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Trifluralin Residues in Runoff and Infiltration Water from Tomato Production

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Runoff from agricultural watersheds carries enormous amounts of pesticides (Ray et al. 2002). During plant production, pesticides may move from application site into runoff water and runoff sediment following irrigation or natural rainfall. Rainfall intensity and flow rate are critical factors in determining a pesticide movement from application sites into surface runoff, rivers, and streams. Highest concentrations of pesticides are usually detected in the first runoff event after pesticide application (Keese et al. 1994; Antonious and Byers 1997). In recent years, there has been a major shift by U.S. farmers from plow tillage towards systems with reduced tillage. The reduced forms of tillage (conservation tillage) generally minimize soil erosion and water runoff, improve soil physical structure and productivity, but increase water infiltration rates into the vadose zone (Gaynor et al. 1995; Antonious 1999; 2000). Concern has been raised regarding the environmental soundness of conservation tillage because of higher use of pesticides and generally greater rates of water infiltration, leading to leaching of pesticides into groundwater (Antonious 2003a). Conservation tillage, therefore may increase the potential for pesticide leaching. Water infiltration through the soil profile provides the soil with the moisture content needed for seed germination and seedling establishment. Infiltration may also carry substantial amounts of pesticides (originating primarily from surface agricultural use) into the plant root area. However, infiltration (seeping) of pesticides through the soil into the vadose zone, the layer that connects the point of chemical input and surface practices to the groundwater zone (the saturated water zone), must be reduced to ensure the safety of groundwater used as a drinking water supply. Unfortunately, a low water infiltration rate accompanied by a heavy rain leads to flooding or runoff and erosion, particularly when agricultural operations occur on highly erodible lands. This distribution of pesticides throughout the soil profile, as a function of time, represents the integration of several processes such as mass flow, diffusion, adsorption/desorption, degradation, volatility, runoff, and plant uptake. One method of reducing overland flow by soil chemicals (e.g., nutrients, pesticides) is to reduce their concentration at the immediate soil surface. This can be done by incorporating the chemical at lower depths, either by tilling the soil or by irrigation shortly after chemical application and/or development of pesticides that have high degradation rates on the soil surface. Knowledge of how, when, and where pesticide residues reach the edge of the field and streams and how these residues can be minimized is essential in order to reduce the quantity of pesticides reaching surface water and the nation's water resources. Minimizing soil erosion is vital to long-term crop production. Therefore, proper soil management practice is an important key element in reducing soil erosion and pesticide movement. Composting provides an organic amendment useful to improve soil structure and nutrient status and generally stimulates soil microbial activity (Burriuso et al. 1997). It also increases pesticide sorption (Martinez and Almendros 1992; Guo et al. 1993), and decreases pesticide leaching (Zsolnay 1992). Trifluralin, a tertiary aromatic amine and dinitrotoluene

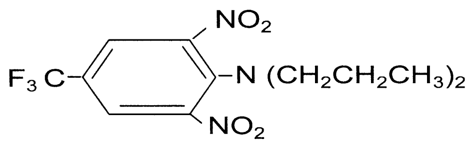

Figure 1. Chemical structure of trifluralin [Treflan, (2,6-dinitro-N,N-dipropyl-4-trifluoromethyl) benzenamine].

derivative (Figure 1), is widely used as a pre-emergence herbicide on a variety of field crops, fruits, vegetables, and ornamentals (Anonymous 2003) for control of annual grasses and broadleaf weeds. Due to its high vapor pressure (1.99×10^{-4} mm Hg at 29.5^{O} C) and sensitivity to photochemical degradation, trifluralin has to be incorporated into the soil in order to avoid undesirable loss under field application (Francioso et al. 1992). Despite its low solubility in water, 0.22 $mg.L^{-1}$ at pH 7 (Anonymous 1995), trifluralin was investigated in this study because of its intensive use in agriculture and its relatively high toxicity to fish (Anonymous 1994). Pesticide adsorption to soil is related to soil organic matter than other soil chemical and physical properties (Jacques and Harvey 1979; Patel 2002). The objectives of this investigation were 1) to study the effect of mixing soil with yard waste compost (having considerable amount of organic matter) and growing living fescue strips (across the contour of the land slope) on the movement of trifluralin from soil into runoff and infiltration water, and 2) to study the impact of each of these two soil management practices (yard waste compost vs. living fescue strips) on tomato yield.

