

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

R. W. Malone,<sup>1</sup> R. C. Warner,<sup>1</sup> M. E. Byers<sup>2</sup>

<sup>1</sup>Biosystems and Agricultural Engineering Department, University of Kentucky, Lexington, Kentucky 40546, USA

<sup>2</sup>Community Research Service, Kentucky State University, Frankfort, Kentucky 40601, USA

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Soil erosion has been shown to result in decreased crop yields and reduced agricultural sustainability (Mississippi Agriculture and Forestry Experiment Station Technical Bulletin, 1989; Littleboy et al., 1992; and Craft et al., 1992). To address the problems associated with soil erosion, Congress passed the Food Security Act in 1985. To comply with this law, farmers must implement conservation plans on highly erodible land to "significantly reduce" erosion rates.

One widely used method of soil conservation is no-tillage agriculture. But water runoff is reduced under conservation tillage and infiltration increases, possibly resulting in more pesticide movement through the unsaturated zone into the groundwater (Gish et al., 1991 and Donigan and Carsel, 1987). 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). The addition of commercially composted yard waste when mixed with soil to increase the organic carbon content and adding to soil surface to reduce erosion and water runoff may reduce pesticide loading to groundwater compared to no-till.

Surface applied organic mulches in general have been shown to reduce soil erosion (Adams, 1966; Kramer and Meyer, 1969; and Vleeschauwer et al., 1978). Yard waste compost in particular has been shown to reduce erosion when surface applied (Ettlin and Stewart, 1993). Since beneficial uses are needed for yard waste compost (BioCycle Guide to Yard Waste Composting, 1989a and 1989b), adding compost to high value horticultural fields should provide a beneficial use for an ever increasing waste product.

Research comparing pesticide runoff in no-till versus conventional-till have been mixed. Kenimer et al. (1987) concluded that no-till may reduce pesticide loading to surface water while Sauer and Daniel (1987) reported no significant differences. Both reported that any reduction in pesticide runoff is due to reduced water runoff (pesticide runoff concentration was found to be larger in no-till). A compost amended soil should also show the benefit of reduced runoff compared to conventional-till and may show reduced pesticide runoff concentration compared to no-till due to pesticide sorption to organic carbon.

Metribuzin [4-amino-6-(1,1dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one] has the potential to be transported into the environment (USEPA, 1992, exhibit 4-1 and USEPA, 1985)

*Correspondence to:* R. W. Malone

and it is used to control broadleaf weeds in tomato production (University of Kentucky Cooperative Extension Service, 1992). The use of yard waste compost to reduce erosion will be beneficial in horticulture due to the value and scale of production.

The objectives of this research were to study the influence of three soil treatments: 1) yard waste compost amended soil with compost added to soil surface after rototilling, CA; 2) no-till, NT and; 3) conventional-till, CT on metribuzin concentration and loading to surface water via runoff and in sediment

## MATERIALS AND METHODS

Standard USLE field plots (22.0 m x 7.3 m) were separated by metal borders. A gutter system conveyed runoff to two tipping buckets installed at the bottom of each plot. Tipping buckets were calibrated to determine total runoff. A percentage of each tip was directed into one of four-liter collection jars. Two collection jars on each plot were designed to collect a large percentage of each tip (i.e., for low runoff quantity) and two collection jars were designed to collect a small percentage of each tip (i.e., for high runoff quantity). This allowed enough water to be collected on low runoff events for analysis and a sample to be collected without overflow on high runoff events. All apparatus that metribuzin contacted were made of glass, stainless steel, or teflon except the low runoff tubing which was tygon. Field plots were uniform and the slope was approximately 10 %. Three plots were studied: compost amended (CA), no-till (NT), conventional-till (CT). The 1994 treatments included adding 115.7 metric ton/ha (metric ton=1000 kg) 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 metric ton/ha ywc (dry basis) on June 2 for CA. The other two plots were treated the same way in both 1994 and 1995. Tomatoes were planted in 1994 only. The 1995 treatments included: CA) adding 115.7 metric ton/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; NT) sow rye (winter 1994-95), then apply 4.6 L/ha Roundup and; CT) simply rototilling to 15 cm. All plots had metribuzin applied at a rate of 0.816 kg/ha (c.v.=2.4%) on May 8 and at a rate of 0.686 kg/ha (c.v.=6.3%) on June 6 using a CO<sub>2</sub> pressurized backpack sprayer.

Soil was a Lowell silt loam with an average carbon content of 1.3%; clay content of 12 %, silt content of 75 %, sand content of 13 %. 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.

Sediment was separated from water by passing up to 1000 ml of the runoff through glass fiber filter paper in a buchner-type funnel attached to a 2000 ml vacuum flask. The filter was air-dried overnight then weighed. The sediment concentration was then determined by simply dividing the dry sediment weight by the water volume passed through the filter.

