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Atrazine Loss in Runoff from No-Tillage and Chisel-Tillage Systems on a Houston Black Clay Soil

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ABSTRACT

Herbicide concentration and mass load of runoff depends, to a large extent, on soil management. This study was conducted to determine how tillage impacts herbicide losses in runoff from a vertisol soil on the Blackland Prairie of Texas. Atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] was applied at a rate of 2 kg a.i. ha^{-1} to a Houston Black clay soil (fine, montmorillonitic, thermic Udic Pellustert) in 1993 at the Blackland Research Center in Temple, TX. For 4 yr, the test area was under continuous management using a wide-bed system with a wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), and grain sorghum [*Sorghum bicolor* (L.) Moench] rotation. Tillage treatments consisted of no-tillage or chisel-tillage. All experiments were repeated four times. A rainfall simulator with an intensity of 12.5 cm h^{-1} was used to apply rainfall 24 h after the atrazine application. Sediment and runoff samples were collected during five time periods (from runoff initiation to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 40 min). No differences in atrazine concentrations were found among treatments in either the runoff water or sediment from any of the five time periods; however, crop residues prevented surface seal development and erosion resulting in reduced runoff and sediment losses. No-tillage treatments significantly reduced runoff and sediment yield, rather than the atrazine concentration of the runoff, resulting in a 42% decrease of the atrazine load in the runoff and a 77% decrease in atrazine associated with the sediment. As a percentage of the total amount applied, runoff accounted for <2% of the atrazine. Sediment-transported atrazine was much less important and represented <0.03% of the total amount applied.

HERBICIDES are an important component of zero and minimum tillage soil management systems. By using chemical weed control, mechanical weed control by tillage can be minimized and make no-tillage systems practical (Morrison et al., 1990). Although these systems can help reduce erosion and decrease energy inputs, the increased herbicide load is of concern with respect to nonpoint source pollution.

Many studies have shown reduced soil erosion and runoff volume with conservation tillage systems (Laflen et al., 1978; Potter et al., 1995). Herbicide runoff, however, is more complex; some studies have reported reduced transport with conservation tillage (Triplett et al., 1978; Wauchope, 1978), whereas others have reported increased transport (Gaynor et al., 1995; Sauer and Daniel, 1987). For example, Gaynor et al. (1995) observed a 30% increase in herbicide concentration in runoff with conservation tillage as compared with conventional tillage; however, uncontrolled environmental factors, such as timing and intensity of rainfall, were more important than tillage with respect to herbicide transport. If a herbicide is relatively insoluble and highly adsorbed to soil colloids, losses in the runoff and sediment may be reduced by conservation tillage systems (Daniel et al., 1989; Wauchope, 1978). Herbicide runoff for chemicals such as atrazine with somewhat greater solubilities (Erickson and Lee, 1989) and relatively small adsorption affinities (Clay and Koskinen, 1990; Weber, 1970) may be reduced, increased, or unchanged by reduced tillage systems (Gaynor et al., 1995; Glenn and Angle, 1987; Sauer and Daniel, 1987; Triplett et al., 1978).

In many studies, herbicide concentration in runoff was highest in those samples taken soon after runoff initiation, decreasing rapidly, and leveling off at a much lower concentration (Hall et al., 1983; Pantone et al., 1992; Wauchope and Leonard, 1980). Pantone et al. (1992) observed a strong fit between the atrazine concentration and the natural logarithm of the time after the rainfall began. Similarly, herbicide concentration is typically greatest in those rainfalls that occur soon after herbicide application, and the greater the period of time between application and the rainfall, the lower the concentration in the runoff (Baker and Johnson, 1979; Gaynor et al., 1992; Pantone et al., 1992; Triplett et al., 1978). Triplett et al. (1978) found a consistent relationship between the natural logarithm of herbicide concentration in runoff and the natural logarithm of the number of days after herbicide application.

