# Effect of Plot Size on Runoff of Herbicides and Suspended Sediment

L. M. Southwick<sup>1</sup>, J. L. Fouss<sup>1</sup>, and R. L. Bengtson<sup>2</sup> <sup>1</sup>Soil and Water Research Unit, Agricultural Research Service U.S. Department of Agriculture, 4115 Gourrier Ave., Baton Rouge, Louisiana <sup>2</sup>Department of Biological and Agricultural Engineering Louisiana State University Agricultural Center, Baton Rouge, Louisiana

# INTRODUCTION

In investigations and descriptions of the contribution of runoff from agricultural fields to nonpoint source pollution problems, the effect of study area size on the applicability of results at the watershed and basin scale becomes an important concern. Spatial variability of rainfall and other weather factors, soil characteristics, topography, geology, vegetation, and drainage patterns lead to uncertainties when applying results from field and small plot studies to larger geographical areas (Bailey and Swank 1983; Smith et al. 1985).

Baker and coworkers (Richards and Baker 1993) have made the following observations with regard to pesticide concentration patterns in the Lake Erie Basin: peak observed concentrations increase as watershed size decreases; and the average length of time during which intermediate pesticide concentrations are continuously exceeded tends to increase with watershed size. These workers assert that scale effects are to be expected down to the plot scale. An additional scale effect that has been reported is that sediment yield (sediment/unit area) decreases as watershed size increases (Johnson and Moldenhauer 1970; Gottshalk 1964).

#### FIELD METHODS

Since 1985 we have been studying runoff of various herbicides and insecticides, nitrate, and suspended sediment from fields planted to corn. Our early work was performed on 2- to 4-ha plots (Southwick et al. 1990b); since 1994 we have made investigations on 0.2-ha study areas (Willis et al. 1991). The earlier work was done on Commerce clay loam, a Mississippi River alluvial soil graded to 0.1% slope; the later studies were conducted 0.2-0.5 km away on Commerce silt loam graded to 0.2 % slope. This work has been conducted on plots with and without subsurface drains. Table I lists relevant properties of the chemicals treated in this paper.

#### OBJECTIVES

In this paper we compare/contrast runoff of herbicides and suspended sediment to test for trends that might be due to the differences in plot sizes in our field work.

-120-

We look at results for atrazine and metolachlor in runoff from 4.4-ha plots in 1987 (Southwick et al. 1990b) and from 0.21-ha plots in 1995 (Southwick et al. 1997a) and 1996. We also compare/contrast runoff of trifluralin from the 4.4-ha plots in 1992 (Southwick et al. 1997b) with results for pendimethalin from the 0.21ha plots in 1996. We discuss the suspended sediment in runoff in these studies (Southwick et al. 1997a; Bengtson et al. 1998). We consider here results only from plots without subsurface drains. In our comparisons we also assess the size of an "elemental area" (Huggins and Burney 1982) in these field studies.

# **RESULTS AND DISCUSSION**

# Concentrations of Atrazine and Metolachlor in Runoff

Disappearance of pesticides from soil usually shows an exponential decrease with time and often approximates to first order kinetics. These kinetics are properly called pseudo first order, since the mechanism of disappearance is a complicated combination of physical and chemical processes such as irreversible sorption to the soil, volatilization, leaching, runoff, and chemical and microbiological decomposition (Benson 1960; Guenzi 1974; Sawhney and Brown 1989; Cheng 1990). Similarly, concentrations of pesticides in runoff diminish exponentially with time, corresponding to the decrease in concentration in the runoff-active zone of the soil (Leonard et al. 1979).

Our field studies with atrazine have routinely shown that the concentration of this herbicide in runoff quickly drops with increase in elapsed time after application (Figure 1). This disappearance of atrazine in runoff closely fits modified first order decay curves (Table II). These equations predict that at t = 0, the initial concentration is (a + b)  $\mu$ g/L; k is the modified first order rate constant. As t increases, these equations predict that  $C_{ro}$  approaches (a)  $\mu g/L$ . The equations allow calculation of  $DT_{50}s$  (50% disappearance times) for the chemical in runoff. Runoff DT<sub>50</sub> values in Table Il correspond to soil DT<sub>50</sub>s of 35 (Southwick et al. 1990a [1987]), 18 (Southwick et al. 1997a [1995]), and 15 (Southwick et al. 1998 [1996]) days. In our field work, we observe that DT<sub>50</sub> (runoff conc.) < DT<sub>50</sub> (soil conc.).

