We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Reducing Herbicide Residues from Agricultural Runoff and Seepage Water

George F. Antonious

Additional information is available at the end of the chapter

Abstract

Herbicide use while being of a great benefit in controlling weeds in agricultural systems can also pose a threat to environmental quality due to off-target and off-site impacts. The increasing concern about risks associated with agricultural chemicals and specifically their impact on surface and groundwater quality is a national and international concern. In Kentucky, herbicide off-site movement occurs, allowing them to enter the Kentucky River watershed and impact surface and groundwater quality. Accordingly, it is necessary to assess the distribution and degradation/dissipation of herbicides in agricultural soils and runoff water after field application and develop management practices and/or remediation techniques to mitigate environmental pollution by agrochemicals. The overall goal of the best management practices is to develop sustainable agricultural techniques that strike an acceptable balance between crop production benefits and ecological conservation by reducing herbicide impact on environmental quality to 1) protect watersheds by reducing the mobility of herbicides from soil into runoff and seepage water using binding agents; 2) enhance soil microbial activity that mineralizes herbicides in soil; and 3) enhance growers' knowledge about bioremediation techniques (soil amendments, biofilters, biochar, and soil microorganisms) that could be implemented to reduce herbicide mobility and protect natural water resources.

Keywords: Biofilter, Biochar, Soil amendments, Organic matter, GC-MSD

1. Introduction

In Kentucky agriculture, herbicides (metribuzin, bensulide, dacthal, halosulfuron, carfentrazone, trifluralin, napropamide, and pendimethalin) are applied according to crop production guidelines [1]; however, their application period typically coincides with seasonal rainfall. In intensively cultivated areas, agriculture is a significant source of herbicides associated with

runoff. According to the US Environmental Protection Agency (EPA), over 441 million kg of conventional pesticides were used in the USA in 2001 [2]. Of that total, about 340 million kg were used in agricultural applications, and 48 million kg were used for home and garden purposes. In the USA, pesticide residues caused about 1,200 water-body impairments [3]. The USEPA also reported the consumption of 3 billion kg of herbicides during 2001 [4].

Pesticides play an important role in the success of modern farming and food production [5]. A commonly quoted estimate is that farmers save $ 3 to $ 5 for every $ 1 spent on pesticides [6]. In the USA, herbicides are used on > 90 % of most crops. Prior to the adoption of herbicides, 120 hours of labor and 16 cultivation trips per acre were used to control weeds. Without herbicides, the US food and fiber production would be reduced by 13.3 billion due to less effective weed control. Pesticides play an important role in the success of modern farming and food production [7]. The total loss in production would amount to 288 billion pounds, which represents approximately 21 % of the national production. In addition, the adoption of no-till practices prevents annual erosion of 304 billion pounds of soil every year [7]. Approximately 41,511 water-body impairments across the USA are attributed to pesticides, and of that total, 1,300 water-body impairments are within the state of Kentucky [8]. Based on estimated pesticide sales data for agricultural applications in 2000, a total of 1.5 million pounds of herbicides were applied in the Kentucky Green River Basin. Five herbicides (atrazine, sima-zine, metolachlor, tebuthiuron, and prometon) were detected in eight karst springs water in the Green River drainage basin [9]. Runoff water and sediment are frequent in sloping areas where most of the arable lands are highly erodible. Concerns about soil erosion, nutrient runoff, loss of soil organic matter, and the impairment of environmental quality from sedi-mentation and pollution of natural water resources by agrochemicals, N, P, trace elements, and other environmental contaminants have stimulated interest in proper management of natural resources. Herbicides cause water pollution by running off agricultural fields and domestic gardens into nearby water sources. Although agriculture has been identified as a source of pesticides found in surface water, other sources exist. Other sources may be pesticide manufacturing industries, industries using pesticides in their processes (such as woolen goods manufacturers), and direct application of herbicides to surface waters to control aquatic plants, lawn care, and golf course care.

A wide range of active ingredients are used as pesticides, and millions of tons of so-called "inert" ingredients are added to pesticide formulations as carriers, stabilizers, emulsifiers, etc. Some of these ingredients are dangerous in their own right. Ethylene dichloride, a nerve poison, is an example of an inert ingredient linked with damage to the eyes, heart, liver, and adrenal glands [10].
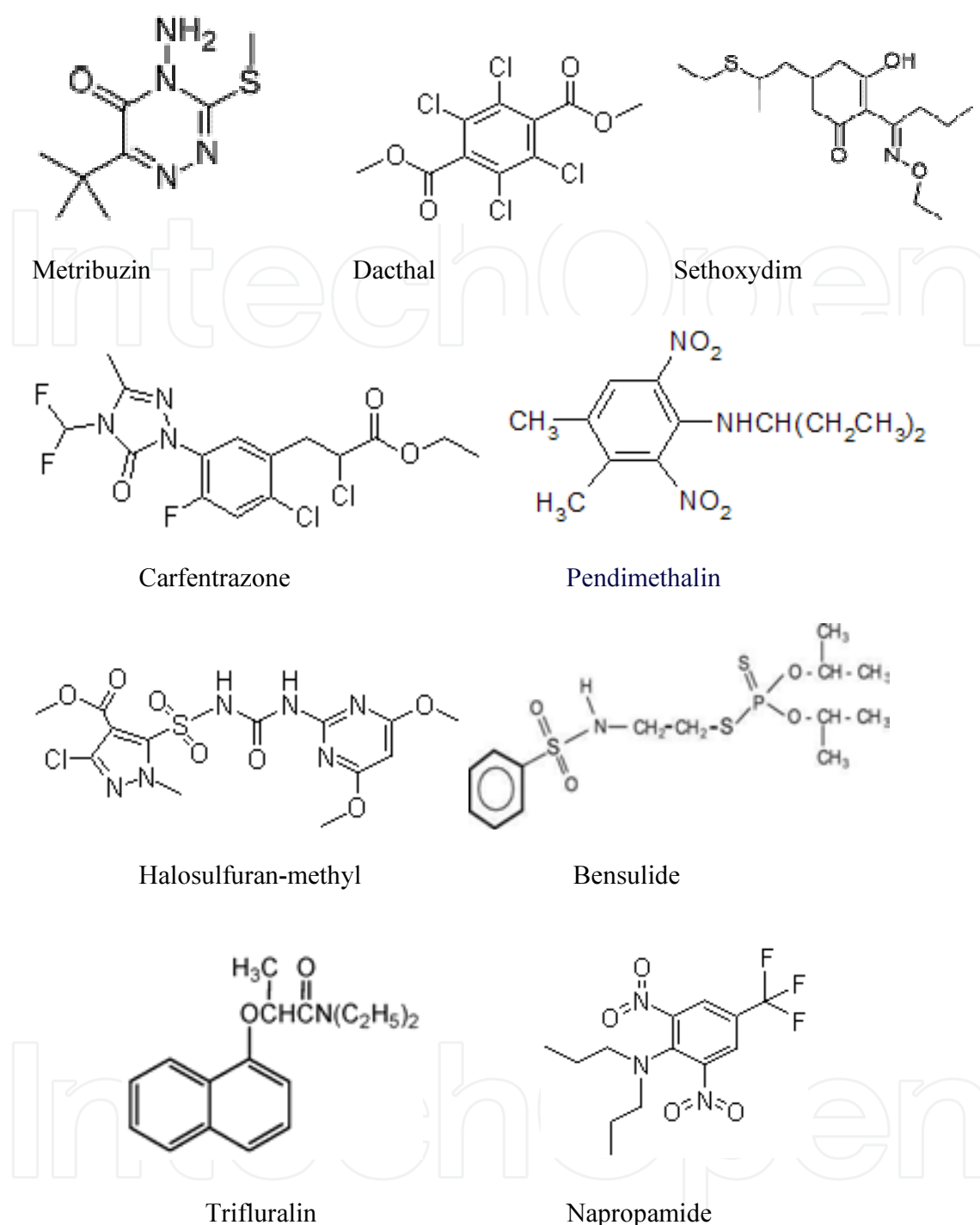
Portions of the active ingredient may transport to neighboring water bodies via drift during pesticide spraying, wind erosion, and runoff. Accordingly, it is necessary to assess and monitor the distribution and degradation/dissipation of herbicide residues in soil and water after field application. Runoff from agricultural watershed is found to carry enormous amounts of pesticides [11]. Following natural rainfall events, water flow may change from < 1 to > 10,000 ft^3/s^{-1} (1 ft^3 is equal to 28.3 L) in a matter of minutes to hours, enhancing pesticide transport to receiving water [12]. Streams and their tributaries that drain into the Kentucky River add

fertilizers and herbicides. In Kentucky, the watershed lies above thick layers of easily dissolved limestone that form carbonate aquifers. Groundwater flows through channels in the limestone, so caves and springs—and sinkholes—are common in regions with this karst geology [13]. Accordingly, Kentucky's citizen who uses fertilizer, herbicides, and other chemicals on his lawn, landscaping, and gardens adds to this water pollution problem.

A significant association was found between the season of elevated agrichemicals in surface water in April–July and higher risks of birth defects in live births in the USA [14]. The most frequently detected herbicides in surface waters include several triazines (atrazine, cyanazine, and simazine), acetanilides (metolachlor and alachlor), and 2, 4-dichlorophenoxyacetic acid (2, 4-D) [15]. In Missouri men, high urine levels of atrazine and alachlor were associated with abnormal sperm [16]. Concentrations of the herbicide atrazine and other pesticides also were higher in the months of April–July. Chlorophenoxy herbicides are widely used in the USA for broadleaf weed control in grain farming and park maintenance. In Minnesota, Montana, North Dakota, and South Dakota, about 85 % of the spring and durum wheat acreage is treated with chlorophenoxy herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA).

Schreinemachers [17] found that infants in these four wheat-producing states conceived in April–June, the time of herbicide field application, were more likely to have circulatory/respiratory (excluding heart) malformations compared to births conceived during the other months. According to the EPA's most recent data, public water systems using groundwater as a drinking source serve about 105 million people nationwide [18]. The total number of people drinking groundwater increases when factoring in households supplied by private drinking water wells. Halosulfuron-methyl is a pyrazole sulfonylurea (Figure 1) used as a selective broadleaf postemergence herbicide. When applied preemergence or to the paddy water, intact halosulfuron-methyl was not detected or recovered in maize, sugarcane, and rice, indicating extensive metabolism of halosulfuron-methyl, probably initiated by a breakdown of the molecule in the soil or water. Chlorosulfonamide acid was the major metabolite identified in all commodities tested [19]. Halosulfuron-methyl exhibited very high to medium mobility in soil. Toxicological studies were carried out on two metabolites. The metabolite chlorosulfonamide acid (CSA) was found in plants and in groundwater at levels potentially exceeding 0.1 μg L^{-1}, whereas its metabolite halosulfuron-methyl showed low acute toxicity. Mitigation of herbicides, fungicides, and insecticide residues in soil and natural water resources could be achieved using modern management practices such as biofilters [20], adsorption techniques [21, 22] or biochar [23], soil microorganisms and the enzymes they produce [24], and wetland microcosms [22]. Among these management practices is the use of soil amendments.

