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Formulation and Tillage Effects on Atrazine and Alachlor in Shallow Ground Water in Upland Corn Production

S. Smith, Jr.,[1] R. M. Johnson,[2] A. B. Pepperman[2]

[1] Water Quality and Ecological Processes Research Unit, USDA-ARS-National Sedimentation Laboratory, 598 McElroy Drive, Post Office Box 1157, Oxford, MS 38655-1157, USA
[2] Commodity Utilization Research Unit, USDA-ARS-Southern Regional Research Center, 1100 Robert E. Lee Boulevard, Post Office Box 19687, New Orleans, LA 70179, USA

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Only in about the last decade has agrichemical leaching to ground water been considered an important component of agricultural nonpoint-source pollution. Just more than a decade ago, it was assumed that pesticides would not leach to underlying ground water (Bouwer, 1990). However, ground water quality surveys conducted during this decade have revealed the contamination of some U. S. aquifers with both inorganic and organic compounds, several of which are agrichemicals (Williams et al., 1988). Some current agricultural practices appear to have adverse impacts on ground water quality and among those practices being questioned is conservation tillage (U. S. Department of Agriculture, 1989). Conservation tillage (especially no-till, NT) is generally considered to be a best management practice (BMP) for improving surface water quality by reducing agrichemical losses via runoff (Bailey and Wadell, 1979; Kenimer et al., 1987; Christensen et al., 1993). Estimates are that by the year 2000, 60-90% of U.S. farmland will be under NT or some other form of conservation tillage (Crosson, 1981; U. S. Department of Agriculture, 1988). In a 3-year study comparing 8 conventional-till (CT) and 14 NT watersheds in Ohio, runoff losses of both atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and simazine [2-chloro-4,6-bis(ethylamino)-1,3,5-triazine] were lower from the no-till systems (Triplett et al., 1978). Glenn and Angle (1987) also reported reductions in runoff losses of atrazine and simazine from a NT corn (*Zea mays L*) watershed compared to a CT corn watershed. Similar results were reported by others and were attributed to reduced seasonal runoff volumes under NT conditions (Edwards et al., 1980). In a recent report on BMPs to reduce runoff of pesticides in surface water, Christensen et al. (1993) concluded that "controlled studies have shown that the use of conservation tillage systems has usually reduced pesticide runoff." However, they also noted exceptions including Baker and Johnson (1979) and Sander et al. (1989) who reported increases in pesticide losses in runoff for NT compared to CT. Still others have reported that conservation tillage had no effect on runoff losses of pesticides (Logan, 1990; Smith, 1992). Wauchope (1987) pointed out that the results and conclusions of several recent studies on the effects of tillage on runoff and leaching losses of pesticides are generally inconsistent and often contradictory. Logan et al. (1991) believe that these inconsistencies probably result from differences in the hydrologic response of the soils studied.

Correspondence to: S. Smith, Jr.

In conservation tillage systems, the generally higher infiltration rates and the increased initial use of pesticides, particularly herbicides, increase the potential for agrichemicals to leach below the root zone. To what extent this actually increases pesticide levels in ground water has only recently come under investigation. For example, Isensee and Sadeghi (1992) reported increases in herbicide concentrations in soil (4-12") in NT plots compared to CT plots. In addition, Smith (1992) and Smith et al. (1994) reported that herbicide movement into the soil profile was greater in a NT system than in a CT system. These studies were all conducted with conventional (emulsifiable concentrate, EC) formulations of herbicides. In an attempt to enhance herbicide performance/efficacy in field situations and perhaps reduce losses from areas of application via leaching and volatilization, various types of alternate formulations have been produced and tested over the last couple of decades. One of these has been termed "controlled-release" (CR). According to Lewis and Cowsar (1977), CR formulations in general provide improved ease and safety in handling, require lower application rates (for active ingredients), and reduce leaching potentials. For example, Pepperman and Kuan (1993) reported that a granular CR alginate formulation of metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one, Lexone™) greatly reduced the release rate of metribuzin compared to a conventional EC formulation. Similar studies were conducted with the herbicide dichlorobenil (2,6-dichlorobenzonitrile) using both alginate and carboxymethylcellulose CR formulations (Connick et al., 1984).

