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Impact of Soil Amendments on Broccoli Quality and Napropamide Movement Under Field Conditions

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Many studies have indicated the potential ecological damage due to the widespread use of synthetic pesticides (Sances et al. 1992; Antonious 2003a; Antonious 2004; Antonious and Patterson 2005). Herbicides used for broccoli (*Brassica oleracea* L.) production are usually incorporated into soil before seeding or transplanting (Anonymous 2004). Pesticide use, while being of great benefit in controlling weeds, insects and pathogens in agricultural systems, can also threaten environmental quality. New soil management practices related to the fate and transport of agricultural chemicals are needed to meet the challenge of conservation, remediation, and environmental quality.

The Environmental Protection Agency estimates that 15 million tons of biosolids (USEPA, 1989) and 31 million tons of yard waste (USEPA, 1991) are discarded annually in the United States. Recycled wastes have unique properties that should be thoroughly investigated in the soil/water/plant ecosystem. Adsorption of two herbicides, imidazolinone and imazethapyr, to sewage sludge amended soils indicated that imazethapyr interacts with organic matter in sludge through multiple-binding mechanisms including ionic and hydrogen bonds (Senesi et al. 1997). Pesticides binding to the organic layer that surrounds the soil solids can enhance detoxification by suppressing herbicide movement. A chemical placed in soil will be partitioned between soil organic matter and soil water and between soil water and soil air based on its hydrophobic character. Accordingly, the organic matter applied as sludge or yard compost to soil can modify the mechanism of pesticide adsorption to soil, and can play a prominent role in the pesticide availability and removal process. The mobility of any pesticide in soil and water is one of the principal parameters controlling the extent to which a pesticide may represent a risk for surface and groundwater contamination. Compost in soil has been shown to increase pesticide sorption (Martinez and Almendros 1992; Guo et al. 1993; Antonious et al. 2004) and decrease pesticide leaching (Zsolnay 1992; Zbytniewski and Buszewski 2002). In addition, the organic matter in compost helps improve soil fertility, and provides an organic amendment useful for improving soil structure and nutrient status for stimulating soil microbial activity (Barriuso et al. 1997; Antonious 2003b) that may break down pesticides.

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Currently, 60% of all biosolids produced are recycled as soil amendments for reclamation sites, and agricultural and forest lands. However, less than 1% of all agricultural lands in the US are amended with recycled biosolids (National Research Council 2002). Recycling this material as a soil amendment would reduce the need for landfill disposal and/or incineration and reduce the impact of disposal methods on environmental quality. The addition of yard waste compost to soils has been shown to increase yields of a wide variety of crops including pepper (Antonious and Patterson 2005), kohlrabi (Vogtmann and Fricke 1989), and tall fescue (Sullivan et al. 2002). Increased crop yields are attributed to increased organic matter content and improvements in the physical properties of the soil after the addition of composted materials. The proportion of sewage sludge recycled for agricultural use is growing steadily in the US (Beck et al. 1995). Nutrients in sludge are used to replace commercial fertilizers, while sludge organic matter has been reported to improve soil structure, reduce soil erosion, and improve crop yield (Bevacqua and Mellano 1993; USEPA, 1999; Antonious et al. 2003; Antonious and Patterson 2005). Additional research is needed to investigate pesticide mobility and mitigation in soil and water following land application of soil amendments, especially on sloped lands. The challenge is to develop a sustainable agricultural technique that strikes an acceptable balance between crop production benefits and ecological conservation by reducing pesticide impact on water quality. Mitigation and cleanup of excess pesticide residues in soil before they runoff and enter bodies of water is the focus of this plan of work.

The objectives of this study were 1) to study movement of napropamide (an herbicide) into runoff and infiltration water from a broccoli field that has been treated with two soil amendments (yard waste and sewage sludge compost) and 2) to study the impact of soil amended with yard waste or sewage sludge on spring and fall broccoli yield and head quality.

MATERIALS AND METHODS

The study was conducted on a Lowell silty loam soil (2.7% organic matter, pH 6.9) at Kentucky State University Research Farm, Franklin County, KY. The soil has an average of 12% clay, 75% silt, and 13% sand. Eighteen (18) universal soil loss equation (USLE) standard plots of 22 × 3.7 m each were established on a 10% slope. 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, replicated six times, were used: 1) municipal sewage sludge treated with lime and pasteurized for land farming (class-A obtained from Nicholasville Wastewater Treatment Plant, Nicholasville, KY) was mixed with native soil at 50 t acre^{-1} on dry weight basis, 2) yard waste compost made from yard and lawn trimmings, and vegetable remains (produced at Kentucky State University Research Farm, Franklin County, KY) was also mixed with native soil at 50 t acre^{-1} on dry weight basis with a plowing depth of 15 cm, and 3) no-mulch (NM) treatment (roto-tilled bare soil) was used for comparison purposes.