The USA produces nearly 15 million dry tons of municipal sewage sludge each year, and the tonnage is increasing due to population growth. In addition, the rapid growth in poultry industry has resulted in significant manure generation. More than 11.4 million tons of poultry litter was generated in the USA [25]. Sewage sludge and chicken manure, that must be disposed, are excellent fertilizers [26-29]. Addition of soil amendments such as chicken manure and sewage sludge to native agricultural soil increased water infiltration, lowering runoff

Metribuzin   Dacthal   Sethoxydim

Carfentrazone   Pendimethalin

Halosulfuran-methyl   Bensulide

Trifluralin   Napropamide

FIGURE 1. Chemical structures of metribuzin [4-amino-6-*tert*-butyl-4, 5-dihydro-3-methylthio-1, 2, 4-triazin-5-one]; dacthal [1, 4-Benzenedicarboxylic acid, 2, 3, 5, 6-tetrachloro-, dimethyl] ester; and sethoxydim [2[1(ethoxyimino) butyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexen-1-one]; carfentazone, ethyl (RS)-2-chloro-3-[2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-

Figure 1. Chemical structures of metribuzin [4-amino-6-*tert*-butyl-4, 5-dihydro-3-methylthio-1, 3, 4-triazin-5-one]; dac-thal [1, 4-Benzenedicarboxylic acid, 2, 3, 5, 6-tetrachloro-, dimethyl] ester; sethoxydim [2[1(ethoxyimino) butyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexen-1-one]; carfentazone, ethyl (RS)-2-chloro-3-[2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorophenyl]propionate; pendimethalin, Prowl 3.3 E, N-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-5-[(4, 6-dimethoxypyri-midin-2-yl) carbamoylsulfamoyl]-1-methyl-pyrazole-4-carboxylic acid methyl ester; bensulide [O, O-diisopropyl S-2-phenylsulfonylaminoethyl phosphorodithioate]; trifluralin [Treflan, (2,6-dinitro N,N-dipropyl-4-trifluoromethyl) benzenamine]; and napropamide [Devrinol, (N, N-diethyl-2-(1-naphthyloxy) propionamide)].

water volume and herbicide residues in runoff following natural rainfall events. Studies revealed that increasing soil organic matter by the addition of soil amendment to native soil reduced the transport of dimethyl tetrachloroterephthalate (DCPA, dacthal) herbicide down the land slope into runoff water [30]. The use of sewage sludge in land farming could become a useful technique for trapping herbicides such as trifluralin [31] and dimethazone [32, 33], metribuzin [30], and napropamide [34]. In addition to soil amendments, slot-mulch techniques (biobeds or biofilters—a cavity in the ground filled with a mixture of composted organic matter, topsoil, and a grass layer on top) provide a potential solution to herbicide contamination of surface waters arising from agricultural fields. Antonious [20] installed the first biofilter in the USA (www.biobed.org) for mitigation of herbicides in runoff water from vegetable fields. The use of biobeds and adsorption techniques are unique ways of treating contaminated soil and agricultural runoff. The filling materials of biobed systems (mixture of straw, peat moss, and native soil) have increased sorption capacity and microbial activity for degradation of pesticides [35]. The mechanism of biosorption process includes chemisorption, complexation, adsorption, diffusion through the pores, and ion exchange [36]. 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). Degradation of the three pesticides in biobeds was found to be faster than published values for degradation of these pesticides in soil. The half-life of the three pesticides used was less than 14 days compared to literature values of 60–70 days in bare soil [37]. In addition, microorganisms in biobeds and soil are capable of degrading both sorbed and bound pesticide residues [38]. These findings indicated that biobeds or biofilters could substantially reduce pesticide concentrations in agricultural runoff. The biobed system can also be built on the farmland using locally available materials. This developed methodology to mitigate the impact of pesticides on the ecosystem is urgently needed. The risk of groundwater contamination resulting from rapid leaching of dimethazone and trifluralin herbicides was minimized through herbicide adsorption on the biobed filling materials under field conditions [20, 22]. In addition, biobeds (biofilters) have been used in northern Europe for minimizing point-source contamination of water resources by pesticides [39]. Antonious [20] provided evidence that biobeds enhanced dimethazone (a hydrophilic herbicide) and trifluralin (a lipophilic herbicide) dissipation and reduced their residues in runoff. To the best of the author's knowledge, the use of biobeds at Kentucky State University (KSU)/College of Agriculture (Frankfort, KY) represents the first field application of biobed systems in the USA for reducing runoff water loss and mitigation of off-site movement of herbicides. Installing biobeds in Kentucky farms (current project at KSU), where most of the arable lands are highly erodible, is a unique way of mitigating environmental pollution by herbicides before they enter rivers and streams.

Biochar, a product of the pyrolysis of organic material, has been credited with many desirable properties as a soil amendment, including soil conditioning [40], enhanced soil fertility [41], and sorption of pollutants [23] and soil hormones [42], and as an agent of C sequestration [43-45]. Although one study did report enhanced biological N fixation in biochar-amended soils [46], the effects of biochar on the biological activity of soil need greater investigation to evaluate the potential repercussions of wide application of such material when amended with municipal sewage sludge or chicken manure used for land farming. Currently, little informa-

tion exists in literature if biochar amendment to soil can reduce the plant uptake of pesticide residues and/or trace-element bioavailability. Such practice, if found effective, can assist in the management of contaminated agricultural and urban soils from current and past use of herbicides and other contaminants. Interest in biochar, made by pyrolysis of biomass, as a multifaceted solution to agricultural and pesticide pollution issues is growing at a rapid pace both nationally and internationally. The use of biochar in the US agricultural field is a new area of research. The infiltration of harmful quantities of nutrients and herbicides into groundwater as well as soil erosion and runoff into surface waters could be limited with the use of biochar [47] as a soil amendment. Biochar reduced the release of nitrous oxide [48]. About 40 % decrease in nitrous oxide emissions has been reported when biochar was applied to soil. This gas is approximately 310 times stronger than CO_2 in terms of global warming potential [49].

Greenhouse gas emission reductions might be 12 %–84 % greater if biochar is land applied instead of combusted for energy purposes [47, 48]. Biochar's fate as a viable component of the long-term solution to mitigate climate change by way of carbon sequestration depends upon further development by the scientific and technology transfer communities. Little is known about how biochar could successfully be implemented in the agricultural fields. Improving methods of pesticide detection and monitoring the performance and impact of soil amendments (such as sewage sludge, chicken manure, and biochar) and soil management practices on concentrations and transport of pesticides, nutrients, and trace elements into runoff and seepage water are the main focus of the current agricultural remediation methods. About $ 2.1 million was spent in 2009 on biochar research by the Agricultural Research Service (ARS) [50]. Converting biomass into biochar and bio-oil at various labs nationwide is one of ARS's priorities. The USA could use biochar to sequester 139 Tg of carbon annually if it were to harvest and pyrolyze 1.3 billion tons of biomass [50]. A series of presentations delivered at the United Nations Climate Change Conferences elevated interest in biochar as an immediate response to mitigate climate change, given its carbon sequestration ability. Biochar sequesters carbon while simultaneously enhancing the fertility of the soil. In addition, Ute et al. [51] found that some microorganisms were able to live on biochar as C source. The activity of purified N-acetyl glucosaminidase increased 50 to 75 % following biochar exposure, suggesting a chemical enhancement of enzyme function [52].

Biochar also is a potential solution to environmental contamination by herbicides. A survey of current adsorbents indicated that the large surface area of activated carbon (ranging from 500 to 2,000 m^2 g^{-1}) makes it a perfect candidate for pesticides and trace-element adsorption. Adsorption on activated charcoal occurs through van der Waals forces that allow it to adsorb different types of pollutants including pesticides [53-55]. Knowledge about the environmental problems and adoption of appropriate solutions and practices to enhance and protect our national water quality from environmental pollution by herbicides require timely delivery of research and educational technology. The development of production systems and mitigation techniques that reduce the introduction of agrochemicals like herbicides into the environment presents a continuing challenge.

2. Literature review

Soil erosion reduces crop productivity by decreasing soil depth, removing nutrients required for plant growth, and altering soil physical properties resulting in less water infiltration, poorer crop establishment, and root penetration. Intensive use of herbicides and other pesticides in many parts of the USA increases the potential for non-point source contamination of soil and receiving water. One of the major problems with the application of pesticides is targeting the chemicals to the pest. Often, less than 0.1 % of the pesticides applied to crops under field conditions reach the target pests. The remaining 99.9 % residues can have a number of adverse effects that include health risks to both humans and wildlife. The amount of herbicides reaching target weeds is generally much higher. From 0.1 to 5 % of postemergence herbicides applied reach the target weeds [56]. Occurrence of herbicides and other pesticides in runoff and infiltration water [32-34, 57-64] increases the potential impact on human health and environmental quality. The lack of pesticide field dissipation data and the increasing concern about herbicides and other agricultural chemicals and their impact on surface and ground-water quality have made environmental pollution by herbicides a national concern.

In addition, an increase of organic waste originating from different human and productive activities is a continuous concern. Waste application to soil is a solution to disposal. This practice is popular in the agricultural fields because of the value of this waste as organic fertilizer. Application of organic amendments to agricultural soils makes good use of natural resources and reduces the need of synthetic fertilizers. Recently, increased interest has been focused on assessing the influence of organic waste added to the soil on pesticide (herbicides, fungicides, and insecticides) adsorption, movement, and biodegradation. There is a continuing search for inexpensive, locally available sources of organic matter for use in growing horti-cultural crops. The addition of organic amendment to soil normally results in an increase in the microbiological activity [24, 65-67] due to the availability of simple organic molecules such as sugar and amino acids. Composting provides an organic amendment useful for improving soil structure and nutrient status [65] and generally stimulates soil microbial activity [24, 68, 69]. Among the major parameters of soil fertility and biological properties, special emphases are given to enzyme activity. As more sewage sludge treatment districts turn to composting as a viable means of sludge stabilization, sewage sludge will become available in increasing quantities. With the increased interest in recycling waste, there is a need to monitor the three enzymes (invertase, urease, and phosphatase) of the C, N, and P cycles, respectively, as indicators of increased soil microbial populations in the rhizosphere of growing plants [24]. Soil microorganisms (bacteria, fungi, protozoa, algae) in sewage sludge and chicken manure excrete ureases, invertases, dehydrogenases, cellulases, amylases, and phosphatases to degrade herbicides in soil and water ecosystems. Microorganisms produce sticky substances (polysaccharides) that help soil particles adhere to one another and help the soil resist erosion that could diminish agriculture productivity [70]. Emphasis has been given to soil enzymes in relation to reclamation management and the enzymatic processes that play a significant role in bioremediation of pesticides and heavy metals. Work carried out by Antonious [22, 24] has

provided detailed information on enzymatic and microbial population responses in soil in a series of ecosystems. Remediation of contaminated soils is based on the degrading activity of soil microbiota. However, sewage sludge and chicken manure contain significant amounts of heavy metals that may impact soil microorganisms and the enzymes they produce by blocking of either the enzyme or substrate when present in excessive concentrations [71]. Accumulation of trace elements in plants grown in biosolids (sewage sludge) varied among plant species and even among accessions of the same species [72]. The application rate of sewage sludge and chicken manure applied to agricultural soil is proposed according to soil nitrogen, phosphorus, and potassium requirements, with a maximum application rate of 15 t year^{-1} [73]. In fact, a specific rule for animal manure application to soil does not exist, but is proposed through good agricultural practices for use as fertilizer and as herbicide binding agent due to its organic matter content. Several studies have shown that an increase in soil pH results in an increase in soil microbial biomass and enzymatic activities, favoring a rapid growth-linked degradation of phenylurea isoproturon herbicides as a result of interaction between degradative *Sphingomonas spp.* and pH [74] and biodegradation of fenamiphos [75]. Therefore, the question here is what can be done to increase soil pH? The answer is the use of either lime (CaO) or biochar mixed with native soil.

3. Overview of soil amendments and herbicide field studies

At Kentucky State University H.R. Benson Research and Demonstration Farm (Franklin County, KY), studies were conducted on a Lowell silty loam soil of 12 % clay, 75 % silt, and 13 % sand. Plots (18) of 22 × 3.7 m each were established on 10 % slope to investigate herbicide mobility in relation to soil amendments under field conditions. The plots were separated using metal borders 20 cm above ground level to prevent cross contamination between adjacent treatments (Figure 2). In the first year, three soil management practices were used: i) sewage sludge (Figure 3) obtained from Nicholasville Wastewater Treatment Plant, Versailles, KY, was treated with lime (CaO) at 1:10 (w/w) ratio and mixed with yard waste compost (made from yard and lawn trimmings and vegetable remains) at 15 t acre^{-1} (on dry-weight basis) with a plowing depth of 15 cm, ii) sewage sludge was mixed with native soil at 15 t acre^{-1} (on dry-weight basis) with a plowing depth of 15 cm, and iii) a no-mulch (NM) control treatment (rototilled bare soil) was used for comparison purposes to monitor the herbicide bensulide (Figure 1) and its metabolite mobility. In year 2, the three soil management practices were chicken manure, sewage sludge (Figure 3), and no-mulch native soil used for comparison purposes to monitor the impact of soil amendments on metribuzin and DCPA (dacthal) herbicide mobility under field conditions. In subsequent years, the persistence of trifluralin and napropamide herbicides (Figure 1) was also investigated. Herbicides selected in this research are commonly used in Kentucky agriculture and were applied according to Kentucky-recommended rates of application [1]. Following herbicide treatment, total runoff water loss per runoff event per each 0.02-acre plot was used to monitor mobility of herbicides tested.