Ground water contamination is not yet considered to be a major problem in the state of Mississippi. However, the State's ground water is very susceptible to contamination because of the very permeable soils in many areas, relatively shallow depth to ground water, and high average annual rainfall. Only limited research has been conducted in the State concerning agrichemical movement in shallow ground water. This is especially true of the loessial uplands of north Mississippi with its restrictive layer soils. Thus, the purpose of this study was to compare the movement in shallow ground water of atrazine and alachlor (2-chloro-2′,6′-diethyl-*N*-methoxymethylacetanilide), each applied in two different formulations (EC and CR), in upland corn production under two tillage practices (NT and CT).

MATERIALS AND METHODS

The study was conducted at the North Mississippi Branch of the Mississippi Agricultural and Forestry Experiment Station located at Holly Springs, Mississippi. The soil at the study site (Loring silt loam, *Typic Fragiudalf*) is a loess with a genetic fragipan (restrictive layer) at about 0.5m. In 1992, 12 hydrologically-isolated plots (4m x 4m) were established and instrumented to collect shallow ground water from observation wells (at depths of 0.30, 0.46 and 0.91m in each plot). Shallow ground water sampling was similar to that previously described (Cullum et al., 1992) and occurred after each rainfall event. The experimental design was a randomized complete block with 4 treatments (two tillages, NT and

CT and two herbicide formulations, EC and CR), each with three replications.

In late April 1993, early May 1994, and mid-May 1995, nominal rates of atrazine (Aatrex™ 4L) at 1.12kg a.i./ha and alachlor (Lasso™ 4L) at 2.24kg a.i./ha were applied broadcast by ground equipment (CO_2-pressurized small plot sprayer) to two (one CT and one NT) of the 4 plots in each block for preemerge weed control. Simultaneously, the other two plots (one CT and one NT) in each block received a broadcast application of an alginate CR formulation of atrazine (1.5% a.i.) and alachlor (1.6% a.i.) at the same rate. The CR formulations were prepared by a method similar to that of Pepperman and Kuan (1993), to contain 1% Na-alginate (Kelgin MV, Kelco, Division of Merck and Company, San Diego, CA), 10% kaolin (Thiele Kaolin Company, Wrens GA), 0.5% TWEEN 20® (Sigma Chemical Company, St. Louis, MO), 4% linseed oil, and technical grade atrazine or alachlor. On the same day, corn (Pioneer 3157, F14) was planted by hand to each plot (6 seeds per meter of row length, 1m row spacing). Two of the four plots in each block were thoroughly disked via rototiller just prior to herbicide application and corn planting. These were designated CT. The other two plots in each block were left undisturbed prior to herbicide application and corn planting. These were designated NT. Also, on the same day, granular fertilizer (13-13-13) was applied at 560 kg ha^{-1} based on soil test recommendations. In late May, the corn was side-dressed with pelletized NH_4NO_3 at 224kg/ha. Observation wells were covered during all herbicide and fertilizer applications. The CT plots were cultivated twice via rototiller at about 4 and 6 weeks after corn planting. *Note: All plots had received a "burndown" application of paraquat dichloride (1,1'-dimethyl-4,4'-bipyridylium dichloride, Gramoxone™) about 2 weeks prior to herbicide application and corn planting.*

Preparation of runoff and shallow ground water samples for pesticide analyses was similar to that previously reported (Smith et al., 1991; Smith, 1992). Methodology involved extraction by sonication with EtOAc and drying of EtOAc extract over anhydrous Na_2SO_4, followed by volume reduction for gas chromatographic analysis. Tracor model 540 gas chromatographs were equipped with J & W DB1 megabore columns (15m x 0.53mm i.d. x 1.5μm film thickness), dual ^{63}Ni electron capture detectors, a flame photometric detector, a nitrogen-phosphorus detector, and Dynatech Precision GC-411V autosamplers to facilitate unattended injection of samples. A PE Nelson 2700 chromatography data system consisting of three model 970 interfaces, Turbochrom 3.3™ software, and a microcomputer with color printer, was used for automated quantification and reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample. Gas chromatograph inlet, column oven, and detector temperatures were 240, 180, and 350°C, respectively, with a column flow rate of 6.5 cc/min helium. Limits of detection were 0.05-0.5ppb depending upon the pesticide. Under these conditions, retention times were 3.07and 5.66min for atrazine and alachlor, respectively. Mean extraction efficiencies, based on fortified samples, were >90% for both herbicides.

