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On-farm bioremediation of dimethazone and trifluralin residues in runoff water from an agricultural field

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Bioremediation is the use of living organisms, primarily microorganisms, to degrade environmental contaminants into less toxic forms. Nine biobeds (ground cavity filled with a mixture of composted organic matter, topsoil, and a surface grass) were established at Kentucky State University research farm (Franklin County, KY) to study the impact of this practice on reducing surface runoff water contamination by residues of dimethazone and trifluralin herbicides arising from an agricultural field. Biobed (biofilter) systems were installed at the bottom of the slope of specially designed runoff plots to examine herbicides retention and degradation before entering streams and rivers. In addition to biobed systems, three soil management practices: municipal sewage sludge (SS), SS mixed with yard waste compost (SS + YW), and no-mulch rototilled bare soil (NM used for comparison purposes) were used to monitor the impact of soil amendments on herbicide residues in soil following natural rainfall events. Organic amendments increased soil organic matter content and herbicide residues retained in soil following rainfall events. Biobeds installed in NM soil reduced dimethazone and trifluralin by 84 and 82%, respectively in runoff water that would have been transported down the land slope of agricultural fields and contaminated natural water resources. Biobeds installed in SS and SS+YW treatments reduced dimethazone by 65 and 46% and trifluralin by 52 and 79%, respectively. These findings indicated that biobeds are effective for treating dimethazone and trifluralin residues in runoff water.

Keywords: Biobed, biofilter, tipping bucket, infiltration water, herbicides, GC-MSD.

Introduction

Pesticides are used on most major crops in the United States and worldwide. The world market for pesticides is estimated at $33.59 billion, of which the United States represents the largest part, in terms of dollars (33%) and pounds (22%) of active ingredients.[1] According to the USEPA, more than 441 million kg of conventional pesticides were used in the United States.[2] Of that total, 77% was used in agricultural applications, and 11% was used for home and garden purposes. Approximately 1,200 water body impairments across the United States are attributed to pesticides.[3] Bioremediation is defined as the process whereby wastes are biologically degraded under controlled conditions by microorganisms or their enzymes to an innocuous state, or to levels below concentration limits established by regulatory authorities.[4] In its most simple form bioremediation uses naturally occurring bacteria and fungi or plants.[5]

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Recent decades have brought increasing concerns for potential adverse human and ecological health effects resulting from the production, use, and disposal of numerous chemicals that offer improvements in agriculture, industry, medical treatment, and even household chemicals. Protecting the integrity of soil and water resources is one of the most essential environmental issues of the 21st century. Agricultural production is an important part of the nation's economy and pesticide use on crops is extensive.[6–8] Agricultural activities are frequently conducted in close proximity to lakes, reservoirs, and streams. According to Moore et al.,[9] more than 500 million kg of pesticides are used each year in the United States in both agricultural and urban settings. Contaminated runoff from farmland contributes a significant proportion of the pesticide load released to surface waters. There is concern over the risks of contamination of food and drinking water by residues of synthetic agrochemicals, and the negative impact of agrochemicals on the countryside. A central hope in these concerns is the safe use of agrochemicals, development of new soil management practices, and use of mitigation techniques. Mitigation techniques must be simple, inexpensive, energy-conserving, safe and effective for pesticide removal, nutrient recycling and erosion control. Although many factors are responsible for decomposition of pesticides in soils, two are considered the most important: a) adsorption increases the availability of the pesticide for degradation processes, and b) microbiological activity increases pesticides metabolism.

Agriculture makes relatively little use of soil microorganisms as producers of several detoxifying enzymes capable of breaking down pesticides and other contaminants. With the decline of many ecosystems in the world and lack of knowledge of soil microbial community, increasing awareness concerning the importance of soil microorganisms has emerged. Soil microorganisms constitute a large dynamic source and sink of nutrients in all ecosystems and play a major role in N-, C-, and P-cycling.[10]

A low-cost biobed system (a hole filled with a mixture of chopped wheat straw, peat moss and top soil) was developed and used in Sweden since 1993[11] to degrade pesticides from point sources. Biobeds rely on the use of a mixture of organic matter and soil as a biofilter for retaining and biodegrading pesticide spillage or contaminated waste water generated during cleaning of agricultural equipment. High quality compost made from garden residues or municipal waste contains numerous microorganisms with differing activities and has demonstrated a good retention capacity for pesticides.[12] The soil in biobeds provides sorption capacity and degrading microorganisms, and the peat contributes to high sorption capacity and regulates the humidity of the system. The grass layer that covers the the biobed system helps to keep the system humid. Castillo and Torstensson[13] reported that a straw: peat: soil at 50: 25: 25% ratio is a recommended biomixture composition for biobeds. This is because organic amendments that increase soil organic matter content offer enhanced pesticide sorption capacity. [14,15]

Biobeds originated in Sweden in response to the need for simple and effective methods to minimize environmental contamination from pesticide use, especially when filling spray equipment (a typical point source of contamination). Replacement of some of the original materials in the Swedish biomixture (straw, peat, and soil) can also change the performance of the system.[16] The biobed system has attracted attention in several countries, where work is being conducted to adapt it to local conditions and applications. As a consequence, the biobed system has been more or less modified and sometimes renamed as biomassbed in Italy, biofilter in Belgium, and Phytobac and biobac in France. The potential of using biobeds to contain and degrade pesticides has been evaluated in a series of experiments using laboratory-scale biobeds located in greenhouses in Utah, in the United States. The study was performed by Earthfax Development Corporation and funded by the U.S. EPA. In general, the experiments in Utah involved application of selected herbicides to the surface of the biobeds, which were prepared to assess various factors (e.g., substrate mixtures with and without fungal inoculation). The herbicide-degrading potential of the biobed substrate mixtures was determined by analyzing the soil/peat/straw (or corn stover or corn cob) mixture of subsamples taken from various depths in the beds to determine residual herbicide concentrations over time. According to Castillo et al.,[16] the degradative performance of biobeds for several of the most commonly used herbicides in the United States was exceptional, particularly for the most heavily used herbicide in the United States, namely, atrazine.

Methodologies to mitigate the impact of pesticides on the ecosystem are urgently needed. Since 1991, Kentucky State University (KSU) Water Quality & Environmental Toxicology Research of the Land Grant Program in Franklin County, KY has been involved in several field and laboratory projects to investigate the relationships between soil farming practices, soil erosion processes, vegetable yield, fate of pesticides and pesticide metabolites in runoff and infiltration water. Various agricultural and management practices have been used to mitigate environmental pollution by pesticides. Planting living fescue strips against the contour of the land slope reduced runoff, but has the disadvantage of increasing the potential of soil infiltration by pesticides. [17,18] Unfortunately, plastic mulch, which can cover between 50–70% of a field, increased surface water runoff from both rainfall and irrigation.[19] This means much of the pesticides applied in living fescue or in plastic-mulched fields may seep into groundwater or leave the field into surface runoff. Agricultural runoff is the main contributor to poor water quality.[20] Composting and use of sewage sludge in agriculture as an organic amendment is useful for improving soil structure and nutrient status [21–24] and generally stimulates soil microbial activity.

Biobeds have been used in northern Europe for minimizing point-source contamination of water resources by pesticides.[25] Biobeds were tested for their ability to retain and degrade chlorpyrifos (an insecticide), metalaxyl (a fungicide), and imazamox (an herbicide) using farm available materials (vine-branch, citrus peel, urban waste and green compost). The filling materials (mixture of modified straw, peat moss, and native soil) of biobeds have increased sorption capacity and microbial activity for degradation of pesticides. Degradation of the pesticides in biobeds was found to be faster than published values for degradation in soil. The half-life of pesticides tested was less than 14 days, compared to literature values of 60–70 days in soil.[26] Biobeds also reduced the concentration of sediment, so they might reduce the concentration of pesticides that are strongly sorbed to sediment. Little is known regarding biobed use in the United States. To the best of the author's knowledge, the present investigation is the first application of biobed systems for reducing runoff water loss and mitigation of off-site movement of pesticides in runoff (non-point source contamination) in Kentucky agriculture, where most of the arable lands are highly erodible. The main objective of the present investigation was to assess the performance of biobed systems in treating residues of two herbicides dimethazone and trifluralin in runoff and seepage water arising from agricultural production under three soil management practices (municipal sewage sludge, sewage sludge mixed with yard waste and no-mulch native soil).