**FIGURE 2** Kentucky State University/ College of Agriculture erosion field plots.

Figure 3. Soil amendments, chicken manure (left) and sewage sludge (right) used for mitigation of herbicide residues at Kentucky State University/College of Agriculture (Franklin Conty, KY).

3.1. Runoff water measurement

Runoff water was collected and quantified at the lower end of each plot throughout the growing season using a tipping-bucket runoff metering apparatus (Figure 4). Buckets were calibrated (one tip represents 3 L of runoff) and maintained to provide precise measure of amount of runoff per tip. Numbers of tips were counted using mechanical runoff counters (ENM Company, 5617 Northwest Highway, Chicago, IL 60646). Collection of samples in 3.79 L borosilicate glass bottles was carried out through a flow-restricted composite collection system (approximately 40 mL per tip was collected). Following rainfall events, runoff water samples were transported on ice to the laboratory, stored at 4 $^{\circ}$C for extraction and analyses of herbicide residues. Runoff water volume (L acre^{-1}) from each soil treatment was based on total runoff water loss per runoff event per 0.02-acre plots.

FIGURE 3. Soil amendments, chicken manure (left) and sewage sludge (right) used for mitigation of herbicide residues at Kentucky State University/College of Agriculture (Franklin Conty, KY).
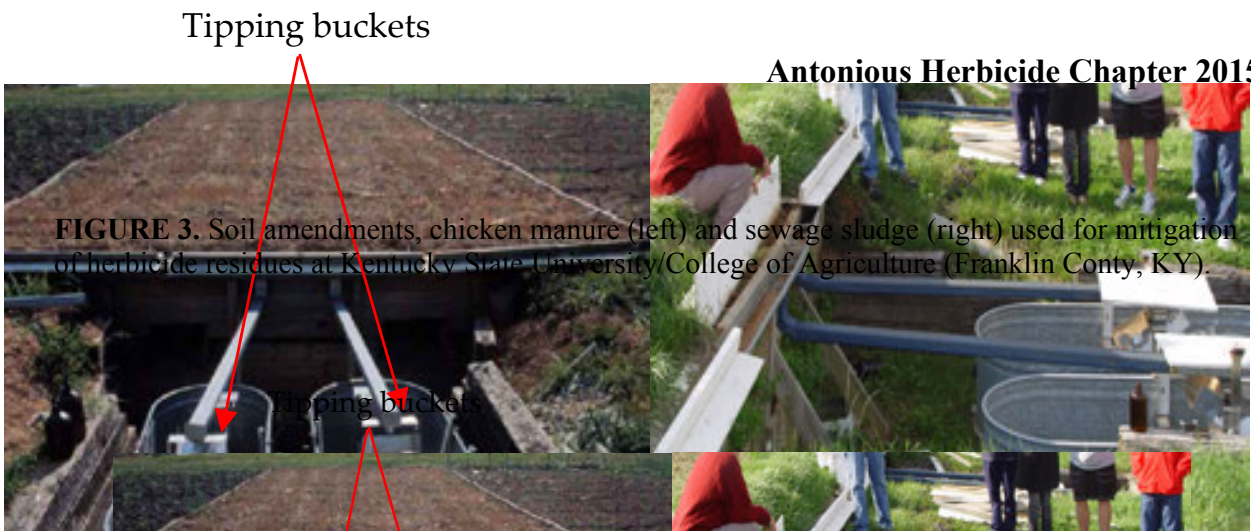
Tipping buckets

FIGURE 4. Surface runoff water collection using tipping buckets installed down the field slope. 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

3.2. Leaching

Pan-lysimeters were installed to monitor the presence of herbicides like bensulide residues and/or its metabolites in the vadose zone (the unsaturated water layer below the plant root zone). Pan-lysimeters (Fig. 5) were installed down and were installed in a summer at 2.0 m underground, leaving the soil column above it intact. This system allowed the collection of infiltration water under normal field conditions (zero tension). Leachate water percolated into the vadose zone was collected in borosilicate amber bottles. Volumes of water collected were recorded following each rainfall or irrigation event.
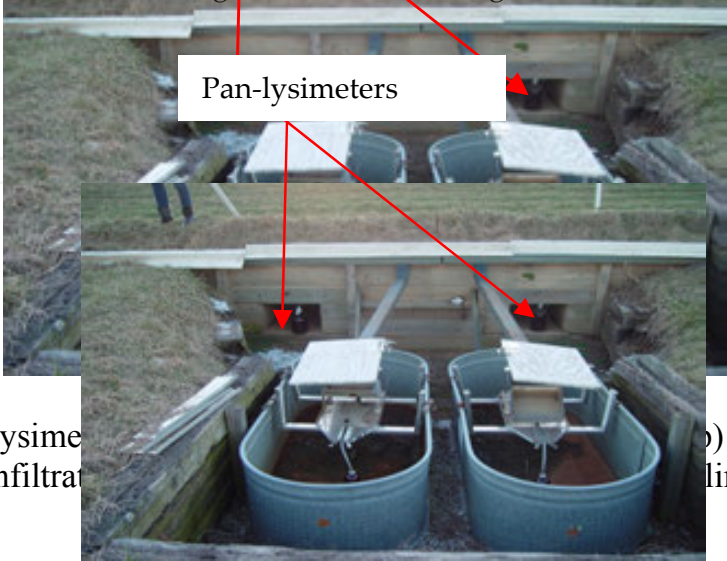
Pan-lysimeters

FIGURE 5. Pan lysimeters installed down the soil column (2 m deep) at the end of field plots for collection of infiltration water (Kentucky State University (Franklin County, KY).

3.3. Monitoring herbicide residues in soil

Soil samples (6 replicates per treatment) were collected from the different treatments using a soil core sampler (Figure 6) equipped with a plastic liner tube (Clements Associates, Newton, IA) of 2.5 cm ID for maintenance of sample integrity. Soil samples were taken to a depth of 15 cm from the rhizosphere of growing plants within the treatments prior to and after herbicide application during the course of the study. Samples were air-dried in the dark at room temperature for 48 h and sieved to a size of 2 mm for herbicide residue analyses. At KSU College of Agriculture, nine biobed systems were installed. 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 [35] to degrade pesticides from point sources. High-quality compost made from garden residues or municipal waste contains numerous microorganisms with differing activities and has provided a good retention capacity for pesticides [37]. 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 (living fescue) that covers the biobed system helps to keep the system humid. Castillo et al. [76] reported that a straw to peat to soil ratio of 50:25:25 % is a recommended biomixture composition for biobeds. This is because organic amendments that increase soil organic matter content offer enhanced pesticide sorption capacity [77, 78]. Concentration of herbicide residues adsorbed to yard waste, sewage sludge, or chicken manure-amended soils was calculated as described by Antonious et al. [21]. The adsorption coefficient (Kd) was calculated using the Freundlich equation (q = Kd C 1/n), where q is the amount of solute (pesticide) adsorbed per unit mass of soil, C is the equilibrium concentration of the solute, and n is the correction factor. Plotting the linear form of the above equation as log q vs (1/n log c + log Kd) provides the slope of the regression line as 1/n and the intercept with the y-axis as log Kd. Pesticide residue data from three soil treatments and from adsorption isotherm experiments were statistically analyzed by analysis of variance (ANOVA) and Duncan's multiple range test for mean comparisons. Replacement of some of the original materials in the Swedish biomixture (straw, peat, and soil) can also change the performance of the biobed system [76].

Figure 6. Collection of soil samples using a core sampler equipped with a plastic liner tube (left photo) and a schematic representation of sorption on soil particle (right sketch).

The biobed system has been 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, USA. The study was performed by EarthFax Development Corporation and funded by the US EPA. The study in Utah involved application of selected herbicides to the surface of the biobed system, which were prepared to assess various factors (e.g., substrate mixtures with and without fungal inoculation). In Utah, the herbicide degrading potential of the biobed substrate mixtures was determined by analyzing 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. Accordingly, the degradative performance of biobeds for several of the most commonly used herbicides in the USA was exceptional, particularly for the most heavily used herbicide in the USA (atrazine). Biobeds have been used in northern Europe for minimizing point-source contamination of water resources by pesticides [39]. 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 [37]. 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 used in the USA. The installation and application of biobed system under field conditions (Figures 7 and 8) is the first application of biobed systems for reducing runoff water loss and mitigation of off-site movement of herbicides in runoff (non-point source contamination) in Kentucky agriculture, where most of the arable lands are highly erodible. In Kentucky agriculture, nine biobeds were used for testing the performance of these systems in treating residues of the two herbicides dimethazone and trifluralin (Figure 1) 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). 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 (USA), 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 soil, runoff, and infiltration water. Various agricultural and management practices have been used to mitigate environmental pollution by herbicides. 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 [61, 79], whereas, plastic mulch, which can cover between 50 and 70 % of a field, increased surface water runoff from both rainfall and irrigation [32]. This means that much of the herbicides applied in living fescue strips used as frequent barriers to runoff or in plastic-mulched fields may seep into groundwater or leave the field into surface runoff. In addition, bensulide (O, O-diisopropyl S-2-phenylsulfonylaminoethyl phosphorodi-

thioate) is one of the few herbicides from the organophosphate group used for control of weeds that threaten numerous crops. Half-life ($T_{1/2}$) values of bensulide in soil were 44.3, 37.6, and 27.1 d in sewage sludge mixed with yard waste at 1:1 ratio, sewage sludge alone, and no-mulch bare soil treatments, respectively. The addition of sewage sludge mixed with yard waste and sewage sludge alone to native soil increased water infiltration, lowering runoff water volume and bensulide residues in runoff following natural rainfall events.

Figure 7. Preparation of soil cavity for biofilter installation at Kentucky State University (Franklin Connty, KY) for trapping herbicides residues in surface runoff water.

4. Herbicide residue analysis

Soil samples (100 gm) was shaken with methylene chloride: acetone (1:1 v/v) for 1 h using a Multi-wrist shaker (Lab-Line Instruments Inc., Melrose Park, IL, USA) to extract the herbicide bensulide. The solvent mixture was filtered through Whatman 934-AH glass microfiber discs (Fisher Sci., Pittsburg, PA). Extracts were passed through anhydrous Na_2SO_4 to remove any traces of water and concentrated by rotary vacuum (Buchi Rotavapor Model 461, Switzerland) and N_2 stream evaporation. Each concentrated extract was subsequently passed through a 0.45
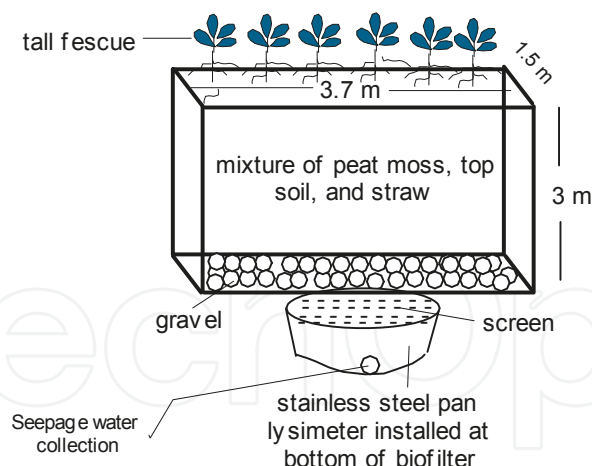
Figure 8. A biofilter system installed at Kentucky State University Research Farm for trapping herbicides and other contaminants in surface water runoff before they enter the Kentucky River.

