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BIOBEDS Phase 3: THE DEVELOPMENT AND EVALUATION OF A BIOLOGICAL SYSTEM FOR THE DISPOSAL OF PESTICIDE WASTE AND WASHINGS

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The Voluntary Initiative is a programme of measures, agreed by Government, to minimise the environmental impacts of pesticides.

Summary

Biobeds provide an effective and affordable system for treating pesticides from mixing / handling areas as well as washdown areas. Studies have shown the ability for biobeds to retain and subsequently degrade high concentrations of relatively complex mixtures of pesticides when applied repeatedly. Water management is crucial in terms of construction costs, performance and the level of management required. The use of unlined biobeds removes many of the problems associated with treating large volumes of liquid. However, in previous studies whilst >99% of the most mobile pesticides tested were retained and subsequently degraded, peak concentrations in leachate did not meet the standards required by regulatory authorities. The specific aim of this study was therefore to optimise the biobed system such that regulatory approval for use could be achieved.

Experiments performed to investigate the relationship between biobed depth and water loading showed that biobeds need to have a minimum depth of 1 - 1.5m. The surface area dimensions of the biobed depends on the water loading which is controlled by the nature and frequency of pesticide handling activities on the farm. However, as a guide a biobed with a surface area of 30 – 40m^2 should be able to treat 33,000 litres – 45,000 litres of pesticide waste and washings, such that the annual average concentration of all but the very mobile (Koc <15) pesticides does not exceed 5 $\mu g\ L^{-1}$.

The microbial biomass of three contrasting soil types (sandy loam, silty clay and clay) was significantly increased by adding straw and compost. There was no significant difference in pesticide concentrations in leachate from lysimeters filled with the 3 different biomix soils, with degradation rates for isoproturon, dimethoate, mecoprop-P and metsulfuron-methyl applied at 4 times the maximum recommended rate similar to published rates for soil. DT_{50} values for each of the compounds showed that pesticide interactions are possible. However, for the 4 pesticides tested DT_{90} values were ≥ 167 days indicating little chance of accumulation from one season to the next.

When subjected to multiple treatments with high volumes of dilute waste, with the exception of isoproturon, losses of pesticide in leachate from 1.5m deep biobed columns were significantly higher than from those receiving a single treatment applied in a low volume. Data suggest higher infiltration rates and therefore a reduced retention time within the biobed matrix allowing less time for sorption and biodegradation as the main reason for the high losses of pesticide from biobeds subjected to “real world” use.

Under optimised conditions biobeds appear able to treat all but the most mobile pesticides. The fact that the different biomix soils achieved the same level of treatment both in terms of leaching potential and degradation suggest that the biobed technology should be readily transferable to farms across the UK and provided that minimum depths and maximum water loading levels are followed biobeds should achieve the same level of performance on the farm as observed under controlled conditions.

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1 Introduction

Pesticides may be released to farmyard surfaces as a result of spillages, leakages and the decontamination of tractors and sprayers, (Ramwell et al., 2001). Recent studies have demonstrated that residues on the yard surface may subsequently be washed off to surface waters and that losses from the farmyard can contribute a significant proportion of the pesticide load being released to surface waters, (Mason et al., 1999). Such 'point source' releases can be minimised by modifying handling practices in order to minimise losses. However, it is inevitable that some releases will occur. Additional treatment methodologies are therefore required to reduce these releases. These treatments would supplement good handling practices that reduce inputs to aquatic systems. These methodologies need to be cheap to use and require low labour 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 in the ratios 25%:25%:50% respectively. A number of researchers in Europe have investigated the use of biological systems which sorb and degrade pesticides (e.g Henriksen *et al*., 1999, Linde *et al*., 2003, Pussemier *et al*., 1998, Rose *et al*., 2001, Spliid *et al* 2003, Torstensson 2000, Torstensson *et al*., 1997). More than 1000 biobeds have been established in Sweden and studies have demonstrated that the system can effectively retain and degrade pesticide spillages (Torstennson 2000). The majority of the retained residues are degraded before the start of the next spraying season thus reducing the risk of contamination to surface and ground water.

In order to assess the suitability of biobeds to treat releases of pesticides to UK farmyards, a number of studies have been performed. These studies have investigated the persistence and mobility of a range of commonly used pesticides in biobeds and the effects of range of factors (including pesticide concentration, mixtures and repeat applications) on biobed performance (Fogg *et al*., 2003a, Fogg *et al*., 2003b, Fogg *et al* 2003c). Results to date have demonstrated that a biobed can treat high concentrations of complex mixtures of pesticides applied repeatedly. Water management is crucial in terms of performance, construction cost and management. Using unlined biobeds > 99.3% of the applied pesticide is retained with a significant proportion of the retained pesticide degraded within ten months. Whilst a small proportion of the applied pesticide may leach, optimisation of the biobed design should result

in pesticide concentrations of < 0.1µg L^{-1}. Biobeds therefore appear to offer a simple, low cost system for treating accidental spills and drips as well as tank and equipment washings.