This observation is reasonably presumed to be due to rapid leaching of the runoff-available residue to just below the runoff extraction zone (Leonard 1990; Leonard and Wauchope 1980; Southwick et al. 1998) but not as quickly below the zone removed in soil sampling procedures (in our case, usually the top 2.5 cm soil layer). The analyses reported in Table II yield identical rate constants k for 1987 and 1995; consequently, the  $DT_{50}$ s are the same for these two study seasons. Therefore, the plot size differences between these two studies did not influence the persistence of atrazine in runoff.

Similar to that of atrazine, our field work has revealed rapid decreases of metolachlor runoff concentration with time after application (Figure 2). The disappearance curves of Figure 2 fit modified first order equations (Table III) that provide  $DT_{50}$ s that are shorter than the respective soil  $DT_{50}$  values: corresponding metolachlor soil  $DT_{50}$ s were 20 (Southwick et al. 1990a [1987]), 29 (Southwick et al. 1997a [1995]), and 17 (Southwick et al. 1998 [1996]) days. As for atrazine in Table II, the metolachlor results of Table III show a similarity in rate constant k (and therefore in persistence in runoff) across plot size (1987 and 1996).

# Concentrations of Atrazine and Metolachlor in Runoff as Functions of Soil Concentrations

Leonard et al. (1979) developed a power equation, Y = 0.05X<sup>1.2</sup>, R<sup>2</sup> = 0.86, to describe the relation between runoff concentrations (Y) of various herbicides transported in the water phase and their respective soil surface concentrations (X). These investigators viewed the soil concentration coefficient to be an "extraction coefficient" and suggested that the greater distance from unity shown by the exponent reflected lower extraction efficiency with increasing time after application. Therefore, runoff extraction was more efficient early after application when soil concentrations were at their highest. Thus, when aged soil residues become more tightly bound or degraded, extraction becomes less efficient and hysteresis is observed (Koskinen and Harper 1990; Ma et al. 1993). We have related the runoff concentrations of atrazine (Figure 3) and metolachlor (Figure 4) to their respective soil surface concentrations and have developed power regression equations (Table IV) to describe these relationships.

The analyses of Table IV reveal a generally consistent statistically significant difference between the extraction coefficients b with respect to plot size and/or year. For both chemicals the extraction coefficient is lower with the smaller plot size (except for the 1995 atrazine value). For atrazine,  $b_{0.21} = 0.59b_{4.4}$ ; for

metolachlor,  $b_{0.21} = 0.40b_{4.4}$ . If these trends are due to the plot size differences, the longer runs of the larger plots before the samples passed through the sampling flumes conceivably could have led to increased extraction efficiency from the runoff-active zone of the soil. With the larger plots there is greater time for the herbicides to desorb from the soil. Figures 1 and 2 indicate that higher runoff concentrations of atrazine and metolachlor occur in the larger plots as a function of time after application. Another observation to make in Table IV is that extraction coefficients are consistently higher for atrazine than for metolachlor: the 10-fold differences (within same year, atrazine > metolachlor) seen in this table are consistent with the two-fold differences in K<sub>oc</sub>s (Table I, metolachlor > atrazine).