Devrinol 50-DF also known as Napropamide [N, N-diethyl-2-(1-naphthyloxy) propionamide] was obtained from United Phosphorus, Inc. (PO Box 570, Exton, PA; EPA Registration No.10182-258-70506) and sprayed on soil as a pre-emergent herbicide at the rate of 4 lb of formulated product $acre^{-1}$ using a 4-gallon portable backpack sprayer (Solo) equipped with one conical nozzle operated at 40 p.s.i. and the herbicide was incorporated into the soil surface. Broccoli (*Brassica oleracea* L. cv. Packman F1) seeds were obtained from Holmes Seed Co. (Canton, Ohio, USA) and planted in the greenhouse. Seedlings of 45 d old were planted on April 15, 2003 (spring broccoli) and August 13, 2003 (fall broccoli) at 10 rows $plot^{-1}$ along the contour of the land slope at 10 plants row $^{-1}$. The plants were sprayed with dimethoate 4E to control aphids (Anonymous 2004) and irrigated using overhead sprinklers. No mineral fertilizer was applied. During the growing season, runoff water from irrigation and/or rain was collected and quantified at the lower end of each plot using a tipping-bucket runoff metering apparatus (Department of Agricultural Engineering, University of Kentucky, Lexington, KY 40546, USA). Homogeneous samples of runoff water were collected in amber borosilicate glass bottles and transported to the laboratory on ice in coolers. Total runoff water lost per runoff event, per each 0.02-acre plot was used to calculate napropamide movement into runoff water. To monitor the presence of napropamide residues 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 lower end of the plots down the land slope at a depth of 1.5 m. Infiltration water was also collected for napropamide residue analysis.

Duplicate 500 mL aliquots of runoff and infiltration water were filtered through Whatman 934-AH glass microfibre discs. Napropamide residues in water were extracted three times by liquid-liquid partition with 100, 60, and 40 mL of acetone-methylene chloride mixture (1:1). CH_2Cl_2 fractions (bottom layer) were combined and passed over anhydrous Na_2SO_4, then evaporated to dryness using a N_2 stream and reconstituted in acetone for GC/NPD quantification. Napropamide residues were quantified 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 DB-5 high resolution column (15 m × 0.53 mm i.d.) with 0.5 μm film thickness (J & W Scientific, Folson, CA, USA). 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 1μL injections obtained from external standard solutions of napropamide ranging from 1 to 10 ng μL^{-1}. Napropamide technical material of 97.9% purity was obtained from Chem Service (660 Tower Lane, West Chester, PA, USA). Under these conditions the retention time of napropamide was 10.99 min. Peak identity was confirmed by consistent retention time and coelution with standards under the conditions described. Napropamide residues also were confirmed using GC/MS that showed spectral data with a molecular ion peak (M^+) at m/z 271, along with other characteristic fragment ion peaks. Linearity over the range of concentrations was determined using regression analysis (R^2 =0.99). Standard solutions were used to spike blank water samples for evaluating the reproducibility and efficiency of the analytical procedures to recover napropamide residues. Recoveries (means ± SE) of napropamide from fortified water samples averaged 90.6 ± 2.4%. Quality control samples included three field blanks to detect possible contamination during sampling, processing, and analysis. The lack of napropamide residues in the blank samples suggested there was no contamination from sampling, processing, or laboratory procedures.

At harvest, total yield from the top 5 rows and bottom 5 rows of each plot were compared to assess the impact of the land slope on nutrient mobility and crop yield. Broccoli head weight and diameter, stalk diameter and length were also recorded. Spring and fall broccoli heads were quartered and examined for small and large instars of *Pieris rapae* L. larvae (Pieridae: Lepidoptera). Broccoli yield and head quality and napropamide residues in runoff and infiltration water under three soil management practices were statistically analyzed using ANOVA (SAS Institute, 2001).