μm GD/X disposable syringe filter (Fisher Scientific, Pittsburg, PA). One μL of the concentrated extracts was injected into a gas chromatograph (GC) equipped with an NP detector. The gas chromatograph (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 ^{O}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 ($R^2 > 0.95$). Quantification was based on average peak areas from three consecutive injections obtained from external standards of bensulide. Peak identity was confirmed by consistent retention time and coelution with standards under the conditions described. Bensulide residues were also confirmed using a gas chromatograph/mass selected detector (GC/MSD, Hewlett Packard Model 5971a, Palo Alto, CA) operated in total ion monitoring with electron impact ionization (EI) mode and 70 eV electron energy. Under these conditions, retention times (R_t) of bensulide averaged 19.6 min. Bensulide standard material of 99 % purity was obtained from Chem Service (West Chester, PA, USA). Bensulide standard solutions in acetone ranging from 0.1 to 15 ng L^{-1} were prepared and used to spike blank soil, runoff, and infiltration water samples obtained from soil treatments for evaluating the reproducibility and efficiency of the analytical procedures used. After fortification at 30 and 45 μg g^{-1} soil and 30 and 45 μg mL^{-1} water samples, bensulide in fortified samples was extracted and determined using the same procedures described above. Bensulide residues detected in soil were used to calculate half-lives in each of the three soil treatments. Half-lives were calculated from regression lines using the equation $T_{1/2} = \ln 2/K$, where $K = -2.302 \times$ slope of the line. 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 bensulide in soil and water and volume of runoff and infiltration water were related to soil management technique and statistically analyzed using ANOVA procedure and Duncan's multiple range test for mean comparisons.

5. Quantification of herbicide residues

A mass spectrometer is an excellent tool for identifying the chemical structure of a single herbicide when present with a mixture of compounds. Bensulide residues were confirmed using GC/MSD which showed spectral data with molecular ion peaks (M+) at m/z 170, 141, 77, and 51 (Figure 9) and at m/z 157, 141, 93, 77, and 51 that correspond to benzenesulfonamide ($C_6H_7NSO_2$), a bensulide metabolite, along with other characteristic fragment ion peaks (Figure 10). These mass spectral data are in agreement with those reported by the National Institute of Standards and Technology [80]. The organic carbon sorption coefficient (K_{OC}) of the herbicide bensulide is 3,900 mL g^{-1}, whereas azafenidin (an herbicide) K_{OC} is 298, which indicates that azafenidin does not bind strongly to soil particles [81]. Herbicides with a strong sorption rate remain near the soil surface, increasing the chances of being carried to a stream via surface runoff. On the contrary, herbicides with high persistence and a weak K_{OC} may be readily leached through the soil column and are more likely to contaminate groundwater. Herbicides having high K_{OC} value, i.e., bensulide, will bind to soil and organic matter. Accordingly, herbicides can be ranked as leachers or non-leachers to assess their potential for off-site surface or subsurface movements under field conditions. Pesticide adsorption to soil is related more to soil organic matter than to other soil chemical and physical properties [81, 82]. Therefore, addition of soil amendments having high organic matter content (such as sewage sludge and chicken manure) is a management practice that should be exploited to trap nonionic herbicides like bensulide to reduce its surface and subsurface mobility under field conditions.
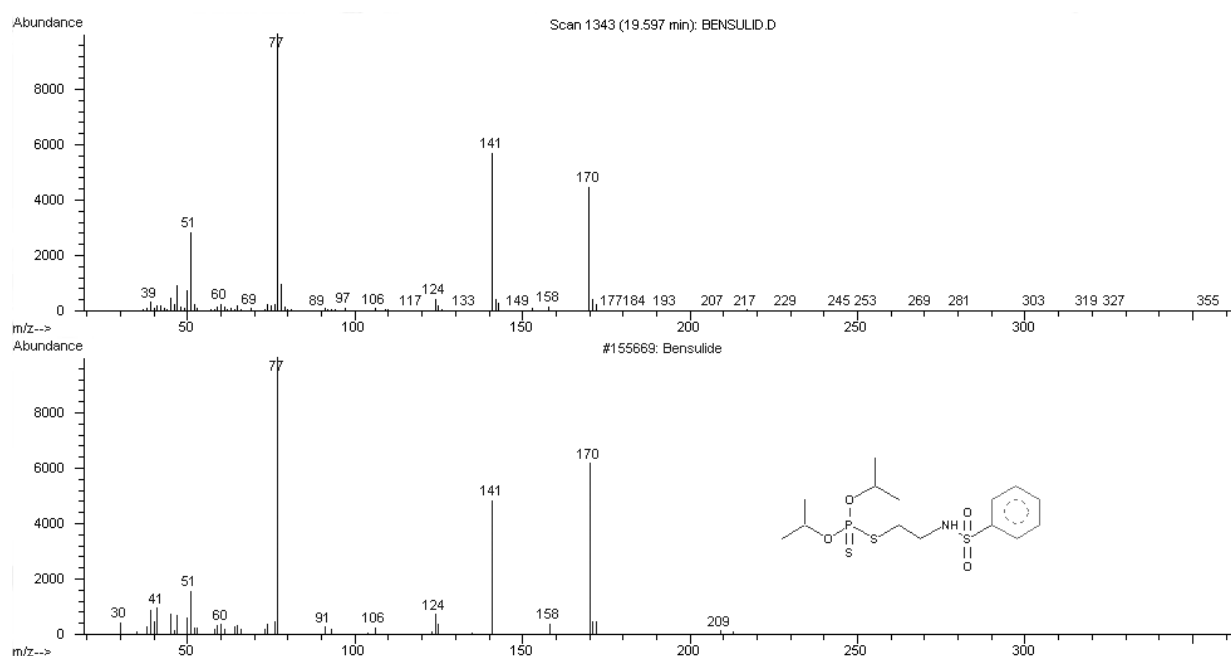
Figure 9. Electron impact mass spectrum of bensulide ($C_{14}H_{24}NO_4PS_3$) extracted from soil indicating the molecular ions of m/z 51, 77, 141, and 170, along with characteristic fragment ions.
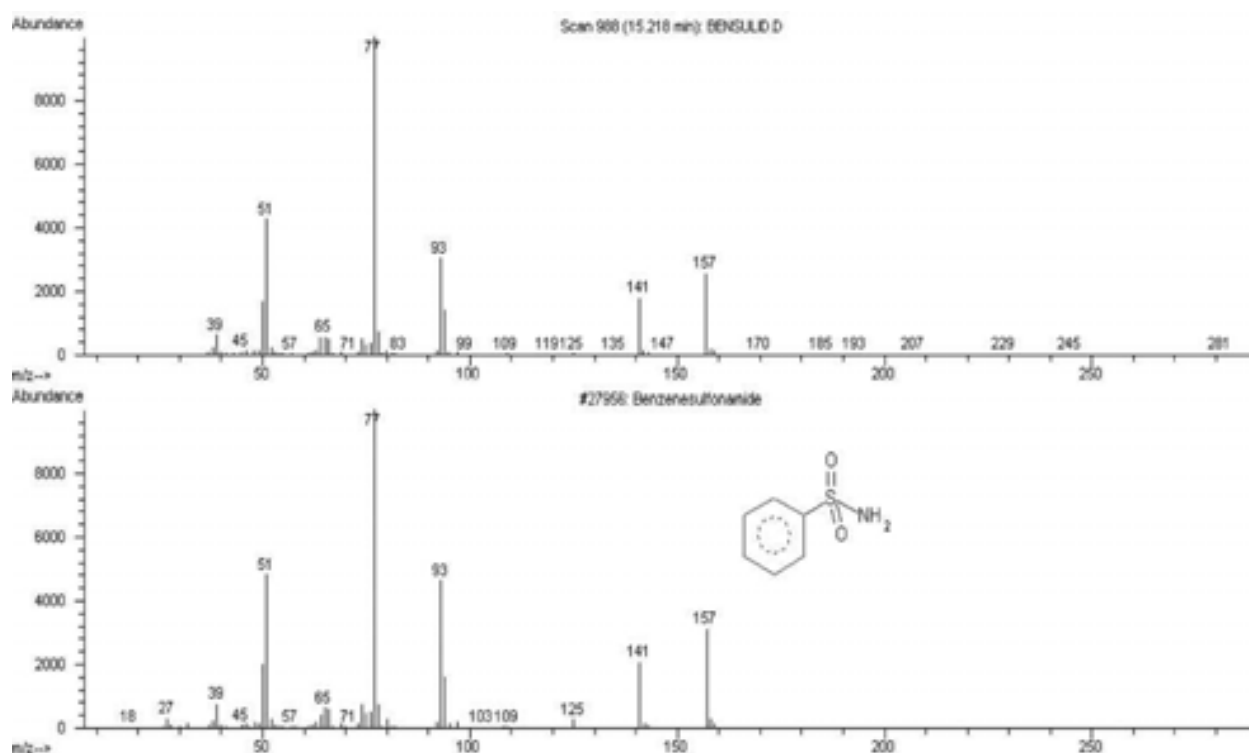
Figure 10. Electron impact mass spectrum of benzenesulphonamide ($C_6H_7NSO_2$), a bensulide metabolite, detected in soil indicating the molecular ions of m/z 157, 141, 93, 77, and 51, along with characteristic fragment ions.

Humic acids (Figure 11), the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values, are dark brown to black in color, whereas fulvic acids, the fraction of humic substances that is soluble in water under all pH conditions, are light yellow to yellow brown in color. Humin, the fraction of humic substances that is not soluble in water at any pH value, is black in color. The presence of carboxylate and phenolate groups gives the humic acids the ability to form complexes with ions such as Mg^{2+}, Ca^{2+}, Fe^{2+}, and Fe^{3+}. Many humic acids have two or more of these groups arranged to enable the formation of chelate complexes [83-85]. The formation of chelate complexes is an important aspect of the biological role of humic acids in regulating bioavailability of metal ions [86] and binding of pesticides to soil organic matter.

The soil organic matter content and the water solubility of the pesticide are the two most important characteristics determining soil adsorption of a pesticide. Adsorption of nonionic pesticides on soil particles depends directly on the organic carbon content (K_{OC}) of the compound and the adsorbing phase. 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 [21, 83, 87]. Walker and Welch [88] studied the degradation rates of three herbicides and their strengths to adsorption; their results showed an order of degradation rate of metribuzin > alachlor > atrazine and an order of adsorption of alachlor > atrazine > metribuzin. Metribuzin mineralization to $^{14}CO_2$ proceeded more slowly in amended soil than in un-amended soil [89].
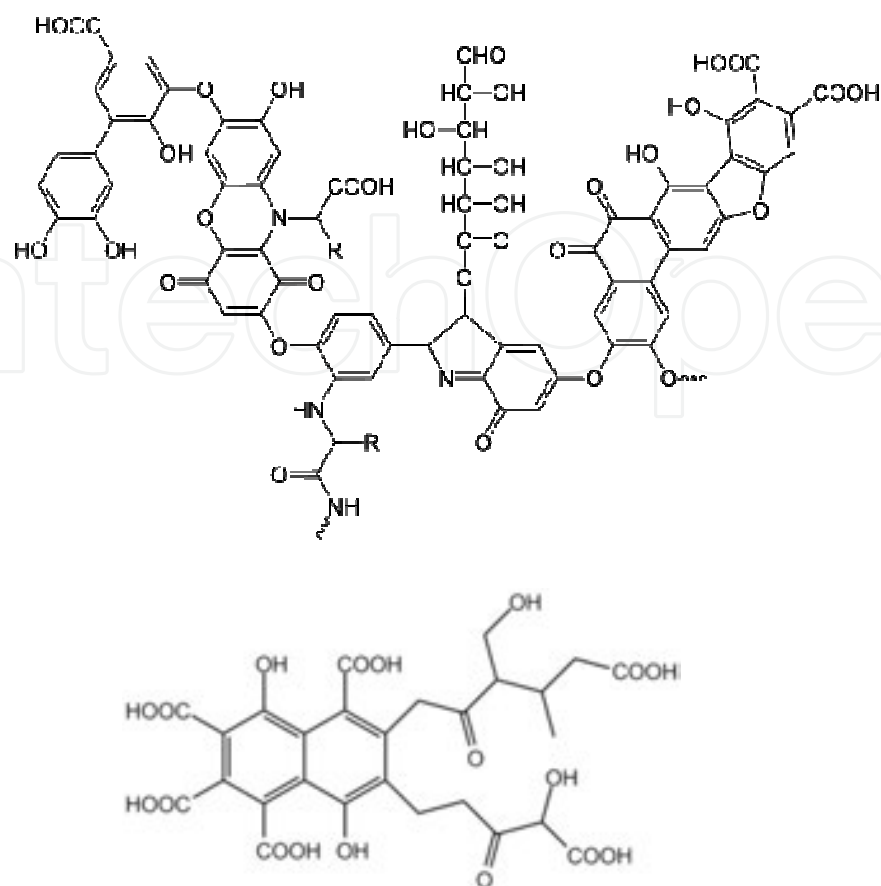
FIGURE 11. Chemical structure of a typical humic acid (upper structure) and fulvic acid (lower structure) having quinone, phenol, catechol and sugar moieties.