#### Trifluralin and Pendimethalin Yield in Runoff

In 1992, we studied runoff of the dinitroaniline herbicide, trifluralin. Our 1996 work considered runoff of another dinitroaniline, pendimethalin. Since both water solubilities (0.3 ppm) and Kocs (8000 mL/g, trifluralin; 5000 mL/g, pendimethalin) are the same or similar for the two compounds (Table I), we have compared the yield in runoff as a function of flow and have developed regression equations for these relationships (Table V). We express yield as percent of application since the dinitroaniline application rates for the two years differed slightly. The flow coefficient b (Table V) is statistically higher for the 1996 (0.21 ha)data than for the 1992 (4.4 ha) results (b<sub>0.21 ha</sub> = 1.86b<sub>4.4 ha</sub>). This higher coefficient for the smaller plots is consistent with the application difference between the two years -- incorporated in 1992 but not in 1996. Trifluralin and pendimethalin exhibit water solubilities and Kas (Table I) that favor association with sediment in runoff (Leonard 1990; Wauchope 1978): the greater coefficient b from the smaller plots also corresponds to the larger sediment yields from these plots (see below).

#### Sediment Yield in Runoff

From our 4.4 ha plots we have a series of years of monthly sediment yields in runoff. For a 9-year period, 1988-1996, we have calculated means and standard errors of the means (yields normalized with respect to flow, kg/ha/mm) for each of the months April, May, June (Table VI). We have also calculated the respective means and standard errors of sediment yields from the 0.21 ha plots for the 1995 season (mostly in May) and the 1996 season (mostly in April). The trend is toward higher sediment yields from the smaller plots. Averaging the Sediment Yield (Y)/Runoff Volume (V) for the respective plot sizes, we calculate  $(Y/V)_{0.21 ha} = 3.0(Y/V)_{4.4 ha}$ 

-121-

where Y is in kg/ha, and V is in mm. When ANOVA is used to compare the 1995 and 1996 4.4 ha data with the 0.21 ha results of the same years,

$$(Y/V)_{0.21 \text{ ha}} = 3.2(Y/V)_{4.4 \text{ ha}}$$

a difference significant at  $P \le 0.016$ . This greater yield of sediment from smaller plots translates to higher yields of sediment-associated chemicals from these plots.

# SUMMARY AND CONCLUSION

In this assessment of field data of the runoff of herbicides of both moderate and low water solubility, we have observed that this runoff shows trends variably assignable to plot size differences. From both plot areas of our studies, the water soluble compounds atrazine and metolachlor demonstrated rapid concentration declines with increasing time between application and the runoff event. When these runoff concentration data are regressed with time after application (Tables II and III), the resulting modified first order equations produce the same  $DT_{50}$ s across plot size. Regression of atrazine and metolachlor runoff concentrations against those of soil (Table IV) indicated more effective desorption from the soil in the larger plots.

The herbicides of low water solubility (trifluralin and pendimethalin) also show trends that are consistent with a plot size influence. The probability of this effect is enhanced since the observed trend (Table V) is in the same direction as that of sediment. But the issue is clouded by the fact that application differences (year effect) are also in line with the trends of Table V.

Sediment yield in runoff (Table VI) seems to show a definite trend attributable to plot size. In the analysis of these sediment runoff data, the three 4.4-ha data sets, each extending over a 9-year period, demonstrate a consistently lower runoff sediment yield compared to the two 0.21-ha studies. This difference stands when the 1995 0.21-ha data (collected mostly in May) are compared with the May 1995 4.4-ha data and when the 1996 smaller plot data (mostly from April) are compared with the larger plot data of April 1996.

Huggins and Burney (1982) assign to an elemental agricultural area the following characteristics: uniform soil type, constant vegetation cover, constant overall slope, and uniform distribution of precipitation. In our studies, these conditions are generally met at both plot size levels. The lack of a consistent trend attributable to plot size in our runoff data for atrazine and metolachlor points to a general similarity of the above plot characteristics across the areas of our studies, as these characteristics affect runoff of these compounds of high water solubility. The data do indicate that from soil of similar atrazine and metolachlor concentrations, larger concentrations result in a runoff event from the larger plot size. But a general breakdown in elemental area across the plot sizes in the work described in this paper shows up in our sediment data. The runoff of herbicides of low water solubility may suggest a plot size effect between the two areas of our studies with respect to these two chemicals.

The possibility of plot size effects on field results of studies of agricultural practices on water quality should always be of concern. But in many (probably most) cases, the conditions of an elemental agricultural area are not met. Thus, the results coming out of the Mississippi Delta Management Systems Evaluation Area (MD MSEA) generally cannot be assessed with respect to a plot size effect because of the variability in soil type, vegetation cover, slope, and precipitation across the various areas of this study. This variability is a result of the sizes of the individual study areas (small watersheds) and of the separation between the study sites.

