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Effect of Different Soil Textures on Leaching Potential and Degradation of Pesticides in Biobeds

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Biobeds can be used to intercept pesticide-contaminated runoff from the mixing/washdown area, creating optimum conditions for sorption and biodegradation such that the amount of pesticide reaching adjacent water bodies is significantly reduced. The biobed is built on the farm using locally available materials, which include, straw, compost, and topsoil. The topsoil acts as the inoculum for the system and is likely to vary in terms of its physical, chemical, and microbiological characteristics from one farm to another. This study therefore investigated the effects of using different soil types on the degradation and leaching potential from biobeds. Three contrasting topsoils were investigated. Leaching studies were performed using isoproturon, dimethoate, and mecoprop-P, which were applied at simulated disposal rates to 1.5 m deep biobeds. Annual average concentrations were similar for each soil type with leaching losses of even the most mobile (K_{oc} = 12−25) pesticide <1.64% of the applied dose. Greater than 98% of the retained pesticides were degraded in all matrices. Degradation studies investigated the persistence of individual pesticides and pesticide mixtures in the different matrices. DT_{50} values for isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl applied at 4 times the maximum approved rate were similar across the biomix types and were all less than or equal to reported DT_{50} values for soil treated at approved rates. When applied as a mixture, DT_{50} values in each biomix increased, indicating that interactions between pesticides are possible. However, DT_{90} values of <167 days were obtained in all circumstances, indicating a negligible risk of accumulation. Studies therefore indicate that substrate will have little impact on biobed performance so it should be possible to use local soils in the construction process.

KEYWORDS: Biobeds; pesticide waste; treatment; soil types; design

INTRODUCTION

The presence of pesticides in environmental waters is well documented (*1*−*6*). These pesticide residues can be attributed to a number of sources including releases from fields during and after application, leakage from equipment, spillages, and incorrect disposal of waste and washings (*4*, *7*). Recent research suggests that the contribution from sources other than those originating from approved applications to agricultural land may be more significant than previously realized (*8*−*11*). Such "point source" releases can be reduced by modifying handling practices to minimize losses (*12*). However, due to time constraints and other pressures, small drips and spills are still likely to occur (*8*, *9*). Additional methods of control are therefore required. A number of possible approaches are available including (1) the washing of spray equipment in the field (*13*, *14*), thus reducing the requirements for decontamination at the farmyard and the disposal of any associated waste; (2) better design of the farmyard to minimize release of pesticides to nearby surface waters (*12*, *15*); or (3) treatment systems that are installed on the farmyard to treat any waste arising from spray equipment and during the filling process. One possible treatment approach is to use a biobed to intercept and treat contaminated runoff from the farmyard and/or drips and spillages arising during the filling process (*16*, *17*). In its simplest form, a biobed is a clay-lined hole in the ground filled with a mixture of topsoil, peat, and straw (biomix) and covered with grass (*16*, *18*). The biobed is equipped with a ramp enabling the tractor and sprayer to be driven over the bed and thus intercept drips and spills. Alternatively, the biobed is connected to an adjacent concrete intercept area on which all mixing and washdown activities take place (*19*). Studies have demonstrated that biobeds can effectively retain and degrade pesticides, (*15*, *20*−*27*), such that the concentrations of pesticide leaving the mixing/washdown area are significantly reduced.

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Table 1. Characteristics of Soils Used for Leaching and Degradation Experiments

	soil series		
	Wick	Worcester	Blacktoft
% sand (63 μm–2 mm)	65.4	19.6	12.9
% silt (2 μm–63 μm)	18.7	36.1	46.5
% clay (<2 μm)	15.9	44.3	40.6
pH (water)	6.2	7.3	7.7
% organic carbon	0.9	1.0	3.6
texture	sandy loam	clay	silty clay
maximum water-holding capacity (% w/w)	33.0	55.3	64.6

Typically, the constituent components of the biomix (topsoil, peat, and straw) are mixed in volumetric proportions of 1:1:2, respectively (*18*). The peat or compost provides numerous sites for pesticide sorption and also helps to maintain aerobic conditions due to its high water-holding capacity, whereas the straw acts as an additional food source for the microorganisms. The topsoil acts as the inoculum for the biomix and should be rich in humus but must have a low clay content (*16*). However, the model biobed described is generally adapted to satisfy site-specific conditions (*21*) and to utilize locally available materials, in particular topsoil. There is evidence that soil texture influences the rate at which a pesticide degrades (*28*, *29*). Furthermore, water movement is largely controlled by soil texture, with susceptibility to leaching typically associated with low organic matter content, low moisture-holding capacity, and a relatively sandy texture (*30*). In a clay-textured soil, water movement is much slower, however, and can be complicated by large cracks and macropores, which may result in bypass flow and very rapid water movement (*31*). The contrasting characteristics of the different topsoil textures may not be as relevant in the biobed as for in situ soils due to (a) the destructive mixing process and (b) the inclusion of peat and straw. However, as the topsoil represents 25% of the overall mix and is the major source of microorganisms, it is likely to have a controlling influence in the performance of the biobed. The objective of the experiments reported here was to assess the impacts of substrate on biobed performance by (a) determining whether concentrations of pesticide leaching from biobeds were affected by different topsoils being used to make the biomix and (b) investigating degradation in the different biomix types.

MATERIALS AND METHODS

Preparation of Biomix. Three arable topsoils with a range of physical characteristics were collected (**Table 1**). On the basis of texture, these were representative of 46% of agricultural land in England and Wales (*32*). Each soil type was mixed separately with peat-free compost (Levington Peat Free Universal) and winter wheat straw in the volumetric proportions of 1:1:2, respectively. The mixtures were composted in uncovered heaps, outside, for 71−97 days prior to use. The heaps were turned twice throughout this period. Biomix for use in the degradation experiments was then macerated using a food processor, air-dried to ∼25−40% w/w (depending on topsoil texture), and refrigerated at 0−10 °C prior to use. A disturbed subsample was then repacked into 222 cm^3 volumetric tins and the maximum water-holding capacity determined by capillary rise (*33*). The microbial biomass of the three topsoils and the three biomix mixtures was also measured to give an indication of microbial activity (*34*).

To replicate the anticipated field conditions, the biomix for use in the semifield lysimeter experiments was not macerated. Field biobeds are likely to contain several cubic meters of biomix, and following consultation with potential users of the biobed systems, it was felt that sourcing the required volume of chopped straw would be difficult.

Test Chemicals. Test pesticides were selected on the basis of their physicochemical properties (*35*−*37*), in particular their sorption potential and water solubility, and represent compounds that are of relatively high average annual usage in the United Kingdom (*38*) (**Table 2**).