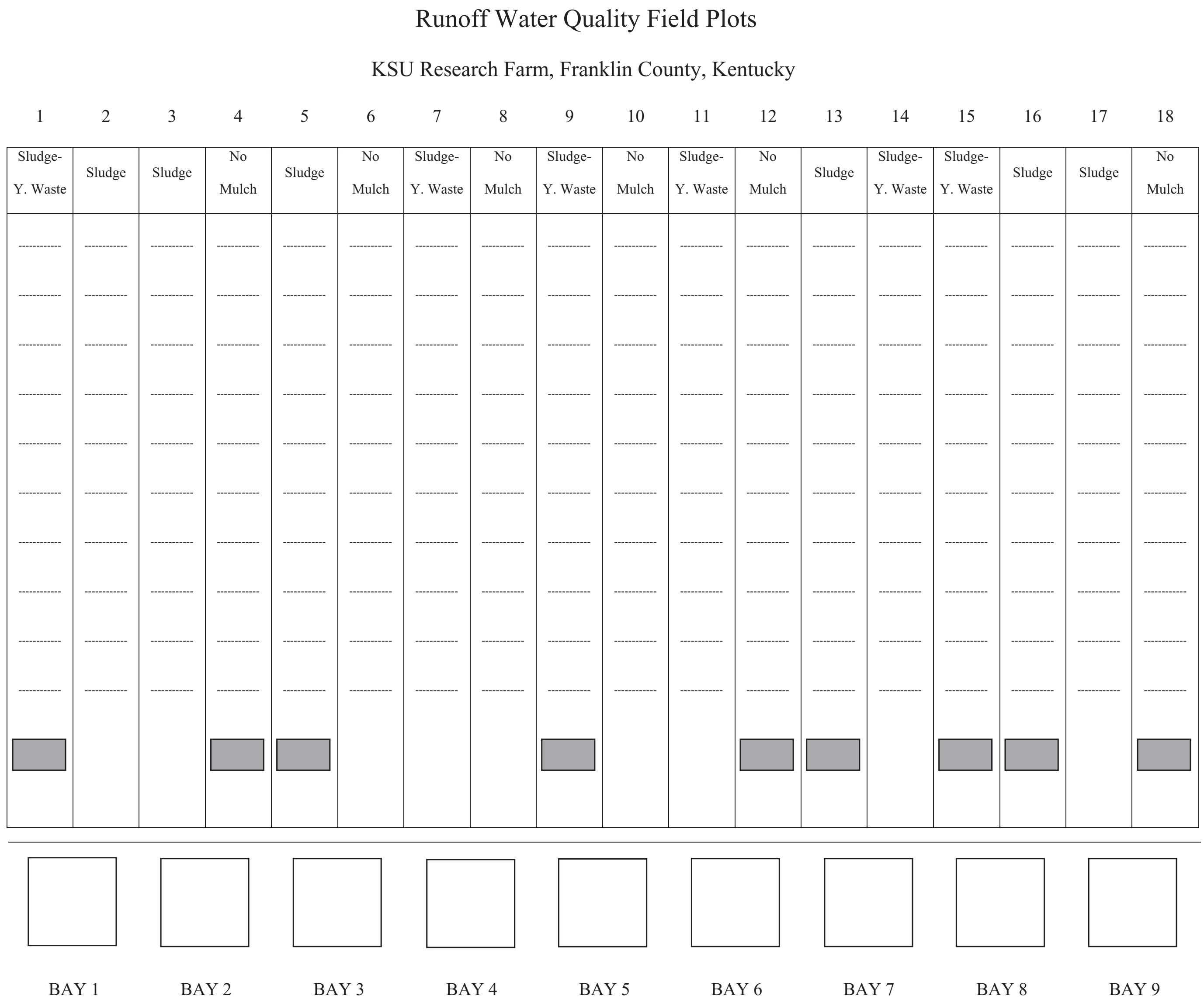


Fig. 1. Diagram of KSU water quality & environmental toxicology field study indicating runoff plots (n = 18) design and soil treatments. Note that each bay has two tipping bucket runoff metering apparatus (see Fig. 2) for collecting runoff water down the land slope following rainfall events. A pan lysimeter (n = 18) was also installed 1.6 m deep at the end of each plot for collecting infiltration water from the vadose zone. ▆ Indicate a biobed system. □ Indicate two tipping buckets installed in each bay for collecting and measuring runoff water from two adjacent plots.

Materials and methods

Field description

The field trial area was established on a Lowell silty loam soil (pH 6.7, 2% organic matter) of 10% slope located at the Kentucky State University (KSU) Research Farm (Franklin County, KY). The farm is located in the Kentucky River Watershed in the Blue Grass Region. Eighteen (18) field plots (Fig. 1) of 3.7 m wide and 22 m long each were installed with stainless steel borders along each side to prevent cross contamination between adjacent treatments. A gutter was installed across the lower end of each plot with 5% slope to direct runoff to the tipping buckets and collection bottles for runoff water measurement and sampling (Fig. 2). Each of the 18 tipping-buckets was calibrated (one tip represented 3L of runoff water) and was maintained to provide precise measure of amount of runoff per tip. Number of tips was counted using mechanical runoff counters (ENM Company, 5617 Northwest Highway, Chicago, IL 60646). At the bottom of each plot, a pan lysimeter (n = 18) of 1.5 m deep was installed for collecting infiltration water following natural rainfall events.

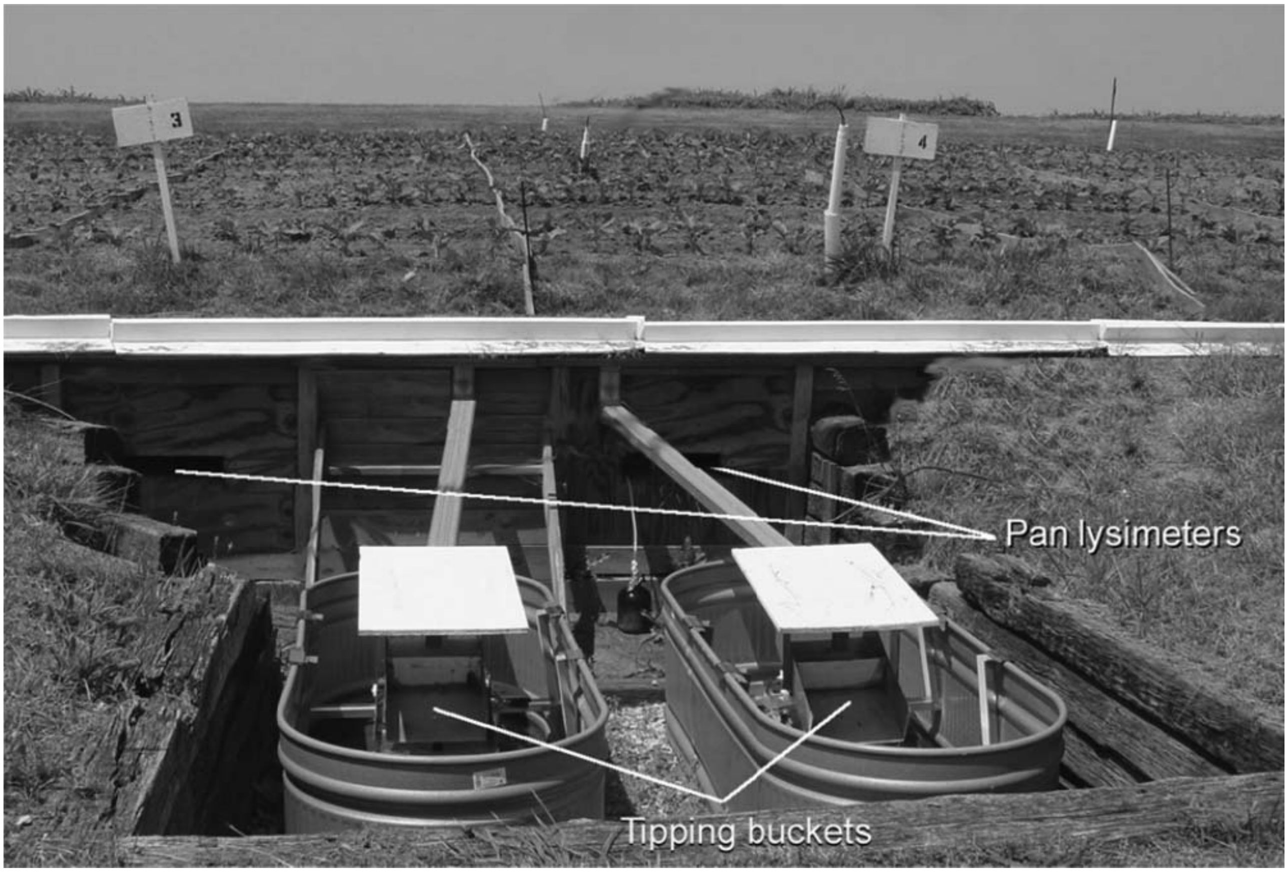


Fig. 2. Design of tipping bucket apparatus (n = 18) installed down the farm slope at Kentucky State University research farm (Franklin County, KY). One tipping bucket apparatus for each of the 18 experimental plots for measuring and collecting runoff water samples.

