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Subsurface Losses of Surface-Applied Metribuzin as Influenced by Yard Waste Compost Amendments, No-Tillage, and Conventional-Tillage

R. W. Malone,[1] R. C. Warner,[1] M. E. Byers[2]

[1]Biosystems and Agricultural Engineering Department, University of Kentucky, Lexington, Kentucky 40546, USA
[2]Community Research Service, Kentucky State University, Frankfort, Kentucky 40601, USA

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Metribuzin is effective as a broadleaf weed control for no-till tomatoes (Shelby et al., 1988) but has the potential to contaminate groundwater (USEPA, 1992; USEPA, 1985). No-till practices reduce water runoff and erosion but increased infiltration possibly results in more pesticide movement through the unsaturated zone and into groundwater (Gish et al., 1991; Donigian and Carsel, 1987). In contrast, Gish et al. (1995) reported that no-till can have a positive impact on groundwater quality. Therefore, it is desirable to design a tillage system that would reduce both erosion and decrease subsurface pesticide transport.

Most research suggests that pesticide sorption to soil is primarily a function of pesticide partitioning into the soil organic matter rather than adsorption into the total soil mass (Karickhoff et al., 1979). Yard waste compost reduces erosion when surface applied (Ettlin and Stewart, 1993). Therefore, since yard waste compost is carbon-rich and reduces erosion, using as a soil amendment and surface applying should decrease erosion and subsurface pesticide migration.

Guo et al. (1993 and 1991) found that amending soil with carbon-rich wastes reduced pesticide movement through repacked soil columns but field studies that included macropore flow (e. g., worm holes, cracks, root channels, freezing-thawing, etc.) were not investigated. Research indicates that macropore flow is a major factor in pesticide transport (Tindall and Vencill, 1995; Harris et al., 1994; Levanon et al., 1993). The more macropore flow that occurs in a system, the smaller the percentage of the total soil mass that will contribute to partitioning and the soil water will flow at a faster rate possibly causing non-equilibrium sorption, therefore, more pesticide will be transported through the soil profile.

The objectives of this study were to research the influence of three infield tillage systems: 1) yard waste compost amended soil with compost added to the soil

Correspondence to: R. W. Malone

surface after rototilling, CA; 2) no-till, NT and; 3) conventional-till, CT on metribuzin subsurface concentration and loading.

MATERIALS AND METHODS

During the 1994 and 1995 growing seasons, standard USLE length field plots (22.0 m x 7.3 m) were used to study metribuzin movement on three treatments: compost amended (CA), no-till (NT) and, conventional-till (CT). Plots were separated by metal borders. Two pan lysimeters (61 cm x 61 cm) were installed in May 1994 on each plot at 76 cm via horizontal tunneling leaving the soil column above the lysimeters undisturbed. Effluent from pans was directed to 4 L glass collection jars using Teflon lined tubing. Field plots were uniform and the slope was 10%. Treatments in 1994 included: CA) adding 115.7 Mg/ha of yard waste compost (ywc) (dry basis) on May 24, rototilling to 15 cm, then planting tomatoes on May 25 and finally adding 96.5 Mg/ha ywc (dry basis) on June 2; NT) sow rye (winter 1993-94), then apply 4.6 L/ha Roundup and; CT) simply rototilling to 15 cm. The 1995 CA treatment included adding 115.7 Mg/ha ywc (dry basis), rototilling to 15 cm (4-7-95 and 4-10-95), then applying 20.9 Mg/ha ywc (dry basis) to the soil surface. The other two plots were treated the same in 1994 and 1995; tomatoes were planted on all plots only in 1994. All plots had metribuzin applied at a rate of 0.816 kg/ha (C.V.=2.4%) on May 8, 1995 and at a rate of 0.686 kg/ha (CV=6.3%) on June 6, 1995 using a CO2 pressurized backpack sprayer. The summer of 1994 was used to install, acclimate and test all equipment and laboratory procedures.