Weed assessments were made each year in all 12 plots at about 4 weeks after planting and immediately prior to the first cultivation of the CT plots. This was accomplished by counting the emerged weed seedlings within 3 randomly selected 0.5m X 0.5m areas within each plot.

RESULTS AND DISCUSSION

Throughout each crop year (planting through harvest), shallow ground water concentrations of atrazine and alachlor decreased with increasing time after application (Table 1). In crop year 1993, there were five ground water producing rainfall events (i. e. sufficient rainfall to result in water in sampling wells) with a total rainfall of about 22cm. The first three events occurred within three weeks after herbicide application and each were the result of about a 2-3cm rainfall. The highest herbicide concentrations in shallow ground water occurred in the NT-EC plots at 11 days after application, reaching values of 125 and 254μg/L (ppb) for atrazine and alachlor, respectively. For the first three ground water producing rainfall events (i.e. up through 19 days after herbicide application), the EC formulation produced higher concentrations (mean of about 4.6 times) in shallow ground water compared to the CR formulation. For the last two events (i.e. 105 and 157 days after application), the concentrations were either about the same for all treatments or slightly higher for the CR formulation. There was a trend toward faster and more extensive dissipation with the EC formulation compared to the CR formulation. With regard to tillage effects, concentrations were generally higher (about 1.2-1.8 times) in the NT plots compared to the CT plots for the EC formulation, but were about the same for the CR formulation.

Four ground water producing rainfall events occurred in crop year 1994. In contrast to crop year 1993, these events were all within about 7 weeks (i.e. 49 days) after herbicide application and about 18cm rainfall occurred. However, herbicide concentrations and dissipation trends were quite similar to those in 1993. Again, highest concentrations in shallow ground water occurred in the NT-EC plots, reaching levels of 127 and 241ppb for atrazine and alachlor, respectively. During the first 35 days after application, concentrations in the EC plots averaged about 3.2 times those in the CR plots. As with the previous crop year, concentrations were generally higher in the NT plots compared to the CT plots for the EC formulation, but were about the same for the CR formulation. In addition, dissipation was faster and more extensive in the EC plots, especially for alachlor. Concentrations in the CR plots remained nearly constant for the first 49 days as they did for the first 19 days in 1993.

Crop year 1995 also had four ground water producing rainfall events. These occurred during the first 84 days after herbicide application and were the result of a total of about 21cm rainfall. Atrazine and alachlor concentrations reached

Table 1. Concentrations of atrazine and alachlor in shallow ground water

Date	Time after application (day)	Rainfall (mm)	Cumulative rainfall (mm)	Mean Concentration($\pm$SD) (ug/L)[a] Atrazine				Alachlor			
				NT-EC	NT-CR	CT-EC	CT-CR	NT-EC	NT-CR	CT-EC	CT-CR
Crop year 1993											
4/27/1993	4	25	25	113(17)	28(2)	75(9)	21(3)	229(23)	41(4)	185(24)	30(7)
5/4/1993	11	30	55	125(15)	24(3)	70(8)	22(3)	254(32)	47(6)	188(19)	33(4)
5/12/1993	19	25	80	98(9)	31(4)	59(7)	20(4)	187(21)	39(5)	171(15)	29(7)
8/6/1993	105	79	159	15(1)	19(4)	8(3)	17(4)	23(3)	22(3)	19(5)	21(3)
9/27/1993	157	63	222	3(1)	11(5)	5(2)	10(3)	3(1)	13(2)	4(1)	11(4)
Crop year 1994											
5/9/1994	3	23	23	127(20)	30(5)	88(12)	29(4)	241(31)	39(9)	222(35)	49(7)
6/7/1994	32	54	77	77(11)	33(4)	41(9)	32(4)	159(23)	44(8)	138(23)	45(8)
6/10/1994	35	67	144	80(9)	33(5)	40(5)	33(7)	161(31)	47(9)	145(19)	50(7)
6/24/1998	49	40	184	59(7)	22(4)	21(3)	35(8)	52(8)	38(5)	39(22)	41(4)
Crop year 1995											
5/17/1995	2	18	18	135(17)	41(8)	108(19)	38(9)	255(21)	58(11)	243(24)	49(5)
5/19/1995	4	35	53	141(11)	45(7)	104(12)	47(7)	268(19)	57(8)	254(19)	55(7)
6/1/1995	17	44	97	124(9)	39(5)	98(8)	43(7)	239(15)	51(7)	233(12)	44(8)
8/7/1995	84	117	214	43(7)	19(3)	15(4)	22(3)	25(4)	35(4)	30(9)	31(4)