Preparation of biobed mix

Biomix was prepared by mixing 50% chopped wheat straw (Anderson County Farm Services, 145 Hawkins St, Lawrenceburg, KY 40342), 25% peat moss (Lowe's, 350 Leonardwood Rd., Frankfort, KY 40601) and 25% top soil (12% clay, 75% silt, 13% sand) obtained from the native soil at KSU Research Farm. The mixture was composted outside in open air, for 2 months prior to use. The mixture in the heap was covered with plastic sheets (Lowe's, KY) and turned twice during this period. The microbial biomass of the mixture in the heap was monitored using the methods described by Antonious[10] to give an indication of microbial proliferation and activity.

Biobed design and installation

At the lower end of each of nine experimental plots, biobeds were installed while other nine plots having no biobed systems were used for comparison purposes. Each biobed system was a hole ($3.7 \times 3 \times 1.5$ m^3) in the ground down the field slope filled with a 10 cm layer of limestone gravel at the bottom, then filled with biobed mix, and then with grass on top (Fig. 3). Each biobed was covered with a tall fescue

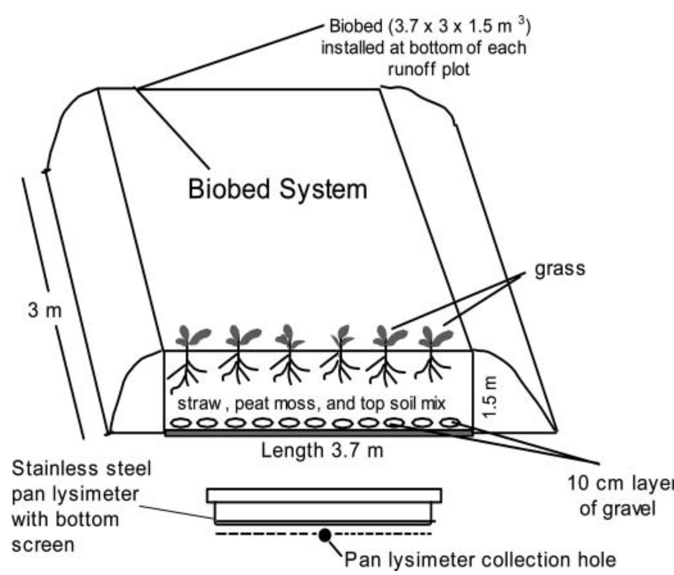
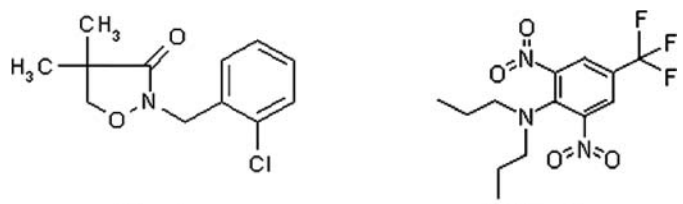


Fig. 3. Schematic diagram of a slot-mulch biobed system. Note that a pan lysimeter is installed at the bottom of each biobed system to collect infiltration water and monitor herbicide mobility.



Dimethazone Trifluralin

Fig. 4. Chemical structures of dimethazone 2-[(2-chlorophenyl) methyl]-4, 4-dimethyl-3-isoxazolidinone in Clomazone formulation and trifluralin [(2,6-dinitro-N,N-dipropyl-4-trifluoromethyl) benzenamide] herbicides in Treflan formulation.

(*Festuca sp.*, Kentucky 31) grass layer to help maintain a suitable level of temperature for microbial activity.

Three soil management practices were used in experimental plots: 1) municipal sewage sludge obtained from Metropolitan Sewer District, Louisville, KY was mixed with yard waste compost (obtained from Con Robinson Company, Lexington, KY) and then incorporated into native soil at 15 t acre^{-1} (on dry weight basis) with a plowing depth of 15 cm; 2) municipal sewage sludge was mixed with native soil at 15 t acre^{-1} (on dry weight basis) with a plowing depth of 15 cm; and 3) a no-mulch (NM) control treatment (roto-tilled bare soil) was used for comparison purposes. The soil in the experimental area was sprayed with a mixture of two pre-emergent herbicides, dimethazone and trifluralin (Fig. 4) formulations. One hundred-twenty five mL of Command 3ME formulation obtained from Platte Chemical Company (18th street, Greeley, CO) and 300 mL of Treflan formulation (Dow Agro Sciences) were used at the recommended rates of application in Kentucky.[8] The two herbicides were mixed in a total volume of 15 gallons of water and sprayed uniformally on the field plots on July 14, 2009 using a portable backpack sprayer equipped with one conical nozzle operated at 40 psi (275 kPa). Seedlings of muskmelon (*Cucumis melo* cv. Athena) and bell pepper (*Capsicum annuum* cv. Artistotle) were grown in the greenhouse for five and eight weeks, respectively, prior to transplant. Seedlings were transplanted in the field plots. Peppers and melons were planted with 25 and 60 cm in-row spacing, respectively. Rows were spaced 1.1 m apart. Plants were watered by a uniform drip irrigation system and grown using standard production practices for Kentucky growers.[8]

Runoff measurement

Runoff water under three natural rainfall events (July 17, July 27, and October 7, 2009) was collected and quantified at the lower end of each plot throughout the growing season using tipping-bucket runoff metering apparatus established by the Department of Agricultural Engineering, University of Kentucky, Lexington, KY. Each of the 18 tipping buckets was calibrated (one tip represents 3L of runoff) and maintained to provide precise measure of amount of runoff per tip. Numbers of tips were counted using mechanical runoff counters. Collection of water samples was carried out in 3.79-L, borosilicate glass bottles through a flow-restricted composite collection system (approximately 40-mL per tip were collected). Runoff water samples were transported on ice within 2 hrs to the laboratory, stored at 4°C for extraction and analyses of the studied herbicides.

Leachate measurement

Eighteen (18) pan lysimeters (see locations in Fig. 2 and 3) were used to monitor the presence or absence of pesticide residues in the vadose zone (the unsaturated water layer below the plant root). Water percolated through the vadose zone from each of the 18 plots was collected. The pan lysimeters (4 square feet each) were tunnel installed, leaving the soil column above it intact. This system allowed collection of infiltration water under normal field conditions (zero tension). Borosilicate amber bottles were used for sample collection. Volumes of water collected were recorded following each rainfall or irrigation event and transported to the laboratory on ice in coolers for measurement and herbicide residue analysis.

Herbicide residue analyses in soil, runoff, and infiltration water

Fifty g representative soil samples (taken from 3 cores per plot) were collected biweekly from the different field treatments using a soil core sampler equipped with a plastic liner tube (Clements Associates, Newton, IA) of 2.5 cm i.d. for maintenance of sample integrity. Soil samples were taken prior to and after herbicides application during the course of the study. Since the depth of sampling influences soil enzyme activity, therefore, soil cores were taken to a depth of 15 cm from the rhizosphere of growing plants within the treatments. This top layer is the layer of increased microbial activity. Soil samples were dried, sieved to a size of 2 mm, and extracted by shaking using 100 mL of acetonitrile : hexane : methanol mixture (45:45:10 v/v). The extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary vacuum (Buchi Rotavapor Model 461, Switzerland) and N_2 stream evaporation.