Degradation. Samples (112) of each biomix type were weighed out (25 g) into clear glass bottles (125 mL) fitted with Bakelite screw cap lids to provide three treated replicates and one untreated control per sampling time point. Subsamples of each biomix were taken and moisture contents determined by oven-drying at 105 ± 2 °C for 24 h. Formulated isoproturon (Alpha Isoproturon 500, 43.6% w/w), chlorothalonil (Cropgard, 41.57% w/w), mecoprop (Optica, 48% w/w), and metsulfuron-methyl (Jubillee 20 DF, 20% w/w) were used to make up individual as well as mixture stock suspensions in tap water. For the biomix made using the sandy loam topsoil 1233, 824, 571, and 34 mg of active substance (a.s.) L^{-1} of each respective product was used. For the clay-textured biomix 2543, 1699, 1177, and 71 mg of a.s. L^{-1} were added, and for the silty clay, 665, 445, 308, and 18 mg of a.s. L^{-1}. To achieve final dry weight concentrations in the biomix substrate of 100 mg kg^{-1} (isoproturon), 60 mg kg^{-1} (chlorothalonil), 48 mg kg^{-1} (mecoprop-P), and 1.2 mg kg^{-1} (metsulfuron-methyl) and moisture content of 50% w/w, 3.3 mL of the respective pesticide solution was added to the sand loam biomix, 6.9 mL to the clay biomix, and 1.5 mL to the silt clay biomix. Tap water was applied to the remaining untreated samples. Immediately after treatment, three treated replicates and one untreated control were taken for each different biomix type and pesticide treatment and frozen (−20 °C). The remaining samples were loosely capped and incubated in the dark at 20 °C. At intervals of 5, 10, 20, 30, and 60 days after treatment (DAT) three samples were collected from each different biomix and pesticide treatment, with a single sample from the untreated controls. The samples were stored at −20 °C prior to analysis.

Leaching Potential. Twelve lysimeters were prepared using unplasticized poly(vinyl chloride) (PVC-u) piping (22.5 cm internal diameter), cut to 165 cm length. Each pipe section was filled with 5 cm of washed gravel (10−15 mm diameter) followed by 150 cm of biomix, to give four replicates for each of the three biomix types. The base of each core drained via Teflon tubing to a 2.5 L amber glass collection vessel located in a central collection pit (*39*). Lysimeters were connected using plastic guttering to 0.16 m^2 concrete slabs. Silicon sealant was placed on three sides of the slab to prevent water loss from the sides. Formulated isoproturon (Alpha Isoproturon 500, 43.6% w/w), dimethoate (Rogor L40, 37.4% w/w), and mecoprop (Optica, 48% w/w) were used to make up stock suspensions in tap water of 3200, 435.2, and 1536 mg of a.s. L^{-1} of isoproturon, dimethoate, and mecoprop, respectively. All 12 lysimeters were treated in January 2003 with 50

Table 2. Study Compounds and Their Reported Physicochemical Characteristics[a]

active substance	product	concn (% w/w)	K_{oc} (mL g^{-1})	mobility class[b]	DT_{50} soil (days)	solubility water (mg L^{-1})
isoproturon	Alpha Isoproturon 500	43.6	125	moderately mobile	6–28	65
chlorothalonil	Cropgard	41.6	1600–14000	slightly/nonmobile	5–36	0.6–1.2
dimethoate	Rogor L40	37.4	16–52	mobile	2–16	23800
mecoprop	Optica	48	12–25	very mobile	3–13	860
metsulfuron-methyl	Jubilee 20 DF	20	4.6–35	very mobile	7–35	27900

[a] Values taken from refs *35*–*37*. [b] From ref *32*.

mL of the pesticide mixture to give final treatment rates of 298 mg (isoproturon), 40.5 mg (dimethoate), and 143 mg (mecoprop-P). Application rates were based on a number of field studies and long-term pesticide usage data for a number of large arable farms (*9*, *15*). Potassium bromide (KBr) was applied at the same time as the pesticides (314 mg core^{-1}) to check the hydrological integrity of the lysimeters, as well as to determine the breakthrough timing of infiltrating water. Leachate collection vessels were monitored after all rainfall events, and the total volume of leachate was recorded. Volumes in excess of 200 mL were collected and frozen prior to analysis. When possible, a 60 mL subsample was also taken for KBr analysis. At the end of the study (115 DAT), the top 30 cm of the lysimeters was removed and sectioned (0−10, 10−20, and 20−30 cm) and the sections were homogenized and frozen prior to analysis. Artificial irrigation was applied to all 12 lysimeters in February, March, and April. The cumulative total applied was 91.4 mm, equivalent to 18.3 L per lysimeter.

Analysis. *Water Extraction.* For isoproturon, dimethoate, and mecoprop-P added as mixture, samples (200 mL) were extracted into 3 × 40 mL of dichloromethane (DCM) using a glass separating funnel (250 mL). Following extraction, DCM extracts were dried over anhydrous sodium sulphate and then evaporated to dryness using a rotary evaporator at 40 °C. The resulting residues were redissolved into 2 mL of methanol. Concentrations of isoproturon and mecoprop-P were then determined by HPLC, and dimethoate concentrations were determined by GC.

Biomix Extraction. Biomix samples (40 g) from the semi-field experiments treated with isoproturon, dimethoate, and mecoprop-P added as mixture were placed into glass 250 mL bottles and extracted into 80 mL of methanol for 1 h using an end-over-end shaker. Following extraction, samples were allowed to stand until clear. An aliquot of the methanol solution was then taken for analysis. Isoproturon and mecoprop-P concentrations were determined by HPLC, and dimethoate concentrations were determined by GC. Laboratory samples (25 g) treated with isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl applied individually and as a mixture were shaken for 1 h on an end-over-end shaker with methanol (50 mL). Samples were allowed to stand until clear, after which an aliquot of the solution was taken for HPLC analysis.

Recoveries for all of the extraction methods were >94%.

HPLC Analysis. Concentrations of isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl were determined by HPLC using a Spectra Physics SP8810 pump linked to a Kontron 430 UV detector. Samples (20 μL) were injected using a Spectra Physics SP8775 autosampler. Separation was achieved using a Hypersil C18 column (250 × 4.6 mm) (Jones Chromatography, Hengoed, U.K.). The mobile phase used was acetonitrile/methanol/0.05 M acetic acid (35:30:35) with a flow rate of 1.5 mL min^{-1}, which gave retention times of 2.6, 3.4, 4.1, and 5.6 min for metsulfuron-methyl, mecoprop-P, isoproturon, and chlorothalonil, respectively. The detection wavelength was 230 nm for all three substances. The limits of quantification were 0.05 μg L^{-1} for metsulfuron-methyl and mecoprop-P, 0.03 μg L^{-1} for isoproturon, and 0.02 μg L^{-1} for chlorothalonil.

GC Analysis. Concentrations of dimethoate were determined on a Hewlett-Packard HP5890 gas chromatograph fitted with a split/splitless injector, a 12 m × 0.53 mm BPX5 column (SGE), and a nitrogen−phosphorus detector. The carrier gas (helium) flow rate was 7 mL min^{-1}, and detector gas flow rates were 100 mL min^{-1} (air) and 4 mL min^{-1} (hydrogen). The oven temperature was raised from 90 to 190 °C (40 °C min^{-1}) and then to 220 °C (10 °C min^{-1}) and finally to 245 °C (15 °C min^{-1}). Samples (2 μL) were injected using a Hewlett-Packard HP7673 autosampler. Under these conditions dimethoate had a retention time of 3.1 min. Quantification was achieved by comparison of peak areas with results from external standards. The limit of quantification was 0.08 μg L^{-1}.

