crop cover. This range of runoff responses is quite similar to results of previous mesoplot and microplot studies on these sandy soils (*38*, *39*). Rainfall events of this magnitude and intensity have a probability of occurrence of about once a year in this region. Forcing the storm to occur within 24 h after chemical application is considered a "reasonable worst-case" chemical runoff scenario (*16*).

Spray Rate Validation. Spray trap (Petri dish) results from the field experiments are shown in **Table 4**. These measured deposit amounts are used to calculate runoff losses as a fraction of applied amounts. The Petri dish deposit data were not normally distributed; extreme value or log-normal distributions generally gave better fits. Although (or perhaps because) the usual high variability in individual spray trap values was observed, the average calculated spray rates for all plots and years were not significantly different at the $P < 0.05$ level for all of the measured pesticides, except for metolachlor in the 2 years (**Table 4**). This is excellent spray application precision and accuracy between years and plots, in terms of average application rate. Average application rates found in the Petri dishes were 105 (118% in 1998 and 91% in 1999), 85, and 143% of nominal for metolachlor, chlorothalonil, and rhodamine, respectively.

Field Washoff Experiment. If we subtract the amounts of chlorothalonil and rhodamine found in the below-canopy traps from the above-canopy traps (**Table 4**), this is a measure of the amounts of spray intercepted by the plant tops. The results are 1.05 kg/ha for chlorothalonil and 2.5 kg/ha for rhodamine. If we assume a plant density of 215 000 plants/ha, these translate into 4.8 and 11.6 mg/plant chlorothalonil and rhodamine, respectively. The 4 L water extracts of these plants contained 3.2 (1998) and 4.4 (1999) mg/plant chlorothalonil and 3.4 (1998) and 5.8 (1999) mg/plant rhodamine. Thus, chlorothalonil

Table 3. Rainfall, Runoff, and Chemical Losses from Simulated Worst-Case Runoff Events on 0.045 ha Mesoplots: Chemicals Applied to Bare Soil and Mature Peanut Crop

			water runoff		chemical runoff					
					load			load		
year	plot	rain applied (cm)	total (mm)	max flow (L/s)	mass (g/ha)	fraction of appl. (%)	event avg. concn (ppb)	mass (g/ha)	fraction of appl. (%)	event avg. concn (ppb)
		event 1 (soil-applied chemicals)				metolachlor			ethalfluralin	
1998	A	6.4	7.01	1.20	2.0	0.07	29	0.34	0.04	5
	B	5.7	8.73	2.00	6.0	0.24	69	0.45	0.05	5
1999	A	5.6	3.76	0.86	6.6	0.33	185	0.41	0.05	11
	B	5.1	2.99	0.74	4.0	0.20	134	0.14	0.02	5
		event 2 (foliar-applied chemicals)				chlorothalonil			rhodamine	
1998	A	nm[b]	2.59	0.56	4.5	0.39	155	6.0	0.17	233
	B	nm[b]	3.56	0.65	5.7	0.46	140	11.4	0.32	320
1999	A	5.0	3.70	0.46	3.5	0.31	95	3.8	0.11	102
	B	5.6	5.97	0.52	15.5	1.32	260	3.5	0.08	59

[a] Nominal application rates were ethalfluralin, 0.84; metolachlor, 2.2; chlorothalonil, 1.3; and rhodamine, 2.1 kg/ha. [b] Not measured.

Table 4. Chemical Application Rates as Determined by Spray Traps and Recoveries of Chemical Washed off Foliage[a]

chemical	metolachlor	chlorothalonil	rhodamine WT
position of field spray traps	soil surface	below and above canopy	below and above canopy
amounts recovered in spray traps—field (kg/ha)	2.6 ± 0.5 (1998) 2.0 ± 0.2 (1999)	1.1 ± 0.4 above 0.05 ± 0.04 below	3.0 ± 1.3 above 0.5 ± 0.9 below
washoff amounts (mg/plant): before rain		3.2 ± 1.1 (1998) 4.4 ± 1.4 (1999)	3.4 ± 1.3 (1998) 5.8 ± 1.7 (1999)
washoff amounts (mg/plant): after rain		1.0 ± 0.4	0.36 ± 0.08 (1998A) 0.170 ± 0.003 (1998B) 0.9 ± 0.5 (1999)
% washoff[b]		69 (1998) 77 (1999)	92 (1998) 83 (1999)