Figure 11. Chemical structure of a typical humic acid (upper structure) and fulvic acid (lower structure) having quinone, phenol, catechol and sugar moieties.

The presence of metribuzin (an herbicide) in soil was confirmed using GC/MSD which showed spectral data with molecular ion peaks (M+) at m/z 198 along with characteristic fragment ion peaks at 57, 74, 103, 144, and 171 (Figure 12, upper graph), whereas the presence of DCPA (dacthal) in soil and water was confirmed using molecular weight of 332 and spectral ions of m/z 59, 107, 142, 177, 221, 273, and 301, along with characteristic fragment ions (Figure 12, lower graph). These mass spectral data are in agreement with those reported by the National Institute of Standards and Technology [80]. DCPA has a low vapor pressure, 2.5×10^{-6} mmHg, and very low water solubility, 0.5 ppm. DCPA with its low water solubility, <0.5 ppm, high K_{OC} of 5,900 and stability to UV light has great affinity for binding to soil particles. Consequently, low residue levels of DCPA would be available on the soil surface. In soil, biodegradation of DCPA into tetrachlorophthalic acid, which is extremely mobile in the environment, is slow [90]. Work carried out by Antonious et al. [30] revealed that runoff water volume from no-mulch soil (200,000 L plot^{-1}) was significantly greater than runoff from soil amended with chicken manure and sewage sludge-amended soils (45,000 and 85,000 L plot^{-1}, respectively). This might be due to reduced bulk density and increased soil interspaces after addition of soil amendments that increased water infiltration into the soil column toward the vadose zone (the unsaturated water layer below the plant root), reducing surface water runoff from chicken

manure and sewage sludge incorporated soil. Water infiltration into the vadose zone also varied between soil treatments. Generally, substantial portions of soil-applied herbicides are leached from the site of application by percolation into the vadose zone and enter the ground-water supply. DCPA residues were detected at very low concentrations in infiltration water collected from the vadose zone. One should consider that precipitation during June and July storms resulted in increased water infiltration from chicken manure and sewage sludge compost treatments compared to no-mulch treatment. The decrease of DCPA residues in runoff and infiltration water from chicken manure and sewage sludge treatments might be due to DCPA environmental fate characteristics (i.e., high sorption capacity) that increased its adsorption to the soil particles and the greater organic matter content of chicken manure (5.37 %) and sewage sludge treatments (5.35 %) compared to 2.2 % in no-mulch treatment which might have increased DCPA binding to humic substances, reducing its mobility in the soil column into the vadose zone and down the land slope into surface water. This may be explained by the nonpolar properties of the herbicide DCPA which increases its adsorption to soil particles, thereby decreasing its availability in leachate water at lower depth.

Other reports also suggested that the mobility of metribuzin within soils is limited in organic soils [91, 92] because metribuzin is tightly bound to soils with high clay or organic matter content. In addition, Nicholls et al. [93] reported little movement (<10 cm) of metribuzin applied at the surface of sandy loam that was maintained fallow over the entire growing season. Khoury et al. [94] indicated that soil microorganisms contribute to the rapid degrada-tion of metribuzin and the increase in soil organic matter favored microbial development and subsequently accelerated the degradation of metribuzin. They concluded that the degradation speed of metribuzin in non-sterile soils was found to be 7–12 times higher than that in sterilized soils. Benoit et al. [95] investigated metribuzin sorption and found that metribuzin is weakly sorbed in different soils and concluded that the observed relationship between organic carbon and herbicide mineralization was related to the activity of soil microorganism.

The persistence of an herbicide is defined as the time in which the molecule remains in the soil and is usually expressed as half-life ($T_{1/2}$). The leaching index (LI) of an herbicide can be calculated using the equation developed by Laskowski et al. [96]

($LI = (S) (T_{1/2})/ (VP) (K_{OC})$), where S is the water solubility of a pesticide in mg L^{-1} at 25 ^{O}C, $T_{1/2}$ is the half-life of a pesticide in soil in days, VP is the vapor pressure in mmHg at 25 ^{O}C, and K_{OC} is the organic carbon partition coefficient that can be calculated using the equation $K_{OC} = Kd/\%$ soil organic carbon. Using S and VP values from the pesticide manual [97], $T_{1/2}$ in no-much soil taken from Antonious et al. [30] and K_{OC} from Kim and Feagley [98], the LI value of metribuzin in soil was calculated as [$LI = (1050) (12)/(5.8 \times 10^{-7}) (96)] = 2.26 \times 10^{8}$, whereas LI value of DCPA in soil was calculated as [$LI = (0.5) (26.17)/(1.57 \times 10^{-6}) (5900)] = 1.41 \times 10^{3}$, indicating the weak soil leaching of DCPA and the high leaching of metribuzin into the soil column.

In other studies conducted in a field experiment, a silty loam soil was sprayed with a mixture of two preemergent herbicides, dimethazone and trifluralin (Figure 1) formulations. One hundred twenty-five milliliters of Command 3ME (dimethazone) formulation obtained from Platte Chemical Company (18th street, Greeley, CO) and 300 mL of Treflan (trifluralin)
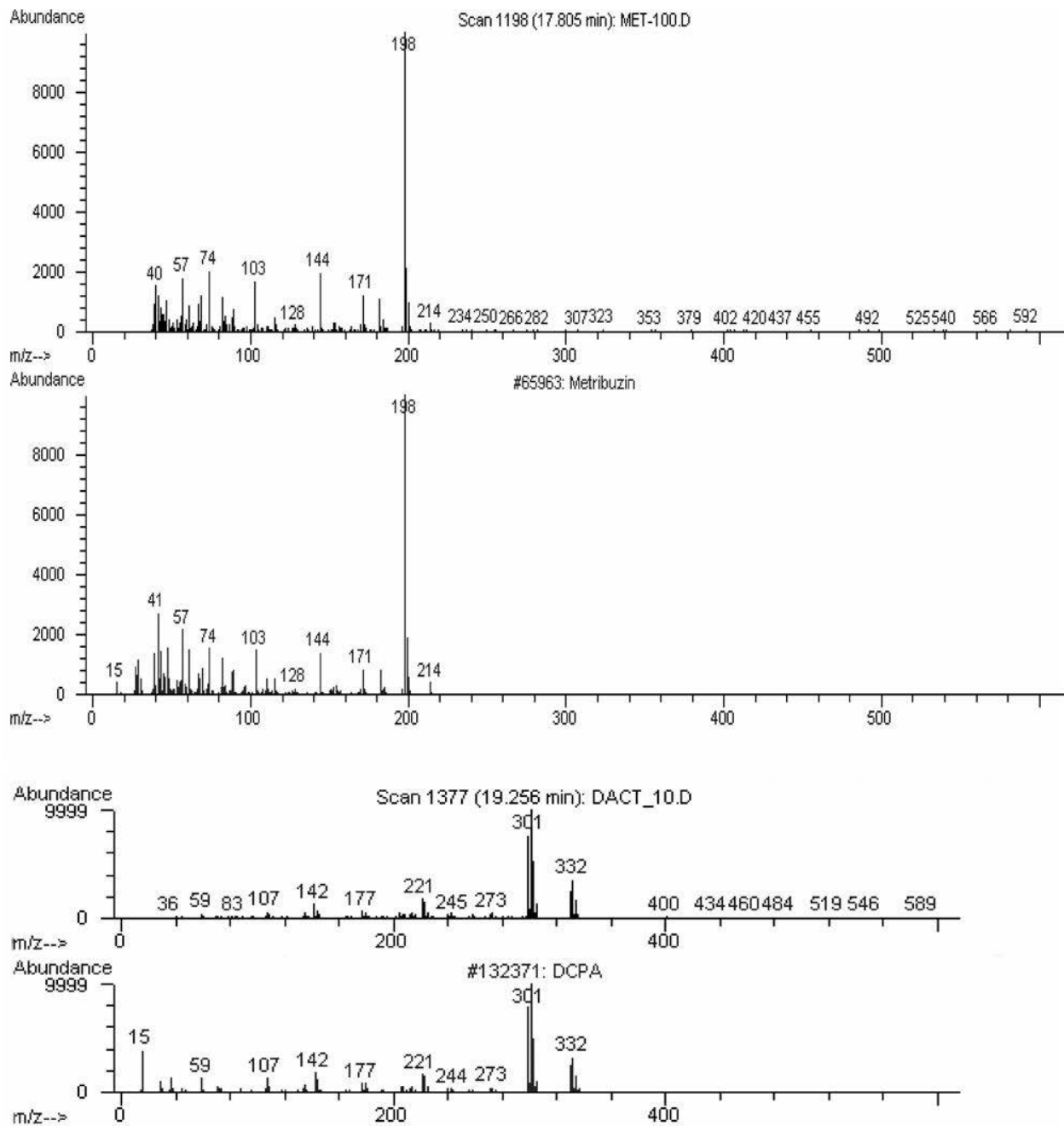
Figure 12. Electron impact mass spectrum of metribuzin extracted from soil indicating the molecular weight of 214 and molecular ions of m/z 57, 74, 103, 144, 171, and 198, along with characteristic fragment ions (upper graph) and DCPA extracted from soil indicating the molecular weight of 332 and molecular ions of m/z 59, 107, 142, 177, 221, 273, and 301, along with characteristic fragment ions (lower graph).

formulation (Dow AgroSciences) were used at the recommended rates of application in Kentucky [1]. The two herbicides were mixed in a total volume of 15 gallons of water and sprayed uniformly on the field plots (total area = 0.36 acre) using a portable backpack sprayer equipped with one conical nozzle operated at 40 psi (275 kPa). Following herbicide spraying, soil samples were collected, dried, sieved to a size of 2 mm, and extracted with 100 mL of acetonitrile: hexane: methanol mixture (45:45:10 v/v) using Soxhlet extraction apparatus

(Figure 13). The extracts were dried over anhydrous Na_2SO_4 to remove any traces of water and concentrated by rotary vacuum (Buchi Rotavapor Model 461, Switzerland) and N_2 stream evaporation.


Figure 13. Use of soxhlet extraction units and liquid-liquid partition for extraction of dimethazone and trifluralin herbicides from soil.

Trifluralin and dimethazone herbicides were extracted from runoff and infiltration water samples with a mixture of methylene chloride (CH_2Cl_2) + acetone (6:1, v/v) and sodium chloride solution by liquid-liquid partition. 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 to a known volume. Concentrated extracts were injected into a gas chromatograph (GC) equipped with flame ionization detector (FID). Retention times (Rt) of trifluralin and dimethazone averaged 16.29 and 17.43 min, respectively (Figure 14). The molecular weight of trifluralin (335) is greater than that of dimethazone (239). However, a 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 (Figure 15) showed spectral data with molecular ion peaks (M+) at m/z 306, 290, 264, and 43. Dimethazone electron mass spectrum (Figure 16) with spectral data at m/z 204, 125, 89, and 41 is consistent with those reported by the National Institute of Standards and Technology [80]. In soil, the ion m/z 204 is formed by 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.