Metribuzin was extracted from filtered sediment using supercritical fluid extraction (SFE) by adding up to 9 g of sediment 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 pump (to modify supercritical CO<sub>2</sub> with solvent) with 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; CO<sub>2</sub> 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 91.2% (n=8, c.v.=17%).

Metribuzin was separated from 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 sediment 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 (terb.).

## RESULTS AND DISCUSSION

Total rainfall and runoff for the three plots are presented in Table 1; each rainfall and runoff event is presented in Figure 1. As expected runoff was highest on CT.

Where data were available from all three plots, the mean concentration of metribuzin in runoff was higher (Refer to Table 1) and metribuzin concentrations were higher on each runoff event except Julian day 186 (Refer to Figure 1) for CA and NT compared to CT. Baker et al. (1978) and Kenimer et al. (1987) also found that pesticide concentration increased with an increase in residue cover. This may be attributed to the higher soluble organic matter in the runoff which could affect the solubility of metribuzin in runoff water (Baker et al., 1978) or this may be attributed to foliar washoff (Kenimer et al, 1987).

Little difference was found between NT and CA water concentrations. Kenimer et al. (1987) found no-till to have higher pesticide concentration than conventionally-tilled plots with organic residue added after tillage. CA should partition more metribuzin compared to NT due to the higher organic carbon content of CA, therefore, the concentration was expected to be less on CA than NT. This did not occur because NT had less than half the runoff of CA on each runoff occurrence (Refer to Figure 2), therefore metribuzin may have infiltrated prior to runoff. Most research shows that the highest runoff pesticide concentration is during the beginning of an event (Kloppel et al., 1994 and Baker et al., 1978). Compared to NT, CA runoff was generally darkest in color, indicating more soluble organic material and thus higher metribuzin water solubility (Baker et al., 1978).

The metribuzin load in runoff was less for NT compared to both CA and CT (Refer to Table

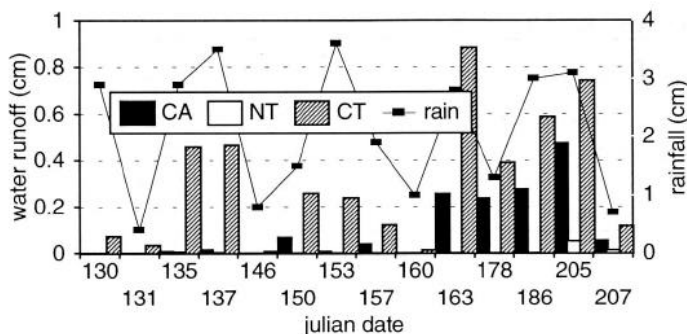


Figure 1. Runoff and rainfall. KSU Research Farm, 1995.

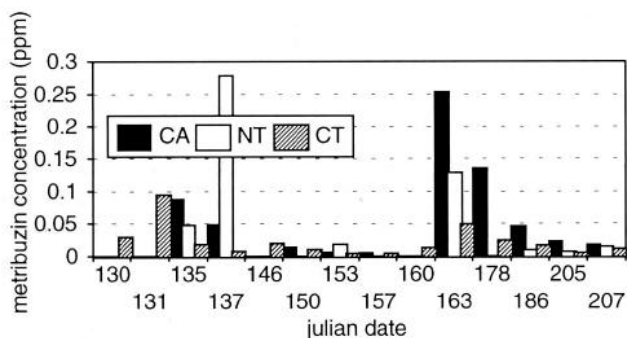


Figure 2. Metribuzin runoff concentration. KSU Research Farm, 1995.

1 and Figure 3). This is consistent with Kenimer et al. (1987). The reduction was due to reduced runoff volume in NT compared to both CA and CT (Refer to Table 1 and Figure 2).

The metribuzin load in runoff was higher on CA compared to CT (Refer to Table 1). But the results were mixed when comparing the metribuzin load in runoff for CT and CA after each metribuzin application (Refer to Figure 3). During the first metribuzin application the cumulative metribuzin runoff was less for CA and during the second application the cumulative metribuzin runoff was less for CT. This may be due to an unmeasured quantity of compost washoff during an intense Julian date 138 rainfall (6.8 cm, no runoff collected on this date due to instrumentation failure). Therefore, the runoff curve number (CN) increased after this date generating a comparatively higher volume of runoff after day 138 (Refer to Figure 1). To illustrate this, the CA:CT average concentration ratio during the first two runoff events after the first and second metribuzin applications were 5.6 and 5.4 respectively, while the average CA:CT runoff volume ratios were 0.024 and 0.45 respectively (approximately 20 times greater). Most research suggests that reduced pesticide loadings to surface waters on surface-applied residue plots compared to conventional-till plots with no residue is due to reduced runoff (Kenimer et al., 1987 and Sauer and Daniel, 1987).

