

## Leaching of Pesticides from Biobeds: Effect of Biobed Depth and Water Loading

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Pesticides may be released to farmyard surfaces as a result of spillages, leakages, and the decontamination of tractors and sprayers. Biobeds can be used to intercept and treat contaminated runoff, thus minimizing losses to the environment. Previous studies using lined and unlined biobeds showed that water management was the limiting factor for both systems. While lined biobeds effectively retained pesticides, the system rapidly became water logged and degradation was slow. Studies using unlined biobeds showed that >99% of the applied pesticides were removed by the system, with a significant proportion degraded within 9 months. However, peak concentrations of certain pesticides ( $K_{oc} < 125$ ) were unacceptable to the regulatory authorities. These experiments were designed to optimize the design and management of unlined biobeds. Experiments performed to investigate the relationship between biobed depth and water loading showed that biobeds need to have a minimum depth of 1–1.5 m. The surface area dimension of the biobed depends on the water loading, which is controlled by the nature and frequency of pesticide handling activities on the farm. Leaching losses of all but the most mobile ( $K_{oc} < 15$ ) pesticides were <0.32% of the applied dose from 1.5 m deep biobeds subject to a water loading of 1175 L m<sup>-2</sup>. These were reduced to <0.06% when a water loading of 688 L m<sup>-2</sup> was applied and down to <0.0001% for a water loading of 202 L m<sup>-2</sup>. On the basis of these data, a 1.5 m deep biobed, subject to a maximum water loading of 1121 L m<sup>-2</sup> and with a surface area of 40 m<sup>2</sup> should be able to treat ≤44000 L of pesticide waste and washings such that the average concentration of all pesticides, other than those classified as very mobile, does not exceed 5 μg L<sup>-1</sup>. This level of treatment can be improved by further reduction in the hydraulic loading.

**KEYWORDS:** Biobeds; pesticide waste treatment; leaching potential; water management; design; regulation

### INTRODUCTION

Routine monitoring of environmental waters has shown that contamination with pesticides does occur (1–3). Where the water serves as a drinking water supply, treatment is often required in order to meet the standards set by, e.g., the European Drinking Water Directive 80/778/EEC (4). Such a treatment can be expensive, with around £1 billion being invested by the water industry in England and Wales since 1990 (5). Pesticides are generally applied for agricultural purposes on to land where a microbiologically active soil layer is present and where degradation and dissipation processes can take place (6). However, under these normal use conditions, losses to the environment can still occur due to processes such as leaching, runoff, and drainflow (7–10). However, contamination arising from other sources such as nonapproved use, poor practice,

illegal operations, accidental releases, and inputs of washings is reported to contribute between 18 and 84% of the pesticide load measured in some individual catchments (11–20). Better training of sprayer operators and good machinery maintenance can reduce the number of accidental releases (21). However, because of time constraints and other pressures, small drips and spills are still likely to occur (17, 18). Direct inputs from the decontamination of tractors and sprayers (22) and residues that remain in the sprayer sump after infield tank rinsing are also an unavoidable feature of the spraying operation (14, 23).

The filling and cleaning of agricultural spray equipment is often performed at the same site in the farmyard year after year due to the location of the farm pesticide store and the convenience of a clean water supply (24, 25). The design, management, and operation of these mixing/handling/washdown areas are therefore considered a primary target in reducing the amount of pesticide leaving the farmyard (26). Traditionally, these areas have been on concrete pads, which offer little

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**Table 1.** Study Compounds and Their Reported Physicochemical Characteristics<sup>a</sup>

active substance	product	concn (% w/w)	Koc (mL g <sup>-1</sup> )	mobility class <sup>b</sup>	DT <sub>50</sub> soil (days)	solubility water (mg L <sup>-1</sup> )
isoproturon	Alpha Isoproturon 500	43.6	125	moderately mobile	6–28	65
pendimethalin	Stomp 400 SC	36.4	5000–17200	nonmobile	90–120	0.3
chlorpyrifos	Dursban 4	44.65	6000	nonmobile	7–15	1.4
chlorothalonil	Cropgard	41.6	1600–14000	slightly/nonmobile	5–36	0.6–1.2
epoxiconazole	Opus	12.1	957–2647	slightly mobile	60–90	6.63
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

<sup>a</sup> Values taken from refs 38–40. <sup>b</sup> Ref 45.

opportunity of sorption and degradation (27, 28) and which often connect directly to a soakaway or water course, resulting in direct and rapid transport of pesticides to water bodies. Alternative materials on which pesticides are mixed and equipment decontaminated therefore need to be considered (21). Any alternative should supplement good handling practices that reduce inputs to aquatic systems and also be cheap to use and require low labor and time inputs. One possible 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. In its simplest form, a biobed is a clay-lined hole in the ground filled with a mixture of topsoil, peat, and straw and covered with grass (29, 30). The biobed is equipped with a ramp enabling the tractor and sprayer to be driven over the bed and thus enabling the biobed to intercept drips and spills. The biobed can also be connected to an adjacent concrete intercept area on which all mixing and washdown activities take place (31). Studies have demonstrated that biobeds can effectively retain and degrade pesticides (26, 32–35), such that the concentrations of pesticides being released from the farmyard are significantly reduced. However, studies have shown the potential risk to groundwater from mobile pesticides leaching through the clay layer in the base of the biobed (36). To safeguard against the potential contamination of groundwater, the UK regulatory authorities insisted that a butyl liner be installed into the base of all experimental biobeds constructed in the United Kingdom. However, studies performed at the semifield scale using lined biobeds showed that while pesticides were effectively retained, the biobeds quickly became water logged. Covers had to be placed over the biobeds to exclude clean rainwater. However, once covered, the top 10 cm became hydrophobic, forming an impermeable layer, which restricted water loss and impeded degradation of the retained pesticides (37). The use of unlined biobeds removed the need to manage water inputs while at the same time maintaining near optimum conditions for pesticide degradation. Only the most mobile ( $K_{oc} < 125$ ) compounds leached to any great extent, and even for these compounds, the biobed system appeared to retain or degrade more than 99% of the applied dose (37). However, maximum concentrations of pesticide leaching from the biobed were considered unacceptable. In order for biobeds to be approved for use, it is likely that the performance of the system will have to improve such that maximum concentrations of pesticide in leachate are close to the standard of  $0.1 \mu\text{g L}^{-1}$  set by the European Drinking Water Directive 80/778/EEC.

This study was performed to understand the relationship between biobed size, water load, and concentration of a range of pesticides in order to provide guidance on the construction and operation of biobeds in the United Kingdom. Experiments were therefore made to examine the effects of (i) the hydraulic load and (ii) the depth of the biobed, such that the optimum

dimensions and maximum hydraulic loading with respect to concentrations of pesticide in leachate could be determined and regulatory approval for use could be granted. The studies were performed at the semifield scale.

## MATERIALS AND METHODS

**Preparation of Biomix.** The biomix was prepared by mixing topsoil (69% sand, 13% silt, 18% clay, organic matter 1.95%, pH 6.15, maximum water holding capacity 37% w/w), peat free compost (Levington Peat Free Universal), and winter wheat straw in the volumetric proportions of 1:1:2, respectively. The mixture (organic matter 12.36%, pH 7.5, maximum water holding capacity 75–127% w/w) was composted outside in uncovered heaps for 71–97 days prior to use. The heaps were turned twice throughout this period.

**Test Chemicals.** Test pesticides were selected to cover a range of their physicochemical properties (38–40) and which were of high average annual usage in the United Kingdom (41) (Table 1). Formulated isoproturon (Alpha Isoproturon 500), 43.6% w/w; pendimethalin (Stomp 400 SC), 36.4% w/w; chlorpyrifos (Dursban 4), 44.65% w/w; chlorothalonil (Cropgard), 41.57% w/w; epoxiconazole (Opus) 12.1% w/w; dimethoate (Rogor L40), 37.4% w/w; mecoprop (Optica), 48% w/w; and metsulfuron-methyl (Jubilee 20 DF), 20% w/w, were used to make up stock suspensions in tap water.