Pesticide concentration is not the only index of pesticide runoff. Pesticide mass load, the total amount of pesticide transported, is also important. Often, short-term effects are best evaluated by concentrations; whereas, pesticide load can be a better estimate of the long-term biological consequences (Daniel et al., 1989). Pesticide concentrations are not necessarily correlated with pesticide loads (Baker and Johnson, 1979) as rainfalls that result in large volumes of runoff may tend to dilute the pesticide concentration, while maintaining or increasing the pesticide load. In a study by Kenimer et al. (1987), atrazine was applied in conventional and no-tillage systems, each with three residues levels (0, 750, and 1500 kg ha^{-1}). In both tillage systems, runoff and sediment losses decreased with increased residue cover. Interestingly, atrazine concentrations were higher with no-tillage but mass loads were less.

Although studies have indicated that most of the atra-

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zine mass load is transported in runoff rather than on sediment (Hall et al., 1972; Triplett et al., 1978), atrazine transport via sediment can be significant (Baker and Johnson, 1979). A significant amount of atrazine can be adsorbed to sediment, particularly in soils with high organic matter, and concentrations associated with sediment can exceed that of runoff (Hall, 1974). For a Barnes loam soil with 32.1 g organic C kg^{-1}, Pantone et al. (1992) reported that sediment-transported atrazine equaled or exceeded the load in the water phase, particularly in rainfalls that occurred a week or longer after herbicide application. If rainfall occurred soon after application, the bulk of the lost atrazine was transported in runoff.

One difficulty in determining the effect of conservation tillage on pesticide runoff is lack of replicated studies. Often different watersheds or fields are compared, and rainfall intensity and timing is not controlled (Baker and Johnson, 1979; Triplett et al., 1978). Rainfall simulator experiments (Baker et al., 1978; Gaynor and van Wesenbeeck, 1995; Haan, 1971; Meyer, 1960; Pantone et al., 1992) incorporating replicated small plot research techniques allow more precise control of rainfalls and are a practical alternative to relying on natural rainfall. Recently, a no-tillage soil management system was developed for the Blackland Prairie of Texas (Morrison et al., 1990). The objective of this research was to characterize the influence of wide bed no-tillage and chisel-tillage soil management systems on the concentration and mass load of atrazine in the surface water and sediment of a Houston Black clay soil. A rainfall simulator was used to control rainfall timing, intensity, and duration.

MATERIALS AND METHODS

Field Experimental Design and Sampling

Rainfall simulator studies were conducted in the field each week from 26 July 1993 to 20 Aug. 1993 on a Houston Black clay with <1% slope at the Blackland Research Center in Temple, TX. All treatments were replicated four times. This soil, a self-mulching vertisol, is one of the most common agricultural soils in the Blackland Prairie (Potter et al., 1995). The textural analysis for the soil was 48 g kg^{-1} sand, 390 g kg^{-1} silt, and 562 g kg^{-1} clay, and the organic C content was approximately 15 g kg^{-1}.

The test area had been under continuous management for 4 yr preceding the rainfall simulation experiment using the wide-bed system developed by Morrison et al. (1990). Under this system, raised beds were 1.5 m wide and 0.15 m high, and separated by 0.5 m furrows (Fig. 1). Prior to the pesticide runoff experiment, the site was in a wheat, corn, and grain sorghum rotation. The rainfall simulation experiment was conducted after the wheat harvest. Two tillage regimes, no-tillage and chisel-tillage, had been established. In the no-tillage system, the soil was not tilled and the soil and surface residues remained undisturbed except for reshaping bed shoulders every 3 yr. For the chisel-tillage system, beds were chiseled, tandem-disked, field-cultivator tilled, and reformed annually. The chisel plow had 80-mm concave shanks that were spaced 0.30 m and operated 15 cm deep. The chisel-tillage incorporated most of the residues, leaving some exposed to the surface, but anchored in the soil. Both tillage systems would be considered to be conservation-tillage because of minimized field trips and incomplete burial of residues. Before each rainfall simulation, the percentage of residue cover was measured using the number of interceptions by a 2 mm diameter rod at 100 different points along the rod, which was positioned along two diagonal transects. Soil cores to a depth of 10 cm were taken before the final rainfall simulation and used to estimate bulk densities at 2-cm increments.