Results indicated that dimethazone residues extracted from sewage sludge and sewage sludge 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 sewage sludge and sewage sludge mixed with yard waste compost, respectively (data not shown), compared to no-mulch native soil. This could be explained by the adsorption properties of dimethazone on soil particles that varied with increasing percentages of soil organic matter following the addition
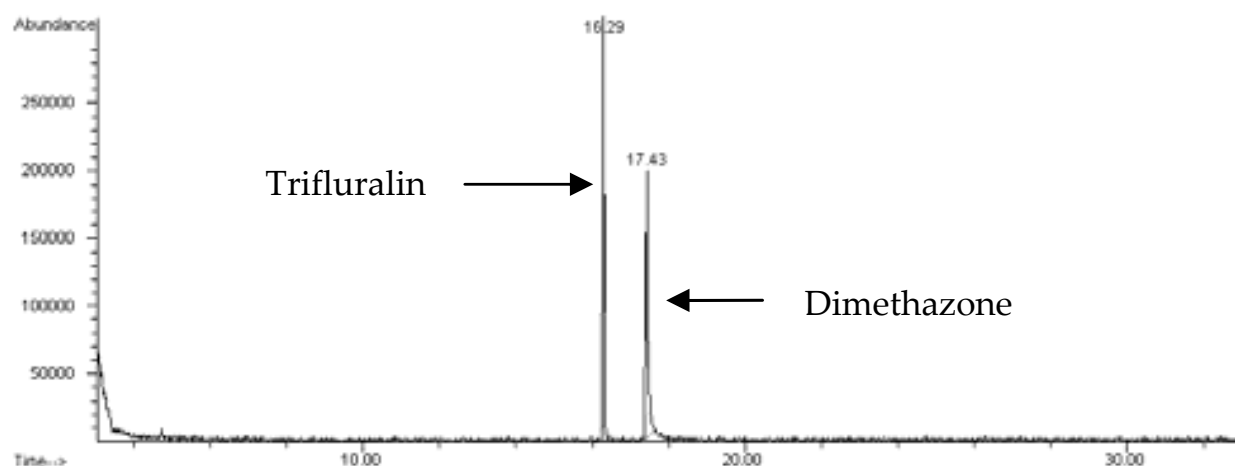
Figure 14. Gas chromatographic (GC) chromatograms of soil extracts prepared in acetonitrile: hexane: methanol (45:45:10 v/v) one hour following spraying with a mixture of dimethazone and trifluralin formulations.
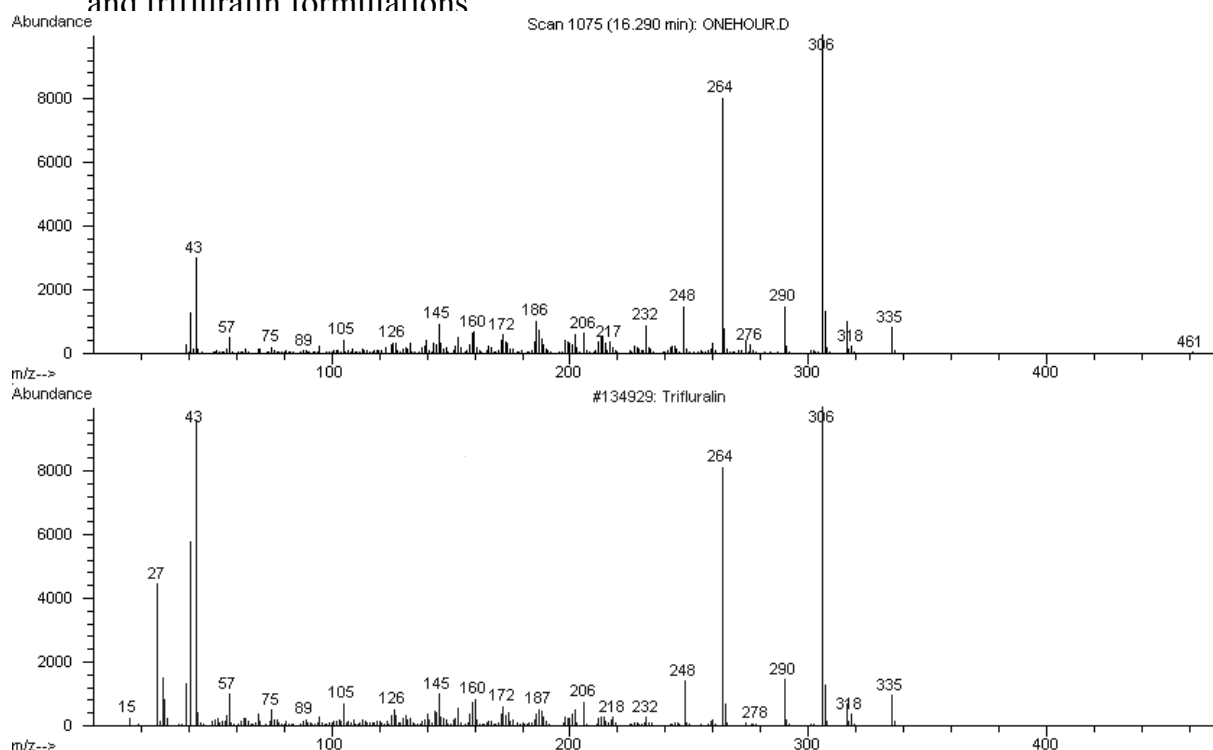
Figure 15. Electron impact mass spectrum of trifluralin ($C_{13}H_{16}N_3O_4F_3$) extracted from soil indicating the molecular ions of m/z 306, 290, 264, and 43 along with other characteristic fragment ions.

of amendments. Loux et al. [99] 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. Soil amendments such as yard waste compost contain significant concentrations of humic acid, the main constituent of soil organic matter. Tavares and Rezende [100] indicated that functional groups in humic acid, namely, carboxylic and phenolic groups (Figure 11) appeared to be the principal
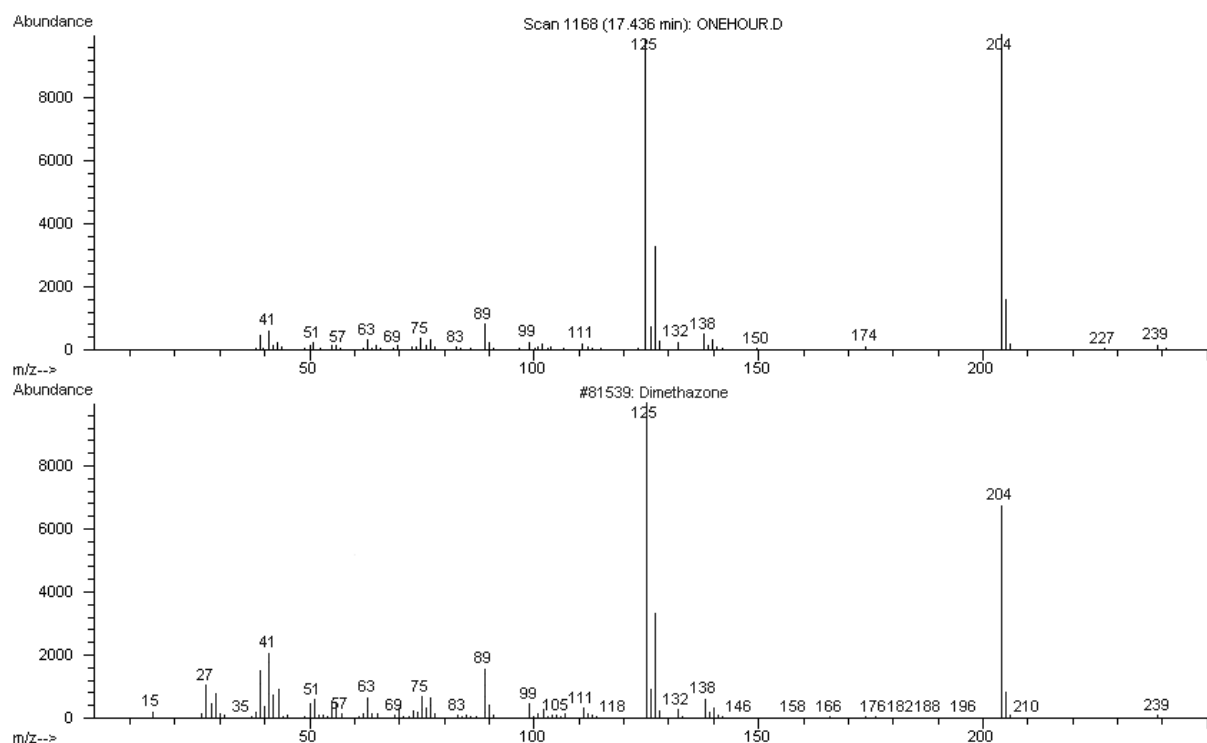
Figure 16. Electron impact mass spectrum of dimethazone ($C_{12}H_{14}$ Cl NO_2) extracted from soil indicating the molecular ions of m/z 204, 125, 89, and 41 along with other characteristic fragment ions.

sites for the adsorption and interaction with trifluralin. This might explain why trifluralin residues were higher in compost-amended soil than in no-mulch 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 [101]. Accordingly, recyclable wastes have unique properties that should be thoroughly investigated in the soil/water/plant ecosystem. Binding of pesticides to humus [83] 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 particularly important because the extensive use of herbicides such as trifluralin has a high toxicity to fish (Table 1). Some herbicides are highly soluble in water, but because of their ionic properties, they bind tightly to the soil particles and organic matter in recycled waste and pose minimal risk for ground and surface water contamination.

Table 1 indicated 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 [102, 103]. Occurrence of trifluralin at concentrations of 50 to 130 ng g^{-1} on dry-weight basis has been reported in soils 30 months after the last application [104], and since the adsorbed herbicide becomes biologically inactive, therefore higher volume application rates are needed for soils rich in organic matter. Dimethazone is soluble in water

Property	Dimethazone	Trifluralin	Reference
Water Solubility (g L^{-1})	1.1	0.22	[92]
Fish LC_{50} (mg L^{-1}) Rainbow trout Bluegill sunfish	19 34	0.01-0.04 0.02-0.09	[92] [92]
Log K_{OW} [†]	2.5	5.1	[100] [101]
K_{OC} (mL g^{-1}) [‡]	150-562	8,000	[102] [82]
Vapor Pressure (mm Hg at 29 ^{O}C)	1.44×10^{-4}	1.99×10^{-4}	[92]
Concentration (μg g^{-1} Soil)	0.4	1.1	[15]
Concentration (mg $Plot^{-1}$) in infiltration water	0.08	0.009	[15]

† Partition coefficient between n-octanol and water (as log value)

‡ Organic carbon partition coefficient

Note that one plot is 0.02 of an acre

Table 1. Physical and chemical properties of dimethazone and trifluralin herbicides sprayed at Kentucky State University Research Farm, Franklin County, Kentucky, USA and their concentrations in runoff and infiltration water following natural rainfall.

and hence poorly bonds to most soils, giving it a potential for leaching into the soil column. These findings indicated that soil amendments and farm management practices play a major role in influencing herbicide residue levels in soil and their off-site mobility into natural water resources.