MATERIALS AND METHODS

A field study was conducted on a Lowell silty loam soil (2.8% organic matter, pH 6.9) located at Kentucky State University Research Farm, Franklin County, KY. The soil has an average of 12% clay, 75% silt, and 13% sand. Plots (universal soil loss equation (USLE) standard plots) of 22×3.7 m (n=18), on a soil of 10% slope were established. Plots were separated using metal borders 20 cm above the ground level to prevent cross contamination between treated and untreated plots. Three soil management practices were used 1) yard waste compost made from yard and lawn trimmings, and vegetable remains (produced at Kentucky State University Research Farm, Franklin County, KY) mixed with native soil at 50 t. $acre^{-1}$ (on dry weight basis) with a plowing depth of 15 cm, 2) grass filter strips (tall fescue, *Festuca* *elatior*), 3 feet wide, planted between every two tomato rows perpendicular to the land slope at 5 rows. $plot^{-1}$ to slow runoff and trap sediment, and 3) no- mulch (NM) treatment (roto-tilled bare soil) for comparison purposes. Sixty day old tomato *(Lycopersicon esculentum* cv. Fabulous) seedlings were planted at 10 plants. row^{-1}. Plots were irrigated by drip tape irrigation and no fertilizer was applied. Trifluralin (430 $g.L^{-1}$ EC; Treflan) was sprayed on May 31, 2000 and incorporated into the soil surface at the rate of 0.75 lb. $acre^{-1}$ using a 4-gallon portable backpack sprayer (Solo) equipped with one conical nozzle operated at 40 p.s.i. Soil samples (6 replicates per treatment) were collected at different time intervals (n=11) during 45 days following spraying to a depth of 15 cm from the field plots using a soil core sampler equipped with a plastic liner tube (Clements Associates, Newton, IA, USA) of 2.5 cm i.d. for maintenance of sample integrity. Soil samples were air-dried in the dark, sieved to a size of ≤2 mm. Ten-gram soil samples were used to determine soil moisture content to report the results on dry weight basis. Fifty g soil were shaken with 100 mL mixture of acetonitrile- water (99:1, v/v) for 1 hour using a Multi-wrist shaker (Lab-Line Instruments, Inc., Melrose Park, IL, USA). The solvent was filtered through Whatman 934-AH glass microfibre discs (Fisher Sci, Pittsburgh, PA) of 90 mm diameter, concentrated by rotary vacuum (Buchi Rotavapor Model 461, Switzerland) and N_2 gas stream evaporation. A Supelco Envi-C_{18} cartridge was conditioned first with 4 mL of 50% acetonitrile in water and then with isooctane (3 mL). Four mL of the soil extract were loaded onto the cartridge and passed through at a flow rate of 1-2 mL. min^{-1}. Finally, the cartridge was eluted with 3 mL of hexane and 3 mL of isooctane, and the eluate was dried under a gentle stream of N_2 gas (99.99% purity) and reconstituted in isooctane for GC/NPD determination.