RESULTS AND DISCUSSION

Runoff water collected from plots treated with sewage sludge was significantly less than plots treated with yard waste compost (Figure 1). Runoff water collected from the no mulch (NM) soil was significantly greater than runoff from plots treated with sewage sludge and yard waste compost. Napropamide residues were significantly higher in runoff water from NM soil compared to yard waste and sewage sludge treatments (Figure 1, upper graph). The organic matter content was significantly higher in soil mixed with sewage sludge (5.95±0.17%) and soil mixed with yard waste compost (5.72±20%) compared to NM soil (2.8±0.77%). These results confirm the notion that the sorption of pesticides was highest in soils with the greatest organic matter content (Zbytniewski and Buszewski 2002; Antonious et al. 2004). Application of compost to soil has increased the retention or removal of hydrophobic compounds like trifluralin (an herbicide) from runoff water (Antonious 2004) and retention of pyrethrins (natural insecticides) on soil solids (Antonious et al. 2004). Addition of sludge also increased soil pH compared to native soil (Antonious et al. 2003). An increase in soil pH can promote metal precipitation or adsorption to soil particles, reducing metal accumulation in plant tissues (Straton and Rechcigl 1998). Organic matter (or organic carbon) is normally the predominant adsorbing component in soil (Barber and Parkin 2003). Application of carbon-rich waste to soils may be useful for reducing pesticide leaching to groundwater (Guo et al. 1993). Concentration of napropamide in infiltration water from soil treated with sewage sludge was similar to the control (NM) treatment but lower than napropamide in infiltration water from yard waste compost treatment. However, the volume of water collected from the vadose zone of the two amended soils was equal (Figure 1, lower graph). Addition of sewage sludge to soil may reduce napropamide

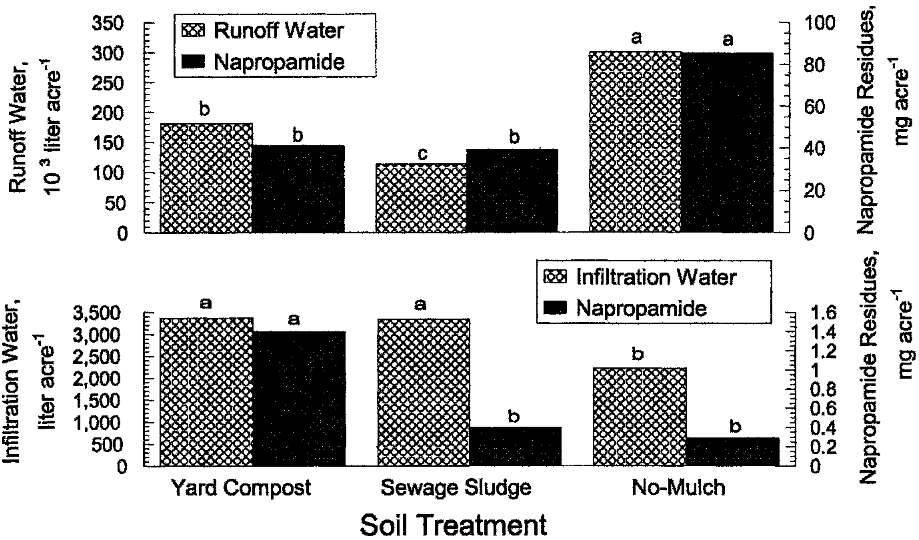

Figure 1. Volume of spring runoff water and napropamide residues in runoff water (upper graph) and infiltration water and napropamide residues in infiltration water (lower graph) collected from the vadose zone of broccoli plants grown under three soil management practices. Bars accompanied by different letter in each soil treatment are significantly different ($P < 0.05$) from each other using Waller LSD test (SAS Institute, 2001).

contamination of groundwater, especially in areas with a high water table or heavy rainfall events. Figure1 (upper graph) indicates that a substantial amount of runoff was being retarded by the two soil amendments (sewage sludge and yard waste compost) that would otherwise have been transported down hill into streams and rivers. Yard waste compost was also associated with increased water infiltration and napropamide residue in the vadose zone (Figure 1, lower graph). Napropamide residues in the vadose zone were 0.3 mg acre^{-1} in the NM treatment compared to 1.4 mg acre^{-1} in yard waste compost treatment. Previous results have indicated that the complexation of pesticides with a water-soluble carrier such as dissolved organic matter (DOM) may facilitate chemical movement through the soil. A strong positive relationship was found between napropamide concentration and DOM content in soil leachates (Lee et al. 1990). DOM, therefore, can affect the distribution and availability of solutes between soil solution and sorbed phases and may explain our results. The increased napropamide movement through the soil mixed with yard waste compost into the vadose zone (Figure 1, lower graph) could be attributed to the formation of napropamide-DOM complexes that lack adsorption affinity for the solid phase (Lee et al. 1990; Nelson et al. 2000) or due to reduced bulk density and increased soil particle interspaces after addition of yard compost. Napropamide seeping into the vadose zone was lowest in NM soil compared to yard waste compost treatment. A large fraction of napropamide mass moved horizontally on the soil surface of the NM soil in runoff water compared to yard waste or sewage sludge mixed soils (Figure 1, upper graph), reducing the concentration of napropamide in infiltration water. No napropamide residues were collected during the fall season (data not shown) due to reduced rainfall.