However, before biobeds are approved for use in the UK, there are a number of issues that need to be addressed, namely:

1. The effects of soil type on performance - Studies to date have only used one soil type as the inoculum for the biomix. Biobeds will be built on farms using locally available materials. It is therefore necessary to determine biobed performance when different soil types are used in the preparation of the biomix.

2. The leaching behaviour of highly mobile substances – The most mobile compound studied to date is dimethoate (Koc = 16-52). A number of pesticides are likely to be more mobile than dimethoate.

3. The effects of large rainfall events soon after treatment - Unlined biobeds rely on sorption between pesticides in solution and the biomix matrix. Sufficient contact time is required in order for equilibrium between the liquid and solid phases to be established. High water loadings soon after the application of pesticide waste may result in insufficient time for equilibration and may result in higher concentrations of pesticide in leachate. It is therefore necessary to investigate the effects of realistic worst case hydraulic loading events being applied to the biobed soon after treatment.

4. Behaviour of pesticide degradation products - Studies to date have focused on the fate and behaviour of different active substances. However certain degradation products may be more persistent, more mobile and more toxic than the parent product. It is therefore necessary to identify any relevant metabolites and investigate their fate and behaviour within the biobed.

5. The long term performance of biobeds - Semi-field experiments have lasted for up to 12 months. Performance over an extended period of time should be measured to ensure that the level of performance does not decline. Studies are also required to look at the management requirements of the system and to determine the fate of spent biomix when / if complete replacement is required.

6. Optimisation of the biobed design – Relationships between hydraulic load, biobed dimensions and concentrations of pesticide in leachate would allow the design of the biobed to be optimised.

7. The effects of repeated applications – Studies to data have focused on single applications of pesticide instead of multiple applications over time as would occur on the farm. Also the application volumes used have not been representative of actual on farm conditions. It is therefore necessary to test a semi-field biobed when subject to 'real world' use.

This report describes a series of studies that were performed by Cranfield Centre for EcoChemistry to address many of these issues.

2 Objectives

The overall aim of this project was to address many of the remaining uncertainties over the performance of biobeds in the treatment of waste containing pesticides. The specific objectives were to:

1. Investigate the effect of biobed depth on concentrations of pesticides in leachate for a range of hydraulic loadings

2. Investigate biobed performance with respect to leaching risk and degradation rates when different soil types are used as the inoculum for the biomix.

3. Fully characterise the leaching risk from unlined biobeds by testing a number of highly mobile pesticides.

4. Determine the performance of an unlined biobed in response to extreme rainfall events immediately following the addition of pesticide.

5. Determine biobed performance when pesticides are applied at high volume and on multiple occasions in order to replicate 'real world' use.

3 Methodology

3.1 Test pesticides

A number of pesticides were investigated (Table 1). These were selected on the basis of their physico-chemical properties, in particular their mobility class, in order to fully characterise the leaching risk posed by the use of unlined biobeds.

Table 1 Study compounds and their reported physico-chemical charactersistics

Active substance	Product	Concentration in product (% w/w)	Koc (mL g^{-1})	Mobility class (Hollis 1991)	DT_{50} soil (days)	Solubility water (mg L^{-1})
Isoproturon	Alpha Isoproturon 500	43.6	125	Moderately mobile	6 - 28	65
Dimethoate	Rogor L40	37.4	16 - 52	Mobile	2 - 16	23800
Mecoprop-P	Optica	48	12 - 25	Very mobile –mobile	3 - 13	860
Metsulfuron-methyl	Jubilee 20 DF	20	4.6 - 35	Very mobile - mobile	7 - 35	2790
Chlorothalonil	Cropguard	41.6	1600 - 14000	Slightly / Non-mobile	5 - 36	0.6 – 1.2

Roberts et al., 1998, Roberts et al., 1999, Tomlin 2000

3.2 Biomix preparation

Biomix was prepared by mixing topsoil, peat free compost (Levington Peat Free Universal) and winter wheat straw in the volumetric proportions of 1:1:2 respectively.

A sandy loam soil was used in all of the studies. In the study to assess the effects of soil type on biobed performance, a clay soil and a silty clay soil was also used. The three arable topsoils had a range of physical characteristics, (Table 2) and, based on texture, represented 46% of Agricultural land in England and Wales. Biomix was stored in the open for at least 70 d prior to use in the experiments.