[a] Within each column, year or plot values are reported separately if significantly different ($P < 0.05$). [b] Fraction of rates found in traps (above canopy minus below canopy values) and assuming 215 000 plants/ha.

washoff amounts found are similar to expected spray deposit amounts and indicate that washoff was nearly total. This was confirmed by the water extraction of plants after they had been exposed to rainfall: about 3/4 less chlorothalonil was found. Troiano and Butterfield (*27*) observed large chlorothalonil washoff fractions (50−67%) under 1 cm of simulated rainfall. Other studies have shown that highly insoluble pesticides can be relatively washable in the first day or so after application, probably because of the presence of formulation components, which promote suspension and solubilization. Examples include [solubility in mg/L (*40*), washability in %] EPN, 0.5 mg/L, 62% (*41*); fenvalerate, 0.002 mg/L, 50% (*28*); lactofen, 0.1 mg/L, 50−80% (*29*); and permethrin, 0.006 mg/L, 58% (*42*).

For rhodamine, amounts found in washings from prerain plants were only about half or less than expected, but these were reduced to near zero by rain in 1998 and to 0.9 mg/plant in 1999. In summary, (i) actual application rates, as determined by spray traps, were close to nominal for all chemicals; (ii) foliar residues of chlorothalonil were approximately in agreement with spray trap values, but rhodamine residues were half or less; and (iii) both rhodamine and chlorothalonil residues were essentially completely removed by water washing, either by rain or by immersion.

Chemical Runoff. Runoff loads of all chemicals were small. Losses of the two soil-applied herbicides (**Table 3**) were consistent with previous studies of incorporated and surface-applied herbicides (*6*, *7*). Ethalfluralin runoff has not been studied before, but results may be compared with trifluralin, which is also incorporated and has a solubility of 0.3 mg/L and K_{oc} of 8000 g/mL (*40*); losses of trifluralin under severe conditions have been 0.1−0.3% of the amounts applied (*6*, *7*). Metolachlor has been the subject of several runoff studies; under severe rainfall, losses have ranged from 1 to 12% (*43*−*45*). Thus, our losses are at the low end of other study results, probably because of our very sandy surface soil.

In comparison with the soil-applied herbicides, chlorothalonil and rhodamine lost larger fractions of applied amounts (**Table 3**), but these losses are still relatively small as compared to other chemicals under these severe conditions (*5*). Our sandy soil may be a general explanation, but the large microplot losses observed by Potter et al. (*21*) are on essentially the same soil. This raises the possibility of a plot scale effect (*15*, *46*, *47*).

Chlorothalonil fractional losses are significantly larger ($P < 0.05$) than rhodamine. This tends to support the hypothesis that the more rapidly dissolved rhodamine would be leached into the soil profile to a greater extent than chlorothalonil. Clearly, an experiment is needed in which the timing of washoff is compared with the timing of runoff during the rainfall/washoff/runoff process.

In terms of the overall pollution potential of these pesticides when used in peanut production, ethalfluralin does not appear to be susceptible to large runoff losses due to its soil adsorption properties and typical use pattern of soil incorporation. Metolachlor was more readily lost in runoff because it was applied to the soil surface. Chlorothalonil appears to be the most susceptible to runoff losses under worst-case conditions; it is perhaps fortunate that it is so quickly degraded on both foliage and soil in this climate (*32*, *33*). However, a large proportion of peanut acreage is treated with multiple applications of chlorothalonil. It is thus probable that a significant runoff of chlorothalonil may take place in any given season.