**Water Loading.** Twelve lysimeters were prepared using unplasticized poly(vinyl chloride) (PVC-u) piping (19 cm internal diameter  $\times$  65 cm length) filled with 5 cm of washed gravel (10–15 mm diameter) followed by 50 cm of biomix. The base of each core drained via Teflon tubing to either 10 L high-density polyethylene (HDPE) bottles or a 2.5 L amber glass collection vessels (depending on the hydraulic loading) located in a central collection pit (42). Three hydraulic scenarios were investigated. To give a “high” water loading, four lysimeters were connected using plastic guttering to  $0.54 \text{ m}^2$  concrete slabs. A further four lysimeters were connected to  $0.135 \text{ m}^2$  concrete slabs to give an “intermediate” loading. The four remaining lysimeters received only direct inputs of rainfall. Silicon sealant was placed on three sides of each slab to prevent water loss from the sides. Three lysimeters from each hydraulic loading scenario were treated with 50 mL of the pesticide mixture containing 5100, 4080, 1468, 3060, 1020, and 694 mg a.s.  $\text{L}^{-1}$  of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole, and dimethoate, respectively, in January 2000, to achieve a final treatment rate of 255 (isoproturon), 204 (pendimethalin), 73.4 (chlorpyrifos), 153 (chlorothalonil), 51 (epoxiconazole), and 34.7 mg (dimethoate). Application rates were based on a number of field studies and long-term pesticide usage data for a number of large arable farms (15, 24). Potassium bromide (KBr) was applied ( $314 \text{ mg core}^{-1}$ ) at the same time as the pesticides 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. Where possible, a 60 mL subsample was also taken for KBr analysis. At the end of the study (244 days after treatment, DAT), all 12 lysimeters were destructively sampled and sectioned (0–5, 5–10, 10–20, 20–30, and  $> 30$  cm), and the sections were then homogenized and frozen prior to analysis.

**Depth and Water Loading.** A further 18 lysimeters were prepared using PVC-u piping (22.5 cm internal diameter), cut to either 65, 115, or 165 cm length. Each pipe section was filled with 5 cm of washed gravel (10–15 mm diameter) followed by either 50, 100, or 150 cm of biomix. The base of each core drained via Teflon tubing to a 2.5 L amber glass collection vessel located in a central collection pit (40). Six lysimeters (two from each depth) were connected using plastic guttering to 0.32 m<sup>2</sup> concrete slabs. A further six lysimeters were connected to 0.16 m<sup>2</sup> concrete slabs. The six remaining lysimeters received only direct inputs of rainfall. Silicon sealant was placed on three sides of the slabs to prevent water loss from the sides. All 18 lysimeters were treated with 50 mL of the pesticide mixture containing 3200, 435.2, 1536, and 7.68 mg a.s. L<sup>-1</sup> of isoproturon, dimethoate, mecoprop, and metsulfuron-methyl, respectively, in March 2002, to achieve a final treatment rate of 298 (isoproturon), 40.5 (dimethoate), 143 (mecoprop), and 0.72 mg (metsulfuron-methyl). Application rates were based on a number of field studies and long-term pesticide usage data for a number of large arable farms (15, 24). KBr was applied (314 mg core<sup>-1</sup>) at the same time 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. Where possible, a 60 mL subsample was also taken for KBr analysis. At the end of the study (197 DAT), all 18 lysimeters were destructively sampled in the same manner as the lysimeters used in the water loading studies.

**Analysis. Water Extraction.** For the water loading studies, samples (200 mL) were extracted three times into 30 mL of dichloromethane (DCM) in a 500 mL glass separating funnel. The DCM extracts were passed through anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and then evaporated to dryness at 40 °C. The resulting residues were redissolved in 2 mL of a mixture containing 10% methanol and 90% DCM. Concentrations of all six pesticides were determined by gas chromatography (GC). For the water loading and depth studies, samples (200 mL) were extracted into 3 × 40 mL DCM using a glass separating funnel (250 mL). Following extraction, DCM extracts were dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and then evaporated to dryness using a rotary evaporator at 40 °C. The resulting residues were redissolved into 2 mL of methanol. Recovery values for all pesticides from biomix leachate were >94%. Concentrations of isoproturon and mecoprop-P were then determined by high-performance liquid chromatography (HPLC), dimethoate concentrations were determined by GC, and metsulfuron-methyl concentrations were determined by liquid chromatography/mass spectrometry (LC/MS).

**Biomix Extraction.** For the water loading studies, duplicate samples (40 g) of the homogenized biomix were placed into 250 mL glass bottles. Anhydrous Na<sub>2</sub>SO<sub>4</sub> (40 g) plus 160 mL of a mixture containing 90% DCM and 10% methanol was added, with samples shaken for 1 h using an end-over-end shaker. The samples were allowed to stand until clear, with an aliquot of the solution taken for analysis using GC. With the exception of chlorothalonil (82%), the recovery of all six pesticides from biomix exceeded 95%. For the water loading and depth studies, duplicate samples (40 g) of the homogenized biomix 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, the samples were allowed to stand until clear. An aliquot of the methanol solution was then taken for isoproturon, mecoprop-P, and metsulfuron-methyl determination by HPLC.

**GC Analysis.** Concentrations of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole, and dimethoate from the water loading studies were determined on a Hewlett-Packard HP5890 gas chromatograph fitted with a split/splitless injector, 12 m × 0.53 mm BPX5 column (SGE), and a nitrogen-phosphorus detector. The carrier gas (helium) flow rate was 7 mL min<sup>-1</sup>, and detector gas flow rates were 100 (air) and 4 mL min<sup>-1</sup> (hydrogen). The oven temperature was raised from 90 to 190 °C (40 °C min<sup>-1</sup>) and then to 220 °C (10 °C min<sup>-1</sup>) and finally to 245 °C (15 °C min<sup>-1</sup>). Samples (2 µL) were injected using a Hewlett-Packard HP7673 autosampler. Under these conditions, all six pesticides were baseline separated with retention times of 3.1 (dimethoate), 3.5 (chlorothalonil), 3.9 (isoproturon), 4.2 (chlor-

pyrifos), 4.7 (pendimethalin), and 7.2 min (epoxiconazole). Quantification was achieved by comparison of peak areas with results from external standards. Recoveries with DCM extraction of water spiked at 0.01 mg L<sup>-1</sup> were >94% for all compounds. The limit of quantification was 0.23 µg L<sup>-1</sup> for isoproturon, 0.12 µg L<sup>-1</sup> for pendimethalin, 0.11 µg L<sup>-1</sup> for chlorpyrifos, 0.22 µg L<sup>-1</sup> for chlorothalonil, 0.10 µg L<sup>-1</sup> for epoxiconazole, and 0.08 µg L<sup>-1</sup> for dimethoate.

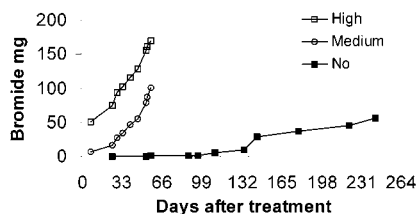
**HPLC Analysis.** Concentrations of isoproturon, mecoprop, and metsulfuron-methyl in extracts from the water loading and depth studies were determined by HPLC using a Spectra Physics SP8810 pump linked to a Kontron 430 UV detector. Samples (20 µL) were injected using a Spectra Physics SP8775 autosampler. Separation was achieved using a Genesis C8 column (250 mm × 4.6 mm) (Jones Chromatography, Hengoed, United Kingdom). The mobile phase used was acetonitrile:methanol:0.05 M acetic acid (27:28:45) with a flow rate of 1.7 mL min<sup>-1</sup>, which gave retention times of 3.4, 5.0, and 7.5 min for metsulfuron-methyl, isoproturon, and mecoprop-P, respectively. The detection wavelength was 230 nm for all three substances. The limit of quantification was 0.05 µg L<sup>-1</sup> for metsulfuron-methyl and mecoprop and 0.03 µg L<sup>-1</sup> for isoproturon.

**LC/MS Analysis.** Concentrations of metsulfuron-methyl in water were determined by LC/MS, operated in positive electrospray reaction monitoring mode (ES +MRM). Separation was achieved using a Spherisorb C8 3 µm ODS2 column (150 mm × 1.0 mm) (Jones Chromatography). The mobile phase used was methanol:10 mM ammonium formate:acetonitrile (47.5:47.5:5) with a flow rate of 50 µL min<sup>-1</sup> and an injection volume of 2.5 µL. Quantification was achieved by comparison between the two transitions (*m/z* 382/167) quantification and (*m/z* 382/199) confirmation. Metsulfuron-methyl was reported if both transitions were present at around the correct ratio (10:1). The estimated limit of detection was 0.6 µg L<sup>-1</sup>.