#### ACKNOWLEDGEMENTS

The authors are grateful for the statistical assistance of Dr. David W. Meek, USDA, ARS, Ames, Iowa, and of Deborah L. Boykin, USDA, ARS, Stoneville, Mississippi.

# LITERATURE CITED

- Bailey, G.W., and R.R. Swank, Jr. 1983. Modeling agricultural nonpoint source pollution: A research perspective. p. 27-47. In F.W. Schaller and G.W. Bailey (ed.) <u>Agricultural management and water</u> <u>guality</u>. Ames, Iowa: Iowa State University Press.
- Bengtson, R.L., C.E. Carter, and H.F. Morris. 1998. Surface water quality from soybeans on shallow water table soils. p. 530-537. In L.C. Brown (ed.) <u>Drainage in the 21<sup>st</sup> century: food production and the environment</u>. St. Joseph, Michigan: American Society of Agricultural Engineers.
- Benson, S.W. 1960. <u>The foundations of chemical</u> <u>kinetics</u>. New York, New York: McGraw-Hill Book Company.
- Cheng, H.H. 1990. <u>Pesticides in the soil environment:</u> <u>Processes, impacts, and modeling</u>. Madison, Wisconsin: Soil Science Society of America, Inc.
- Gottschalk, L.C. 1964. Sedimentation. Part I. Reservoir sedimentation. p. 17-1 to 17-34. In V. T. Chow (ed.)

-122-

Handbook of applied hydrology. New York, New York: McGraw-Hill.

- Guenzi, W.D., Ed. 1974. <u>Pesticides in soil and water</u>. Madison, Wisconsin: Soil Science Society of America, Inc.
- Hornsby, A.G., R.D. Wauchope, and A.E. Herner. 1996. <u>Pesticide properties in the environment</u>. New York, New York: Springer-Verlag, Inc.
- Huggins, L.F., and J.R. Burney. 1982. Surface runoff, storage and routing. p. 169-225. In C.T. Haan, H. P. Johnson, and D.L. Brakensiek (ed.) <u>Hydrologic</u> <u>modeling of small watersheds</u>. St. Joseph, Michigan: American Society of Agricultural Engr.
- Johnson, H.P., and W.C. Moldenhauer. 1970. Pollution by sediment: Sources and the detachment and transport processes. p. 3-20. In T.L. Willrich, and G.E. Smith (ed.) <u>Agricultural practices and water quality</u>. Ames, Iowa: Iowa State University Press.
- Koskinen, W.C., and S. Harper. 1990. The retention process: mechanisMississippi. p. 51-77. In H.H. Cheng (ed.) <u>Pesticides in the soil environment:</u> <u>Processes, impacts, and modeling</u>. Madison, Wisconsin: Soil Science Society of America, Inc.
- Leonard, R.A. 1990. Movement of pesticides into surface waters. p. 303-349. In H.H. Cheng (ed.), <u>Pesticides in the soil environment: Processes</u>, <u>impacts, and modeling</u>. Madison, Wisconsin: Soil Science Society of America, Inc.
- Leonard, R.A., G.W. Langdale, and W.G. Fleming. 1979. Herbicide runoff from upland piedmont watersheds-data and implications for modeling pesticide transport. J. Environ. Qual. 8:223-229.
- Leonard, R.A., and R.D. Wauchope. 1980. The pesticide submodel. p. 88-112. In W.G. Knisel (Ed.), <u>Creams: A field scale model for chemicals</u>, <u>runoff, and erosion from agricultural management</u> <u>systems</u>. Washington, DC: U. S. Dept. of Agriculture.
- Ma, L., L.M. Southwick, G.H. Willis, and H.M. Selim. 1993. Hysteretic characteristics of atrazine adsorption-desorption by a Sharkey soil. <u>Weed Sci.</u> 41:627-633.
- Richards, R.P., and D.B. Baker. 1993. Pesticide concentration patterns in agricultural drainage networks in the Lake Erie Basin. <u>Environ. Toxicol.</u> <u>Chem.</u> 12:13-26.