Bromide. Concentrations of potassium bromide were determined using a Metrohm (Herisau, Switzerland) 790 personal ion chromatograph and an 813 compact autosampler. Analytical columns used were Metrohms' Metrosep RP guard, Metrosep A Supp 4/5 guard, and Metrosep A Supp 4 (250 × 4.0 mm). A 20 μL injection loop and isocratic eluent of composition 1.8 mM sodium carbonate/1.7 mM sodium hydrogen carbonate were used, giving a typical retention time of 8.5 min. All samples were filtered at 0.45 μm (Whatman 13 mm polysulfone syringe) prior to loading into the proprietary autosampler cartridges. Limit of quantification was 0.5 mg L^{-1}, with a limit of detection at 0.1 mg L^{-1}.

Biomass. Total microbial biomass was determined by fumigation extraction (*34*). Chloroform (2 mL) was added to triplicate samples (20 g) of soil and biomix. A control sample was left untreated. Treated and untreated samples were sealed and incubated at 30 °C for 7−10 days. Following incubation, fumigated samples were evacuated 4−6 times in a vacuum desiccator to remove the chloroform and then shaken for 50 min with 50 mL of 2 M potassium chloride. Samples were then centrifuged, and a 1 mL extract was taken to which 0.5 mL of ninhydrin was added. The samples were then immersed in a boiling water bath for 20 min. After cooling, samples were made up to 10 mL using a 50:50 mixture of ethanol and water and transferred to plastic cuvettes, and the absorbance was measured using a spectrophotometer at 570 nm. The absorbances were corrected for the unfumigated controls and the amounts of ninhydrin reactive N derived from a calibration curve produced using different concentrations of L-lucine. The results were corrected for moisture content, and the total biomass C (mg kg^{-1}) was calculated (*34*).

Data Analysis. When possible, the first-order rate equation was fitted to the observed concentrations

$$dC/dt = -kC \quad (1)$$

where C is the concentration (mg kg^{-1} of soil), t is the time (days), and k is the degradation rate (days^{-1}). The integrated form of this equation (eq 2) was fitted to nontransformed data using the least-squares method in order to give the best agreement between calculated and observed concentrations.

$$C_t = C_0 \exp(-kt) \quad (2)$$

However, the first-order rate equation is often considered to be unacceptable if the determination coefficient (r^2) falls below 0.7 (*40*). When data indicated increasing rates of degradation with time, DT_{50} and DT_{90} values were calculated using an empirical two-parameter relationship

$$S/S_0 = \exp\{k_1[1 - \exp(k_2 t)]\} \quad (3)$$

where S_0 and S are the concentrations of pesticide at time 0 and time t, respectively. Microsoft Excel Solver was used to estimate parameters k_1 and k_2 using the least-squares method in order to give the best agreement between calculated and observed concentrations. The degradation data were summarized by calculating the time to 50% degradation (DT_{50}) and the time to 90% degradation (DT_{90}) from the calculated degradation curves using the relationship

$$DT_{50} = \ln[1 - \ln(0.5)/k_1]/k_2 \quad (4)$$

$$DT_{90} = \ln[1 - \ln(0.1)/k_1]/k_2 \quad (5)$$

Similarly when the pattern of degradation was biphasic with residue concentrations decreasing slowly after an initial rapid decline, data were fitted to a biexponential decay curve. The biexponential curve consists of two exponential terms

$$C_t = A \exp(-k_1 t) + B \exp(-k_2 t) \quad (6)$$

where C_t (mg kg^{-1} of soil) is the concentration at time t, A (mg kg^{-1} of soil) and B (mg kg^{-1} of soil) are constants, and k_1 (days^{-1}) and k_2 (days^{-1}) determine the decline of the first and second components of the curve, respectively (*40*).

RESULTS

Microbial Biomass. The microbial biomass was measured to give an indication of microbial activity. Values of 83.47, 229.4, and 185.5 mg kg^{-1} carbon were measured for the sand,

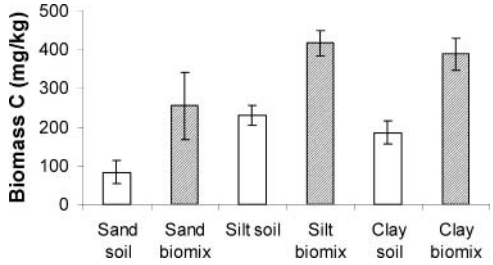

Figure 1. Microbial biomass measured in the sand, silt, and clay topsoils and biomixes.

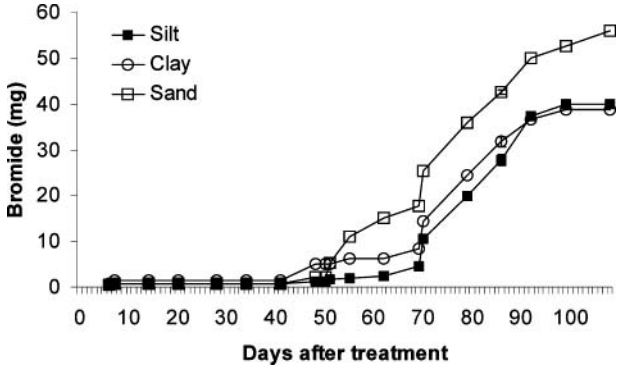

Figure 2. Bromide leaching (± 1 SE) from lysimeters filled with different biobed mixtures made using sand-, silt-, and clay-textured topsoils.

silt, and clay topsoils, respectively. By mixing the three topsoils with straw and compost, a significant (Anova $P < 0.05$, $F = 5.01$, df = 2) increase in microbial biomass was measured with values of 255.4, 416.7, and 388.2 mg kg^{-1} carbon being obtained for the sand, silt, and clay biomixes, respectively (**Figure 1**).

Degradation. *Effect of Different Soils on Pesticide Degradation.* Results from the experiments to investigate the degradation of isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl in biomix made using different topsoil inocula are summarized in **Table 4**. With the exception of the silt biomix, the pattern of degradation for isoproturon could be fitted to first-order kinetics (equation 2), with <5% of the applied dose remaining in the sand and clay biomixes after 20 days. In the silt biomix, after an initial period of rapid degradation, residue levels persisted at low levels until the end of the experiment (**Figure 4a**). DT_{50} values of 6.3, 13.4, and 5.9 days were calculated for the sand, silt, and clay biomix soils, respectively. The slower rate of isoproturon on the silt biomix resulted in recovered residues of >15% at the end of the experiment, which were significantly higher (Anova $P < 0.05$, $F = 40.16$, df = 2) than in the sand and clay biomixes. Degradation of chlorothalonil was biphasic (eq 6) in all three biomix substrates, with similar DT_{50} values measured, ranging from 8.0 days in the sand biomix to 9.4 days in the clay biomix. In the sand and clay biomixes <13% of the applied dose was recovered at the end of the experiment with DT_{90} values of 49.5 days calculated for both matrices. In the silt biomix a DT_{90} of 71.3 days was calculated, explaining why significantly (Anova $P < 0.05$, $F = 7.05$, df = 2) more (23%) of the applied dose was recovered after 60 days (**Figure 4b**). Mecoprop-P degraded rapidly in all three biomix types (**Figure 4c**). The data indicated increasing rates of degradation with time (eq 3). DT_{50} values were between 4.3 days (silt biomix) and 6.2 days (sand biomix) with DT_{90} values of <9 days in all three biomix types. Recovered residues were <1% after 10 days. The pattern of metsulfuron-methyl degradation could be fitted to first-order kinetics in all three biomix types (**Figure 4d**). The rate of degradation was quickest in the sand biomix (DT_{50} = 13.4 days) and slowest in the clay biomix (31.4 days). Similarly, DT_{90} values ranged from 44.4 days in the sand biomix to 104.3 days in the clay. Recovered