**Bromide.** Concentrations of potassium bromide were determined using two methods of ion chromatography. For the water loading experiment, water samples (0.5 mL) were filtered (0.2 µm) and analyzed using a Dionex DX-100 (Dionex UK Ltd., Macclesfield, Cheshire). Samples (25 µL) were injected neat with a typical retention time of 2.3 min. The system was calibrated using a series of standards with known concentrations of bromide with a limit of detection set at 1.1 mg L<sup>-1</sup>. For the depth and water loading experiments, a Metrohm (Herisau, Switzerland) 790 Personal ion chromatograph and 813 compact autosampler were used. Analytical columns used were Metrohms', Metrosep RP guard, Metrosep A Supp 4/5 guard, and Metrosep A Supp 4 (250 mm × 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. The limit of quantification was 0.5 mg L<sup>-1</sup>, with a limit of detection at 0.1 mg L<sup>-1</sup>.

## RESULTS

**Water Loading.** The rainfall for the study period (January to September 2000) was 11% above average and totaled 486.3 mm. The leachate samples were collected on 28 occasions over the 244 day monitoring period. Cumulative leachate volumes from lysimeters receiving only direct inputs of rainfall ranged from 3.4 to 5.1 L. From lysimeters connected to the 0.135 m<sup>2</sup> concrete slabs, leachate volumes ranged from 45.2 to 56.4 L and from those connected to the 0.54 m<sup>2</sup> concrete slabs the volume recorded ranged from 103.7 to 177.6 L. A rapid breakthrough of bromide was observed 7 DAT for the lysimeters connected to the 0.54 and 0.135 m<sup>2</sup> concrete slabs as compared to 57 DAT for the lysimeters receiving only direct inputs of rainfall (**Figure 1**). The maximum concentrations of bromide were measured 7 DAT from lysimeters connected to the 0.54 m<sup>2</sup> slabs, 29 DAT from those connected to the 0.135 m<sup>2</sup> slabs, and 221 DAT from those receiving only direct inputs of rainfall. With the exception of chlorpyrifos in lysimeters connected to 0.135 m<sup>2</sup> slabs, the highest concentrations of



**Figure 1.** Cumulative amounts of bromide measured in leachate collected from lysimeters filled with 50 cm of biomix and subjected to three different hydraulic loadings.

pesticide were measured in leachate collected from lysimeters connected to 0.54 m<sup>2</sup> slabs (**Figure 2**). For lysimeters receiving the highest hydraulic loading, concentrations of pesticide ranged from 1.21  $\mu\text{g L}^{-1}$  for epoxiconazole to 1167  $\mu\text{g L}^{-1}$  for isotroturon. For lysimeters receiving the water loading from 0.135 m<sup>2</sup> slabs, the highest concentrations of pesticide ranged from 0.35  $\mu\text{g L}^{-1}$  for epoxiconazole to 258  $\mu\text{g L}^{-1}$  for isotroturon, and for lysimeters receiving only direct inputs of rainfall, the highest concentrations of pesticide ranged from 0.57  $\mu\text{g L}^{-1}$  for epoxiconazole to 1.65  $\mu\text{g L}^{-1}$  for chlorpyrifos.

The cumulative losses of isotroturon and dimethoate from lysimeters connected to 0.54 m<sup>2</sup> slabs were 6.37 and 6.08% of the amount applied, respectively, with losses of each of the remaining pesticides being <0.2%. From lysimeters connected to 0.13 m<sup>2</sup> slabs, losses of isotroturon and dimethoate were 0.2 and 0.61%, respectively, with losses of the remaining pesticides all below 0.02%. Cumulative pesticide residues in leachate from lysimeters receiving only direct inputs of rainfall were below 0.005% for all six pesticides.

In biomix from lysimeters connected to 0.54 m<sup>2</sup> concrete slabs, 47% of the total applied pesticide remained within the biobed matrix 244 DAT. No pesticide was measured below 30 cm depth with 39% of the retained pesticide measured in the 0.5 cm layer. In lysimeters connected to the 0.135 m<sup>2</sup> slabs, 51% of the applied pesticide was recovered from the biomix with 48% retained within the 0.5 cm layer. No pesticide was measured below 20 cm depth. In lysimeters receiving only direct inputs of rainfall, no pesticide was measured below 10 cm depth, with 72% of the applied pesticide retained within the biomix of which 71% was in the 0–5 cm layer.

**Table 2.** Mass Balance for 0.5 m Long Biobed Columns Subjected to a Hydraulic Loading of 9747 L m<sup>-2</sup> (Connected to 0.54 m<sup>2</sup> Concrete Slabs)

pesticide	% leached	% degraded	% retained	maximum concn ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	average concn ( $\mu\text{g L}^{-1}$ )
isotroturon	6.37	93.53	0.10	568.03	101.63
pendimethalin	0.12	87.08	12.80	23.82	1.78
chlorpyrifos	0.04	99.52	0.44	1.81	0.19
chlorothalonil	0.11	98.04	1.85	9.90	1.20
epoxiconazole	0.05	66.41	33.54	0.50	0.17
dimethoate	6.08	93.90	0.02	96.84	18.71

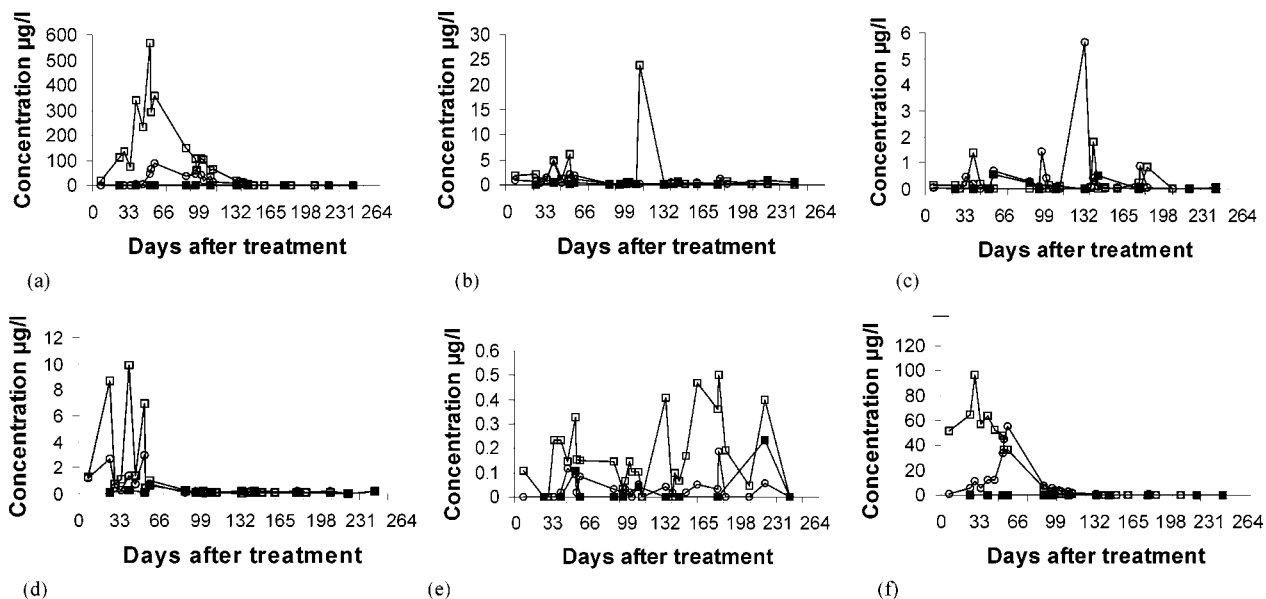
<sup>a</sup> This is the highest concentration averaged across the three treated replicates.

**Table 3.** Mass Balance for 0.5 m Long Biobed Columns Subjected to a Hydraulic Loading of 2797 L m<sup>-2</sup> (Connected to 0.135 m<sup>2</sup> Concrete Slabs)

pesticide	% leached	% degraded	% retained	maximum concn ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	average concn ( $\mu\text{g L}^{-1}$ )
isotroturon	0.20	99.71	0.09	89.38	17.78
pendimethalin	0.01	85.06	14.93	4.58	0.69
chlorpyrifos	0.01	99.27	0.71	5.61	0.39
chlorothalonil	0.01	98.30	1.70	2.99	0.47
epoxiconazole	0.002	66.08	33.92	0.19	0.03
dimethoate	0.61	99.37	0.02	55.00	7.56

<sup>a</sup> This is highest concentration averaged across the three treated replicates.