Trifluralin and dimethazone were extracted from 250 mL of representative runoff water and 500 mL infiltration water samples with 150 mL of a mixture of methylene chloride [CH_2Cl_2] + acetone (6:1, v/v) and sodium chloride solution (40 g litre^{-1}; 50 mL) by liquid-liquid partition for 1 min. The solvent was filtered through a Buchner funnel containing Whatman 934-AH, of 55 mm diameter glass microfiber filter (Fisher Scientific, Pittsburgh, PA), passed through anhydrous sodium sulfate (Na_2SO_4) and concentrated by rotary vacuum evaporator (Buchi Rotavapor Model 461, Switzerland) to a known volume. Concentrated extracts were injected into a gas chromatograph (GC) equipped with flame ionization detector (FID). The gas chromatograph

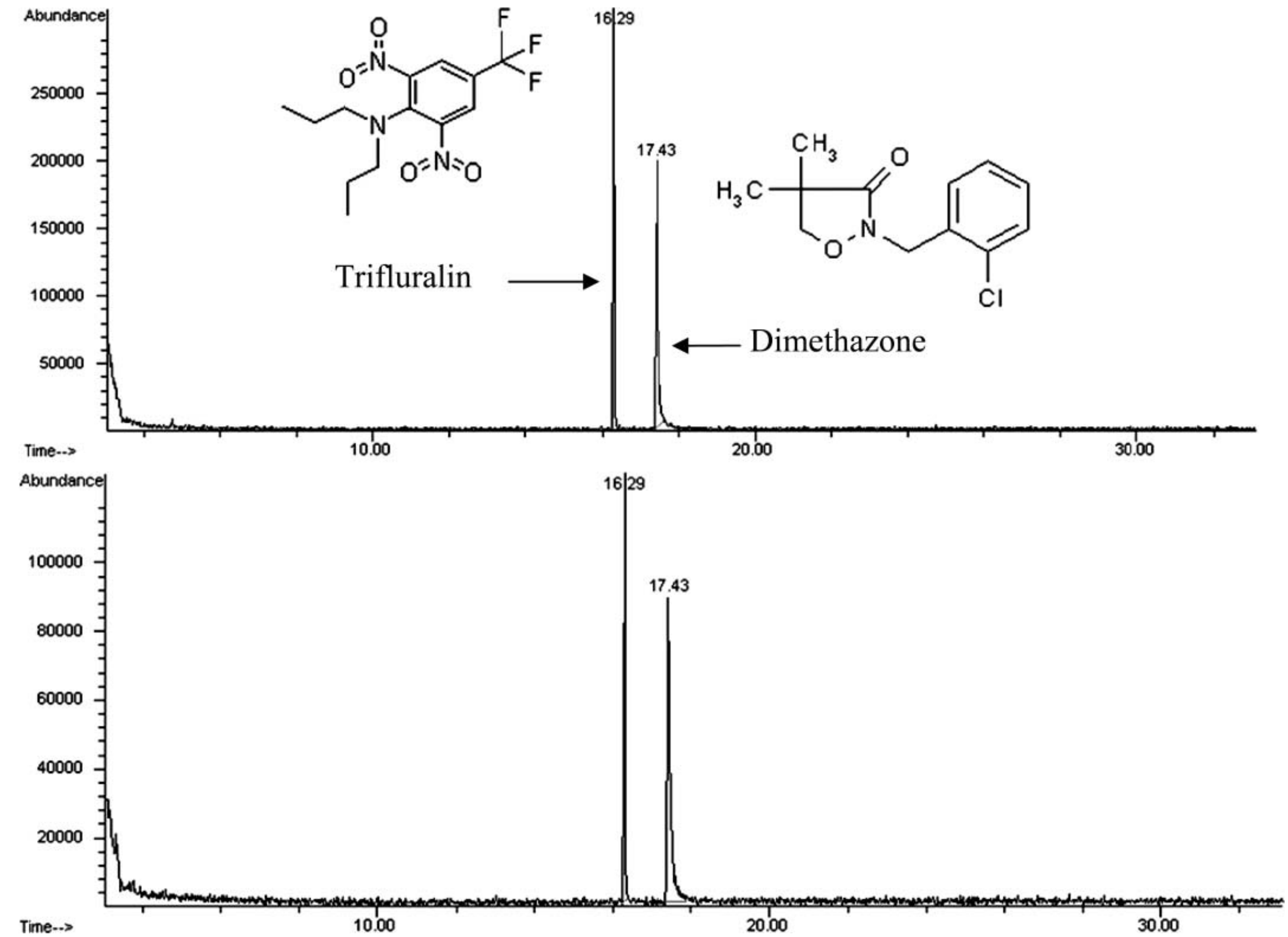


Fig. 5. Gas chromatographic (GC) chromatograms of native soil extracts prepared in acetonitrile: hexane: methanol (45:45:10 v/v) at 1 h (upper graph) and 3 d (lower graph) following spraying with a mixture of Clomazone and Treflan formulations at the recommended rate of application.

(HP 5890, Hewlett Packard, Palo Alto, CA) was equipped with a 30-m (0.23-mm diameter, 0.33-μm film thickness) fused silica capillary column with HP-5 (5% phenyl polysiloxane, 95% methyl polysiloxane) liquid phase. Operating conditions were 230, 250, and 280 °C for injector, oven, and detector, respectively. Area units were obtained from 1 μL injections. Linearity over the range of concentrations was determined using regression analysis ($R^2 > 0.95$). Peak areas were determined on a Hewlett Packard model 3396 series-II integrator. Quantification was based on average peak areas from two consecutive injections obtained from external standards. Under these conditions retention times (Rt) of trifluralin and dimethazone averaged 16.29 and 17.43 min, respectively (Fig. 5). Peak identity was confirmed by consistent retention time and coelution with standards under the conditions described. Dimethazone of 98% purity was purchased from Chem Service (West Chester, PA, USA) and trifluralin of 96.8% purity was obtained from Eli Lilly & Company (Indianapolis, IN, USA). Standard solutions ranging from 1 to 50 ng μL^{-1} were prepared and used to spike blank soil and water samples obtained from each of the soil treatments for evaluating the reproductability and efficiency of the analytical procedures used. After fortification at 30 and 45 $\mu g\ g^{-1}$ soil and 30 and 45 $\mu g\ mL^{-1}$ water samples, dimethazone and trifluralin were extracted and determined using the same procedures described above for field samples. Quality control (QC) samples included three field blanks to detect possible contamination during sampling, processing, and analysis. Three sets of duplicate samples and three sample-matrix spikes were used to evaluate potential bias of the data collected and the ability of the analytical procedure to recover the analyte from field samples. Residues of dimethazone in soil and water samples were related to soil management technique, and statistically analyzed using ANOVA procedure[27] and Duncan's multiple range test for mean comparisons. Recoveries (means $\pm$ SD) of dimethazone from fortified no-mulch soil, sewage sludge, and sludge mixed with yard waste compost averaged 94 ± 1.5, 91.6 ± 2.5, and 88 ± 2.4%, respectively. Recoveries (means ± SD) of dimethazone from runoff water samples were 96 ± 1.5%. Recoveries (means ± SE) of trifluralin from fortified no-mulch soil, sewage sludge, and sludge mixed with yard waste compost samples were 96.6 ± 2.4, 94.5 ± 1.9, and 91.5 ± 2.6, respectively. Recoveries of trifluralin from water samples averaged 93% ± 1.8. The lack of dimethazone and trifluralin residues in the blank samples suggested that there was no contamination from sampling, processing, or laboratory procedures. All chromatographic conditions were optimized as needed. Levels of detected pesticides were reported in μg L^{-1} of water and mg g^{-1} soil and related to soil management technique and statistically analyzed using analysis of variance [27] and Duncan's multiple range test for mean comparisons.