Runoff (soil-water suspension) was collected and quantified at the lower end of each plot using tipping-bucket runoff metering apparatus (Department of Agricultural Engineering, University of Kentucky, Lexington, KY 40546, USA). Homogeneous samples of runoff were collected in amber borosilicate glass bottles and transported to the laboratory on ice in coolers. Sediment in runoff was determined by weighing the sediments collected from a 1-L sample of runoff using Whatman No.1 filter paper. Trifluralin was extracted from sediment samples using C_{18} cartridges as described in soil analysis. Total runoff water lost per runoff event, per each 0.02-acre plot was used to measure trifluralin concentration, which in turn was dependent on natural rainfall events. To monitor the presence of trifluralin in the vadose zone (the unsaturated water layer below the plant root), pan-lysimeters (Department of Agricultural Engineering, University of Kentucky, Lexington, KY 40546, USA) were installed at the end of the experimental plots down the land slope at a depth of 1.5 m. Infiltration water was collected following each rainfall event in amber borosilicate glass bottles. To monitor trifluralin concentration in runoff and infiltration water following each rainfall event, the pH of water samples was adjusted to 2.2 - 2.3 using 15 mL of 2 N HCl per liter of water. Duplicates of 500 mL aliquots were filtered through Whatman 934-AH glass microfibre discs using vacuum filtration. Trifluralin residues in 500 mL of the acidified water samples were extracted three times by liquid-liquid partition with 100, 60, and 40 mL of methylene chloride (CH_2Cl_2). CH_2Cl_2 fractions (bottom layer) were combined and passed over anhydrous Na_2SO_4, then evaporated to dryness using N_2 stream and reconstituted in isooctane. Trifluralin residues were determined using a Hewlett Packard model 5890A Series II gas chromatograph (Hewlett Packard Co., Avondale, PA) equipped with a NP detector. Samples were injected onto a BD-5 high resolution column (15 m × 0.53 mm i.d.) with 0.5 µm film thickness (J & W Scientific, Folson, CA). Operating conditions were 230, 250, and 280 ^{o}C for injector, oven, and detector, respectively. Carrier gas (He) flow rate was 5.2 mL. min^{-1}. Peak areas were determined on a Hewlett Packard model 3396 series II integrator. Quantification was based on average peak areas of 1 µL injections obtained from external standards solutions of trifluralin ranging from 0.1 to 15 ng. µL^{-1}. Under these conditions retention time (Rt) of trifluralin was 6.88 min. Peak identity was confirmed by consistent retention time and coelution with standards under the conditions described. Trifluralin technical material of 96.3% purity was obtained from Dow AgroSciences (Indianapolis, IN, USA). Linearity over the range of concentrations was determined using regression analysis (R^2 =0.99). Standard solutions were used to spike blank soil samples for evaluating the reproducibility and efficiency of the analytical procedures to recover trifluralin. Recoveries (means ± SE) of trifluralin from fortified water and soil samples were 96.6 ± 2.4 and 91.5 ± 3.8, respectively. Quality control (QC) samples included three field blanks to detect possible contamination during sampling, processing, and analysis. The lack of trifluralin residues in the blank samples suggested that there was no contamination from sampling, processing, or laboratory procedures.

RESULTS AND DISCUSSION

Trifluralin residues following application and incorporation into the 10-15 cm top soil, averaged from 0.01 to 0.05 µg. g^{-1} soil (Figure 2). Concentration of trifluralin was much higher in yard waste compost treatments than the NM treatments (rototilled bare soil). Yard waste compost contains significant concentrations of humic acid, the main constituent of soil organic matter (Patel 2002). Tavares and Rezende (1998) have indicated that functional groups in humic acid, namely carboxylic and phenolic groups appear to be the principal sites for the adsorption and interaction with trifluralin. This may explain why trifluralin residues were higher in compost-amended soil than NM soil.

Runoff water control is highest when living fescue strips are established as repeated barriers to runoff across the land slope. Living fescue strips reduced the volume of runoff water (Figure 3, upper graph) as a pesticide carrier and consequently reduced trifluralin transport and concentration in runoff water by 86.2% (Figure 3, lower graph) down the land slope. Trifluralin residues were decreased as the runoff water flowed across the rough soil and grass surfaces along the hill slope that would otherwise have been transported down hill into surface runoff. Filter strips increased water infiltration into the vadose zone as indicated by volume of water collected from the vadose zone (Figure 4, upper graph). Previous results have indicated that living fescue strips reduced runoff but did not reduce leaching of α-endosulfan (Antonious and Byers 1997) and dacthal into the vadose zone (Antonious 1999). On the contrary, this investigation provides evidence of the low potential leaching of trifluralin towards the vadose zone (Figure 4, lower graph). The low concentration of trifluralin in infiltration water from yard waste compost indicates that the risk of groundwater contamination will be low. This can be explained by the adsorption properties of trifluralin on humic acids in compost-amended soil. Due to mechanical incorporation of the pesticide in the top 10-15 cm of soil, an equilibrium is usually established between the pesticide adsorbed to the soil and that in solution. This equilibrium reduces the transport and movement of strongly adsorbed pesticides such as trifluralin (Baker et al. 2000).