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LITERATURE CITED

(1) Frank, R.; Braun, H. E.; Holdrinet, M. V. H.; Sirons, G. J.; Ripley, B. D. Agriculture and water quality in the Canadian Great Lakes Basin: V. Pesticides use in 11 agricultural watersheds and presence in streamwater, 1975−77. *J. Environ. Qual.* **1982**, *11*, 497−505.

(2) Richards, R. P.; Baker, D. B. Pesticide concentration patterns in agricultural drainage networks in the Lake Erie Basin. *Environ. Toxicol. Chem.* **1993**, *12*, 13−26.

(3) Thurman, E. M.; Goolsby, D. A.; Meyer, M. T.; Kolpin, D. W. Herbicides in surface waters of the United States: The effect of spring flush. *Environ. Sci. Technol.* **1991**, *25*, 1794−1796.

(4) Wauchope, R. D.; Baker, D. B.; Balu, K.; Nelson, H. *Pesticides in Surface and Groundwater*; CAST Issue Paper No. 2; Council for Agricultural Science and Technology: Ames, IA, 1994.

(5) Burgoa, B.; Wauchope, R. D. Pesticides in runoff and surface waters. In *Environmental Behavior of Agrochemicals*; Roberts, T. R., Kearney, P. C., Eds.; Progress in Pesticide Biochemistry and Toxicology, Vol. 9; John Wiley & Sons: Sussex, United Kingdom, 1995; pp 221−255.

(6) Leonard, R. A. Movement of pesticides into surface water. In *Pesticides in the Soil Environment: Processes, Impacts and Modeling*; Cheng, H. H., Ed; Soil Science Society of America Book Series No. 2; Soil Science Society of America: Madison, WI, 1990; pp 303−349.