A mass balance was performed to determine the overall environmental fate of the six pesticides under the three hydraulic scenarios investigated (**Tables 2–4**). For lysimeters with a high hydraulic loading between 0.04 (chlorpyrifos) and 6.37% (isotroturon) leached, between 0.02 (dimethoate) and 34% (epoxiconazole) was associated with the biomix matrix and 87% (pendimethalin) to >99.5% (chlorpyrifos) was dissipated. The total amount of pesticide either retained or degraded by the system was >93%. For lysimeters with a medium hydraulic loading between 0.002 (epoxiconazole) and 0.61% (dimethoate) leached, 0.02 (dimethoate) and 34% (epoxiconazole) were associated with the biomix matrix and 85% (pendimethalin) to



**Figure 2.** Average concentrations of (a) isotroturon, (b) pendimethalin, (c) chlorpyrifos, (d) chlorothalonil, (e) epoxiconazole, and (f) dimethoate measured in leachate collected from 0.5 m long biobeds subjected to a high ( $\square$ ) and medium ( $\circ$ ) water loadings and those receiving only direct inputs of rainfall.

**Table 4.** Mass Balance for 0.5 m Long Biobed Columns Subjected to a Hydraulic Loading of 486 L m<sup>-2</sup> (Direct Inputs of Rainfall Only)

pesticide	% leached	% degraded	% retained	maximum concn ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	average concn ( $\mu\text{g L}^{-1}$ )
isoproturon	0.000	98.81	1.19	0.59	0.09
pendimethalin	0.002	82.80	17.20	1.00	0.31
chlorpyrifos	0.002	96.51	3.49	0.55	0.11
chlorothalonil	0.001	90.55	9.45	0.65	0.18
epoxiconazole	0.001	67.15	32.85	0.24	0.03
dimethoate	0.004	99.88	0.11	0.22	0.11

<sup>a</sup> This is the highest concentration averaged across the three treated replicates.

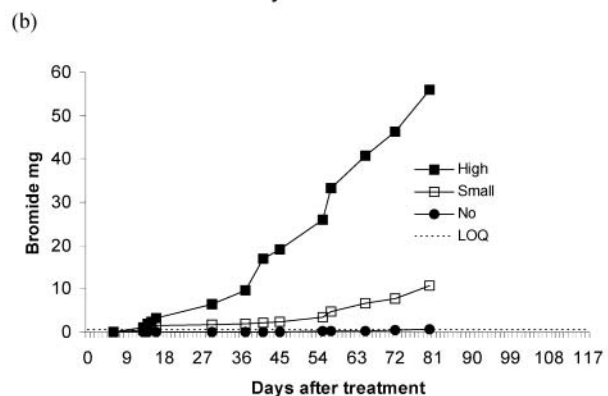
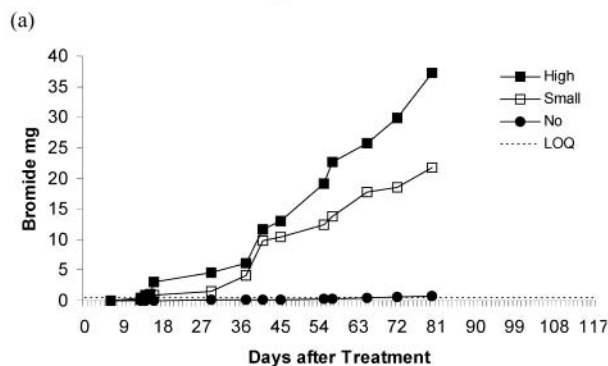
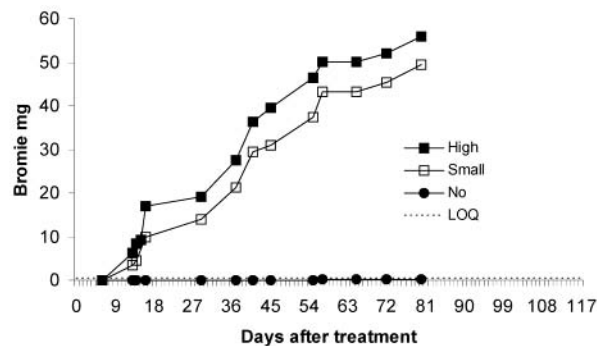
>99.7% (isoproturon) was degraded. The total amount of pesticide either retained or degraded by the system was >99.3%. For lysimeters with no additional hydraulic loading, <0.004% of each chemical applied leached, between 0.11 (dimethoate) and 33% (epoxiconazole) was retained within the biomix, and 67–99.9% was degraded. More than 99.99% of the applied pesticide was either retained or degraded by the biobed.

**Depth and Water Loading.** Including irrigation, rainfall for the period March to July 2002 was 7% above average and totaled 201.5 mm between application (05/03/02) and collection of the last water samples (09/07/02). The leachate samples were collected on 17 occasions providing 293 water samples for analysis. Cumulative leachate volumes ranged from 2.9 to 3.1 L for the lysimeters receiving only direct inputs of rainfall, from 19.8 to 22.6 L for lysimeters connected to the 0.16 m<sup>2</sup> concrete slabs, and from 23.7 to 29.8 L from those receiving the highest water loading (0.32 m<sup>2</sup> slabs).

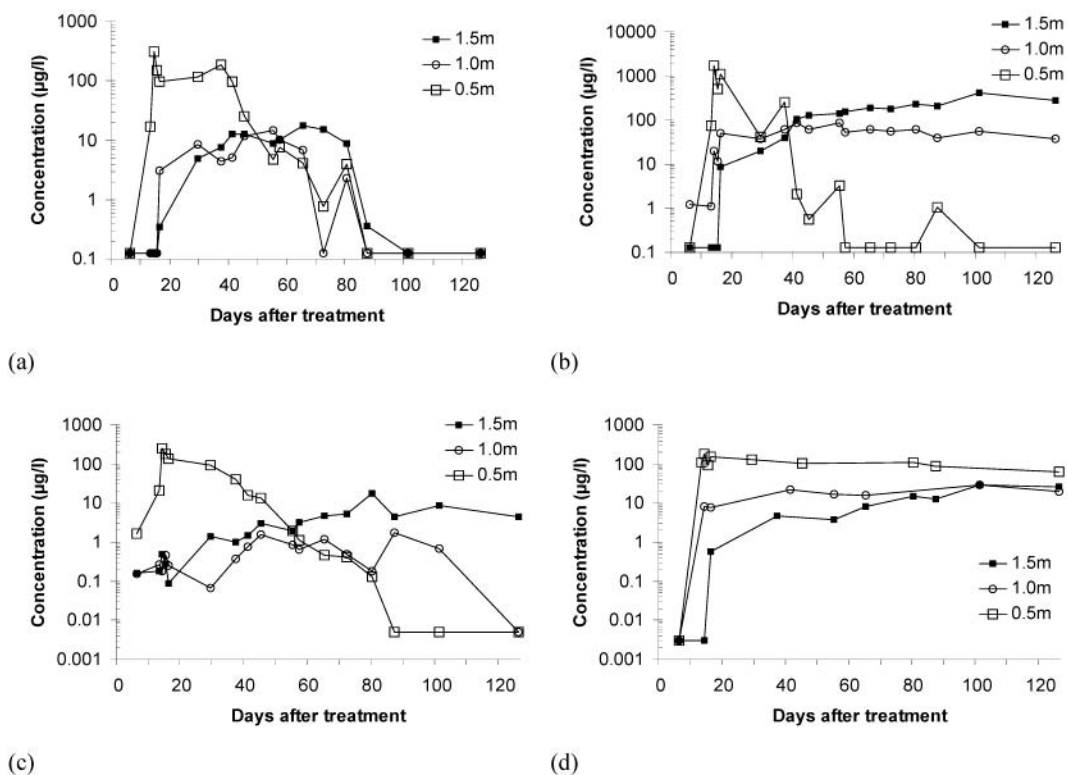
The breakthrough of bromide from all lysimeters receiving high (i.e., connected to 0.32 m<sup>2</sup> slabs) and medium (i.e., connected to 0.16 m<sup>2</sup> slabs) water loads generally occurred 13–16 days after treatment. In contrast, the breakthrough from the 1.0 and 1.5 m lysimeters receiving only direct rainfall inputs occurred much later (41–55 DAT) (**Figure 3b,c**). No bromide leached from the 0.5 m lysimeters that received only direct rainfall inputs (**Figure 3a**). In all 1.5 m columns and the 1.0 m column receiving only direct rainfall inputs, the peak bromide concentrations were observed 80 DAT. The peak concentrations were observed 41 DAT in the 0.5 and 1.0 m columns receiving a medium water loading. The highest concentrations from the 0.5 and 1.0 m columns receiving a high water loading were observed 16 and 65 DAT, respectively. The total amount leached was related to the water loading, and the highest amounts of bromide were leached from columns receiving a high water loading whereas the lowest amounts were leached from the columns receiving only direct rainfall inputs. There appeared to be no relationship between the length of the columns and the amount of bromide leached.