- Sawhney, B.L., and K. Brown, Eds. 1989. <u>Reactions</u> and movement of organic chemicals in soils. Madison: Wisconsin: Soil Science Society of America, Inc.
- Smith, C.N., D.S. Brown, J.D. Dean, R.S. Parrish, R. F. Carsel, and A.S. Donigian, Jr. 1985. <u>Field</u> <u>agricultural runoff monitoring (FARM) manual</u> (EPA/600/3-85/043). Athens, Georgia: U. S. Environmental Protection Agency,
- Southwick, L.M., G.H. Willis, R.L. Bengtson, and T.J. Lormand. 1990a. Atrazine and metolachlor in subsurface drain water in Louisiana. J. Irr. Drain. Engin. 116:16-23.
- Southwick, L.M., G.H. Willis, R.L. Bengtson, and T.J. Lormand. 1990b. Effect of subsurface drainage on runoff losses of atrazine and metolachlor in southern Louisiana. <u>Bull. Environ. Contam. Toxicol</u>. 45:113-119.
- Southwick, L.M., G.H. Willis, J.L. Fouss, J.S. Rogers, and C.E. Carter. 1997a. Influence of water table management on runoff losses of soil-applied pesticides. p. 239-246. In B.J. Daniel (ed.) <u>Proceedings, 27th Mississippi Water Resources</u> <u>Conference</u>. Mississippi State University: Water Resources Research Institute.
- Southwick, L.M., G.H. Willis, O.A. Mercado, and R.L. Bengtson. 1997b. Effect of subsurface drains on runoff losses of metolachlor and trifluralin from Mississippi River alluvial soil. <u>Arch. Environ.</u> <u>Contam. Toxicol</u>. 32:106-109.
- Southwick, L.M., G.H. Willis, and J.L. Fouss. 1998. Water table control effects on leaching losses of soil-applied herbicides. p. 668-675 In L. C. Brown (ed.) <u>Drainage in the 21<sup>st</sup> century: Food production</u> <u>and the environment</u>. St. Joseph, Michigan: American Society of Agricultural Engineers.
- Wauchope, R.D.1978. The pesticide content of surface water draining from agricultural fields–a review. <u>J.</u> <u>Environ. Qual</u>. 7:459-472.
- Willis, G.H., J.L. Fouss, J.S. Rogers, C.E. Carter, and L.M. Southwick. 1991. System design for evaluation and control of agrochemical movement in soils above shallow water tables. p. 195-211. In R.G. Nash and A.R. Leslie (ed.) <u>Groundwater residue sampling design</u>. ACS Symposium Series 465. Washington, DC.: American Chemical Society.

-123-

Table I. Herbicide Properties\*

Herbicide	Sw	K₀∝	V <sub>p</sub>	t <sub>1/2</sub>	Ref.
Atrazine	33	100	2.9 x 10 <sup>-7</sup>	35	t, ‡
Metolachlor	530	200	3.1 x 10 <sup>-5</sup>	23	t. 1
Pendimethalin	0.3	5000	9.4 x 10 <sup>-6</sup>	55	t. 1
Trifluralin	0.3	8000	1.1 x 10 <sup>-4</sup>	31	†, §

\* S<sub>w</sub>, water solubility, mg/L; K<sub>oc</sub>, soil organic carbon sorption coefficient, mL/g; V<sub>p</sub>, vapor pressure, mm Hg; t<sub>1/2</sub>, soil half life, days.
† Hornsby et al., 1996; ‡ Southwick, et al., 1990a; ¶ Southwick et al., 1997a;

† Hornsby et al., 1996; ‡ Southwick, et al., 1990a; ¶ Southwick et al., 1997a; § Southwick et al., 1997b.



Figure 1. Concentration of atrazine in runoff.