Results and discussion

Herbicide residues detected in soil and water were confirmed using gas chromatography (GC)/mass spectrometry (GC/MS) (Hewlett Packard Model 5971a, Palo Alto, CA). GC/MS chromatograms of a mixture of dimethazone and trifluralin detected in soil extracts are presented in Figure 5. The molecular weight of trifluralin (335) is greater than that of dimethazone (239). However, trifluralin peak appeared before dimethazone. This might be because of the greater vapor pressure of trifluralin as indicated in Table 1. The Electron impact mass spectrum of trifluralin (Fig. 6) showed spectral data with molecular ion peaks (M+) at m/z 306, 290, 264, and 43. Dimethazone electron mass spectrum (Fig. 7) with spectral data at m/z 204, 125, 89, and 41 are consistent with those reported by the National Institute of Standards and Technology (NIST).[28] The ion m/z 204 is formed by the loss of the atom of chlorine and the m/z 125 is formed by the breakage of the molecule of dimethazone at the carbon bond with nitrogen, and the subsequent loss of the $-C_5H_8NO_2$ of m/z 114.

Table 1. Physical and chemical properties of dimethazone and trifluralin herbicides sprayed at Kentucky State University Research Farm, Franklin County, Kentucky, USA.

Property	*Dimethazone*	*Trifluralin*	*Reference*
Water Solubility (g L^{-1})	1.1	0.22	[48]
Fish LC_{50} (mg L^{-1})			
Rainbow trout	19	0.01–0.04	[48]
Bluegill sunfish	34	0.02–0.09	
Log K_{OW} †	2.5	5.1	[49] [50]
K_{OC} (mL g^{-1}) ‡	150–562	8,000	[51] [40]
Vapor Pressure (mm Hg at 29 °C)	1.44×10^{-4}	1.99×10^{-4}	[48]

† Partition coefficient between n-octanol and water (as log value).
‡ Organic carbon partition coefficient.

The increased organic matter content of soil due to the addition of soil amendments (sewage sludge and sewage sludge mixed with yard waste compost) increased the concentration of dimethazone and trifluralin retained in soil (Fig. 8). Dimethazone residues extracted from sewage sludge (SS) and SS mixed with yard waste compost increased by 14 and 50%, respectively compared to no-mulch soil. Similarly, trifluralin residues increased by 17 and 75% in SS and SS mixed with yard waste, respectively (Fig. 8), compared to no-mulch native soil. This could be explained by the adsorption properties of dimethazone on soil particles[29] that varied with increasing percentages of organic matter following the addition of amendments as well as the partial degradation of dimethazone by soil microbes. [30, 31] Loux et al.[29] proposed hydrophobic bonding to organic matter to be the primary mechanism of dimethazone sorption and that bioavailability and dissipation of dimethazone in soil are determined by dimethazone adsorption properties. Yard waste compost contains significant concentrations of humic acid, the main constituent of soil organic matter.[32] Tavares and Rezende[33] indicated that functional groups in humic acid, namely carboxylic and phenolic groups appeared to be the principle sites for the adsorption and interaction with trifluralin. This might explain why trifluralin residues were higher in compost-amended soil than in NM bare soil. Due to mechanical incorporation of the herbicide 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.[34] Accordingly, recycling wastes have unique properties that should be thoroughly investigated in the soil/water/plant ecosystem. Binding of pesticides to humus in sewage sludge[32] might decrease the amount of pesticides available to interact with biota, thus reducing the toxicity of the pesticide active ingredients. Binding might inhibit the mobility of xenobiotics via leaching and runoff, thus preventing the contamination of aquatic environments. This is particulary important because of the extensive use of herbicides such as trifluralin and its relatively high toxicity to fish (Table 1). Some pesticides are highly soluble in water, but because of their ionic properties they bind tightly to the soil particles and pose minimal risk for groundwater contamination.

The two most important characteristics determining soil adsorption of a pesticide are the organic matter content of the soil and the water solubility of the pesticide. Adsorption of nonionic pesticides on soil particles depends directly on the organic carbon content of the compound and the adsorbing phase. The general tendency of an organic chemical to be adsorbed by soils may be assessed by the chemical's organic carbon partition coefficient (K_{OC}), which describes the tendency of the chemical to partition between water and organic carbon. K_{OC} is the amount of pesticide

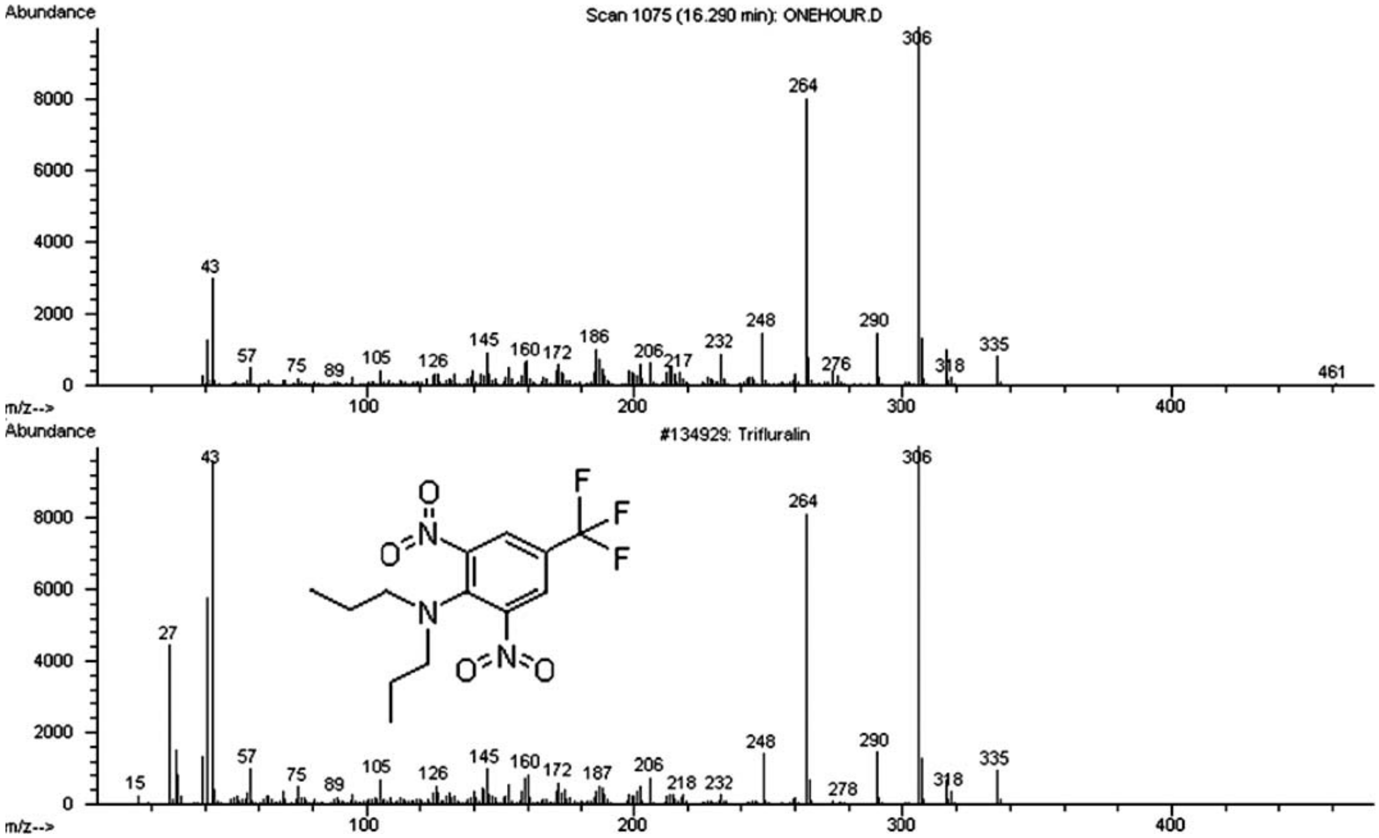


Fig. 6. Electron impact mass spectrum of trifluralin ($C_{13}H_{16}N_3O_4F_3$) extracted from soil indicating the molecular ions of m/z 306, 290, 264, and 43 along with other characteristic fragmentions.