[a]Per plot over all well depths

maximum values of about 141 and 268ppb, respectively, at 4 days after application (again in the NT-EC plots). Trends in concentrations of the two herbicides in shallow ground water were quite similar to those in 1993 and 1994. During the first 17 days after application, concentrations in the EC plots averaged about 3.8 times those in the CR plots. Also during this first 17-day period, concentrations in shallow ground water remained fairly constant for both formulations; similar to the nearly constant concentrations during the first 19-day period in crop year 1993.

It should be noted that shallow ground water collected from these 12 plots a few weeks prior to the beginning of each crop year did not contain any detectable levels of atrazine or alachlor.

Weed counts in the EC plots averaged about 2.8, 3.0, and 3.8 times those in the CR plots in 1993, 1994, and 1995, respectively (Table 2). Counts in 1995 were lower than in the previous two crop years. Main weed species in all three years were signalgrass (*Brachiaria* spp.) and Johnsongrass (*Sorghum halepense*).

Table 2. Weed control assessment

Crop year	Mean Weed Count ($\pm$SD)[a]			
	NT-EC	NT-CR	CT-EC	CT-CR
1993	25(5)	11(2)	29(4)	9(3)
1994	36(9)	12(3)	33(7)	11(2)
1995	14(2)	5(1)	19(3)	4(1)

[a]Per 0.25 square meter per plot, n=9

Dissipation of atrazine and alachlor in soil and aqueous environments occurs mainly via chemical and/or microbial degradation (EXTOXNET, 1998; PPD, 1998; Royal Society of Chemistry, 1987). Within the same treatment and at the same time after application, the higher concentrations of alachlor compared to atrazine occurring in the shallow ground water (Table 1) were likely the result of the 2:1 application ratio of the two herbicides. Other contributing factors are the higher water solubility (242mg/L @ 25°C vs. 28mg/L @ 20°C) and lower organic carbon partition coefficient (124cm^3/g vs. 147cm^3/g) of alachlor compared to atrazine (EXTOXNET, 1998; PPD, 1998). The generally higher herbicide concentrations observed in the EC plots compared to the CR plots is the result of the controlled availability of atrazine and alachlor for leaching in the CR plots. Johnson and Pepperman (1995) conducted studies using uniformly ring-labeled ^{14}C atrazine and two soil series and reported reduced leaching potentials of atrazine from two alginate CR formulations (with and without linseed oil) compared with technical grade atrazine and the commercial formulation of atrazine (Aatrex™ 4L). In their research, they also reported that with the CR formulations, higher amounts of ^{14}C and parent atrazine (58-93%) remained in the soil surface horizon compared with technical grade atrazine (4.7-5.6%) and Aatrex™ (2.1-3.6%). In the present study, this latter finding helps explain the nearly constant concentrations of atrazine and alachlor observed in the shallow ground water of the CR plots in the few weeks during each crop year. Because the CR formulation was controlling the release rate of each herbicide from the formulation matrix, substantial and relatively uniform amounts of each herbicide were available in the surface soil horizon for leaching by rainfall, during the first few weeks after application. This also helps explain the lower weed counts in the CR plots compared to the EC plots (Table 2). In the plots with the EC formulation, much of the atrazine and alachlor leached out of the soil surface during the first few weeks after application and was unavailable to control weed seedlings near the soil surface. In order for CR formulations to be effective, they should maintain herbicide concentrations in the soil surface horizon for a critical time period, which they apparently did in the present study.

The higher concentrations observed in the NT plots compared to the CT plots are likely the result of conducting macropores. This finding was reported previously for larger corn plots adjacent to the small plots in the present study (Smith et al., 1994).

The data and results from the present study demonstrate the positive potential of CR formulations of some commonly used herbicides, namely, improved preemerge weed control with reduced movement in shallow ground water. A critical need exists for further development of this technology in terms of environmental/ecosystem impact, enhanced weed control, and economics of larger scale applications.

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Mention of a pesticide in this paper does not constitute a recommendation for use by the U S Department of Agriculture nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U S Department of Agriculture.

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