Maximum concentrations of pesticide were measured in leachate collected from lysimeters with a high water loading (**Figure 4**). Generally, by increasing the depth of the lysimeter up to 1.0 m and controlling water inputs, the concentrations of pesticide in leachate were significantly (ANOVA  $P < 0.05$ ,  $F_{6,38, df 1}$ ) reduced (**Figure 5**).

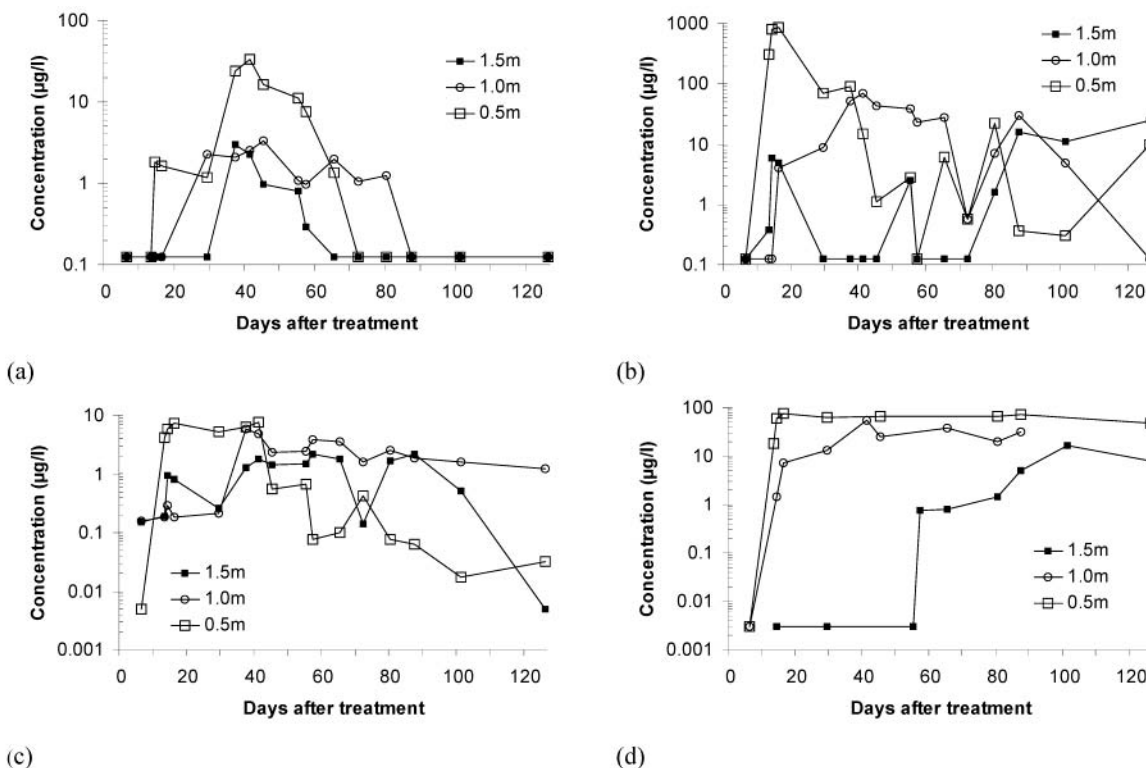
From lysimeters subject to the highest water loading, concentrations of isoproturon were 370.6  $\mu\text{g L}^{-1}$  from 0.5 m lysimeters, 22.9  $\mu\text{g L}^{-1}$  from 1.0 m lysimeters, and 30.0  $\mu\text{g L}^{-1}$  from 1.5 m lysimeters. Breakthrough from the 0.5 m lysimeters was measured 13 DAT with peak concentrations measured 1 day later. The breakthrough from the 1.0 and 1.5 m lysimeters was measured 16 DAT. Peak concentrations were measured 55 DAT from the 1.0 m lysimeters and 65 DAT from

**Figure 3.** Cumulative amounts of bromide leached from (a) 0.5, (b) 1.0, and (c) 1.5 m deep biobed lysimeters when subjected to no (direct input of rainfall), low (0.16 m<sup>2</sup>), and high (0.32 m<sup>2</sup>) water loadings.

the 1.5 m lysimeters. Cumulative losses of isoproturon were 0.4, 0.04, and 0.06% for the 0.5, 1.0, and 1.5 m deep lysimeters, respectively. Maximum concentrations of mecoprop-P were 2217.2  $\mu\text{g L}^{-1}$  from the 0.5 m lysimeters, 157.4  $\mu\text{g L}^{-1}$  from the 1.0 lysimeters, and 515.2  $\mu\text{g L}^{-1}$  from the 1.5 m lysimeters and were measured 14, 41, and 101 DAT, respectively. The breakthrough was measured 6, 13, and 16 DAT from the 0.5, 1.0, and 1.5 m lysimeters, respectively. Cumulative losses were 3.4, 1.0, and 2.1% for the 1.5, 1.0, and 0.5 m lysimeters, respectively. The breakthrough of dimethoate for all depths was measured 6 DAT. Maximum concentrations of 255.8, 2.2, and 21.6  $\mu\text{g L}^{-1}$  were measured 14, 87, and 80 DAT for the 0.5, 1.0, and 1.5 m deep lysimeters, respectively. Dimethoate losses were 1.4, 0.04, and 0.3% for the 0.5, 1.0, and 1.5 m deep lysimeters. Metsulfuron-methyl peak concentrations were 183.0, 28.6, and 29.9  $\mu\text{g L}^{-1}$  from the 0.5, 1.0, and 1.5 m lysimeters, respectively, with breakthroughs measured 13, 14, and 16 DAT, respectively. Peak concentrations from the 0.5 m lysimeters were measured 14 and 101 DAT from the 1.0 and 1.5 m lysimeters. The cumulative losses were 100% for the 0.5 m deep lysimeters, 19% for the 1.0 m lysimeters, and 15% for the 1.5 m lysimeters.



**Figure 4.** Mean concentrations of (a) isoproturon, (b) mecoprop-P, (c) dimethoate, and (d) metsulfuron-methyl from different length lysimeters connected to 0.32 m<sup>2</sup> concrete slabs.



**Figure 5.** Mean concentrations of (a) isoproturon, (b) mecoprop-P, (c) dimethoate, and (d) metsulfuron-methyl from different length lysimeters connected to 0.16 m<sup>2</sup> concrete slabs.

From lysimeters subject to an intermediate water loading, maximum concentrations of isoproturon were 45.81  $\mu\text{g L}^{-1}$  from the 0.5 m lysimeters, 5.0  $\mu\text{g L}^{-1}$  from the 1.0 m lysimeters, and 2.96  $\mu\text{g L}^{-1}$  from the 1.5 m lysimeters and were measured 41, 45, and 37 DAT, respectively. The breakthrough was measured 14, 29, and 37 DAT from the 0.5, 1.0, and 1.5 m

deep lysimeters. Cumulative losses of isoproturon were 0.05, 0.006, and 0.001% from the 0.5, 1.0, and 1.5 m lysimeters. For mecoprop-P, breakthrough at 0.5, 1.0, and 1.5 m depth was measured 14, 16, and 13 DAT, respectively. Maximum concentrations were 1434.3  $\mu\text{g L}^{-1}$  from the 0.5 m lysimeters, 140.7  $\mu\text{g L}^{-1}$  from the 1.0 m lysimeters, and 49.46  $\mu\text{g L}^{-1}$  from the

**Table 5.** Mass Balance for 0.5, 1.0, and 1.5 m Deep Biobed Lysimeters Subjected to a High Water Loading (0.32 m<sup>2</sup> Concrete Slabs)<sup>a</sup>

pesticide	% leached			% retained			% degraded			maximum concn ( $\mu\text{g L}^{-1}$ )			average concn ( $\mu\text{g L}^{-1}$ )		
	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m
isoproturon	0.06	0.04	0.39	0.13	3.51	0.41	99.81	96.45	99.20	17.31	14.92	310.9	5.87	4.01	60.23
dimethoate	0.32	0.04	1.41	0.08	0.53	0.07	99.60	99.43	98.52	18.16	1.77	253.4	3.46	0.58	44.47
mecoprop-P	3.37	1.02	2.07	0	0	0	96.63	98.98	97.93	423.1	88.40	1687.2	123.7	45.78	216.1
metsulfuron-methyl	15.29	19.34	100	0	0	0	84.71	80.66	0	29.90	28.60	183.0	10.09	14.90	103.1

<sup>a</sup> Maximum concentrations are based on the mean from duplicate lysimeters.

