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Loss of Herbicides in Runoff Water[1]

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Abstract. The loss of 2-methoxy-3,6-dichlorobenzoic acid (dicamba), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 4-amino-3,5,6-trichloropicolinic acid (picloram) in runoff water was determined with a gas chromatograph and bioassays. When determined 24 hr after application, losses of dicamba and picloram were greater from sod plots than from fallow plots while 2,4,5-T losses were about equal. Four months after application, losses of all herbicides averaged less than 1% of that lost 24 hr after application. The amount of picloram lost in a simulated rainfall of 0.5 inch varied with rate, but the percentage lost was the same. The slope of the plot and movement over untreated soil influenced the percentage of picloram lost. The maximum loss obtained for any herbicide was 5.5% and the average approximately 3%.

INTRODUCTION

THE movement of farm chemicals via surface water has received increasing attention in the past decade. Johnson *et al.* (3) studied the drainage effluent from irrigated land fertilized for rice (*Oryza sativa* L.) and cotton (*Gossypium sp.*) production and found sufficient nutrients in the effluent to cause significant growth of algae in downstream areas. Barnett *et al.* (2) found 2,4-dichloro-phenoxyacetic acid (2,4-D) esters to be lost much more readily than the amine salts in runoff from fallow soils. Studies on the fate of 2,4-D in natural surface waters showed that little of the herbicide was absorbed by soil particles in the water and that sunlight had little effect on its decomposition (1).

This paper presents results from experiments conducted to determine the amount of herbicide in the runoff from small plots following simulated rainfall.

EXPERIMENTAL METHODS

Two experimental sites were located approximately 10 miles west of College Station, Texas on an Irving clay loam soil. This soil is highly montmorillonitic with a pH of 7.5 and an organic matter content of 1.5 to 2.0%. The slope of one site was 3% and the other 8% as determined with a surveyor's level. Both sites were covered with sod, primarily bermudagrass (*Cynodon dactylon (L.) Pers.*), silver beardgrass (*Andropogon saccharoides Swartz*), and threeawn (*Aristida sp.*), approximately 2 inches high. The sod was destroyed on the fallow plots by plowing and disking to a depth of 4 to 6 inches. A trench 3 inches deep was dug around the periphery of each plot to facilitate the collection of runoff water. Plots were 10 by 10 ft and replicated three times in a completely randomized design.

Unformulated 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) was applied in dilute aqueous sodium hydroxide. Two-methoxy-3,6-dichlorobenzoic acid (dicamba) and 4-amino-3,5,6-trichloropicolinic acid (picloram) were applied in water as the dimethyl amine and potassium salts, respectively. All chemicals were applied in 1 gal of solution per plot. The herbicides were applied with a small hand sprayer uniformly over the plot at rates of 1 or 2 lb/A. In one experiment, only the upper half of 50% of the plots was treated so that the effect of movement over untreated sod could be determined. All plots received a simulated rainfall of 0.5 inch in an hr 24 hr after herbicidal application. The plots received a similar application of water approximately 4 months after herbicidal application. Rain-like droplets were produced by passing water through a spray nozzle with a 50-mesh screen in place but with the tip removed.

The runoff water was collected at the lowest corner of each plot in containers placed below the soil surface. The water was stored at 4 C until analyses were made. The amount of soil present in the runoff from fallow plots also was determined. There was insufficient soil in the runoff from sod plots to obtain a sample.

Moisture content of the surface 3 inches of soil at the time of simulated rainfall was determined as the weight lost by the soil after 5 days in a forced-air oven at 105 C.

Analyses were made with a Barber-Colman 5630 pesticide analyzer equipped with a Ra^{226} detector and a 6-ft spiral glass column packed with 10% DC200 on 100–200 mesh gas chrom Q. Injector, column, and detector temperatures were 260, 210, and 240 C, respectively. The carrier gas was nitrogen at a flow rate of 75 ml/min. Three 100-ml samples were taken from the runoff of each plot. Each sample was acidified with concentrated HCl and extracted with two 100-ml portions of ethyl ether. The ether extracts were combined and evaporated on a steam bath. After evaporating the ether, the picloram and 2,4,5-T samples were esterified with 5 ml of a borontrifluoride-methanol solution containing 0.125 g of borontrifluroide per ml methanol. To obtain quantitative esterification, picloram samples were heated until there was only enough methanol remaining to cover the bottom of the beaker (4). Since dicamba is not readily esterified by borontrifluoride, these samples were methylated by heating to near dryness with a diazomethane solution (5).

The methylated samples were dissolved in 10 ml of hexane and added to 10 ml of water in a 50-ml separatory funnel. The mixture was shaken vigorously and the water portion discarded. One µl of the hexane portion was injected into the chromatograph and the herbicide content determined by comparing the peak height produced by the sample to the peak height produced by known concentrations of herbicide. From the fallow plots, 20-g samples of eroded soil were analyzed by extracting with 100 ml of aqueous base, suction filtering, and then proceeding as with the aqueous samples.

[1]Received for publication January 26, 1968. Cooperative investigations of the Texas Agricultural Experiment Station and the Crops Research Division, Agricultural Research Service, U.S. Department of Agriculture.

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In addition to the chromatographic analyses, 100 ml of runoff water were applied to beans (*Phaseolus vulgaris L.*, var. Black Valentine); their subsequent growth was observed. Beans were grown in the greenhouse in commercial sand and were treated prior to the expansion of the first trifoliate leaf. The runoff water was sprinkled over the plants to simulate conditions of irrigation.