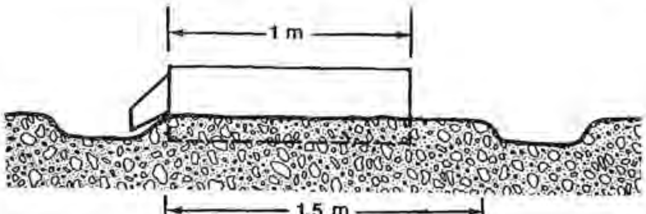

Fig. 1. Diagram of raised wide beds. A square metal frame surrounded the plot area, and the trough at one end was used to collect runoff and sediment samples.

A solenoid-operated, variable intensity rainfall simulator similar to that described by Miller (1987) was used. Plots (1 m^2) were delineated by driving a square metal frame 0.1 m deep into the soil. The frames were positioned at the edge of the raised beds so that runoff moving toward the furrow would flow out of the square frame through a trough (Fig. 1). The results of this study are applicable to field scale scenarios because in the wide-bed system water has to flow only a short distance from the raised beds to the furrow, after which transport out of the field is quite direct.

All plots were brought to a uniform water content 48 h prior to the rainfall by applying 12.5 cm of simulated rainfall so that sampling completed at various dates were not confounded with different soil conditions. The gravimetric water content of the soil was taken before and after rainfall to a depth of 10 cm at 2-cm increments. Twenty-four hours prior to the rainfall, atrazine was applied at a rate of 2 kg a.i. ha^{-1}. Simulated rainfall was applied to the plot and border area that covered 10 m^2 surrounding the plot. Water was delivered with a Spraying Systems HH30 WSQ wide square spray nozzle (Spraying Systems Co., Wheaton, IL) with an average dropsize diameter of 2.5 mm, kinetic energy of 230 J m^{-2} cm, and the flow rated at 12.5 cm h^{-1}. This rate of rainfall is equivalent to that of a 10-yr, 30-min rainfall (Hershfield, 1961). The electrical conductivity of the water was 0.6 dS m^{-1}, which is relatively low and equivalent to that used in similar rainfall simulator studies (Ben-Hur et al., 1995; Pikul and Aase, 1995).

Runoff and sediment were collected from each plot at five different intervals (from runoff initiation to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 40 min) during the rainfall. Runoff was collected in a trough at the edge of the plot and pumped to weighing tanks with peristaltic pumps. Runoff volume was calculated and recorded every five seconds with a Campbell 21X datalogger (Campbell Scientific, Logan, UT). Runoff subsamples were collected in 1 L amber glass bottles with Teflon seals for chemical analysis. Sediment was collected during each time interval from the trough connected to the metal frame surrounding the plots and later added to the suspended sediment that was filtered from the runoff. The sediment and water samples were stored at 4°C until analyzed.

Runoff Water and Sediment Analysis

Sediment suspended in the water was separated by filtration through a Whatman no. 40 filter paper on a Buchner funnel and added to the sediment previously collected from the trough connected to the metal frame surrounding the plots. Water