6. Conclusion

Herbicide washes off from agricultural fields and the Kentucky River watershed impacts surface water quality. Analysis of the herbicide metribuzin in the top soil indicated that considerable residues were detected in soil amended with chicken manure and sewage sludge compared to native soil. Similarly, soil amended with chicken manure or sewage sludge retained DCPA residues up to 99 d compared to unamended soils. Runoff water volume from no-mulch soil (200,000 L $plot^{-1}$) was significantly greater than runoff from soil amended with chicken manure and sewage sludge-amended soils (45,000 and 85,000 L $plot^{-1}$, respectively). Knowledge about the environmental problems and adoption of appropriate solutions and practices to enhance and protect our national water quality from environmental pollution by herbicides require timely delivery of research and educational technology. The development of production systems and mitigation techniques that reduce the introduction of agrochemicals like herbicides into the environment presents a continuing challenge. Soil mixed with chicken manure and sewage sludge increased water infiltration into the soil column toward the vadose

zone, reducing surface water runoff down the land slope. Agricultural runoff is the main contributor to poor water quality. Recycling waste for use as a low-cost fertilizer promoted the restoration of ecologic and economic functions of soil. Composts provide a stabilized form of organic matter that improves the physical properties of soils by increasing nutrient and water holding capacity, total pore space, aggregate stability, erosion resistance, and temperature insulation and decreasing apparent soil density [105] and binding of herbicides to soil particles and organic matter in soil amendments through herbicide sorption process that include chemisorption, complexation, adsorption, diffusion through the pores, and ion exchange [36]. Mobility of herbicides is affected by many site-specific variables, including the amount of soil organic matter, particle size distribution, porosity, rainfall, and application rates [30]. Field trials related to the mobility of trifluralin herbicide were conducted on a Lowell silty loam soil (pH 6.7, 2 % organic matter) of 10 % slope located at the Kentucky State University (KSU) H.R. Benson Research Farm (Franklin County, KY, USA). The farm is located in the Kentucky River watershed in the Bluegrass region. Results indicated that yard waste compost mixed with native soil reduced trifluralin residues in surface runoff water from June to July rainfall by 76 and 84 %, respectively. When sewage sludge and chicken manure were mixed with native soil, half-life ($T_{1/2}$) values of metribuzin were 24, 18, and 12 d in chicken manure, sewage sludge, and no-mulch treatments, respectively, whereas $T_{1/2}$ values of DCPA (dacthal) were greater in chicken manure and sewage sludge-incorporated soil (45.8 and 52.2 d, respectively) compared to NM native soil (26.2 d). A strong positive relationship was found between napropamide (an herbicide) concentrations and organic matter content in soil leachates. Sewage sludge and yard waste mixture added to native soil increased water infiltration, lowering surface runoff water volume and dimethazone (an herbicide) residues in runoff following natural rainfall events. Accordingly, soil amendments could be used to intercept herbicide-contaminated runoff from agricultural fields and might provide a potential solution to herbicide contamination of surface and seepage water from farmlands.

Acknowledgements

Author details

George F. Antonious

Address all correspondence to: george.antonious@kysu.edu

Kentucky State University, College of Agriculture, Food Science, and Sustainable Systems, Frankfort, USA

References

[1] Coolong T, Bessin R, Jones T, Strang J, Seebold K. Vegetable Production Guide for Commercial Growers, Cooperative Extension Service Bulletin ID-36, University of Kentucky, College of Agriculture, 2011, Lexington, KY.

[2] U.S. Environmental Protection Agency (US EPA). Pesticide Sales and Usage Report, 2004a. EPA-733-R-04-001, Washington, D.C., USA.

[3] U.S. Environmental Protection Agency (USEPA), National Summary of Impaired Waters and TMDL Information, 2004b, Washington, D.C. Available at http://iaspub.epa.gov/tmdl waters10/attains nation cy.control?p report type=T.

[4] Mahmood Q, Bilal M, Jan S. Herbicides, pesticides, and plant tolerance: An overview. In: Ahmad P, Rasool S, (Eds). Chapter 17, Emerging Technologies and Management of Crop Stress Tolerance, Volume 1, Academic Press: San Diego, CA, USA, May 8, 2014, pp. 423-448.

[5] De Wilde T, Spanoghe P, Debaer C, Ryckeboer J, Springael D, Jaeken P. Overview of on-farm bioremediation systems to reduce the occurrence of point source contamination. Pest Management Science 2007; 63: 111-128.

[6] Pimentel D, Andow D, Dyson-Hudson R, Gallahan D, Jacobson S, Irish M, Kroop S, Moss A, Schreiner I, Shepard M, Thompson T, Vinzant B. Environmental and economic impacts of reducing U.S. agricultural pesticide us. In: Pimentel D (Ed). Handbook of Pest Management in Agriculture, Volume.1, CRC Press: Boca Raton, FL, 1991, pp. 679-718.

[7] Gianessi, L.P.; Sankula, S. The Value of Herbicides in U.S. Crop Production, National Center for Food and Agricultural Policy, April 2003, Washington, DC. Available at http://www.ncfap.org/documents/FullText.pdf.

[8] US EPA Impaired Waters Listed by State: http://iaspub.epa.gov/tmdl_waters10/attains_nation_cy.control?p_report_type=T (accessed April 5, 2013).

[9] U.S. Geological Survey (USGS). Pesticides and nutrients in karst springs in the Green River Basin, Kentucky, May-September 2001 USGS Fact Sheet 133-01. Available at: http://pubs.usgs.gov/fs/2001/0133/report.pdf.

[10] Inert Ingredients in Pesticide Products. http://www.epa.gov/opprd001/inerts/lists.html (accessed 4/1/15).

[11] Ray C, Soong TW, Lian YQ, Roadcap GS. Effect of flood-induced chemical load on filtrate quality at bank filtration sites. Journal of Hydrology 2002; 266 (3-4): 235-258.

[12] Teifenthaler LL, Schiff K, Leecaster M. Temporal variability of patterns of stormwater concentrations in urban runoff. In: Weisberg S, Elmore D (Eds), Southern California Coastal Water Research Annual Report 1999-2000.

[13] Currents, JC, Kentucky Geological Survey, Mining and mineral resources information, University of Kentucky, Lexington, KY 40506, circular 4, series XII, 2002. Available at: oepos.ca.uky.edu/files/Ky_Karst.pdf.

[14] Winchester PD, Huskins J, Ying J. Agrichemicals in surface water and birth defects in the United States. Acta Paediatrica 2009; 98: 664-669.

[15] U.S. Geological Survey (USGS). Pesticides in surface waters, National Water-Quality Assessment (NAWQA), Fact Sheet FS-039-97, March 4, 2014. Available at: http://water.usgs.gov/nawqa/pnsp/pubs/fs97039/sw4.html.

[16] Swan SH, Kruse RLBarr DB, Drobnis EZ, Redmon JB. Semen quality in relation to biomarkers of pesticide exposure. Environ Health Perspectives 2003; 111: 1478-1484.

[17] Schreinemachers DM. Birth malformation and other adverse perinatal outcomes in four U.S. wheat-producing states. Environ Health Perspect 2003; 111: 1259-1264.

[18] US EPA (2011). A watershed Academy Webcast. Available at http://water.epa.gov/learn/training/wacademy/upload/2011_3_29_flyer.pdf.

[19] European Food Safety Authority. Conclusion on the peer review of the pesticide risk assessment of the active substance halosulfuron. J. European Food Safety Authority 2012; 10: 2987. Available online: www.efsa.europa.eu/efsajournal.

[20] Antonious GF. On-farm Bioremediation of dimethazone and trifluralin residues in runoff water from an agricultural field. J. Environmental Science Health 2012; Part-B 47: 608-621.

[21] Antonious GF, Patel GA, Snyder JC, Coyne MS. Pyrethrins and piperonyl butoxide adsorption to soil organic matter. J. Environ. Sci. Health 2004; B39 (1): 19-32.

[22] Antonious GF. Pesticides: Measurement and mitigation. In: Jorgensen SE (Ed). Encyclopedia of Environmental Management. Taylor and Francis Books, New York, USA, Book Chapter, 2013-2027, published May 1, 2013.

[23] Yu X, Ying GG, Kookana RS. Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 2009; 76: 665-671.

[24] Antonious GF. Enzyme activities and heavy metals concentration in soil amended with sewage sludge. J. Environ. Science & Health, Part-A Toxic/Hazardous Substances and Environmental Engineering 2009; A44: 1019-1024.

[25] Jackson BP, Bertson ML, Cabreta JJ, Camberto JC, Seaman CW. Wood, trace element speciation in poultry litter. J. Environ. Qual. 2003; 32: 535-540.

[26] Antonious GF, Perkins E, Cantor A. Chicken manure increased concentration of organic sulfur compounds in field-grown onions. J. Environ. Science & Health 2009; Part-B Pesticides, Food Contaminants & Agricultural Wastes, B44 (5): 481-487.

[27] Antonious GF, Snyder JC, Dennis SO. Heavy metals in summer squash fruits grown in soil amended with municipal sewage sludge. Journal of Environmental Science and Health 2010; Part-B, 45: 167-173.

[28] Antonious GF, Dennis SO, Unrine JM, Snyder JC. Ascorbic acid, β-carotene, sugars, phenols, and heavy metals in sweet potato grown in soil fertilized with municipal sewage sludge. Journal of Environmental Science and Health 2011; Part-B, 46 (2): 112-121.

[29] Antonious G, Kochhar T, Coolong T. Yield, quality, and concentrations of seven heavy metals in cabbage and broccoli grown in sewage sludge and chicken manure amended soil. J. Environmental Sci. Health 2012; Part-A 47: 1955-1965.

[30] Antonious GF, Turley T, Hill R. Impact of soil amendments on metribuzin and DCPA half-lives and mobility into agricultural runoff water. J. Environmental Science and Health 2014, Part B 49: 313-323.

[31] Antonious GF. Trifluralin residues in runoff and infiltration water from tomato production. Bull. Environ. Contam. Toxicol. 2004; 72 (5): 962-969.

[32] Antonious GF. Clomazone residues in soil and runoff: Measurement and mitigation. Bull. Environ. Contam. Toxicol. 2000; 64 (2): 168-175.

[33] Antonious GF. Mitigation of dimethazone residues in soil and runoff water in agricultural field. Journal of Environmental Science and Health 2011; Part-B 46: 76-83.

[34] Antonious GF; Patterson MA. Napropamide residues in runoff and infiltration water from pepper production. J. Environ. Sci. Health 2005; B40(3): 385-396.

[35] Fogg P, Boxall A, Walker A, Jukes A. Degradation and leaching potential of pesticides in biobed systems. Pest Manage. Sci. 2004; 60: 645-654.

[36] Sud D, Mahajan G, Kaur MP. Agricultural waste material as adsorbent for sequestering heavy metal ions. Bioresour. Technol. 2008; 99: 6017-6027.

[37] Vischetti C, Capri E, Trevisan M, Casucci C, Perucci P. Biomassbed: A biological system to reduce pesticide point contamination at farm level. Chemosphere 2004; 55: 823-828.

[38] Novak JM, Jayachandran K, Moorman TB, Weber JB. Sorption and binding of organic compounds in soils and their relation to bioavailability. Soil Science Society of America, American Society of Agronomy, Crop Science Society, 1995, 13–3, SSSA Special Publication 43, http://afrsweb.usda.gov/SP2UserFiles/Place/66570000/Manuscripts/1995/ Man381.pdf.

[39] Karanasios E, Tsiropoulos N, Karpouzas DG, Ehaliotis C. Degradation and adsorption of pesticides in compost-based biomixtures as potential substrates for biobeds in Southern Europe. J. Food Chem. 2010; 58: 9147-9156.

[40] Novotny EH, Hayes MHB, Madari BE, Bonagamba TJ, De Azevedo ER, De Souza AA, Song GX, Nogueira CM, Mangrich AS. Lessons from the Terra Preta de Indios of

the Amazon region for the utilisation of charcoal for soil amendment. Journal of the Brazilian Chemical Society 2009; 20: 1003-1010.

[41]   Van Zwieten L, Kimber S, Morris S, Chan KY, Downie A, Rust J, Joseph S, Cowie A. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant and Soil 2010; 327: 235-246.

[42]   Kim I, Yu ZQ, Xia BH, HuangWL. Sorption of male hormones by soils and sedi‐ ments. Environmental Toxicology and Chemistry 2007; 26: 264-270.

[43]   Fowles M. Black carbon sequestration as an alternative to bioenergy. Biomass & Bio‐ energy 2007; 31: 426-432.

[44]   Larson RW. Using biochar for cost-effective CO_2 sequestration in soils. In: Proceed‐ ings of Ises Solar World Congress 2007: Solar Energy and Human Settlement 2007; IeV: 2462-2467.

[45]   Lehmann J, Skjemstad J, Sohi S, Carter J, Barson M, Falloon P, Coleman, K, Wood‐ bury P, Krull E. Australian climate-carbon cycle feedback reduced by soil black car‐ bon. Nature Geoscience 2008; 1: 832-835.

[46]   Rondon MA, Lehmann J, Ramirez J, Hurtado M. Biological nitrogen fixation by com‐ mon beans (*Phaseolus vulgaris* L.) increases with bio-char additions. Biology and Fer‐ tility of Soils 2007; 43: 699-708.