Table 3. Mass Balance for Lysimeters Filled with Biomixex Made Using either Sand, Silt, or Clay Topsoil[a]

soil type	% leached	% retained	% degraded	max concn (μg L^{-1})	CV%	av concn (μg L^{-1})	CV%
isoproturon							
sand	0.006	0.50	99.50	6.49	188.8	0.50	129.4
silt	0.002	0.51	99.49	1.62	96.7	0.16	67.4
clay	0.007	0.38	99.61	2.84	158.2	0.44	106.7
mecoprop-P							
sand	1.36	0	98.64	145	116.9	53	114.6
silt	0.04	0	99.96	45	154.8	6.15	88.5
clay	1.64	0	98.36	117	96.1	48	76.4
dimethoate							
sand	0.02	0.48	99.50	6.27	128.2	0.98	62.5
silt	0.004	0.61	99.38	0.53	99.4	0.15	131.6
clay	0.112	0	99.89	1.06	112.0	0.16	108.3

[a] Studies investigating the leaching risk of metsulfuron-methyl are ongoing and will be presented elsewhere.

Table 4. DT_{50} and DT_{90} Degradation Rates, Degradation Rate Constants (k), and Determination Coefficients (r^2) for Isoproturon, Chlorothalonil, Mecoprop-P, and Metsulfuron-methyl When Applied Individually to Biomixes Made Using Sand, Silt, and Clay Topsoils

	sand				silt				clay			
	DT_{50} (days)	DT_{90} (days)	k (deg days^{-1})	r^2	DT_{50} (days)	DT_{90} (days)	k (deg days^{-1})	r^2	DT_{50} (days)	DT_{90} (days)	k (deg days^{-1})	r^2
isoproturon	6.3	20.8	0.111	0.99	13.4	52.9	$k_1 = 1.589$ $k_2 = 0.054$	1	5.9	19.5	0.118	0.98
chlorothalonil	8.0	49.5	$k_1 = 0.038$ $k_2 = 0.43$	0.98	8.2	71.3	$k_1 = 0.0001$ $k_2 = 0.10$	0.95	9.4	49.5	$k_1 = 1.953$ $k_2 = 0.082$	0.85
mecoprop-P	6.2	8.6	$a = 0.038$ $b = 0.477$	1.00	4.3	8.0	$a = 0.343$ $b = 0.256$	1.00	5.1	7.5	$a = 0.067$ $b = 0.476$	1.00
metsulfuron-methyl	13.4	44.4	0.052	0.98	19.5	64.8	0.036	0.99	31.4	104.3	0.022	0.99

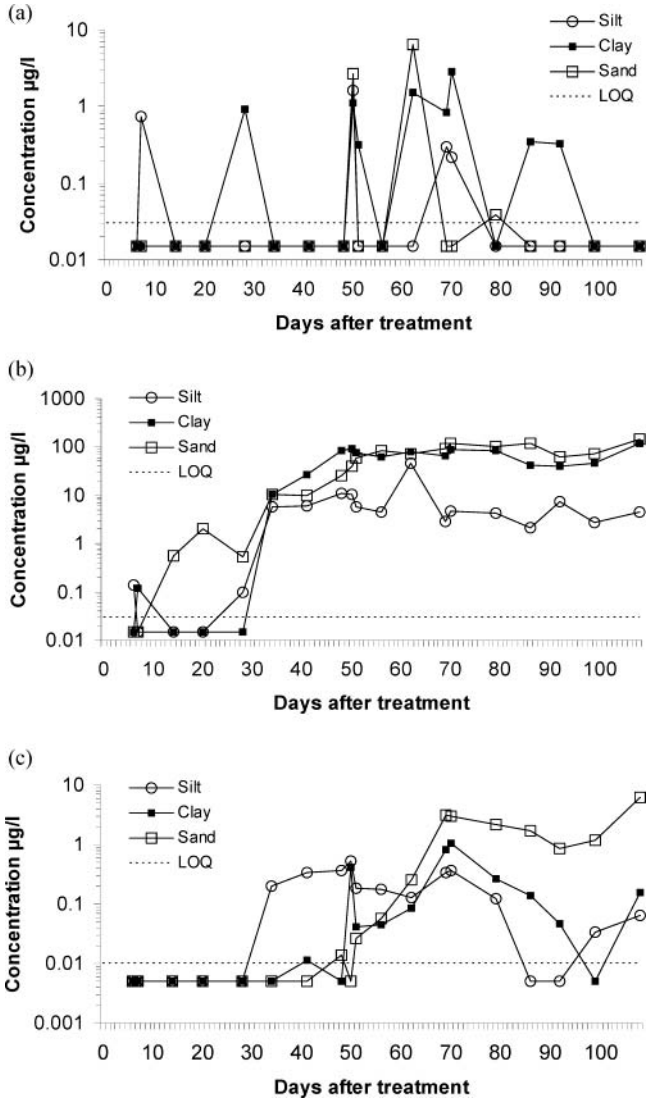

Figure 3. Mean concentrations of (**a**) isoproturon, (**b**) mecoprop-P, and (**c**) dimethoate from 1.5 m deep lysimeters connected to 0.16 m^2 concrete slabs and filled with biomix made from either sand, silt, or clay topsoil.

residues at the end of the study were significantly different (Anova $P < 0.05$, $F = 30.11$, df = 2), with 1.9, 12.7, and 28.3% of the applied dose measured in the sand, silt, and clay biomix soils, respectively.

Effect of Pesticide Mixture on Pesticide Degradation. Results from the experiments to investigate the degradation of isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl in the different biomix types when applied as a mixture are summarized in **Table 5**. The pattern of isoproturon degradation in the sand and clay biomixes was biphasic, showing a slight increase in the rate of degradation with time (**Figure 5a**,**c**). DT_{50} and DT_{90} values of 21.4 and 47.7 days were calculated for the sand biomix and 16.1 and 30.7 days for the clay biomix, respectively. At the end of the experiment, <7% of the applied pesticide was recovered. The pattern of isoproturon degradation in the silt biomix fitted first-order kinetics (**Figure 5b**). DT_{50} and DT_{90} values for the silt soil were 34.7 and 115.4 days, respectively, with 35% of the applied pesticide recovered after 60 days. For chlorothalonil the rates of degradation were similar in all three biomix types. After an initial period of rapid degradation, residue levels persisted at relatively low levels until the end of the study (**Figure 6**). DT_{50} values ranged from 14.2 days in the clay biomix to 19.6 days in the silt biomix, and DT_{90} values between 82 days (sand biomix) and 167 days (silt biomix) were obtained (**Table 5**). At the end of the experiment 17, 20, and 31% of the applied dose was recovered from the sand, clay, and silt biomix soils, respectively. Degradation of mecoprop-P was similar to that observed in the individual treatments. The pattern of degradation was the same for all three biomix types, showing increasing rates of degradation with time (**Figure 7**). DT_{50} values ranged from 5.6 to 6.8 days in the silt and clay biomix soils, respectively, with <2% of the applied pesticide remaining in any of the biomix soils after 10 days. For metsulfuron-methyl in the clay and silt biomix soils, very little degradation was observed for the first 30 days following treatment. However, between 30 and 60 days the rate of degradation was much more rapid (**Figure 8b**,**c**). DT_{50} values of 43.5 and 58.6 days were calculated for the silt and clay biomix soils, respectively. At the end of the study, 23% of the applied dose was recovered from the silt biomix compared with 42% from the clay. Degradation in the sand biomix soil was fitted to first-order kinetics (**Figure 8a**). DT_{50} and DT_{90} vales of 37.4 and 124.3 days were calculated, respectively, with 28% of the applied dose recovered 60 DAT.