(7) Wauchope, R. D. The pesticide content of surface water draining from agricultural fields—A review. *J. Environ. Qual*. **1978**, *7*, 459−472.
(8) Fawcett, R. S.; Christensen, B. R.; Tierney, D. P. The impact of conservation tillage on pesticide runoff into surface water: a review and analysis. *J. Soil Water Conserv.* **1994**, *Mar*, 126−135.
(9) Laflen, J. M.; Baker, J. L.; Hartwig, R. O.; Buchele, B. F.; Johnson, H. P. Soil and water loss from conservation tillage systems. *Trans. Am. Soc. Agric. Eng.* **1978**, *21*, 881−885.
(10) Cole, J. T.; Baird, J. H.; Basta, N. Y.; Huhnke, R. L.; Storm, D. E.; Johnson, G. V.; Payton, M. E.; Smolen, M. D.; Martin, D. L.; Cole, J. C. Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. *J. Environ. Qual.* **1997**, *26*, 1589−1598.
(11) Patty L.; Real, B.; Gril, J. J. The use of grassed buffer strips to remove pesticides, nitrate and soluble phosphorus from runoff water. *Pestic. Sci.* **1997**, *49*, 243−251.
(12) Reddy, K. N.; Locke, M. A. Imazaquin spray retention, foliar wash-off, and runoff losses under simulated rainfall. *Pestic. Sci*. **1996**, *48*, 179−187.
(13) Baker, J. L.; Shiers, L. E. Wash-off characteristics of herbicides applied to corn residue. Presented at the American Society of Agricultural Engineering Winter Meeting, Chicago, 1985; Vol. 85, p 1519.
(14) Wauchope, R. D.; Williams, R. G.; Marti, L. R. Runoff of sulfometuron-methyl and cyanazine from small plots: Effects of formulation and grass cover. *J. Environ. Qual.* **1990**, *19*, 119−125.
(15) Truman, C. C.; Wauchope, R. D.; Sumner, J. G.; Gascho, G. J.: Hook, J. E.; Chandler, L. D.; Johnson, A. W. Slope-length effects on runoff and sediment delivery. *J. Soil Water Conserv.* **2001**, *56*, 249−256.
(16) Wauchope, R. D.; Graney, R. L.; Cryer, S.; Eadsforth, C.; Klein, A.; Racke, K. D. Pesticide runoff: Methods and interpretation of field studies. *J. Pure Appl. Chem.* **1995**, *67*, 2089−2108.
(17) Van Wesenbeeck, I. J.; Peacock, A. L.; Havens, P. L. Measurement and modeling of diclosulam runoff under the influence of simulated severe rainfall. *J. Environ. Qual.* **2001**, *30*, 553−560.
(18) Ma, Q. L.; Hook, J. E.; Wauchope, R. D.; Sumner, H. R.; Johnson, A. W.; Davis, J. G.; Gascho, G. J.; Truman, C. C.; Dowler, C. C.; Chandler, L. D. Surface transport of atrazine under conventional tillage corn: observations versus GLEAMS, Opus, PRZM2β and PRZM3 model simulations. *Soil Sci. Soc. Am. J.* **2000**, *64*, 2070−2070.
(19) Wauchope, R. D.; Truman, C. C.; Johnson, A. W.; Sumner, H. R.; Hook, J. E.; Dowler, C. C.; Chandler, L. D.; Gascho, G. J.; Davis, J. G. Fenamiphos losses under simulated rainfall: Plot size effects. *Trans. Am. Soc. Agric. Eng*. **2004**. *47*, 669−676.
(20) Ahuja, L. R. Characterization and modeling of chemical transfer to runoff. *Adv. Soil Sci.* **1986**, *4*, 149−188.
(21) Potter, T. L.; Truman, C. C.; Bosch, D. D.; Bednarz, C. W. Cotton defoliant runoff as a function of active ingredient and tillage. *J. Environ. Qual.* **2003**, *32*, 2180−2188.
(22) Caseley, J. C.; Coupland, D. Effect of simulated rain on retention, distribution, uptake, movement and activity of difenzoquat applied to *Avena fatua*. *Ann. Appl. Biol.* **1980**, *96*, 111−118.
(23) Cohen, M. L.; Steinmetz, W. D. Foliar wash-off of pesticides by rainfall. *Environ. Sci. Technol.* **1986**, *20*, 521−523.
(24) Pick F. E.; van Dyk, L. P.; de Beer, P. R. The effect of simulated rain on deposits of some cotton pesticides. *Pestic. Sci.* **1984**, *15*, 616−623.
(25) Smith, C. N.; Carsel, R. F. Foliar wash-off of pesticides (FWOP) model: Development and evaluation. *J. Environ. Sci. Health* **1984**, *B19*, 323−342.
(26) Sundaram, A. Effect of adjuvants on glyphosate wash-off from white birch foliage by simulated rainfall. *J. Environ. Sci. Health* **1990**, *B2*, 37−67.
(27) Troiano, J.; Butterfield, E. J. Effects of simulated acidic rain on retention of pesticides on leaf surfaces. *Phytopathology* **1984**, *74*, 1377−1380.
(28) Willis, G. H.; McDowell, L. L.; Southwick, L. M.; Smith, S. Washoff of ultralow-volume-oil-applied insecticides from cotton plants as a function of time between application and rainfall. *J. Environ. Qual.* **1992**, *21*, 373−377.