Table 1. Runoff parameters. KSU Research Farm, 1995.

Trt	Rain (cm)	Runoff water			Sediment		
		Total water (cm)	Mean* metr. conc. (ppm)	Metr. load (g/ha)	Mean load (kg/ha)	Mean metr. conc. (ppm)	Metr. load (g/ha)
CA	29.4	1.431	0.069 125.0**	12.44	153.1 145.6	0.234 77.8	0.297
NT	29.4	0.073	0.072 140.3	0.19	9.2 173.1	0.631 103.7	0.004
CT	29.4	4.383	0.016 98.5	8.86	668.9 57.5	0.096 103.2	0.707

\* all mean values are calculated using only runoff dates where data is available from all three plots.

\*\* coefficient of variation (%).

Metribuzin concentrations in sediment were higher on NT and CA than CT (Refer to Table 1 and Figure 4). Kenimer et al (1987) and Sauer and Daniel (1987) also found the pesticide concentration to be greater in no-till compared to conventional-till. This agrees with water metribuzin concentrations (Refer to Table 1).

The mean sediment metribuzin concentration on NT was greater than CA (Refer to Table 1). Of the six runoff events that sediment metribuzin concentration data were available, CA was greater the last three runoff events which were at least one month after metribuzin application (Refer to Figure 4). Concentration of metribuzin in sediment was higher on NT within the first ten days of metribuzin application. This may indicate that the higher organic matter of CA may retain a larger percentage of metribuzin at the soil surface over a longer period of time.

The metribuzin load from sediment was less in NT compared to CA and CT (Refer to Table 1 and Figure 5). These results are consistent with Kenimer et al. (1987) and Sauer and Daniel (1987) (Sauer and Daniel, 1987, state that the differences were not statistically significant). This was due to the reduced sediment load in NT compared to the other treatments (Refer to Table 1).

The metribuzin load from sediment was less in CA compared to CT (Refer to Table 1 and Figure 5). This was expected despite the higher CA sediment metribuzin concentration (when runoff was received on both plots) because the sediment load was less on CA than CT (Refer to Table 1). To illustrate this, the average sediment metribuzin concentration was 0.234 ppm for CA and 0.096 ppm for CT (242% greater for CA considering only runoff events that metribuzin was detected in sediment on both plots) but the average mass sediment runoff was 153.1 kg/ha for CA and 668.9 kg/ha for CT (437% greater for CT). Also, metribuzin was detected in CT sediment on five dates that metribuzin was not detected in CA sediment (Refer to Figure 4).

Comparing Figures 3 and 5, metribuzin loss was at least an order of magnitude greater in water than sediment. This is consistent with other researchers studying water soluble pesticides like

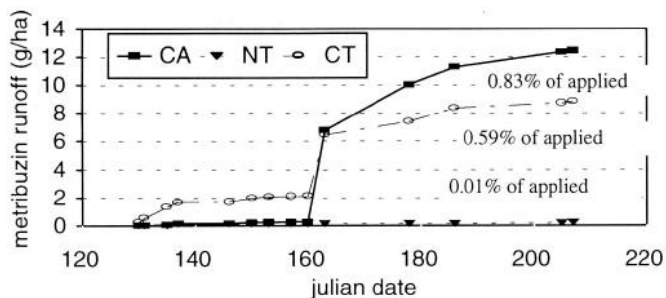


Figure 3. Cumulative metribuzin runoff. KSU Research Farm, 1995.

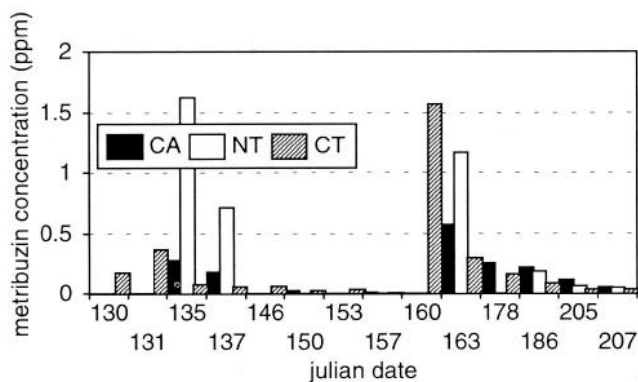


Figure 4. Metribuzin concentration in sediment. KSU Research Farm, 1995.

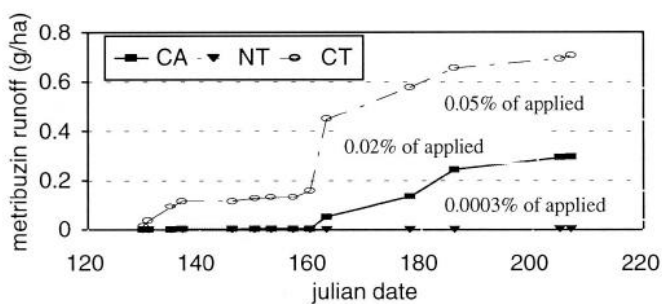


Figure 5. Cumulative metribuzin runoff in sediment. KSU Research Farm, 1995.

metribuzin (Sauer and Daniels, 1987; Kenimer et al., 1987; Baker et al., 1978; and Kloppel et al., 1994).