Leaching. *Rainfall and Leachate Volumes.* With artificial irrigation (91.4 mm) the total water input for the study period was 201.5 mm and was 53% above the long-term average for the period January−April inclusive. Leachate samples were collected on 19 occasions, providing 228 water samples for analysis. Cumulative leachate volumes ranged from 26.2 to 30.6 L from the silt biomix lysimeters, from 30.4 to 33.7 L from the clay biomix lysimeters, and from 27.4 to 34.2 L from the sand biomix lysimeters.

Bromide in Leachate. Bromide breakthrough curves from the three different biobed mixtures were similar (**Figure 2**). Breakthrough was measured 48 DAT for each of the three biobed mixtures. Maximum concentrations were measured 55 DAT from the sand biomix lysimeters, 79 DAT from the clay

Table 5. DT_{50} and DT_{90} Degradation Rates, Degradation Rate Constants (k), and Determination Coefficients (r^2) for Isoproturon, Chlorothalonil, Mecoprop-P, and Metsulfuron-methyl When Applied as a Mixture to Biomixes Made Using Sand, Silt, and Clay Topsoils

	sand				silt				clay			
	DT_{50} (days)	DT_{90} (days)	k (deg $days^{-1}$)	r^2	DT_{50} (days)	DT_{90} (days)	k (deg $days^{-1}$)	r^2	DT_{50} (days)	DT_{90} (days)	k (deg $days^{-1}$)	r^2
isoproturon	21.4	47.7	$a = 0.918$ $b = 0.026$	0.99	34.7	115.4	0.020	0.98	16.1	30.7	$a = 0.399$ $b = 0.062$	1.00
chlorothalonil	15.6	82.0	$k_1 = 0.024$ $k_2 = 0.23$	1.00	19.6	167.0	$k_1 = 0.011$ $k_2 = 0.15$	1.00	14.2	101.9	$k_1 = 0.017$ $k_2 = 0.17$	1.00
mecoprop-P	6.5	7.6	$a = 0.0008$ $b = 1.034$	1.00	5.6	8.6	$a = 0.105$ $b = 0.365$	1.00	6.8	8.8	$a = 0.012$ $b = 0.600$	1.00
metsulfuron-methyl	37.4	124.3	0.019	0.99	43.5	66.5	$a = 0.097$ $b = 0.048$	0.88	58.6	64.7	$a = 0.000008$ $b = 0.195$	0.96

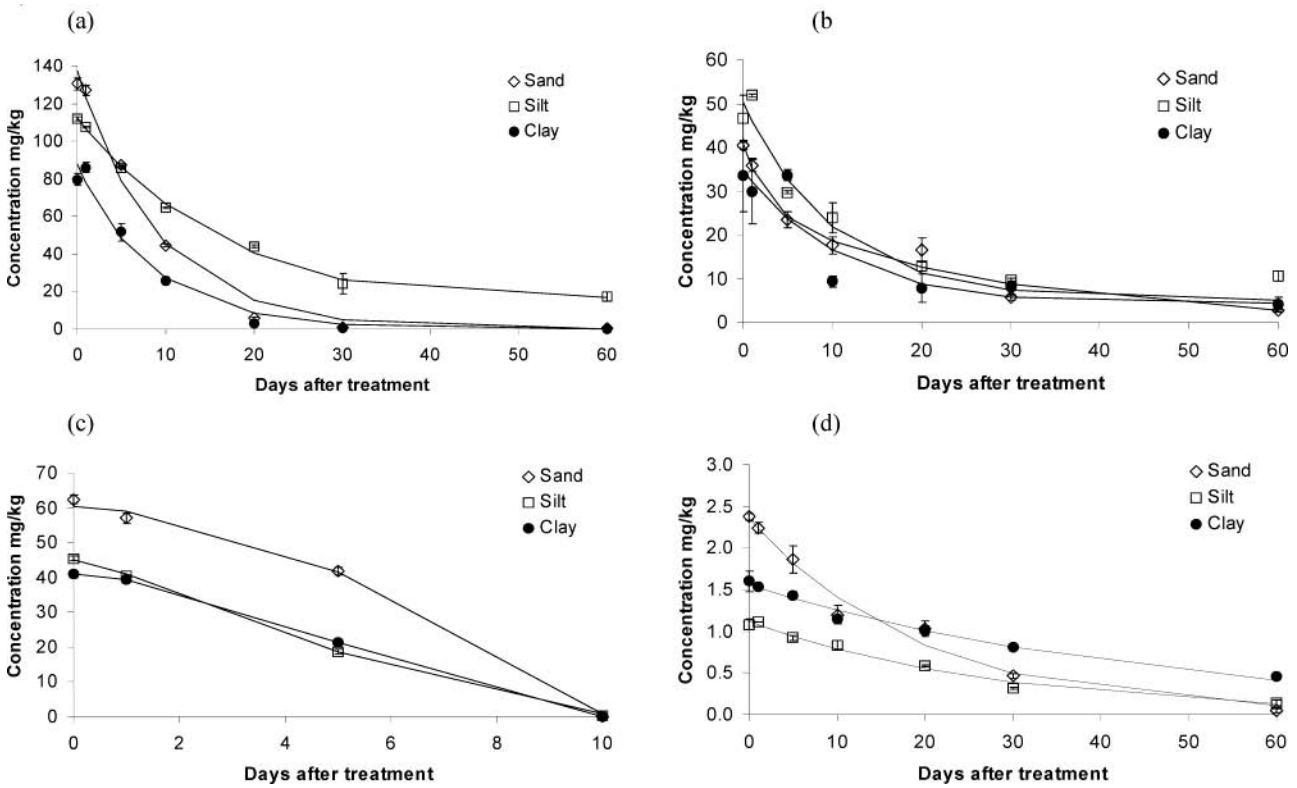

Figure 4. Degradation of (**a**) isoproturon, (**b**) chlorothalonil, (**c**) mecoprop-P, and (**d**) metsulfuron-methyl in biomixes made using three contrasting topsoils.