Weekly (5-8-95 through 7-31-95) 2.54 cm diameter soil cores were obtained to 76 cm and separated by horizon using a subsoil probe equipped with plastic liners (Environmental subsoil probe, zero contamination tubes, Clements Associates, Newton, Iowa). Horizons were as follows: 0-23 cm (A); 23-33 cm (B1); 33-56 cm (B2) and; 56-76 (B3). The 15 cm to 23 cm soil sections were mixed with the B1 horizon so that the plow layer (0-15 cm) could be analyzed separately from the other horizons. Samples were composited by horizon and frozen until analyzed. Pan lysimeter effluent was collected after each rainfall event when greater than 50 ml had accumulated in the collection vessels.

Soil was a Lowell silt loam with an average plow layer carbon, clay, silt and, sand content of 1.3%, 12%, 75%, 13%, respectively. The compost amended soil had a carbon content of about 4.5% as measured on a LECO CR12 carbon determinator. The yard waste compost was 11% carbon, had a moisture content of 50% (mass water per total mass) and; a carbon-nitrogen ratio (C:N) of 16.

Metribuzin was extracted from soil using supercritical fluid extraction (SFE) by adding up to nine g of soil to an SFE thimble. All SFE sediment extractions were performed on a Hewlett Packard Model 7680T supercritical fluid extractor (SFE) module interfaced with a 1050 HPLC modifier pump with a menu driven control from a Vectra 486/33 computer. The extraction parameters were: 15% modifier

by volume (1:5:10 water:MECL:ethanol with 0.05% triethylamine added); 105 C trap temperature; 105 C nozzle temperature; 5 min. static extraction time; 10 min dynamic extraction time; CO2 density of 0.75 g/ml and; an extraction temperature of 40 C. The SFE trap was rinsed with ethyl acetate to achieve a 1 ml sample for GC analysis. Using 0.05 ppm spiked soil, recovery was 92.2% (n=48, CV=14.3%).

Metribuzin was separated from lysimeter water using solid phase extraction (SPE). Up to 500 ml of water was dripped through a 6-ml Bakerbond polarplus column packed with 1000 mg of C18 at a rate less than 5 ml per minute. The column was then air-dried and the metribuzin eluted using 2.2 ml ethyl acetate. The final volume of column rinsate for GC analysis was approximately 1.5 ml. Metribuzin recovery ranged from 91.4% (2 ppb water spike, n=2, C.V.=1.0%) to 115.4% (0.25 ppb water spike, n=2, C.V.=2.5%).

The exact volume of sample in each autosample vial (for both water and soil analysis) was determined by spiking each vial with 0.5 µg terbutylazine then dividing 0.5 µg by the concentration of terbutylazine as determined by GC analysis. Metribuzin analysis was performed using a gas liquid chromatograph (GC, Hewlett Packard Company, Model 5890 Series II, Palo Alto, California), equipped with a nitrogen phosphorus detector. GC mass spectrometry operated in selective ion monitoring mode (m/e=198, 214) was used to confirm metribuzin (HP Model 5971A mass selective detector). GC run conditions included: 225 C injection temperature; oven program was 190 C for 14 min, 10 C temperature increase per min to 220 C, this temperature was held for 5 min; and 240 C detector temperature. Flows were set a 15, 20, 120, and 5-ml per min for carrier (He), auxiliary (He), air, and hydrogen, respectively. The column was an RTX-5 (5% diphenyl-95% dimethyl polysiloxane), 30 m, 0.53 mm inside diameter. Retention times were: 11.1 min (metribuzin) and 7.6 min (terbutylazine).

Results reported and discussed for each treatment includes: the mean (and coefficient of variation) pan lysimeter metribuzin concentration, the mean (and coefficient of variation) pan lysimeter effluent volume; the total pan lysimeter effluent; the total metribuzin leached; the daily lysimeter water volume; the daily lysimeter metribuzin concentration; the cumulative metribuzin leached; the subsoil horizons' metribuzin concentration; the plow layer metribuzin concentration over time and; the plow layer dissipation coefficient.

RESULTS AND DISCUSSION

The mean lysimeter water effluent metribuzin concentration was less for CA than both NT and CT (Refer to Table 1). The metribuzin concentration was also less on each day that lysimeter water effluent was found on all plots (Refer to Figure 1). Guo et al. (1993 and 1991) found pesticide concentration to be less in the carbon amended soil than unamended soil. This was due to metribuzin sorption to the additional organic carbon in CA.