adsorbed by soil divided by the product of fraction of organic carbon (OC) in soil and amount of pesticide in the soil solution.[35] K_{OC} coefficient represents the sorption on a unit carbon basis and could be used for comparison of sorption extent on soils with different organic matter contents. The greater the K_{OC} value of a pesticide, the stronger the binding to the soil.[35,36] According to Haith and Rossi,[37] the organic carbon sorption coefficient (K_{OC}) of bensulide is 3900 mL g^{-1}. Comparatively, the herbicide azafenidin (Milestone) has soil-organic carbon sorption coefficient of 298, which indicates that azafenidin does not bind strongly to soil particles.[38] Pesticides with high persistence and a strong sorption rate are likely to remain near the soil surface, increasing the chances of being carried to a stream via surface runoff. On the contrary, pesticides with high persistence and a weak sorption rate may be readily leached through the soil and are more likely to contaminate groundwater.[39]

Table 1 indicates that the soil binding property (Koc) of dimethazone is only 150–562 mL g^{-1} while Koc of trifluralin is 8,000 mL g^{-1}. Greater Koc values of trifluralin indicated a tighter binding to the soil particles.[36,40] Occurance of trifluralin at concentrations of 50 to 130 ng g^{-1} on a dry weight basis have been reported in soils 30 months after last application [41] and since the adsorbed herbicide becomes biologically inactive, therefore higher volume application rates are needed for soils rich in organic matter. These findings indicated that soil amendments and farm management practices play a major role in influencing pesticide residue levels in soil.

The present investigation is the first use of biobeds for retarding runoff water arising from agricultural fields. Under field conditions and depending on the rainfall events, biobeds reduced runoff water volume in no-mulch treatments by 44–88% compared to treatment with no biobeds (Fig. 9). Sewage sludge and sewage sludge mixed with yard waste compost treatments reduced runoff water by 60 and 79%, respectively in plots with biofilters compared to plots with no biofilters (Fig. 10**).** Biobeds also were successful in reducing the concentrations of the two herbicides dimethazone and trifluralin in runoff water. Dimethazone residues in runoff water collected down the field slope from plots with biobeds were much lower than those in runoff from plots with no biobeds (Fig. 11). Similarly, trifluralin residues in ruoff water from plots with biobeds were lower than trifluralin residues in runoff from plots with no biobeds (Fig. 12). These findings indicated that biobeds are an effective low-cost alternative for treating dimethazone and trifluralin residues in runoff water, providing a matrix to facilitate biodegradation. Studies in

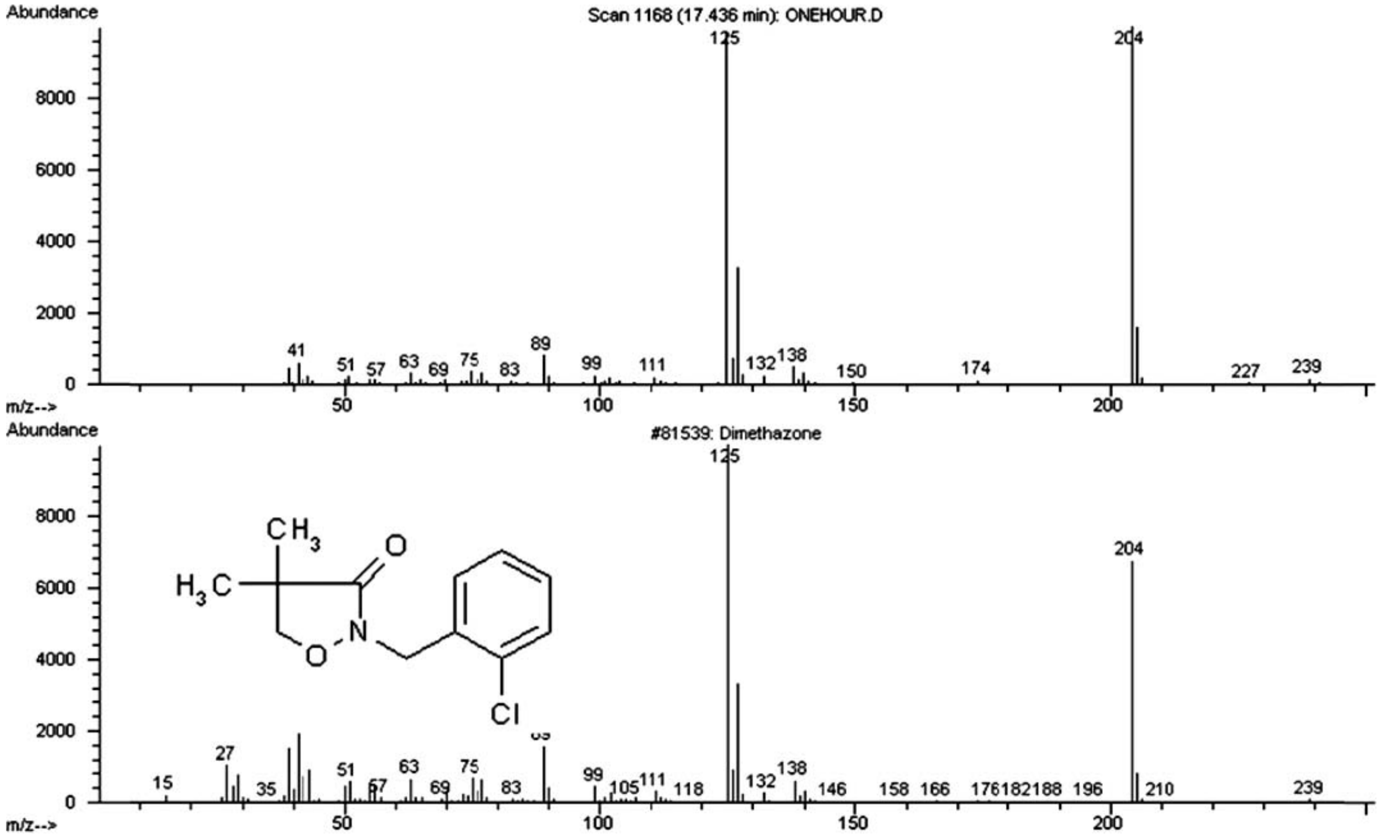


Fig. 7. Electron impact mass spectrum of dimethazone ($C_{12}H_{14}$ Cl NO_2) extracted from soil indicating the molecular ions of m/z 204, 125, 89, and 41 along with other characteristic fragmentions.

Sweden have demonstrated that biobeds can effectively retain and degrade pesticide waste arising from accidental spillages of pesticide concentrate.[42] However, studies performed in Denmark have shown that the clay membrane at the base of the biobed could not retain all of the leachate draining through the biobed.[43] Studies have also shown that whilst less mobile pesticides are effectively retained within the biobed matrix, significant amounts of the more mobile pesticides can leach from the biobed.[43–45] Previous work has shown that biobeds were used to treat pesticide waste arising from spills as well as pesticide washing processes. The literature indicated that total amounts of isoproturon (an herbicide) leached from biobeds were 1947 mg from the soil compared with 32 mg from the biobed and for mecoprop (an herbicide) 574 and 175 mg leached from the soil and biobed, respectively, after in-field tank washing and disposal.[11]

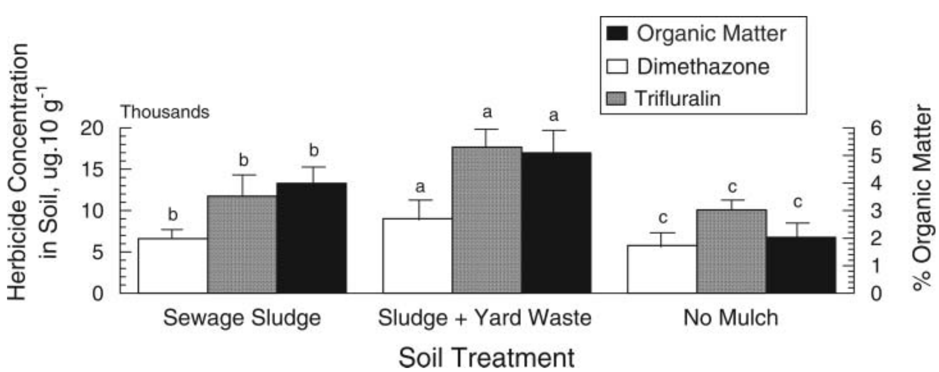


Fig. 8. Dimethazone and trifluralin residues, and organic matter content in no-mulch soil, soil mixed with sewage, and soil mixed with sewage sludge and yard waste compost mixture. Statistical comparisons were done between three soil management practices for each parameter. Bars accompanied by different letter are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