**Table 6.** Mass Balance for 0.5, 1.0, and 1.5 m Deep Biobed Lysimeters Subjected to a Small Water Loading (0.16 m<sup>2</sup> Concrete Slabs)<sup>a</sup>

pesticide	% leached			% retained			% degraded			maximum concn ( $\mu\text{g L}^{-1}$ )			average concn ( $\mu\text{g L}^{-1}$ )		
	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m
isoproturon	0.002	0.01	0.05	0.29	0.47	0.55	99.71	99.52	99.40	2.96	3.34	33.35	0.54	1.09	6.24
dimethoate	0.06	0.12	0.10	0.20	0.21	0.24	99.74	99.67	99.66	2.20	5.93	7.74	1.06	2.06	2.42
mecoprop-P	0.11	0.33	1.54	0	0	0	99.89	99.67	98.46	24.79	70.39	877.9	4.27	19.45	137.2
metsulfuron-methyl	5.94	18.38	48.34	0	0	0	94.06	81.62	51.66	16.60	54.20	75.30	3.64	21.23	52.76

<sup>a</sup> Maximum concentrations are based on the mean from duplicate lysimeters.

1.5 m lysimeters, and these were measured at 16, 41, and 126 DAT, respectively, equivalent to cumulative losses of 1.54% for the 0.5 m lysimeters, 0.34% for the 1.0 m lysimeters, and 0.12% for the 1.5 m lysimeters. The breakthrough of dimethoate occurred 6 DAT from the 1.0 and 1.5 m lysimeters and 6 DAT from the 0.5 m depth. Maximum concentrations of 12.02, 9.46, and 2.87  $\mu\text{g L}^{-1}$  were measured from 0.5, 1.0, and 1.5 m depth at 37, 41, and 87 DAT, respectively. Cumulative losses from the 0.5 and 1.0 m lysimeters were 0.1% of the applied dose and from the 1.5 m lysimeters 0.06%. For metsulfuron-methyl, breakthrough was measured 13 DAT from 0.5 m deep lysimeters, 14 DAT from the 1.0 m deep lysimeters, and 57 DAT from the 1.5 m deep lysimeters. Maximum concentrations for each depth (0.5–1.5 m) were measured 16, 41, and 101 DAT and were 75.3, 54.2, and 16.6  $\mu\text{g L}^{-1}$ , respectively. Cumulative losses were 48, 18, and 6% for the 0.5, 1.0, and 1.5 m lysimeters, respectively.

For lysimeters receiving only direct inputs of rainfall, no concentrations of isoproturon were measured above the LOQ of 0.03  $\mu\text{g L}^{-1}$ . Cumulative losses were estimated to be  $\leq 0.0002\%$  of the applied dose for all depths. Maximum concentrations of mecoprop-P were 2.05  $\mu\text{g L}^{-1}$  at 0.5 m depth, 1.23  $\mu\text{g L}^{-1}$  at 1.0 m depth, and 4.98  $\mu\text{g L}^{-1}$  at 1.5 m depth. Breakthrough and maximum concentrations coincided and were measured 41 DAT at 0.5 and 1.5 m depth and 126 DAT at 1.0 m depth. Cumulative losses were  $\leq 0.0007\%$  for all depths. At 0.5 m depth, concentrations of dimethoate were all below the LOQ. The breakthrough at 1.0 and 1.5 m was measured 41 DAT with a maximum concentration of 1.23  $\mu\text{g L}^{-1}$  measured at 1.0 m depth, 87 DAT, and at 1.5 m depth 0.13  $\mu\text{g L}^{-1}$ , 41 DAT. As for mecoprop-P, losses of dimethoate from the biobed lysimeters receiving only direct inputs of rainfall losses were all  $\leq 0.0007\%$ . Concentrations of metsulfuron-methyl were below the LOQ in leachate collected from 1.0 and 1.5 m depth. At 0.5 m, maximum concentrations coincided with breakthrough and were measured 101 DAT at 4.51  $\mu\text{g L}^{-1}$ . Cumulative losses of 0.2% were measured for the 0.5 m lysimeters and  $\leq 0.0003\%$  for the 1.0 and 1.5 m deep lysimeters.

No mecoprop-P or metsulfuron-methyl was measured in the biobed at the end of the study (197 DAT). No isoproturon or dimethoate was measured below 10 cm depth under either of the water loading scenarios investigated with between 92 and

100% retained in the top 5 cm. For isoproturon, the measured residues (expressed as % of the applied dose) remaining in the biobed lysimeters were 0.41, 3.51, and 0.13% for the 0.5, 1.0, and 1.5 m lysimeters, respectively, and for dimethoate 0.07, 0.53, and 0.08%.

A mass balance was performed to determine the fate of each of the study compounds under the three hydraulic scenarios investigated. For the lysimeters connected to the 0.32 m<sup>2</sup> concrete slabs (high water loading), between 100 (metsulfuron methyl) and 0.39% (isoproturon) leached from the 0.5 m lysimeters, between 0.41 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 0 (metsulfuron-methyl) and 99.2% (isoproturon) was degraded. For the 1.0 m lysimeters, between 19.34 (metsulfuron methyl) and 0.04% (isoproturon and dimethoate) leached, between 3.51 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 81 (metsulfuron-methyl) and 99.4% (dimethoate) was degraded. For the 1.5 m lysimeters, between 15.29 (metsulfuron methyl) and 0.06% (isoproturon) leached, between 0.13 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 85 (metsulfuron-methyl) and 99.8% (isoproturon) was degraded (**Table 5**).

For the lysimeters connected to the 0.16 m<sup>2</sup> slabs (low water loading), between 48.3 (metsulfuron methyl) and 0.05% (isoproturon) leached from the 0.5 m lysimeters, between 0.55 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 52 (metsulfuron-methyl) and 99.6% (dimethoate) was degraded. For the 1.0 m lysimeters, between 18.38 (metsulfuron methyl) and 0.01% (isoproturon) leached, between 0.47 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 82 (metsulfuron-methyl) and 99.7% (dimethoate and mecoprop-P) was degraded. For the 1.5 m lysimeters, between 5.94 (metsulfuron methyl) and 0.002% (isoproturon) leached, between 0.29 (isoproturon) and 0% (metsulfuron methyl) was associated with the biobed matrix, and between 94 (metsulfuron-methyl) and 99.9% (mecoprop-P) was degraded (**Table 6**).

For the lysimeters receiving only direct inputs of rainfall, between 0.24 (metsulfuron methyl) and 0% (dimethoate) leached from the 0.5 m lysimeters, between 0.55 (isoproturon) and 0% (metsulfuron methyl and mecoprop-P) was associated with the

**Table 7.** Mass Balance for 0.5, 1.0, and 1.5 m Deep Biobed Lysimeters Receiving Only Direct Inputs for Rainfall<sup>a</sup>

pesticide	% leached			% retained			% degraded			maximum concn ( $\mu\text{g L}^{-1}$ )			average concn ( $\mu\text{g L}^{-1}$ )		
	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m	1.5 m	1.0 m	0.5 m
isoproturon	0.0001	0.0001	0.0003	1.06	0.44	0.07	98.94	99.56	99.93	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
dimethoate	0.0001	0.0007	0	0.30	0.13	0.06	99.70	99.87	99.94	0.13	0.62	0.05	0.01	0.06	<0.01
mecoprop-P	0.0009	0.0006	0.0005	0	0	0	100	100	100	4.98	0.98	1.96	0.94	0.20	0.36
metsulfuron-methyl	0.0002	0.0003	0.24	0	0	0	100	100	99.76	<0.0006	<0.0006	4.51	<0.0006	<0.0006	0.90

<sup>a</sup> Maximum concentrations are based on the mean from duplicate lysimeters.