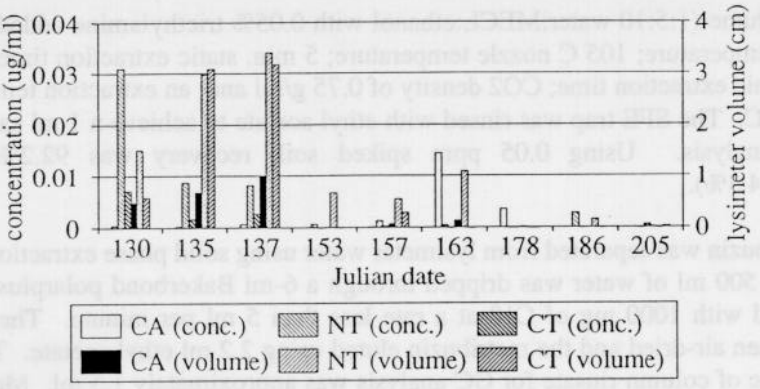

Figure 1. Lysimeter volume and metribuzin concentration. KSU Farm, 1995.

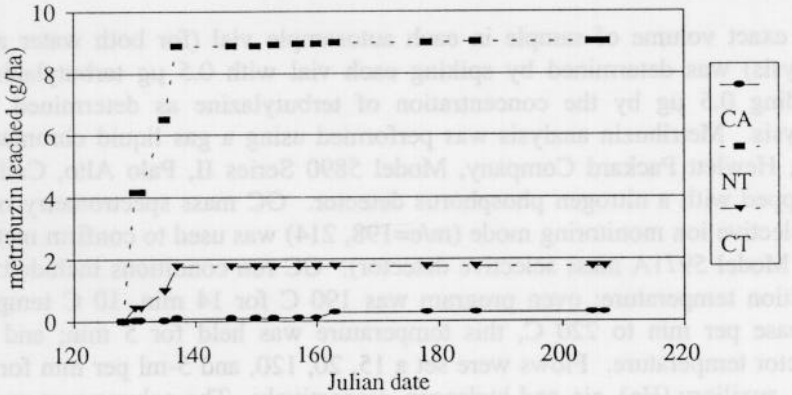

Figure 2. Cumulative metribuzin leaching into lysimeters. KSU Farm, 1995.

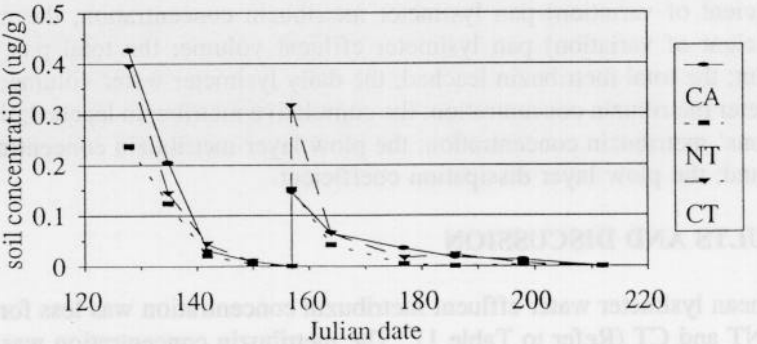

Figure 3. Plow layer metribuzin dissipation. KSU Farm, 1995.

Table 1. Lysimeter effluent parameters and plow layer soil dissipation coefficient (top 15 cm). KSU Research Farm, 1995.

Plot	Mean[1] metribuzin concentration (µg/L)	Mean volume leached (cm)	Total volume leached (cm)	Total metribuzin leached (g/ha)	Dissipation coefficient[3] (day^{-1})
CA	0.38 (99.5%)[2]	0.55 (69.4%)	2.37	0.30	0.12
NT	12.35 (105.0%)	2.11 (62.8%)	10.37	9.03	0.14
CT	2.91 (101.9%)	1.78 (88.0%)	7.16	1.77	0.13

[1]Mean values were calculated from rainfall events when all treatments generated lysimeter effluent (n=4)
[2]Coefficient of variation
[3]Average of two applications (Refer to Figure 3); R^2 was greater than 0.87 for each observation

The mean lysimeter water metribuzin concentration was less for CT than NT (Refer to Table 1). The concentration was also less each day that lysimeter effluent was detected on both plots (Refer to Figure 1). Hall et al. (1991) found herbicide concentration from pan lysimeters to be less under CT than NT and Byers et al. (1995) found the mean clomazone concentration to be less in CT than in conservation-tillage (fescue strips) when sampling using tension lysimeters. Hall et al. (1991) attributed this to the additional macropore flow in NT compared to CT.