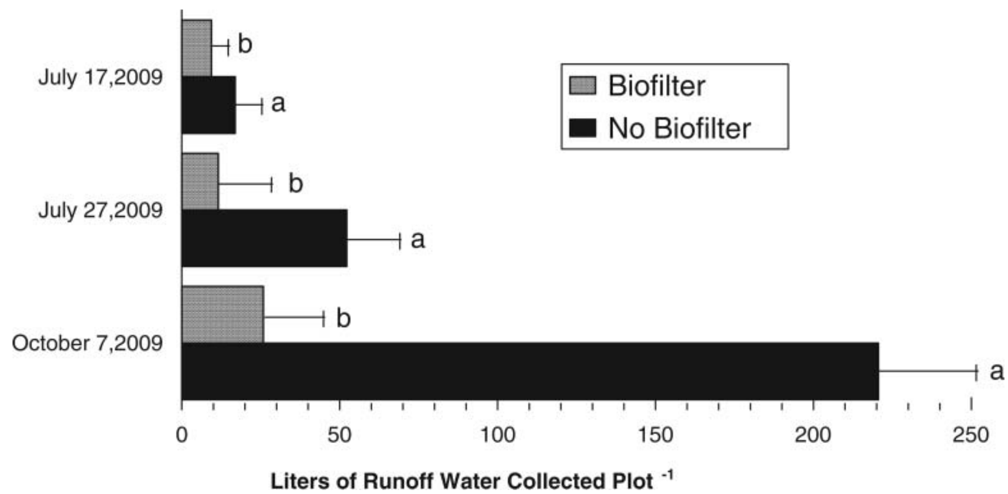


Fig. 9. Overall runoff water volume collected down the field slope on July 17, July 27, and October 7, 2009 following three natural rainfalls of 0.81, 1.31, and 1.95 inches of rain, respectively. Each plot is 3.7 m wide × 22 m long (0.02 acre). Statistical comparisons were done between plots with biofilters and plots with no biofilter for each rainfall event. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

This investigation indicated that large volumes of runoff water containing dimethazone and trifluralin residues arising from normal agricultural practices can be treated, thus minimizing their loss into the environment. The biobed system can be built on the farm land using locally available materials which are topsoil, peat, and straw (Biomix) covered with grass.[11,46] The topsoil represents 25% of the overall mix and is the major source of microorganisms that acts as the inoculum for the system that may receive high concentrations of relatively complex mixtures of pesticides in runoff. The risk of groundwater contamination resulting from rapid leaching of highly soluble pesticides can be minimized through pesticide adsorption on a matrix or carrier.[47] Biobed systems could be used to intercept pesticide-contaminated runoff from agricultural fields, creating optimum conditions for sorption and biodegradation such that the amount of pesticides adjacent to water bodies is significantly reduced. This may provide a potential solution to pesticide contamination of surface and groundwater from farmlands. These data would be of value at the regional level and at state and national levels and might provide economic solutions to environmental pollution by pesticides in runoff released from arable lands. Off-site movement of dimethazone by vapor and liquid route, due

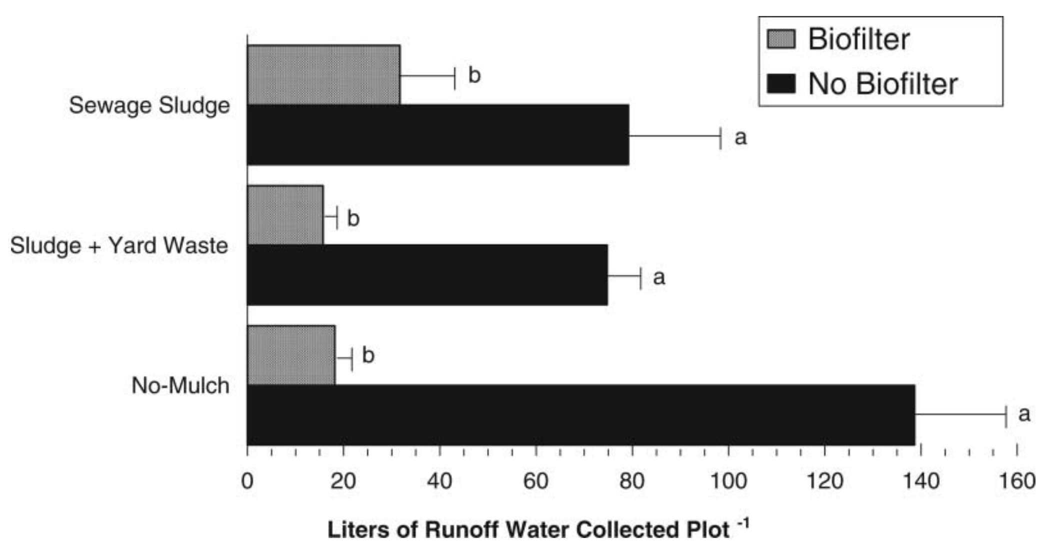


Fig. 10. Runoff water volume collected down the land slope under three soil management practices. Each plot is 3.7 m wide x 22 m long (0.02 acre). Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil treatments. Bars accompanied by different letter are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

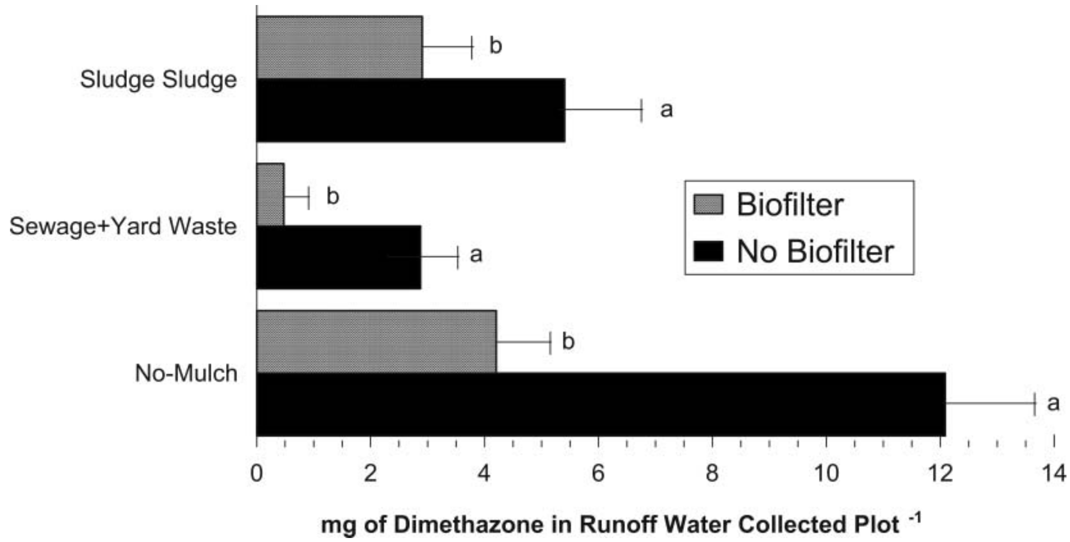


Fig. 11. Dimethazone residues in runoff water collected down the land slope under three soil management practices. Each plot is 3.7 m wide × 22 m long (0.02 acre). Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil treatments. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

to its physical and chemical properties, might be limited by sorption of the herbicide to high levels of organic carbon in soil amendments such as sewage sludge and/or use of biofilters that contain a considerable amount of organic carbon. A spill of a few millilitres of formulated preparation from a container of concentrated pesticide during spraying operations can easily contain 1 g of active ingredient, which require 10,000,000 L (10,000 m^3) of water to dilute this amount to an acceptable concentration of 0.1 μgL^{-1} water. Accordingly, the use of biobeds in on-farm bioremediation of pesticide residues in surface runoff water might provide a potential solution to contaminated runoff and seepage water arising from agricultural production operations.