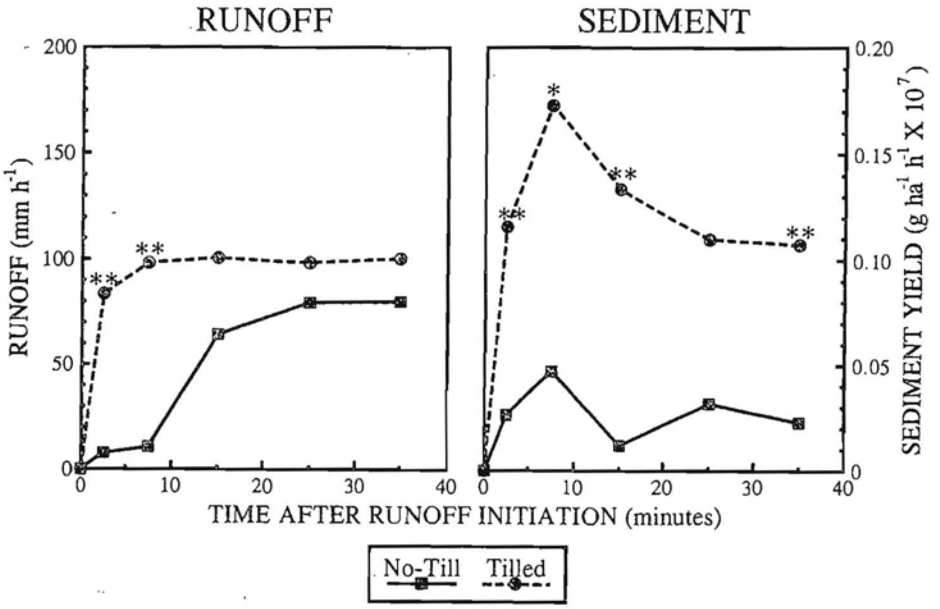

Fig. 2. **Runoff rates and sediment yields for five time intervals (from runoff initiation to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 40 min). Scale of the dependent axis for runoff is 1000× that for the sediment. Significant differences between no-till and tilled treatments for individual time intervals are indicated by * ($P < 0.05$) or ** ($P < 0.01$).**

samples were spiked with 100 µg tetrachloro-m-xylene and 100 µg dibutyl chlorendate as extraction surrogates. Atrazine was extracted three times from the runoff water in dichloromethane (100:6 water/dichloromethane) and extracts were dried by passing through 10 cm by 1 cm columns of anhydrous sodium sulfate followed by 50 mL of dichloromethane to rinse out the columns. Each extracted sample was concentrated to 5 mL on a 500 mL Kuderna-Danish apparatus with three Snyder columns followed by further concentration under a three ball micro column to a final volume of 1 mL. The 1 mL extracts were spiked with 20 µg each of a mixture of deuterated compounds (1,4-dichlorobenzene-d^{4}, napthalene-d^{6}, phenanthrene-d^{8}, chrysene-d^{10}, and perylene-d^{12}) to serve as internal standards.

Aggregate sediment samples were mixed with sodium sulfate, spiked with 100 µg tetrachloro-m-xylene and 100 µg dibutyl chlorendate as extraction surrogates and extracted with 1:1 hexane/acetone on a 250 mL Soxhlet apparatus for 18 h. Extracted solvents were concentrated to 1 mL as described above and spiked with the internal standards mixture.

Extracts were analyzed on a Varian 3400 GC-MS using an ion trap detector. Extracts were injected onto a 30 m 5% (phenyl)-methylpolysiloxane capillary column at 50°C that was then ramped at 10°C per min to 280°C and held until elution of the last internal standard. The data system provided peak confirmation by comparison of the mass spectra of the eluted peaks with standards that were themselves matched with the National Institute of Standards and Technology (NIST) mass spectra library. Extraction efficiencies of the atrazine averaged >80% for the water and sediment; reported concentrations and loads were corrected for extraction efficiencies.

Data Analysis

Differences due to tillage treatments were analyzed for significance by using *t* tests (SAS Institute, 1988) for runoff rates and sediment yields at each time interval. Similarly, *t* tests were used to determine the effect of tillage treatments on atrazine concentrations, atrazine losses, bulk densities, gravimetric water content, and residue cover. Atrazine loss was the product of the atrazine concentration and the runoff rate or sediment yield for the time interval. Atrazine mass loads were calculated by integrating the atrazine losses over the entire period of runoff. Pairwise *t* tests (Zar, 1974) were used to determine if differences in atrazine mass loads for the chisel-tillage and no-tillage treatments were significant.

RESULTS AND DISCUSSION

Runoff and Sediment Yield

Runoff and sediment yield were greater for chisel-tillage compared with no-tillage, especially for the earlier time intervals (Fig. 2). Later in the rainfall (15 to 35 min), differences between runoff rates of the chisel- and no-tillage treatments were less for the water phase. To a large extent, differences are a reflection of the residue cover, which averaged 30% for chisel-tillage and 99% for no-tillage treatments. The greater residue cover of the no-tillage plots would serve to intercept raindrops, limit surface seal development, maintain infiltration, decrease soil detachment, thereby decreasing sediment yield. In addition, no-tillage treatments resulted in significantly lower bulk densities (0.83 g cm^{-3} compared with 0.99 g cm^{-3} for the chisel-tillage) for the soil surface (0 to 2 cm depth) when measured before the rainfall. By limiting surface seal development, infiltration for the no-tillage treatment was maintained. Gravimetric water content of the top 2 cm for no-tillage plots after applying 12.5 cm of rainfall averaged 42%, but was not significantly different from the chisel-tillage plots which averaged 44% (Fig. 3). Therefore, changes in the soil surface rather than differences in antecedent water contents accounted for differences observed in the steady-state runoff between tillage treatments.