Results and Discussion

A 0.5-inch rain required the application of approximately 177 L of water per plot. Of this amount, about 15 L were recovered as runoff water. The runoff was slightly higher from sod plots than from fallow plots. The sod plots had not been cultivated for a number of years and the soil was extremely compact. The average moisture content in the surface 3 inches of soil was 16% at the time the rainfall was applied. Essentially all of the runoff occurred in the final 20 min of the watering process.

The efficiency of the extracting and methylating procedures for detecting dicamba, 2,4,5-T, and picloram was 78, 87, and 88%, respectively. Care was taken that the picloram samples did not go to complete dryness in the methylating process to prevent loss of the methylated sample.

The effect of slope, rate of application, and movement over untreated soil on the concentration of picloram in runoff water following a simulated rainfall is shown in Table 1. The concentration of herbicide varied with rate of herbicide applied, but the percentage lost was essentially the same for both rates. Although the percentage lost was greater from an 8% slope than from a 3% slope, the difference was not significant.

Table 1. Effect of slope, rate of application, and movement over untreated sod on the concentration of picloram in runoff water from Irving Clay Loam soil.[a]

Rate (lb/A)	% slope	Portion of plot treated	Picloram concn. in runoff water[b,c] (μg/ml)	Total Picloram in runoff (lb/A)
2	8	Entire	5.21	0.075
2	3	Entire	5.06	0.063
2	8	Upper half	2.11	0.032
2	3	Upper half	1.32	0.018
1	8	Entire	3.81	0.055
1	3	Entire	1.98	0.028
1	8	Upper half	1.49	0.021
1	3	Upper half	0.65	0.011
Check	3 & 8	0	0.00	0.000

[a]Applied as potassium salt in water equivalent to 400 gpa.
[b]Simulated rainfall applied at 0.5 inch/hr 24 hr after application of herbicide.
[c]Significance at the 5% level between the 2 lb/A entire plot and other rates. Also, significance between 2 lb/A upper half and 1 lb/A entire plot for the 8% slope.

The percentage of herbicide lost decreased when the runoff water passed over untreated sod. When the entire plot was treated at the rate of 1 lb/A, 0.055 lb/A of picloram was lost when the slope was 8%, and 0.028 lb/A when the slope was 3%. However, when the upper half of the plot was treated with 2 lb/A and the lower half remained untreated, the amount of picloram lost dropped to 0.032 and 0.018 lb/A for the 8% and 3% slopes, respectively. The data suggest that the distance between the treated area and the major water arteries is an important factor in determining the amount of herbicide which will enter the water sources.

A comparison of dicamba, 2,4,5-T, and picloram losses from fallow and sod plots is given in Table 2. A simulated

Table 2. Concentration of three herbicides in runoff water following a simulated rainfall of 0.5 inch/hr to an Irving Clay Loam having a 3% slope.

Herbicide	Soil cover	Herbicide concn. (μg/ml)[a] Time after application 24 hr[b]	4 mo	Total herbicide (lb/A × 10⁻³) Time after application 24 hr	4 mo
Picloram[c]....	Sod	2.17	0.027	31.00	0.41
Picloram....	Fallow	0.65	0.015	9.00	0.18
2,4,5-T[d].....	Sod	3.30	0.043	45.00	0.59
2,4,5-T......	Fallow	2.60	0.007	37.00	0.09
Dicamba[c]....	Sod	4.81	0.000	65.00	0.00
Dicamba....	Fallow	1.60	0.018	17.00	0.32
Check.......		0.00	0.000	00.00	0.00

[a]Two lb/A of picloram, 2,4,5-T, and dicamba applied as K, Na, and dimethylamine salts, respectively.
[b]In fallow plots picloram and dicamba were significantly lower than 2,4,5-T at the 5% level. In sod plots picloram and 2,4,5-T were significantly lower than dicamba at the 5% level.
[c]Significant at 5% level between sod and fallow plots in 24 hr runoff.
[d]Significant at 1% level between sod and fallow plots in the 4 months runoff.

rainfall of 0.5 inch in 1 hr 24 hr after herbicidal application resulted in a detectable loss of herbicides from both fallow and sod plots. In general, losses were greater from the sod plots. However, the loss from sod and fallow areas varied for each herbicide. The simulated rainfall removed more dicamba from the sod plots than picloram or 2,4,5-T. On fallow plots, we found more 2,4,5-T in the runoff than either of the other herbicides. Almost four times as much dicamba was found in runoff from sod as from fallow plots and more than three times as much picloram. The difference in amount of 2,4,5-T in runoff from sod and fallow plots was much less pronounced.

The herbicide adsorbed to soil particles in the runoff water was insignificant when compared to the herbicide lost in the water itself. Of course, this could change if the intensity of the rainfall was increased since soil movement then would become more pronounced. Under our simulated rainfall conditions, only 0.057 mg of picloram, 1.028 mg of 2,4,5-T, and 0.092 mg of dicamba were recovered from the eroded soil of the fallow plots. There was insufficient soil lost from the fallow plots to obtain a sample. The total herbicide lost varied from 0.065 lb/A of dicamba on the sod plots to 0.009 lb/A of picloram on the fallow plots.

Four months after herbicidal application, the plots were again subjected to simulated rainfall. Approximately 8.5 inches of natural rainfall occurred between the herbicidal application and the sampling date. Although there was still a detectable amount of herbicide in the runoff water (Table 2) from all treatments except dicamba on sod plots, losses averaged less than 1% of that in the runoff 24 hr after application. Losses of picloram and 2,4,5-T were still greatest from the sod plots, but the reverse was true for dicamba.

In general, bioassays with bean plants supported the chromatographic findings. There were sufficient amounts of all herbicides in 100 ml of runoff water obtained 24 hr after herbicidal application to kill or seriously alter the growth of black valentine beans. When determined 4