The mean pan lysimeter effluent volume was less in CA compared to both NT and CT (Refer to Table 1). The total volume leached (Refer to Table 1) and the amount leached on days when lysimeter effluent was detected on all plots was less on CA compared to NT and CT (Refer to Figure 1). Emerson (1995) reported that water retention increases as organic C increases.

The mean and the total lysimeter effluent volume were less for CT than NT (Refer to Table 1). The volume was also less for CT compared to NT on each event that effluent was detected in all plots except on day 135 (Refer to Figure 1). Hall et al. (1991) found that CT had lower lysimeter effluent volume than NT which they attributed to additional macropore flow in NT compared to CT.

Of the nine deep core soil sampling dates, metribuzin was detected below the plow layer on only three occasions (Refer to Table 2) and all metribuzin concentrations were close to or below the detection limit (approximately 4.0 µg/kg; occasionally lower concentrations were detected due to GC detector

Table 2. Soil metribuzin concentration. KSU Research Farm, 1995.

Julian		Concentration (ppb)		
Date	Depth (cm)	CA	NT	CT
157	15 to 33	8.84	5.89	10.89
	33 to 56	3.53	3.43	2.08
	56 to 76	0.00	4.77	3.00
164	15 to 33	0.00	0.00	0.00
	33 to 56	0.00	0.00	0.00
	56 to 76	2.30	0.00	0.00
177	15 to 33	3.53	0.00	1.98
	33 to 56	2.49	0.00	0.00
	56 to 76	2.15	0.00	0.00

variance). Most NT and CT metribuzin transport were likely due to preferential flow during rainfall events rather than plug flow. Otherwise, pre-day 150 sub-plow layer soil metribuzin would have been detected due to the concentration of the soil water (lysimeter water concentration was greater than 0.0015 µg/ml prior to day 150). The minimum soil-water metribuzin concentration necessary for soil metribuzin detection was about 0.0015 µg/ml considering the soil metribuzin detection limit (approximately 4.0 µg/kg), the soil-water content (approximately 35% ml/ml), the mass of soil extracted (approximately 9 g), and the partition coefficient of the sub-plow layer soil (approximately 0.138 ml/g; Malone, 1995, unpublished). Referring to Figure 1, the lysimeter concentrations of NT and CT were above 0.0015 µg/ml for the first three lysimeter effluent events. Using soil cores, Dao (1995) reported that NT metribuzin center of mass moved 47 to 62% of the distance observed in CT soil after 45 and 175 mm of precipitation. This was attributed to additional surface straw matter and elevated soil organic C levels in NT compared to CT, but pan lysimeters were not utilized, therefore, metribuzin macropore transport would likely not be detected.

The total metribuzin leached was less in CA compared to both NT and CT (Refer to Table 1 and Figure 2). This is consistent with Guo et al. (1991 and 1993). CA had less metribuzin leaching losses due to sorption to the added organic C and due to the increased water retention which reduced the volume of lysimeter effluent.

The total metribuzin leached was less in CT compared to NT (Refer to Table 1 and Figure 2). This is consistent with Hall et al. (1991) who attributed this to the added macropore flow in NT compared to CT.

Metribuzin dissipation coefficients among treatments were similar (Refer to Table 1 and Figure 3). The percent metribuzin lost through leaching (Refer to Table 1) and runoff (Malone et al., submitted 1995) were 0.86%, 0.61% and, 0.76% for CA, NT and, CT, respectively, therefore, little metribuzin escaped the plow layer and dissipation was mainly due to degradation rather than leaching and runoff. Tomlin (1994) states that "in soil, microbial breakdown is the major mechanism of (metribuzin) loss".

The behavior exhibited by CA was as anticipated. The addition of yard waste compost increased the organic carbon content and the water holding capacity of the upper soil profile thereby decreasing the leached water metribuzin concentration and decreasing the leached water volume of CA compared to NT and CT. Therefore, the cumulative metribuzin leached was found to be less in CA compared to the other treatments.

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