Relationships between increased plant residues due to no-tillage and decreased sediment yield have been well

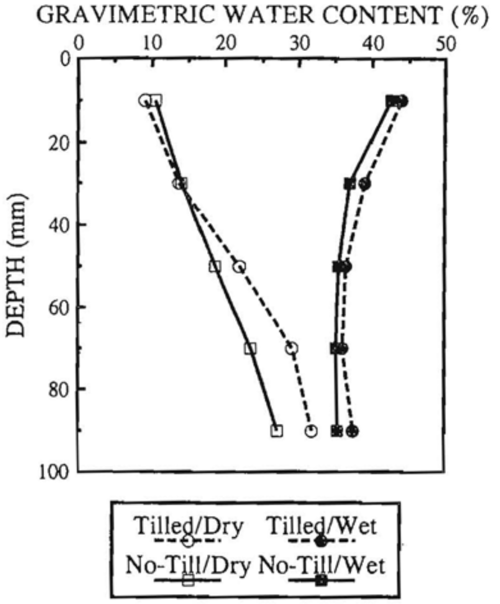

Fig. 3. Gravimetric water content before and after 12.5 cm of rainfall for chisel-till and no-till systems.

documented (Laflen et al., 1978; Potter et al., 1995). Laflen et al. (1978) demonstrated that there is an inverse relationship between sediment yield and percentage of plant residue cover. In a study of the effect of chisel-till and no-till on infiltration in a vertisol, Potter et al. (1995) reported that differences between the no-tillage and chisel-tillage systems were due to alterations in the soil surface by swelling clay minerals (montmorillonite) and raindrop impact. With lower residue levels associated with chisel-tillage, soil cracks were swollen shut soon after rainfall initiation, and soil slaking quickly filled larger surface macropores.

Sediment losses were smaller than the runoff losses (Fig. 2). Note that the scale for runoff is approximately 1000-fold greater than that for sediment. Surface residue cover was an efficient means of controlling sediment losses, especially for the no-tillage treatments.

Atrazine Concentrations of Runoff and Sediment

Atrazine concentrations in the runoff and on the sediment did not differ significantly due to tillage treatment for any of the five time intervals (Fig. 4). Concentrations were higher for samples taken first (0 to 5 min after runoff initiation) for water and sediment phases. Subsequent samples tended to stabilize at a much lower concentration. The hyperbolic relationship between time after runoff initiation and herbicide concentration corresponds to results of previous researchers (Pantone et al., 1992; Triplett et al., 1978).

Atrazine concentrations associated with sediment were about 10 times that of runoff (Fig. 4). Note that in Fig. 4, the ordinate axis (atrazine concentration) for sediment is on a scale ten-fold that for runoff, and therefore, runoff and sediment concentrations were not equal, although they might appear to have been if the different scales were not observed. In a previous study in Minnesota, Pantone et al. (1992) observed a similar trend where atrazine concentrations associated with sediment were one to two orders of magnitude greater than in the water phase.

Not all previous studies agree with our results. Other researchers have reported increased concentrations of atrazine in runoff with conservation tillage as compared with conventional tillage (Gaynor et al., 1995; Sauer and Daniel, 1987). Sauer and Daniel (1987) attempted to account for increased concentrations with no-tillage by postulating that greater surface residues associated with conservation tillage would tend to intercept more herbicide during application as compared with conven-