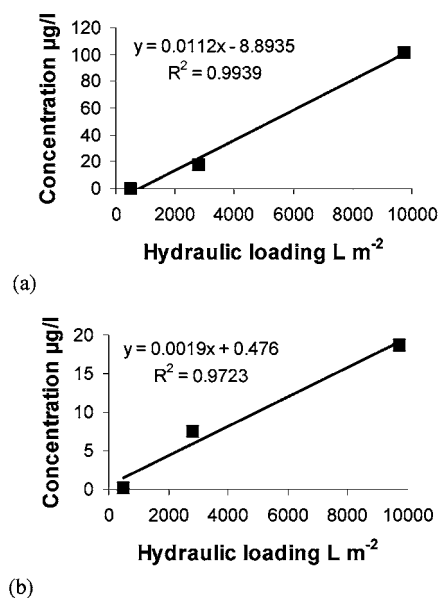
biobed matrix, and between 100 (mecoprop-P) and 99.9% (dimethoate) was degraded. For the 1.0 m lysimeters, between 0.0007 (dimethoate) and 0.0001% (isoproturon) leached, between 0.44 (isoproturon) and 0% (metsulfuron methyl and mecoprop-P) was associated with the biobed matrix, and between 99.6 (isoproturon) and 100% (mecoprop-P and metsulfuron-methyl) was degraded. For the 1.5 m lysimeters, between 0.0009 (mecoprop-P) and 0.0001% (isoproturon and dimethoate) leached, between 1.06 (isoproturon) and 0% (metsulfuron methyl and mecoprop-P) was associated with the biobed matrix, and between 99.7 (dimethoate) and 100% (mecoprop-P and metsulfuron-methyl) was degraded (Table 7).

## DISCUSSION

Biobeds have been in use in Sweden since 1993 with more than 1000 in practical use on farms and other places where pesticide sprayers are filled up (32). The basic design (29, 30) has been shown to be able to treat small drips and spills of pesticide originating from the spray fill site. However, if such a system is to treat dilute pesticide waste and equipment washings in the United Kingdom, it must cope with large volumes of relatively complex mixtures of pesticide, often applied repeatedly. This study was therefore performed to understand the relationship between biobed size, water loadings, and pesticide concentrations in order to provide guidance on the construction and operation of biobeds in the United Kingdom.

Lysimeters (0.5 m) connected to 0.54 and 0.135 m<sup>2</sup> concrete slabs and those receiving only direct inputs of rainfall received a hydraulic loadings equivalent to 9747, 2797, and 486 L m<sup>-2</sup>, respectively. The pesticide leaching potential was clearly affected by hydraulic loading. Amounts of pesticide leaching from lysimeters receiving the highest water loading were <6.4% of the applied, whereas amounts from lysimeters with a medium water loading were <0.7%. From lysimeters receiving only direct inputs of rainfall, the leaching losses were <0.004%. With one exception (pendimethalin at the highest water loading), only the two most mobile pesticides (Koc < 125) leached to any great extent, and even for these, >93% was retained by the biobed lysimeters receiving the highest water loading and >99% from lysimeters receiving a medium water loading. On the basis of the reported physicochemical properties for pendimethalin (Table 1), it would not be expected to represent a leaching risk and is therefore probably an experimental artifact. However, it is possible that the pendimethalin in leachate may have been transported on suspended particulate or colloidal material (43). All pesticides were degraded within the biobed with <35% of the retained pesticide remaining within the biobed matrix after 244 days.

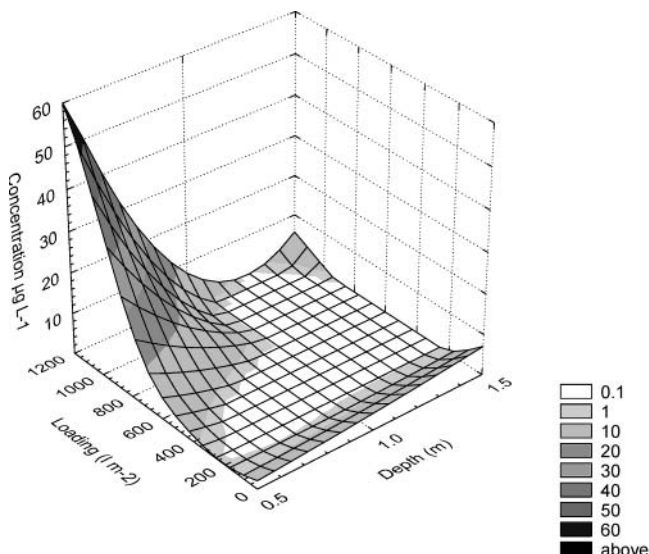
Performance of the biobed with respect to the maximum and average concentrations of isoproturon and dimethoate in leachate for both the high (Table 2) and the medium (Table 3) water loading scenarios was unacceptable to the regulatory authorities.



**Figure 6.** Average concentrations of (a) isoproturon and (b) dimethoate measured in leaches from 0.5 m deep lysimeters correlated against hydraulic loading.

Average concentrations of both isoproturon (Figure 6a) and dimethoate (Figure 6b) were therefore correlated against hydraulic loading to enable the maximum hydraulic loading for a given maximum concentration in the leachate to be calculated. To achieve average concentrations of both compounds of, e.g., <0.1  $\mu\text{g L}^{-1}$ , the maximum hydraulic loading to 0.5 m deep biobed should not exceed 200 L m<sup>-2</sup>. Over the course of a normal spray season, a typical spray applicator can produce between 3800 and 15000 L of pesticide contaminated wastewater (44), not including clean rainwater, and on that basis, a biobed of 0.5 m depth would need to have a surface area of between 19 and 75 m<sup>2</sup>. While an area of up to 40 m<sup>2</sup> is likely to be acceptable to most sprayer operators, anything larger may be seen as impractical. Methods of optimizing biobed performance were therefore investigated. Lysimeters (0.5, 1.0, and 1.5 m) connected to 0.32 and 0.136 m<sup>2</sup> concrete slabs and those receiving only direct inputs of rainfall received hydraulic loadings equivalent to 1175, 688, and 202 L m<sup>-2</sup>, respectively. By controlling water inputs and increasing the retention time within the biobed through increasing depth, studies showed that for mobile [Koc 15–74 (45)] and moderately mobile [Koc 75–499 (45)] pesticides, <1.41% of the applied pesticides leached from 0.5 m deep biobeds receiving the highest water loading, as compared with <0.32% from 1.5 m biobeds. For lysimeters subject to a water loading of 688 L m<sup>-2</sup>, <0.1% of the applied pesticide leached from the 0.5 m deep biobed as compared with <0.06% from the 1.5 m biobeds, and those receiving only direct inputs of rainfall (202 L m<sup>-2</sup>), <0.0007% of the applied pesticide leached. At this low water loading, average concentra-

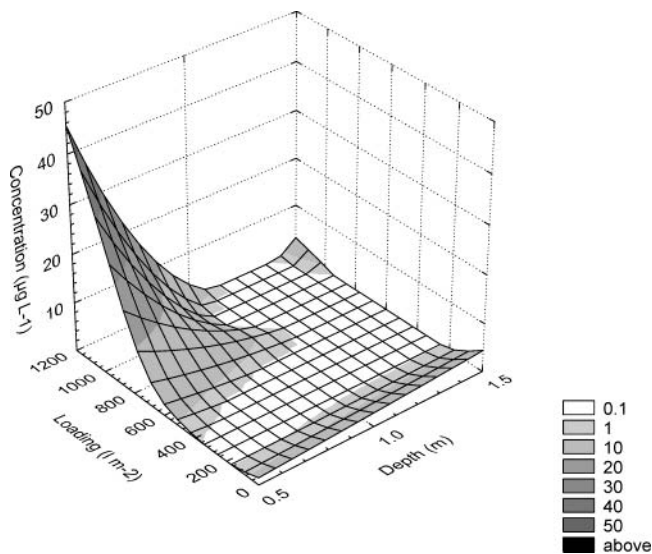




**Figure 7.** Surface area plot showing the combined effects of biobed depth and hydraulic loading on average concentrations of isoproturon in leachate.

tions of both isoproturon and dimethoate from 0.5 m deep biobeds were  $<0.03 \mu\text{g L}^{-1}$  supporting the predictions based on data from the previous experiment discussed. For the two very mobile [ $K_{oc} < 15$ , (45)] pesticides tested, mecoprop-P and metsulfuron-methyl, amounts of pesticide leaching from the biobed lysimeters were higher. However, by controlling water inputs and maximizing the opportunity for sorption and degradation, the amount of pesticide leaching from the biobed was reduced. For example, at the highest water loading, 100% of applied metsulfuron-methyl leached from the 0.5 m deep biobeds as compared with only 15% from the 1.5 m biobeds. Isoproturon, dimethoate, mecoprop-P, and metsulfuron methyl are classified as slightly or moderately persistent,  $DT_{50} < 60$  days (45). In these experiments,  $>96.5\%$  of the retained pesticide was degraded within 197 days.