The 1995 total metribuzin runoff losses were not reduced under CA compared to NT or CT. But the 1994 total metribuzin losses were zero for CA because no runoff occurred, compost was surface applied in 1994 at a rate greater than 4 times the 1995 application. Therefore, higher surface application rates would certainly reduce pesticide loading to surface waters. During the first metribuzin application (before the curve number increased) less total metribuzin losses were detected on CA compared to CT. Since less sediment metribuzin losses were found on CA compared to CT, compost addition to reduce pesticide loading to surface waters may be applicable to pesticides more strongly sorbed than metribuzin. Other researchers have found that strongly sorbed pesticides may be transported mainly by sediment (Kloppel et al., 1994 and Sauer and Daniel, 1987).

The highest metribuzin runoff concentration was less than 0.3 ppm, whereas the LC50 (96 hour) for rainbow trout is 64 ppm (Tomlin, 1994). Therefore, metribuzin concentrations at the edge of the field under the conditions described in this study should cause little environmental concern when natural dilution and degradation (DT50=7 d; Tomlin, 1994) are considered.

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## REFERENCES

- Adams, JE (1966) Influence of mulches on runoff, erosion, and soil moisture depletion. *Soil Sci Soc Amer Proc* 30:110-114
- Baker, JL, JM Laflen, HP Johnson (1978) Effect of tillage systems on runoff losses of pesticides, a rainfall simulation study. *Trans ASAE* 21(5):886-892
- BioCycle Guide to Yard Waste Composting, The (1989a) Key steps for program success. The JG Press, Inc. Emmaus, PA, pp. 19-20
- BioCycle Guide to Yard Waste Composting, The (1989b) Local, regional, and state policies. The JG Press, Inc. Emmaus, PA, pp.17-18
- Craft, EM, RM Cruse, GA Miller (1992) Soil erosion effects on corn yields assessed by potential yield index model. *Soil Sci Soc Am J* 56:878-883
- Donigian, AS, Jr, RF Carsel (1987) Modeling the impact of conservation tillage practices on pesticide concentrations in ground and surface waters. *Environ Toxicol and Chem* 6:241-250
- Ettlin, E, B Stewart ( December, 1993) Yard debris compost for erosion control. *BioCycle*
- Gish, TJ, AR Isensee, RG Nash, CS Helling (1991) Impact of pesticides on shallow groundwater quality. *Trans ASAE* 34(4):1745-1753
- Karickhoff, SW, D S Brown, TA Scott (1979) Sorption of hydrophobic pollutants on natural sediments. *Water Res* 13:241-248
- Kenimer, AL, S Mostaghimi, RW Young, TA Dillaha, VO Shanholtz (1987) Effects of residue cover on pesticide losses from conventional and no-tillage systems. *Trans ASAE* 30(4):953-959
- Kloppel, H, J Haider, W Kordel(1994) Herbicides in surface runoff: a rainfall simulation study on small plots in the field. *Chemosphere* 28(4):649-662
- Kramer, LA, LD Meyer (1969) Small amounts of surface mulch reduce soil erosion and runoff velocity. *Trans ASAE* 638-641

- Littleboy, M, DM Freebairn, GL Hammer, DM Silburn (1992) Impact of soil erosion on production in cropping systems. II. Simulation of production and erosion risks for a wheat cropping system. *Aust. J Soil Res* 30:775-788
- Mississippi Agricultural and Forestry Experiment Station Technical Bulletin. Effects of soil depth, organic matter, and rainfall on soybean yield in the Mississippi Blackland Prairie. Feb. 1989, No. 163, pp. 1-7
- Sauer, TJ, TC Daniel (1987) Effect of tillage system on runoff losses of surface-applied pesticides. *Soil Sci Soc Am J* 51:410-415
- Tomlin, C (ed) (1994) The pesticide manual, tenth edition, Published by the British Crop Protection Council
- USEPA. (1992) National pesticide survey: Phase II Report. EPA/09-91-020, PB92-120831
- USEPA. (1985) Chemical information fact sheet for metribuzin. Fact sheet No. 53, pp. 1-11
- University of Kentucky Cooperative Extension Service (1992) Commercial vegetable crop recommendations. ID-36
- Vleeschauwer, DD, R Lal, MD Boodt (1978) The comparative effects of surface applications of organic mulch versus chemical soil conditioners on physical and chemical properties of the soil and on plant growth. *Catena* 5:337-349