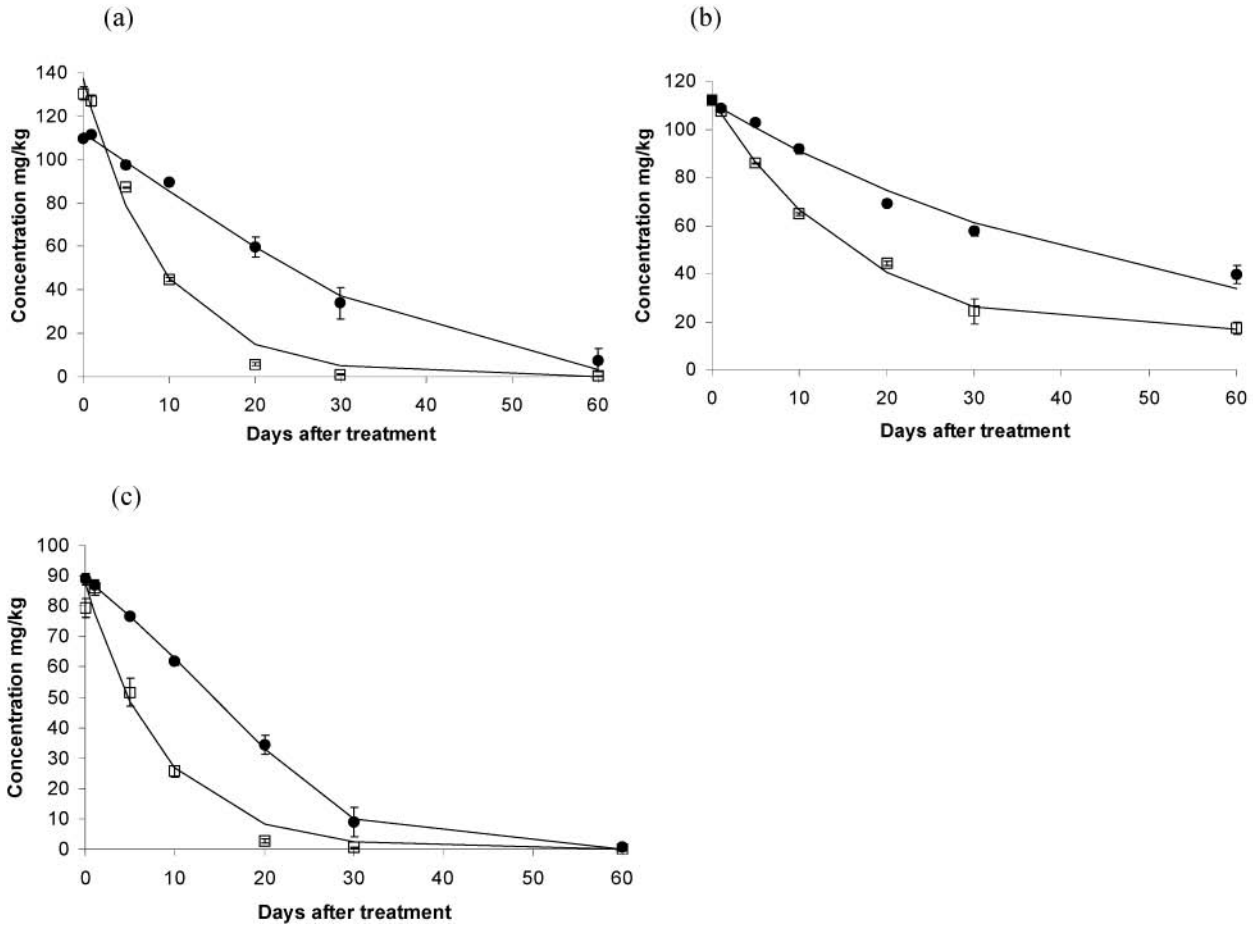

Figure 5. Concentrations of isoproturon in biomixes made using (**a**) sand, (**b**) silt, and (**c**) clay topsoils when applied individually (□) and as part of a mixture (●) containing isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl.

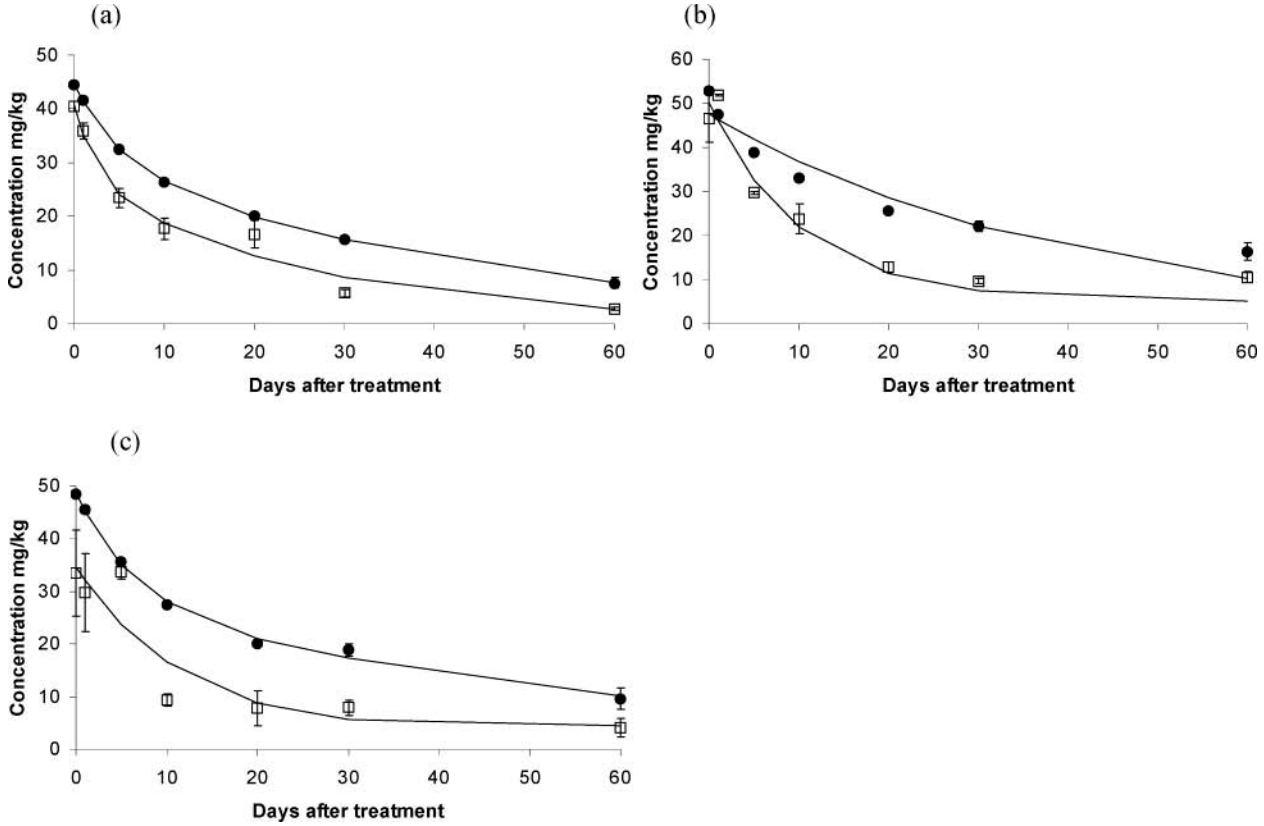

Figure 6. Concentrations of chlorothalonil in biomixes made using (**a**) sand, (**b**) silt, and (**c**) clay topsoils when applied individually (□) and as part of a mixture (●) containing isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl.