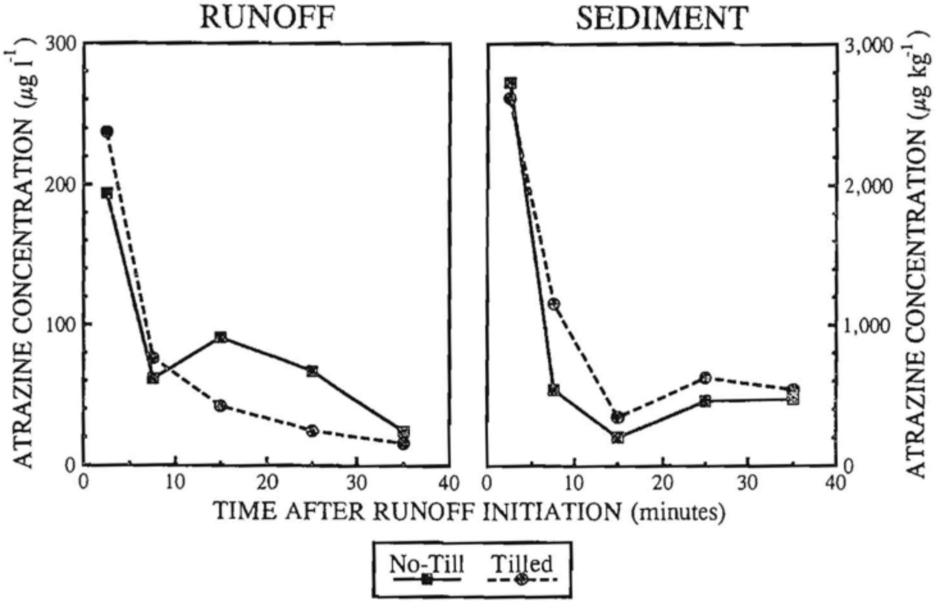

Fig. 4. Atrazine concentration in runoff and sediment for five time intervals (from runoff initiation to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 40 min). Scale of the dependent axis for the sediment is 10× that for runoff. No-till treatments were not significantly different from the tilled treatments for any of the time intervals at the $P = 0.05$ level.

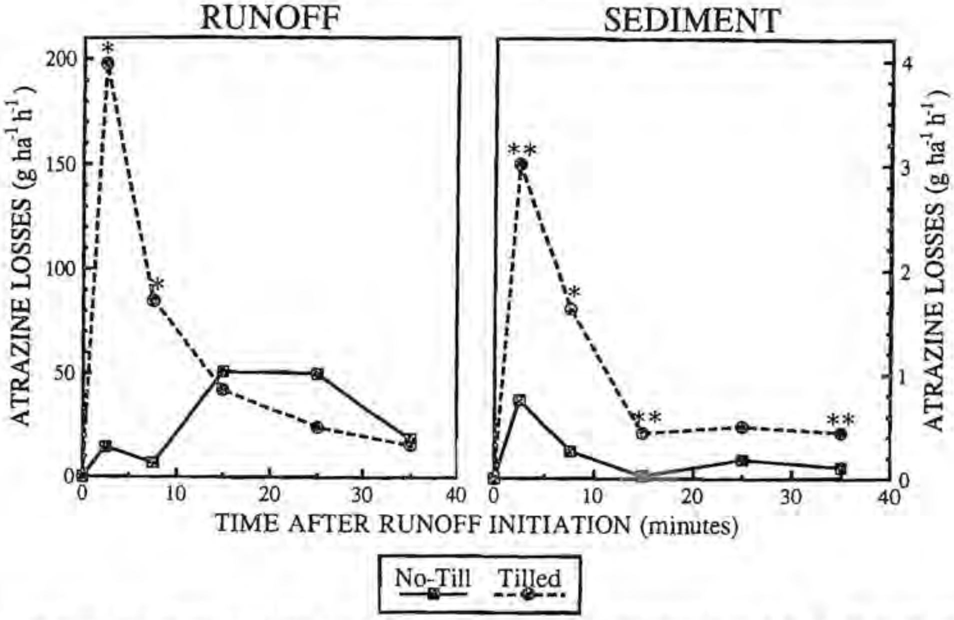

Fig. 5. Atrazine losses in runoff and on sediment for five time intervals (from runoff initiation to 5, 5 to 10, 10 to 20, 20 to 30, and 30 to 40 min). Scale of the dependent axis for runoff is 50× that for sediment. Significant differences between no-till and tilled treatments for individual time intervals are indicated by * ($P < 0.05$) or ** ($P < 0.01$).