[47]   Lehmann J. A handful of carbon, Nature 2007; 447: 143-144.

[48]   Lehmann J. Bio-energy in the Black. Frontiers in Ecology and the Environment 2007; 5 (7): 381-387.

[49]   Hamilton T. The case for burying charcoal. Technology Review 26 April 2007.

[50]   Bracmort K. Biochar: Examination of an Emerging Concept to Mitigate Climate Change CRS Report for Congress Prepared for Members and Committees of Con‐ gress, Congressional Research Service 7-5700, www.crs.gov R40186, May 24, 2010.

[51]   Ute H, Marschner B, Brodowski S, Amelung W. Interactive priming of black carbon and glucose mineralisation. Organic Geochemistry July 2004; 35(7): 823-830.

[52]   Baily VL, Fansler SJ, Smith JL, Bolton H. Reconciling apparent variability in effects of biochar amendment on soil enzyme activities by assay optimization. Soil Biology & Biochemistry 2011; 43: 296-301.

[53]   Pirbazari M, Weber W. Removal of dieldrin from water by activated carbon. J. Envi‐ ron. Eng. 1984; ASCE 110: 656.

[54]   Pirbazari M, Badriyha BN, Miltner RJ. GAC adsorber design for removal of chlorinat‐ ed pesticides. J. Environ. Eng. 1991; ASCE 117: 80.

[55] Hu J, Aizawa T, Ookubo Y, Morita T, Magara Y. (1998). Adsorptive characteristics of ionogenic aromatic pesticides in water on powdered activated carbon. Water Res. 1998; 32: 2593.

[56] Pimentel D, Levitan L. Pesticides: Amounts applied and amounts reaching pests. Bioscience 1986; 36: 86-91.

[57] Antonious GF, Byers ME. Fate and movement of esfenvalerate under field conditions. J. Environmental Toxicol. Chem. 1997; 64 (4): 644-649.

[58] Antonious GF, Byers ME, Kerst WC. Residue levels of pyrethrins and piperonyl butoxide in soil and water. J. Environ. Sci. Health 1997; B32: 621-644.

[59] Antonious GF, Patterson MA, Snyder JC. Impact of soil amendments on broccoli quality and napropamide movement under field conditions. Bull. Environ. Contam. Toxicol. 2005; 75(4): 797-804.

[60] Antonious GF, Snyder JC. Impact of soil incorporated sewage sludge on herbicide and trace metal mobility in the environment. Book chapter, In: Theophanides M (Ed). Environmental Engineering & Economics. Institute for Education & Research, 2006, Chapter 12, pp. 149-164, ISBN: 978-960-6672-13-2.

[61] Antonious GF. Efficiency of grass buffer strips and cropping system on off-site dacthal movement. Bull. Environ. Contam. Toxicol. 1999; 63: 25-32.

[62] Antonious GF. Soil infiltration by pesticides. In: Pimentel D (Ed). Encyclopedia of Pest Management. Volume 3, Marcel Dekker, Inc., New York, 2003, pp. 1-4.

[63] Antonious GF. Trifluralin residues in runoff and infiltration water from tomato production. Bull. Environ. Contam. Toxicol. 2004; 72: 962-969.

[64] Antonious GF. Mobility and half-life of bensulide in agricultural soil. Journal of Environmental Science and Health 2010; Part-B, 45: 1-10.

[65] Antonious GF. Impact of soil management and two botanical insecticides on urease and invertase activity. J. Environ. Sci. Health 2003; B38 (4): 479-488.

[66] Antonious GF, Turley ET, Snyder JC. Soil enzyme activity and heavy metal contamination in soil amended with sewage sludge. Book chapter, In: Theophanides M (Ed). Environmental Engineering & Economics. A paper presented at the International Symposium on Environment, Athens, Greece, Institute for Education and Research, 22-25 May 2008.

[67] Cox L, Cecchi A, Celis R, Hermos'ın M, Koskinen W, Cornejo J. Effect of exogenous carbon on movement of simazine and 2,4-D in soils, Soil Sci. Soc. Am. J. 2001; 65: 1688-1695.

[68] Barriuso E, Houot S, Serra-Wittling C. Influence of compost addition to soil on the behavior of herbicides. Pestic. Sci. 1997; 49: 65-75.

[69] Stratton ML, Rechcigl JE. Organic mulches, wood products, In: Wallace A, Terry R. (Eds). Handbook of Soil Conditioners.. Marcel Dekker, Inc., New York, 1998, pp. 43-95.

[70] Reganold JP, Papendick RI, Parr JF. Sustainable agriculture. Scientific American 1990; 262: 112-120.

[71] Chakrabarti K, Bhattacharyya P, Chakraborty A. Effects of metal-contaminated organic wastes on microbial biomass and activities: A review. In: Ahmed I, Hayat S, Pichtel J. (Eds). Heavy Metal Contamination of Soil, Science Publishers, Plymouth, UK, 2005, 195-204.

[72] Antonious GF, Snyder JC, Berke T, Jarret RL. Screening *Capsicum chinese* for heavy metals bioaccumulation. Journal of Environmental Science and Health 2010; Part-B 45 (6): 562-571.

[73] Antonious GF, Silitonga MR, Tsegaye T, Unrine JM, Coolong T, Snyder JC. Elevated concentrations of trace-elements in soil do not necessarily reflect metals available to plants. J. Environmental Sci. Health 2013; Part-B, 48: 219-225.

[74] Bending G, Lincoln S, Sørensen S, Morgan A, Aamand J, Walker A. In-field spatial variability in the degradation of the phenyl-urea herbicide isoproturon is the result of interactions between degradative *Sphingomonas* spp. and soil pH, Appl. Environ. Microb. 2003; 69: 827-834

[75] Singh B, Walker A, Morgan A, Wright D. Role of soil pH in the development of enhanced biodegradation of fenamiphos, Appl. Environ. Microbiol. 2003; 69: 7035-7043.

[76] Castillo MD, Torstensoon L, Stenstrom J. Biobeds for environmental protection from pesticide uses- a review. J. Agric. Food Chem. 2008; 56: 6206-6219.

[77] Bollag JM, Myers CJ, Minard RD. Biological and chemical interactions of pesticides with soil organic matter. Sci. Total EnViron. 1992; 123: 205-217.

[78] Cox L, Fernandes MC, Zsolnay A, Hermosin MC, Cornejo J. Changes in dissolved organic carbon of soil amendments with aging: Effect on pesticide adsorption behavior. J. Agric. Food Chem. 2004; 52: 5635-5642.

[79] Antonious GF. Soil infiltration by pesticides. In: Pimentel D (Ed). Encyclopedia of Pest Management, volume 3, Marcel Dekker, Inc., New York, 2003. pp. 1-4.

[80] National Institute for Standards and Technology (NIST). Mass Spectrometry Data Center Collection (electron ionization) by U.S. Secretary of Commerce, 2007. Available at: http://webbook.nist.gov/chemistry.

[81] Sharma SD, Singh M. Susceptability of Florida Candler fine soil to herbicide leaching. Bull. Environ. Contam. Toxicol. 2001; 67: 594-600.

[82] Lair GJ, Gerzabek MH, Haberhauer G, Jakusch M, Kirchmann H. Response of the sorption behavior of Cu, Cd, and Zn to different soil management. J. Plant Nutr. Soil Sci. 2006; 169: 60-68.

[83] Patel G. Interactions of pyrethrins and piperonyl butoxide with soil organic matter, MS thesis, 2002, University of Kentucky, Department of Horticulture, Lexington, KY 40546.

[84] Stevenson FJ. Humus Chemistry: Genesis, Composition, Reactions. John Wiley & Sons, 1994. New York.

[85] Tipping E. WHAM – a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Computers and Geosciences 1994; 20(6): 973-1023.

[86] Ghabbour EA, Davies G (Eds). Humic Substances: Structures, Models and Functions. RSC publishing, Cambridge, U.K. 2001. ISBN 978-0-85404-811-3.

[87] Wauchope RD, Buttler TM, Hornsby AG, Augustijn B, Burt JP. The SCS/ARS/CES pesticide properties database for environmental decision making. Reviews of Environmental Contamination and Toxicology 1992; 123: 1-164.

[88] Walker A, Welch SJ. Further studies of the enhanced biodegradation of some soil applied herbicides. Weed Res. 1992; 32: 19-27.

[89] Khoury R, Geahchan A, Coste CM, Cooper JF, Bobe A. Retention and degradation of metribuzin in sandy loam and clay soils of Lebanon. Weed Res. 2003; 43: 252-259.

[90] US EPA. Drinking Water Health Advisory For Dacthal and Dacthal Degradates: Tetrachloroterephthalic Acid (TPA) and Monomethyl Tetrachloroterephthalic Acid (MTP). Health and Ecological Criteria Division, Office of Science and Technology, Office of Water; Washington, DC, 2008. Available at: http://water.epa.gov/drink/index.cfm.

[91] Sharom MS, Stephenson GR. Behaviour and fate of metribuzin in eight Ontario soils. Weed Sci. 1976; 24: 153-160.

[92] Peter CJ, Weber JB. Adsorption, mobility, and efficacy of metribuzin as influenced by soil properties. Weed Sci. 1985, 33: 868-873.

[93] Nicholls PH, Walker A, Baker RJ. Measurement and simulation of the movement and degradation of atrazine and metribuzin in a fallow soil. Pesticide Sci. 1982; 12: 484-494.

[94] Khoury R, Coste CM, Kawar NS. Degradation of metribuzin in two soil types of Lebanon. J. Environ. Sci. Health 2006; 41: 795-806.

[95] Benoit P, Perceval J, Stenrod, M, Moni C, Eklo OM, Barriuso E, Sveistrup T, Kvaerner J. Availability and degradation of metribuzin in alluvial soils as affected by temperature and soil properties. Weed Res. 2007; 47: 517-526.

[96] Laskowski DA, Goring CAI, McCall PJ, Swann RL. Terrestrial environment. In: Conway RA (Ed). Environmental Risk Analysis for Chemicals. Van Nostr and Reinhold Environmental Engineering Series: New York, 1982. Chap. 6, pp. 198-240.

[97] Tomlin C. The Pesticide Manual, Published by the British Crop Protection Council. In: Tomlin C (Ed). Commonwealth Agricultural Bureaux International. 15 Edn. Alton, Hampshire, Wallingford, UK, 2009.

[98] Kim JH, Feagley SE. Adsorption and leaching of trifluralin, metolachlor, and metribuzin in a commerce soil. J. Environ. Sci. Health 1998; B33: 529-546.

[99] Loux MM, Liebl RA, Slife FW. Adsorption of clomazone on soils, sediments, and clays. Weed Sci. 1989; 37: 440-444.

[100] Tavares MC, Rezende MO. Effect of humic acid on the sorption of trifluralin by soils. J. Environ. Sci. Health 1998; B33: 749-767.

[101] Baker JL, Kickelson K, Arora K, Misra AK. The potential of vegetative filter strips to reduce pesticide transport. In: Steinheimer TR, Ross LJ, and Spitter TD (Eds.), Agrochemical Fate and Movement, ACS Symposium Series, American Chemical Society, Washington, DC. 2000, pp. 272-285.

[102] Wauchope RD, Yeh S, Linders J, Kloskowski R, Tanaka K, Rubin B, Katayama A, Kordel W, Gerstl Z, Lane M, Unsworth J. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Management Sci. 2002; 58: 419-445.

[103] Wauchope RD, Buttler TM, Hornsby AG, Augustijn B, Burt JP. The SCS/ARS/CES pesticide properties database for environmental decision making. Reviews of Environmental Contamination and Toxicology 1992; 123: 1-164.

[104] Corbin BR, McClelland M, Frans RE, Talbert RE, Horton D. Dissipation of fluometuron and trifluralin residues after long-term use. Weed Sci. 1994; 42: 438-445.

[105] Shiralipour A, McConnell DB, Smith WH. Uses and benefits of MSW compost: A review and assessment. Biomass and Bioenergy 1992; 3: 267-279.