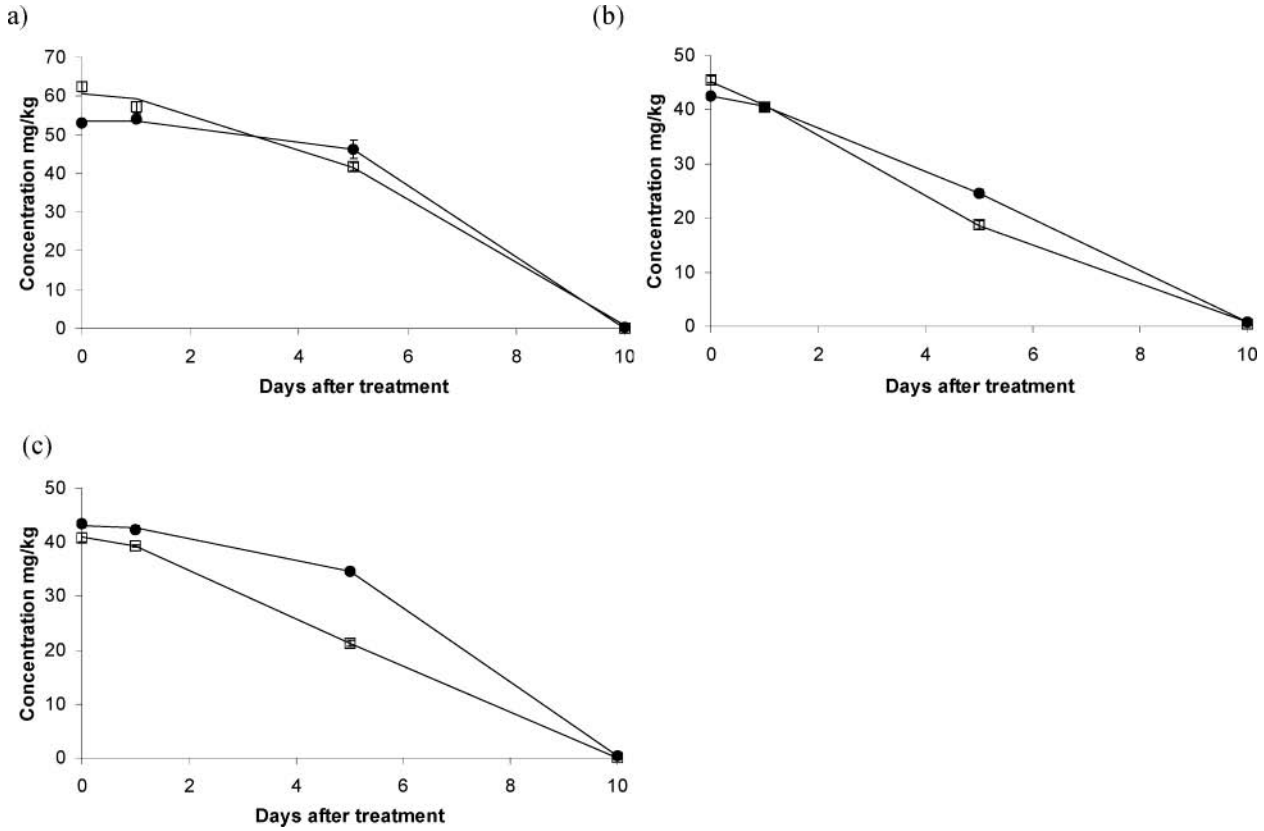

Figure 7. Concentrations of mecoprop-P in biomixes made using (**a**) sand, (**b**) silt, and (**c**) clay topsoils when applied individually (□) and as part of a mixture (●) containing isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl.

biomix lysimeters, and 86 DAT from the silt biomix lysimeters. Concentrations of bromide for the silt and clay biomix lysimeters were below the LOQ (0.5 mg L^{-1}) by the end of the study (108 DAT) and from the sand biomix lysimeters were at 1.7 mg L^{-1}.

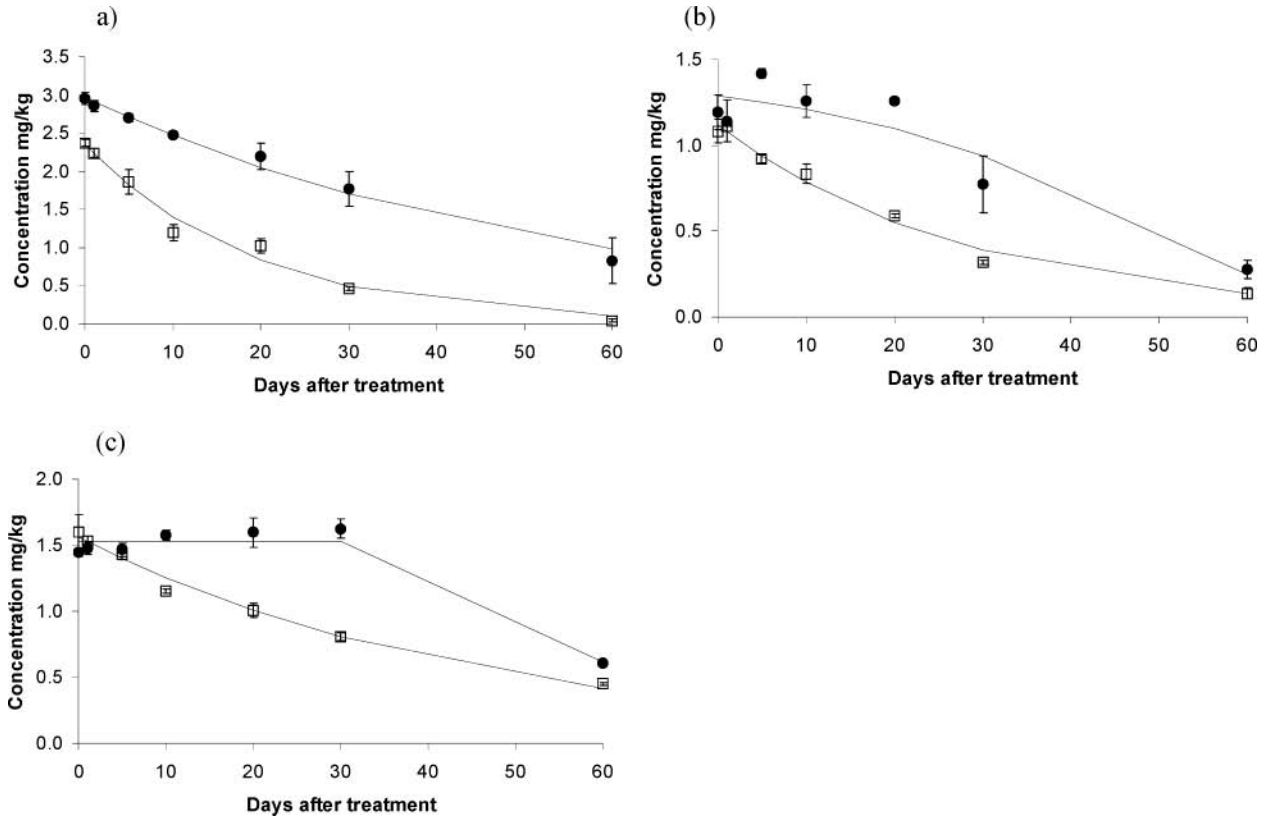

Figure 8. Concentrations of metsulfuron-methyl in biomixes made using (**a**) sand, (**b**) silt, and (**c**) clay topsoils when applied individually (□) and as part of a mixture (●) containing isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl.