Table II. Atrazine Concentration in Runoff Model: C<sub>ro</sub> = a + bexp(-kt) Parameters, and [95% Confidence Intervals]

Year	а	Ь	k	R <sup>2</sup>	DT <sub>50</sub> , days <sup>†</sup>
			<u>4.4 ha</u>		
1987	1.00	923	0.111	0.986	6.23
	[0.50, 1.50]	[705, 1210]	[0.101, 0.122]		[5.68, 6.89]
			0.21 ha		
1995	1.00	206	0.111	0.986	6.23
	[0.50, 1.50]	[164, 259]	[0.101, 0.122]		[5.68, 6.89]
996	1.00	397	0.193	0.986	3.59
	[0.50, 1.50]	[336, 470]	[0.175, 0.211]		[3.29, 3.95]

 $^{*}$  C<sub>ro</sub>, conc.,  $\mu g/L$ ; t, days after application.

<sup>†</sup> 50% Disappearance time.

-124-



Figure 2. Concentration of metolachlor in runoff.

# Table III. Metolachlor Concentration in Runoff<sup>•</sup> Model: C<sub>ro</sub> = a + bexp(-kt) Parameters, and [95% Confidence Intervals]

Year	a	b	k	R <sup>2</sup>	DT <sub>50</sub> , days <sup>†</sup>
			4.4 ha		
1987	0	1944	0.136	0.988	5.12
		[1598, 2364]	[0.122, 0.14	19]	[4.66, 5.6
			0.21 ha		
1995	14.7	1944	0.356	0.988	1.95
	[9.14, 20.32]	[1598, 2364]	[0.311, 0.40	0]	[1.73, 2.23
1996	14.7	232	0.136	0.988	5.12
	[9.14, 20.32]	[205, 263]	[0.122, 0.14	[9]	[4.66, 5.67

 $^{*}C_{ro}$ , conc.,  $\mu$ g/L; t, days after application.  $^{\dagger}$ 50% Disappearance time.

-125-

Table IV.	Atrazine and Metolachlor Concentration in Soil and Runoff"	
	Model: $C_{ro} = a + bC_s^3$	
	Parameters, and [95% Confidence Intervals]	

Year	ha <sup>†</sup>	а	b	R <sup>2</sup>
			Atrazine	
1987	4.4	0	0.0626	0.986
			[0.045, 0.080]	
1005	0.21	0	0.0874	0.085
1775	0.21	0	[0.0532, 0.122]	0.985
1996	0.21	0	0 0369	0.990
			[0.0317, 0.0422]	
			Metolachlor	
1987	4.4	-0.0326	0.00650	0.987
	[-0.0	0521, -0.01	32][0.0054, 0.0076]	
1995,	0.21	0.0159	0.00260	0.990
1996	[0.0]	034, 0.028	4] [0.00230, 0.00289]	

<sup>&</sup>lt;sup>\*</sup> C<sub>ro</sub>, runoff conc.,  $\mu$ g/L; C<sub>s</sub>, soil conc.,  $\mu$ g/kg. <sup>†</sup> Plot size, ha.



Figure 3. Concentration of atrazine in soil and runoff.

-126-





Table V. Yields of Trifluralin (1992) and Pendimethalin (1996) in Runoff \* Model:  $Y = a + bV^{1/2}$ Parameters, and [95% Confidence Intervals]

Year	ha	a	b	R <sup>2</sup>
1992	4.4	-0.0104 [-0.0150, -0.0058]	0.00412 [0.00329, 0.00495]	0.987
1996	0.21	-0.0140 [-0.141, -0.0139]	0.00765 [0.00522, 0.0101]	0.826

\* Y, herbicide yield, % of appl.; V, runoff flow, mm.

Table VI. Sediment Yield/Runoff Flow \*

Year	N	Yield/Runoff Volume <sup>†</sup> kg/ha/mm
	4.4	1 ha
1988-96, April	14	$10.0 \pm 1.6$
1988-96, May	12	$15.6 \pm 3.4$
1988-96, June	13	$16.5 \pm 2.6$
	0.2	21 ha
1995, 33 days	16	$41.6 \pm 6.3$
1996, 41 days	32	$41.4 \pm 4.7$

\* 4.4 ha, 2 reps; 0.21 ha, 4 reps. † mean ± standard error of the mean.