tional tillage. According to their hypothesis, herbicide on the crop residues would be washed off easily into the runoff resulting in higher herbicide concentrations. They also hypothesized that infiltration might be reduced by residue cover resulting in higher concentrations under no-tillage system; however, many studies, including that by Sauer and Daniel (1987), have found that surface residues tend to prevent surface seal development resulting in increased infiltration (Potter et al., 1995). Increased infiltration could favor herbicide transport into the soil profile where it would be unavailable for surface transport. In addition, wheat straw, the residue on the plots in this study, may not have as low an affinity for atrazine as was once thought (Ghadiri et al., 1984). Dao (1991) reported that wheat straw can significantly sorb triazine herbicides. It appears that there are several opposing processes occurring, and depending upon herbicide adsorption to the residue, soil water level, and infiltration characteristics, atrazine concentration can be increased, decreased, or remain unchanged (as in the present experiment) due to conservation tillage.

Atrazine Losses and Loads

Atrazine loss was the product of atrazine concentration and runoff rate or sediment yield (Fig. 5). For runoff, only those samples obtained during the first two time intervals had significantly greater atrazine losses for the chisel-tilled system as compared with no-tillage. Atrazine losses in subsequent runoff samples did not differ due to tillage treatment. This is a reflection of runoff rate, which was greater for the chisel-tilled treatment only during the first two time intervals (Fig. 2). For sediment, with the exception of the 20- to 30-min time interval, the tilled system resulted in greater atrazine losses as compared with the no-tillage system. This was due to sediment yields, which were greater for the chisel-tilled treatment with the exception of the 20- to 30-min time interval. Atrazine losses associated with runoff was greater than that of sediment. Note that the scale for runoff is 50 times greater than the scale for sediment (Fig. 5).

Table 1. Total atrazine loss after 40 min of simulated rainfall with chisel-tillage (tilled) or no-tillage (no-till) treatments.

	Atrazine		
Sample	Tilled	No-till	Tilled − No-till (SE)
	g ha⁻¹		
Runoff water	37.19	21.65	15.54* (6.72)
Sediment	0.62	0.14	0.48** (0.08)

*, ** Significant differences between tillage treatments (tilled − no-till) are denoted by $P < 0.05$ or $P < 0.01$ as determined by one-tailed pairwise *t* tests. Values in parentheses are standard errors (SE).

Atrazine mass loads were calculated by integrating the area under the atrazine loss curves (Table 1). The largest atrazine load occurred in runoff of the chisel-tillage system. Under no-tillage, the mass load for the water phase was reduced 42% as compared with chisel-tillage. Sediment-transported atrazine was reduced by 77% with the no-tillage system. About 2% of the applied atrazine was recovered in runoff with the chisel-tillage treatment. Sediment-transported atrazine accounted for only 0.03% of the amount applied under chisel-tillage.

Previous researchers have also observed that sediment-transported atrazine can be much less than that in the water phase (Hall et al., 1972); however, Pantone et al. (1992) reported that atrazine transport via sediment can exceed that of runoff. In that study, the organic C content of the soil was much greater (3.2%) than the present study where organic C was only 1.5%. Moreover, the field slope was 6% compared with <1% slope in the present study. Greater slopes and higher organic C would tend to increase atrazine transport via sediment as compared with water.

CONCLUSIONS

No-tillage soil management systems can reduce atrazine runoff on the Blackland Prairie of Texas. Although tillage might not affect the concentration of atrazine, as in this study, no-tillage systems can decrease runoff and sediment losses; reduced atrazine mass loads are largely a reflection of the decreased runoff. Atrazine lost in runoff decreased 42% as a result of the no-tillage treatments as compared with chisel-tillage. Likewise, the mass load of atrazine associated with sediment was reduced 77% with no-tillage. The bulk of the atrazine applied was not lost, as <2% of the total amount applied was transported in runoff, and <0.03% was transported with sediment. No-tillage systems represent a management alternative by which runoff and pesticide losses can be reduced.

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