Cumulative losses from the sand, silt, and clay biomix lysimeters were 17, 13, and 12%, respectively.

Pesticide Residues in Leachate. Peak concentrations of isoproturon measured in leachate from the silt, clay, and sand biomix lysimeters were 1.62, 2.84, and 6.49 μg L^{-1} and were measured 50, 70, and 62 DAT, respectively (**Figure 3**). Breakthrough from the silt biomix lysimeters occurred 7 DAT, whereas from the clay and sand biomixes, breakthrough was much later, that is, 34 and 50 DAT, respectively. Mecoprop-P breakthrough from the silt and clay biomixes was measured 6 DAT and that from the sand biomix 14 DAT. Peak concentrations were measured 62 DAT from the silt biomix and 108 DAT from the sand and clay biomixes. The maximum measured concentrations were 45.22, 117.7, and 145.3 μg L^{-1} from the silt, clay, and sand biomixes, respectively. Maximum concentrations of dimethoate were measured 50, 70, and 108 DAT from the silt, clay, and sand biomixes with values of 0.53, 1.06, and 6.27 μg L^{-1} respectively. Breakthrough of dimethoate was measured 34 DAT from the silt biomix, 41 DAT from the clay biomix, and 48 DAT from the sand biomix.

Pesticide Residues in Biomix. No mecoprop-P was measured in either the sand, silt, or clay biomix lysimeters at the end of the study (115 DAT), and no isoproturon or dimethoate was measured below a 10 cm depth. For isoproturon, the measured residues (expressed as percentage of the applied dose) remaining in the sand, silt, and clay biomix lysimeters were 1.46, 1.53, and 1.13%, respectively. No dimethoate was recovered from the clay biomix lysimeter 0−10 cm layer, with 0.2% recovered from this layer in the sand biomix and 0.25% from the silt biomix.

Mass Balance. A mass balance was performed to determine the fate of each of the study compounds when applied to the biobed lysimeters filled with the different biomix substrates (**Table 3**). For isoproturon between 0.007% (clay) and 0.002% (silt) leached, between 0.51% (silt) and 0.38% (clay) was associated with the biobed matrix, and between 99.6% (clay) and 99.5% (silt) was dissipated. For mecoprop-P, between 1.64% (clay) and 0.04% (silt) leached, 0% was recovered from the biobed matrix for either the sand, silt, or clay biomix, with between 99.96% (silt) and 98.36% (clay) dissipated. For dimethoate between 0.11% (clay) and 0.004% (silt) leached, between 0.61% (silt) and 0% (clay) was retained in the biobed matrix, and between 99.89% (clay) and 99.38% (silt) was dissipated.

DISCUSSION

Topsoil is used as the inoculum for the biobed matrix, and as biobeds are likely to be built on farms using locally available materials, it is likely that the physical and chemical characteristics of the topsoil used will vary considerably. In the preparation of the biomix the initial moisture content of the topsoil can be critical, particularly in those soils containing a significant amount of clay. For the clay soil used in these experiments at a moisture content of 38% v/v [field capacity (5 kPa) in this particular soil] it was almost impossible to prepare a homogeneous mix with the straw and peat fractions. However, when a second batch of the clay topsoil was collected in the late summer, following stubble cultivations, the moisture content was only 29% v/v, allowing far easier preparation of the biomix.

The degradation of pesticides applied to soil is mainly carried out by soil microorganisms (*41*); therefore, those factors that effect microbial activity in soil should also influence rates of pesticide loss (*42*). In the three soils tested here, measured biomass levels were highest in the silt topsoil and lowest in the sand. Mixing each of the soils with compost and straw resulted in a 2-fold increase in the measured biomass, indicating a significant increase in the levels of microbial respiration. DT_{50}

values for individual compounds applied at 4 times the maximum approved rate were less than or equal to reported DT_{50} values for soil treated at approved rates. However, in practice, crops and field soils receive repeated applications of tank mixes containing herbicides, fungicides, and insecticides (*43*−*46*). Biobeds are therefore likely to receive complex mixtures of more than one active substance applied repeatedly at concentrations far higher than field treatment rates. When applied as a mixture, DT_{50} values for isoproturon, chlorothalonil, mecoprop-P, and metsulfuron-methyl increased, indicating that interactions between pesticides applied as a mixture are possible. Similar observations have been reported elsewhere (*22*, *23*, *44*, *46*, *47*). This inhibition may be due to a number of factors. The application of the fungicide chlorothalonil may have suppressed the activity of nontarget soil microorganisms (*48*, *49*), thus inhibiting the rate at which the remaining pesticides were degraded. Singh et al. (*46*) reports that all measured microbial characteristics were adversely affected by chlorothalonil treatment when applied individually or in combination with other pesticides. These findings are supported by a previous study (*50*) in which it was reported that soil respiration was suppressed following the application of chlorothalonil. Even though degradation rates of the individual compounds were suppressed when applied as part of a mixture, DT_{90} values were all <167 days, indicating a negligible risk of carry-over from one season to the next.

It is generally accepted that pesticides applied to coarse-textured, sandy soils are subject to greater leaching than those applied to soils with higher clay or organic matter content (*51*). However, this can be complicated by the presence of large cracks and macropores in finer textured soils, which can result in bypass flow and very rapid vertical water movement (*31*). Studies to investigate the leaching risk from biobeds when different biomix soils were used showed there to be no significant difference in the amounts of pesticide leaching. Bromide breakthrough curves showed a similar rate of water movement through each of the biomix soils, indicating similar physical characteristics for the three matrices.

Analysis of the biobed matrix from this study showed that all pesticides were retained in the top 10 cm and that after 4 months >98% of the nonleached pesticide had been dissipated. Previous laboratory investigations compared pesticide behavior in sterile and nonsterile biomixes and concluded that degradation by soil microorganisms was the principal mechanism responsible for the reduction in measured concentrations of pesticide in nonsterile systems and that bound residues were not a significant issue (*22*).

In conclusion, pesticides may be released to farmyard surfaces as a result of spillages, leakages, and the decontamination of tractors and sprayers, and recent studies have demonstrated that contaminated runoff from the farmyard can contribute a significant proportion of the pesticide load being released to surface waters. Biobeds are one possible approach that can be used to intercept this runoff, thus reducing the concentrations of pesticide being released to the environment. The system is cost-effective, requires low technical inputs, and utilizes materials readily available to the end-user. This study has shown that when different topsoils are used, leaching losses and degradation rates were similar. Furthermore, >98% of the applied pesticide was retained by each of the biomix types. Although interactions between pesticides are possible, DT_{90} values suggest that accumulation of pesticides within the biobed should not occur. On the basis of the results presented here, the use of different soil types in the construction of the biobed should not affect the level of treatment achieved. Clearly, soil texture is only one factor contributing to the performance of the biobed system. We have also investigated the relative performance of lined and unlined biobeds as well as the effects of pesticide mixtures applied repeatedly at high concentrations. The results from these experiments have been presented elsewhere. The majority of these studies have been performed over a relatively short time frame, <12 months. Longer term studies are required to fully characterize any risk posed to the environment from the use of biobeds.

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