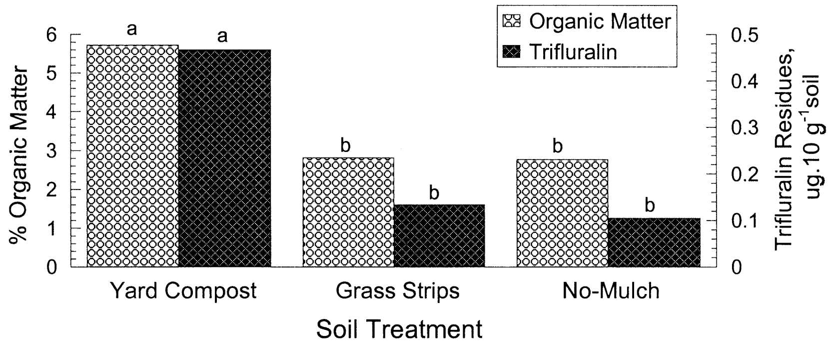

Figure 2. Trifluralin residues and organic matter content of soil collected from the rhizosphere of tomato plants grown under three soil management practices. Statistical comparisons were done between three soil management practices for each parameter. Bars accompanied by different letter are significantly different ($P < 0.05$) from each other using the SAS procedure (SAS Institute, 1999, Duncan's multiple range test).

Yard waste compost is very rich in nutrients (Antonious et al. 2003) and organic matter (Figure 2). Treatments high in organic matter produced high tomato yield (Figure 5). This is because organic substances and nutrients in compost support a vast population of soil organisms that "mine" for soil minerals. Evidence of enhanced microbial activity in the rhizosphere of plants grown with yard waste compost has been reported (Anderson et al. 1994; Antonious 2003b). Much of the effects of application of compost on crop yield is derived from availability of nutrients particularly N in compost. Availability of soluble P had also increased following addition of compost (Swiader and Morse 1984). The competition between living fescue strips and tomato plants on the soil nutrients apparently is the cause of the reduced total tomato yield in fescue treatments. Living fescue strips therefore, may not justify the cost of the occupied soil surface used for growing fescue. However, fescue strips reduced runoff water and trifluralin residues in runoff. This may justify the cost of possible environmental pollution by trifluralin and its high toxicity to fish. Yard waste compost reduced trifluralin residues in surface runoff water from June and July rainfall by 76 and 84%, respectively (Figure 3). The sediment masses in runoff were 0.5 to 8.6 g. L^{-1} with higher amounts in July sampling and lower amounts in June sampling. This corresponds to rainfall intensity during the sampling periods. Rainfall was 5.1 and 6.5 cm with an intensity of 0.9 and 1.3 cm. hr^{-1} on June 19 and July 14, 2000, respectively. Trifluralin concentrations in runoff sediment (data not shown) collected from the three soil management practices at the time of the runoff events showed the same trend of trifluralin in adjoining soil samples. Since pesticide

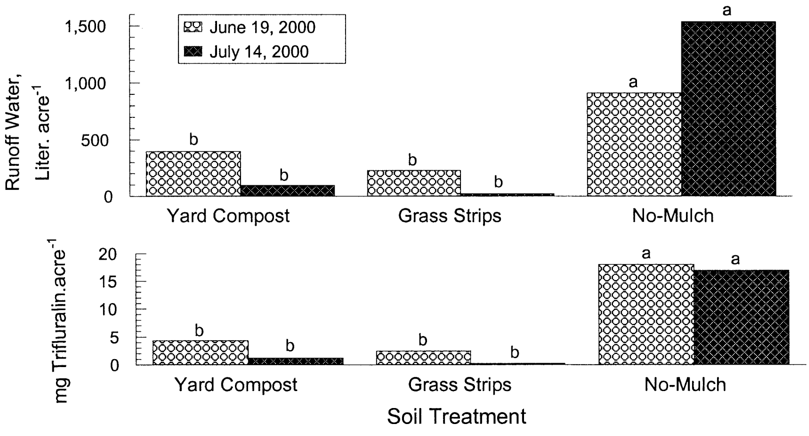

Figure 3. Volume of runoff water (upper graph) and trifluralin residues detected in runoff water (lower graph) from tomato grown on erodible land under three soil management practices. Statistical comparisons were done between three soil management practices for each runoff event. Bars accompanied by different letter for each runoff event are significantly different ($P < 0.05$) from each other using the SAS procedure (SAS Institute, 1999, Duncan's multiple range test).