Plots amended with sewage sludge and yard waste mix increased volume of water percolated into the vadose zone by 55% compared to no-mulch treatments. Plots with

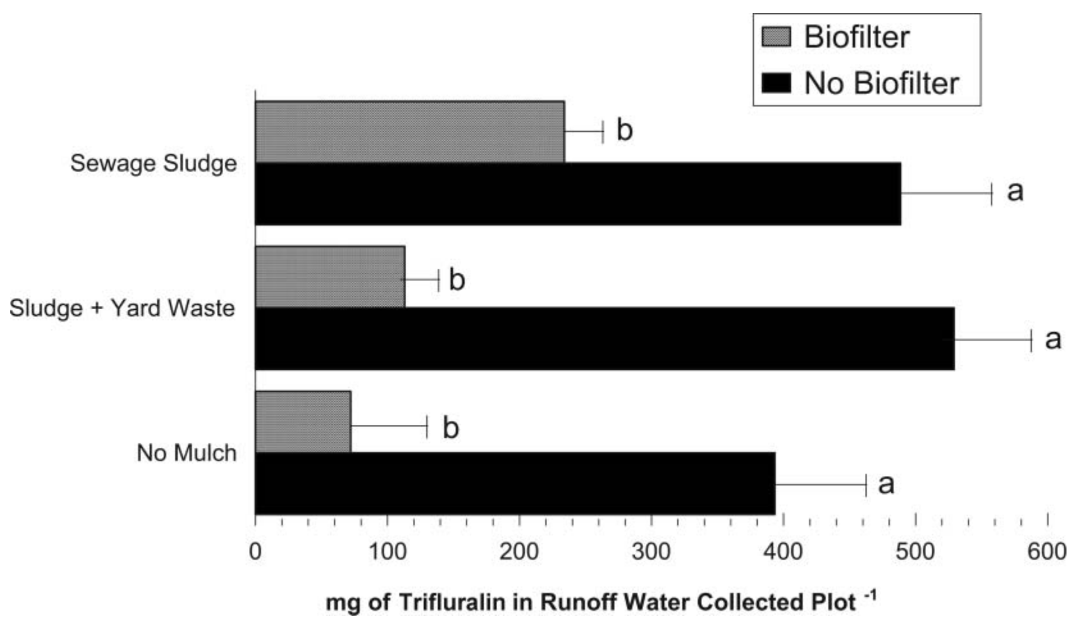


Fig. 12. Trifluralin residues in runoff water collected down the land slope under three soil management practices. Each plot is 3.7 m x 22 m long (0.02 acre). Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil management practices. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

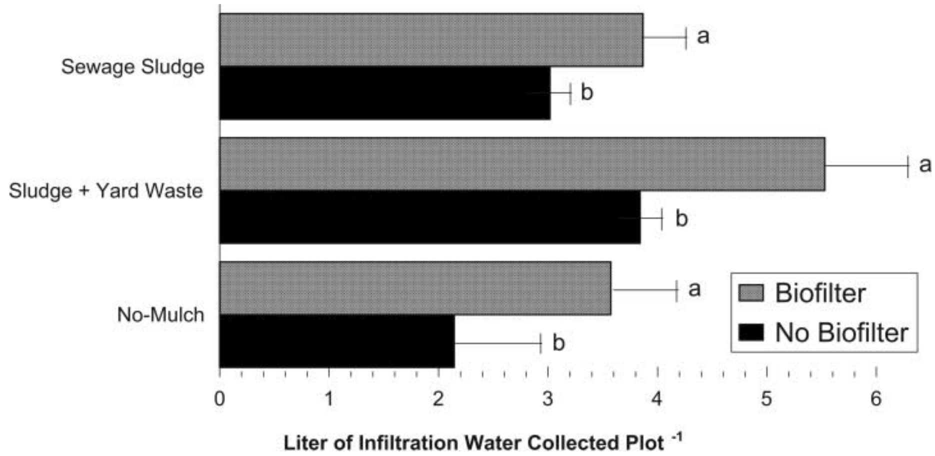


Fig. 13. Infiltration water volume collected under three soil management practices. Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil treatments. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

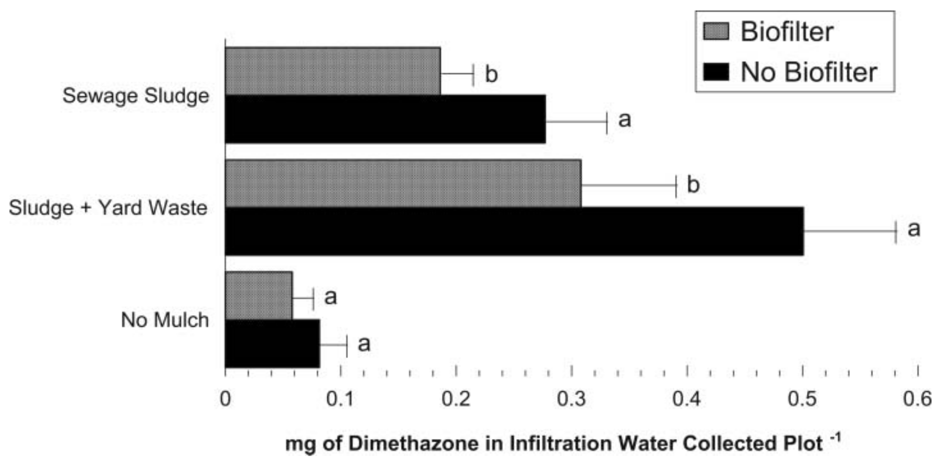


Fig. 14. Dimethazone residues in infiltration water collected under three soil management practices. Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil management practices. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

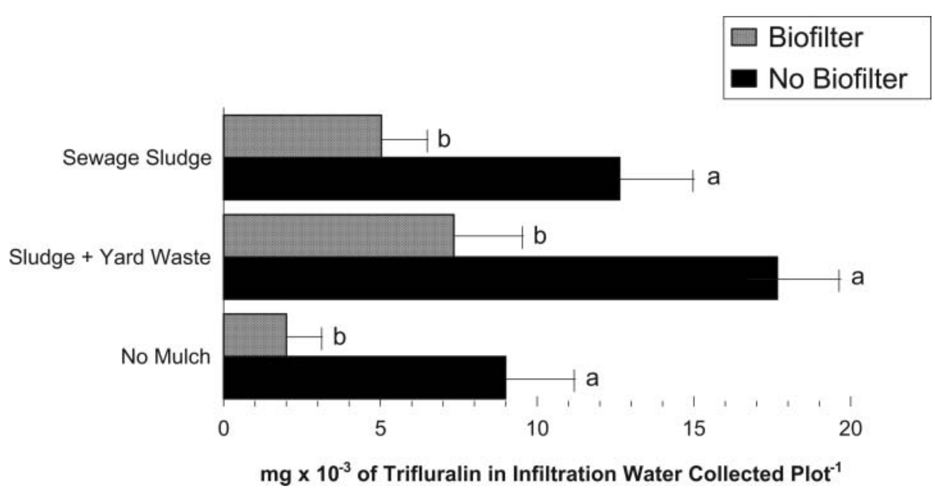


Fig. 15. Trifluralin residues in infiltration water collected under three soil management practices. Statistical comparisons were done between plots with biofilters and plots with no biofilter among three soil management practices. Bars accompanied by different letters are significantly different ($P < 0.05$) using Duncan's multiple range test.[27]

biofilters also increased the volume of water percolated into the vadose zone. This increase was greatest (44%) in sewage sludge mixed with yard waste treatments (Fig. 13). This increase could be attributed to the reduced bulk density and increased soil particle interspaces after addition of yard waste compost.

As indicated previously, water solubility, vapor pressure, and K_{OC} value of a pesticide have a great impact on its mobility and distribution in the environment. Dimethazone residues in infiltration water (Fig. 14) were reduced from 0.5 to 0.31 mg plot^{-1} (38% reduction), while trifluralin residues were reduced from 17.7 to 7.3 mg plot^{-1} (60% reduction). This is attributed to the presence of biobeds (biofilters) (Fig. 15) as well as the physical and chemical characteristics of each of the two herbicides that vary from the high water solubility and low K_{OC} values of dimethazone to the low-water solubility and high K_{OC} values of trifluralin (Table 1).

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