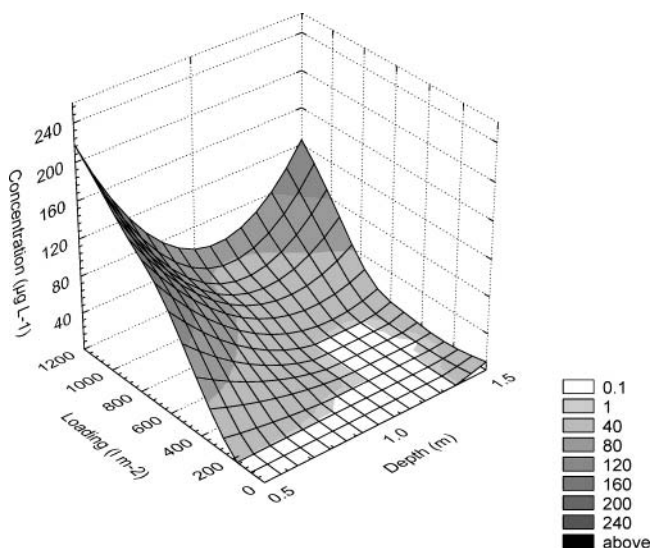
Currently, to gain approval for use in the United Kingdom and the European Union, the annual average concentrations of a pesticide predicted to reach groundwater should not exceed  $0.1 \mu\text{g L}^{-1}$ . Surface water concentrations may be predicted to exceed this value (subject to an ecotoxicological assessment) on the basis that surface waters will require more than minimal treatment in order to obtain suitable quality for human consumption. However, in the future, it is possible that the Water Framework Directive may have impacts in catchments where surface waters are abstracted for drinking water. While the performance of the biobed is not subject to the same strict criteria, it does provide a useful framework in which to assess the level of treatment being achieved by the biobed. Lines of best fit were fixed to the data generated in experiments investigating the combined effects of biobed depth and hydraulic loading. This enabled the minimum depth of the biobed and the maximum hydraulic loading to be calculated such that the average concentration in leachate does not exceed a given maximum concentration, for example,  $0.1 \mu\text{g L}^{-1}$ . Data for isoproturon (Figure 7) and dimethoate (Figure 8) clearly demonstrate the combined effects of hydraulic loading and biobed depth on concentrations of pesticide leaching from the biobed, and for these two compounds, data suggest that a minimum depth of 1.0 m is required. To establish a maximum water loading for the biobed, average concentrations of both isoproturon and dimethoate were correlated separately against hydraulic loading. Lines of best fit were used to calculate hydraulic loadings of  $184 \text{ L m}^{-2}$  for isoproturon and  $469 \text{ L m}^{-2}$



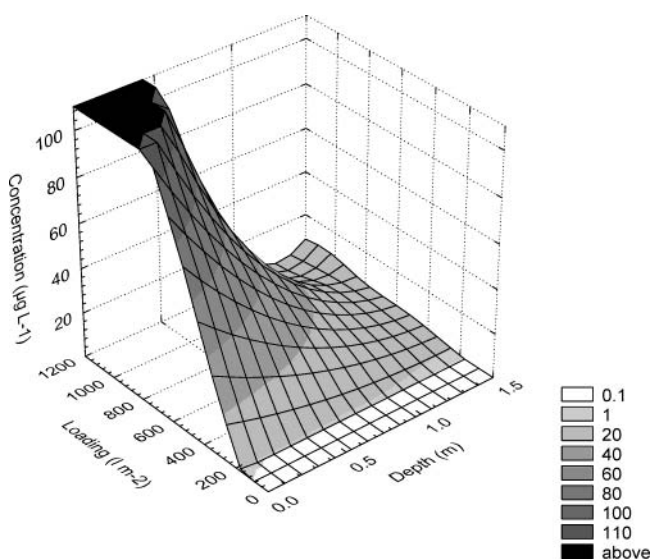
**Figure 8.** Surface area plot showing the combined effects of biobed depth and hydraulic loading on average concentrations of dimethoate in leachate.

for dimethoate such that from a 1.5 m deep biobed concentrations of each pesticide, respectively, should not exceed  $0.1 \mu\text{g L}^{-1}$ . These data can be used to calculate the minimum surface area of a 1.5 m deep biobed in order to treat any given volume of pesticide waste and washings. For example, if the farm had a bunded spray fill area of  $40 \text{ m}^2$ , generated 10000 L of tank and equipment washings, and is located in an area where the annual average rainfall is 650 mm, then the total volume of liquid entering the biobed would be 36000 L. By dividing this figure by the maximum hydraulic loading ( $184 \text{ L m}^{-2}$ ), it can be calculated that the surface area of a 1.5 m deep biobed would need to be  $196 \text{ m}^2$  in order to achieve a maximum average concentration of  $0.1 \mu\text{g L}^{-1}$ . Such physical dimensions are clearly impractical on most agricultural holdings. However, at present, biobeds do not have to comply with European Union and United Kingdom legislation with respect to predicted concentrations of pesticide reaching ground and surface water bodies. Therefore, if a higher maximum average pesticide concentration threshold is set ( $5 \mu\text{g L}^{-1}$  for example), the maximum hydraulic loadings increase significantly to 1161 and  $1121 \text{ L m}^{-2}$  for isoproturon and dimethoate, respectively. By using these data ( $1121 \text{ L m}^{-2}$ ), the surface area of the biobed decreases to only  $32 \text{ m}^2$  in order to treat the same volume of pesticide waste. Data for mecoprop-P (Figure 9) and metsulfuron-methyl (Figure 10) show that extremely mobile pesticides [ $K_{oc} < 15$  (45)] are likely to leach through the biobed. Controlling water inputs does appear to reduce the amount of pesticide leaching from the system; however, increasing biobed depth does not appear to give the same level of improvement in performance as observed for isoproturon and dimethoate. To achieve average concentrations of  $\leq 5 \mu\text{g L}^{-1}$  for mecoprop-P and metsulfuron-methyl, the biobed would have to be at least 1.5 m deep and the hydraulic loading would not have to exceed 387 and  $726 \text{ L m}^{-2}$ , respectively.

On the basis of recent research (21, 26, 33, 34, 37), the Environment Agency has issued interim guidance on the use of biobeds in the United Kingdom. Unlined biobeds may be used for treating the unintentional spillages that occur during the filling, mixing, and handling of pesticides, provided the system is operated in accordance with good agricultural practice. Where the biobed is also used to intercept equipment washings, the biobed will need to be lined with all effluent collected for subsequent appropriate disposal and would also require an



**Figure 9.** Surface area plot showing the combined effects of biobed depth and hydraulic loading on average concentrations of mecoprop-P in leachate.



**Figure 10.** Surface area plot showing the combined effects of biobed depth and hydraulic loading on average concentrations of metsulfuron-methyl in leachate.

authorization under the Groundwater Regulations 1998, including prior investigation of the site and possible monitoring of groundwater. Previous studies (37) with lined biobeds highlighted that water management is crucial and that accumulation of some pesticides may be possible. The data presented here suggest that unlined biobeds may be able to achieve the required level of treatment, such that approval for use for treating equipment washings can also be granted.

In conclusion, pesticide leaching from biobeds is clearly affected by the volume of liquid entering the system. By controlling water inputs and maximizing the opportunity for sorption, biobeds appear able to treat all pesticides other than those classified as very mobile ( $K_{oc} < 15$ ), such that the risk to both surface and groundwater should be acceptable. However, even for highly mobile pesticides, biobed treatment would result in a significant reduction in the amounts of these pesticides reaching surface and groundwater. All pesticides tested dissipated within 12 months; therefore, accumulation from one growing season to the next should not occur. Data suggest a

minimum biobed depth of 1.0–1.5 m. The surface area of the biobed is dependent on the volume of waste and level of treatment required. However, as a guide, a 1.5 m deep biobed with a surface area of 30–40 m<sup>2</sup> should be able to treat  $\leq 44000$  L of pesticide waste such that average concentrations of all but those pesticides classified as very mobile are  $< 5 \mu\text{g L}^{-1}$ . The studies reported here were performed over a relatively short time frame ( $< 12$  months). While biobeds are expected to have an effective lifespan of 5–8 years, subject to appropriate management (30), longer term studies are required in order to fully characterize any risk posed to the environment from the use of biobeds.

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