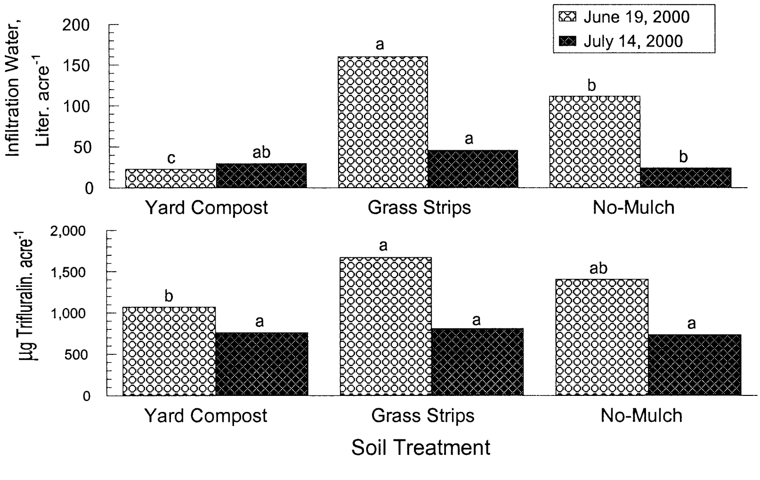

Figure 4. Infiltration water (upper graph) and trifluralin residues detected in infiltration water (lower graph) collected from the vadose zone of tomato plants grown under three soil management practices. Statistical comparisons were done between three soil management practices for each sampling date. Bars accompanied by different letter(s) for each date are significantly different ($P < 0.05$) from each other using the SAS procedure (SAS Institute, 1999, Duncan's multiple range test).

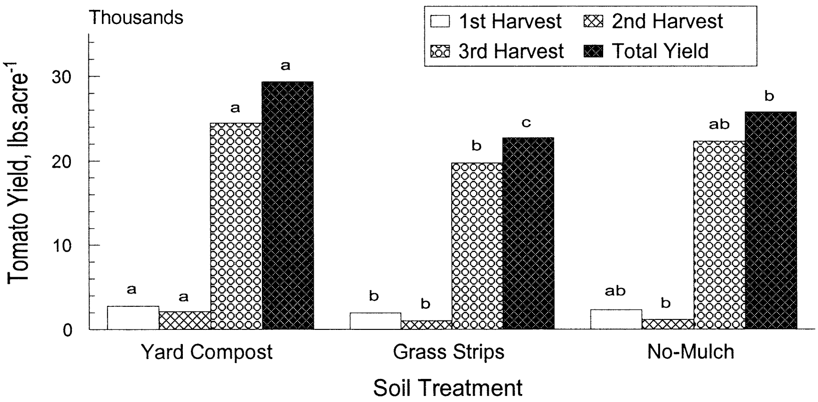

Figure 5. Yield of tomato grown on erodible land with drip irrigation under three soil management practices. Statistical comparisons were done between three soil management practices for each harvest and total yield. Bars accompanied by different letter(s) for each harvest or total yield are significantly different ($P<$ 0.05) from each other using the SAS procedure (SAS Institute, 1999, Duncan's multiple range test).

adsorption to soil is related more to soil organic matter than to other soil chemical and physical properties (Jacques and Harvey 1979; Sparks 1995; Patel 2002), therefore, addition of soil amendments like yard waste compost (having high organic matter content) to native soil will increase the adsorption of trifluralin and reduce its surface and vertical movement under field conditions. Therefore, pesticides strongly adsorbed to soil amended with compost are much better candidates for this method of soil management.

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