Broccoli plants have essentially only one yield component of commercial importance –head size (the harvested portion of the main stem). The addition of sewage sludge to soil increased head weight and diameter as well as stalk diameter and length compared to the NM treatment (Table 1). Broccoli marketable yield (tight, uniform heads with fine beading) is important in establishing and maintaining marketing opportunities (Sterrett et al. 1990). The use of any soil amendment in vegetable production must provide the growers with acceptable and marketable yield in order for them to use this agricultural practice. Organic substances and nutrients in sewage sludge and yard waste support a vast population of soil organisms that "mine" for soil minerals. Evidence of enhanced microbial activity in the rhizosphere of plants grown with soil amendments has been reported (Antonious 2003b). The minimum average head weight should be 195 g to meet the marketing opportunities (Sterrett et al. 1990). This requirement can be achieved when using sludge for spring broccoli production (Table 1).

Table 1. Quality of spring and fall broccoli grown under three soil management practices at Kentucky State University Research Farm (Franklin County, KY).

Soil Treatment	Head Weight, g	Head Diameter, cm	Stalk Diameter, cm	Stalk length, cm	No. of Cabbage Loopers/ Head
Spring Broccoli					
Sewage Sludge	196.3 a	12.7 a	3.9 a	3.5 a	1.1 b
Yard Waste	172.7 a	11.9 b	3.4 b	1.5 b	1.2 b
No Mulch	138.3 b	10.5 c	3.1 c	3.3 a	2.6 a
Fall Broccoli					
Sewage Sludge	186.9 a	10.5 a	4.0 a	5.8 a	0.0 b
Yard Waste	187.5 a	9.7 b	3.6 b	7.1 b	0.2 ab
No Mulch	189.3 a	10.2 ab	3.9 ab	2.7 c	0.3 a

† Each value in the table is an average of 6 replicates. Values within a column for each broccoli season having different letter(s) are significantly different ($P< 0.05$) from each other, using Waller LSD test (SAS Institute, 2001).

Total fall broccoli yield from sewage sludge and yard waste compost amended soils was significantly higher than yield from unamended soils. The effects of compost application on crop yield are derived from availability of nutrients in compost (Swiader and Morse 1984). Total yield from sludge and yard waste compost treatments from top and bottom of plots were not significantly different but greater than NM treatment (Figure 2, upper graph). The use of soil amendments in broccoli production must increase profits in order to become an accepted practice among vegetable growers. Total spring broccoli yield from sewage sludge treatments was significantly higher than unamended soil (Figure 2,

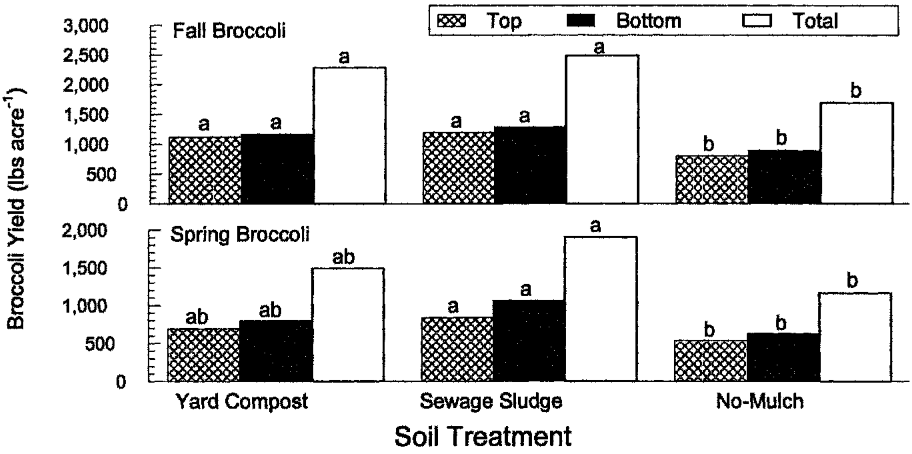

Figure 2. Yield of broccoli plants grown under three soil management practices. Bars accompanied by different letter(s) in each location or total yield are significantly different ($P< 0.05$) from each other using Waller LSD test (SAS Institute, 2001).

lower graph). Further studies are needed to reduce DOM content of municipal waste before land application. This will protect water quailty from off-site movement of pesticides.

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