(29) Reddy, K. N.; Locke, M. A.; Bryson, C. T. Foliar wash-off and runoff losses of lactofen, norflurazon, and fluometuron under simulated rainfall. *J. Agric. Food Chem.* **1994**, *42*, 2338−2343.
(30) Wauchope, R. D.; Leonard, R. A. Maximum pesticide concentrations in agricultural runoff: a semiempirical prediction formula. *J. Environ. Qual.* **1980**, *9*, 665−672.
(31) Burgoa, B.; Wauchope, R. D. Pesticides in runoff and surface waters. In *Environmental Behavior of Chemicals*; Roberts, T. R., Kearney, P. C., Eds.; Progress in Pesticide Biochemistry and Toxicology Vol. 9; John Wiley & Sons: Chichester United Kingdom, 1995; pp 221−255.
(32) Brenneman, T. B.; Sumner, H. R.; Harrison, G. W. Deposition and retention of chlorothalonil applied to peanut foliage: Effects of application methods, fungicide formulations and oil additives. *Peanut Sci.* **1990**, *17*, 80−84.
(33) Potter, T. W.; Wauchope, R. D.; Culbreth, A. K. Accumulation and decay of chlorothalonil and selected metabolites in surface soil following foliar application to peanuts. *Environ. Sci. Technol.* **2001**, *35*, 2634−2639.
(34) Cook, S. M. F.; Linden, D. R. Use of Rhodamine WT to facilitate dilution and analysis of atrazine samples in short-term transport studies. *J. Environ. Qual*. **1997**, *26*, 1438−1440.
(35) Coody, P. N.; Lawrence, L. J. Method and system for conducting meso-scale rainfall simulations and collecting runoff. U.S. Patent 5,279,151, January 18, 1994.
(36) Sumner, H. R.; Wauchope, R. D.; Truman, C. C.; Dowler, C. C.; Hook, J. E. Rainfall simulator and plot design for mesoplot runoff studies. *Trans. Am. Soc. Agric. Eng.* **1996**, *39*, 125−130.
(37) ISCO, Inc. *Instruction Manual, Model 3220 Flow Meter*, *Part #60-3233-036*; ISCO, Inc.: Lincoln, NE, 1990; pp 2−7.
(38) Wauchope, R. D.; Sumner, H. R.; Truman, C. C.; Johnson, A. W.; Dowler, C. C.; Hook, J. E.; Gascho, G. J.; Davis, J. G.; Chandler, L. C. Runoff from a cornfield as affected by tillage and corn canopy: A large-scale simulated-rainfall hydrologic data set for model-testing. *Water Resour. Res.* **1999**, *35*, 2882−2885.
(39) Truman, C. C.; Williams, R. G. Effects of peanut cropping practices and canopy cover conditions on runoff and sediment yield. *J. Soil Water Conserv.* **2001**, *56*, 152−159.
(40) Hornsby, A. G.; Wauchope, R. D.; Herner, A. E. *Pesticide Properties in the Environment*; Springer-Verlag: NY, 1996.
(41) McDowell, L. L.; Willis, G. H.; Southwick, L. M.; Smith, S. Methyl parathion and EPN wash-off from cotton plants by simulated rainfall. *Environ. Sci. Technol*. **1984**, *18*, 423−427.
(42) Willis, G. H.; McDowell, L. L.; Smith, S.; Southwick, L. M. Permethrin and sulprofos wash-off from cotton plants as a function of time between application and initial rainfall. *J. Environ. Qual.* **1994**, *23*, 96−100.
(43) Southwick, L. M.; Grigg, B. C.; Gouss, J. L.; Kornecki, T. S. Atrazine and metolachlor in runoff during seasons of typical rainfall in southern Louisiana. *J. Agric. Food Chem.* **2003**, *51*, 5355−5361.
(44) Buttle, J. M. Metolachlor transport in surface runoff. *J. Environ. Qual.* **1990**, *19*, 531−538.
(45) Zhang, X. C.; Norton, L. D.; Hickman, M. Rain pattern and soil moisture content effects on atrazine and metolachlor losses in runoff. *J. Environ. Qual.* **1997**, *26*, 1539−1547.

(46) Nett, M.; Hendley, P. Designing effective runoff research studies: A review of lessons of scale. In *Pesticide Environmental Fate: Bridging the Gap Between Laboratory and Field Studies*; Phelps, W., Winton, K., Effland, W. R., Eds.; ACS Symposium Series, No. 813; American Chemical Society: Washingon, DC, 2002; pp 23−41.

(47) Steinheimer, T. R.; Ross, L. J.; Spittler, T. D. *Agrochemical Fate and Movement: Perspective and Scale of Study*; ACS Symposium Series 751; American Chemical Society: Washington, DC, 2000.

(48) Everts, C. J.; Kanwar, R. S. Evaluation of rhodamine WT as an adsorbed tracer in an agricultural soil. *J. Hydrol.* **1994**, *153*, 53−70.

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