Table 2 Characteristics of soils used for leaching and degradation experiments

	Soil Series		
	Wick	Worcester	Blacktoft
% sand (63 µm – 2 mm	65.38	19.63	12.85
% silt (2 µm – 63 µm	18.71	36.05	46.56
% clay < 2 µm	15.39	44.32	40.59
pH (water)	6.15	7.3	7.7
% Organic Carbon	0.9	1.0	3.6
Texture	Sandy loam	Clay	Silty clay
Maximum water holding capacity % w/w	32.99	55.32	64.63

3.3 Effect of biobed depth on pesticide leaching

Lysimeter studies were used to investigate the effect of biobed depth on pesticide concentrations in leachate for a range of hydraulic loadings. Three sets of six lysimeters (i.d. 22.5 cm) of 65, 115 or 165 cm length were prepared using PVC-u piping (22.5 cm internal diameter). Each pipe section was initially filled with 5 cm of washed gravel (10-15 mm diameter) followed by biomix to a level 10 cm below the rim of the pipe. The base of each core was sealed and drained via Teflon tubing to a 2.5 litre amber glass collection vessel located in a central collection pit.

Concrete slabs of varying area were connected to the top of 12 of the lysimeters to give a range of hydraulic loadings. Six lysimeters (2 of each depth) were connected to slabs with an area of 0.32 m^2 and six (2 of each depth) were connected to slabs with an area of 0.16 m^2. The six remaining lysimeters received only direct inputs of rainfall. Silicon sealant was placed on three sides of each of the slabs to prevent water loss off the sides of the slabs.

Pesticide formulations were used to make up a stock suspension (in tap water) containing 3.2, 0.44, 1.54 and 0.0077 g $litre^{-1}$of isoproturon, dimethoate, mecoprop-P and metsulfuron-methyl respectively. An aliquot (50 ml) of the suspension was then applied in March 2002 to give a final treatment rate of 298 mg (isoproturon), 40.5 mg (dimethoate), 143 mg (mecoprop-P), and 0.72 mg (metsulfuron-methyl). Treatment rates were based on results from the Cherwell study (Rose et al., 2000, Mason et al., 1999, Higginbotham et al 1999), (Appendix I). At the same time as the pesticides were applied potassium bromide (KBr) was applied (314 mg $core^{-1}$) to check the hydrological integrity of the lysimeters, as well as to determine the breakthrough timing of infiltrating water.

With the exception of one artificial irrigation event in April 2002 with 18.7 mm (equivalent to 4.3 litres for the lysimeters connected to the 0.32m^2 slabs, 2.5 litres for those connected to the 0.16 m^2 slabs and 0.74 litres for lysimeters receiving only direct inputs of rainfall), lysimeters were subject to natural rainfall conditions.
Leachate collection vessels were monitored after all rainfall events and the total volume of leachate recorded. Volumes in excess of 200 mL were collected and frozen prior to analysis. Where possible, a 60 mL sub-sample was also taken for KBr analysis.

At the end of the study, (197 days after treatment, DAT) all 18 lysimeters were destructively sampled and sectioned (0-5, 5-10, 10-20, 20-30, 30-50, 50-70, 70-90, 90-110, 110-130 and > 130 cm), the sections were homogenised and frozen prior to analysis.

3.4 Effect of soil type

Lysimeter experiments were performed on biomix prepared from each of the three soil types described in Table 2 in order to determine the effects of soil type on pesticide leaching behaviour. Laboratory-based studies were also performed to assess effects on degradation rates.

3.4.1 Lysimeter studies

Twelve lysimeters were prepared using PVC-u piping (22.5 cm internal diameter), cut to 165 cm length. Each pipe section was filled with 5cm of washed gravel (10-15 mm diameter) followed by 150 cm of biomix, to give 4 replicates for each of the three biomix types. The base of each core drained via Teflon tubing to a 2.5 litre amber glass collection vessel located in a central collection pit. All 12 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 off the sides of the slabs.

All twelve lysimeters were treated in January 2003 with 50 mL of a mixture containing 3.2, 0.44 and 1.54 g $litre^{-1}$ of isoproturon, dimethoate and mecoprop-P respectively to give a final treatment rate of 298 mg (isoproturon), 40.5 mg (dimethoate) and 143 mg (mecoprop-P). 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 recorded. Volumes in excess of 200 mL were collected and frozen prior to analysis. Where possible, a 60 mL sub-sample was also taken for KBr analysis. At the end of the study, (115 days after treatment, DAT) the top 30 cm of the lysimeters was removed and sectioned (0-10, 10-20, and 20-30cm) and the sections were homogenised and frozen prior to analysis.

Artificial irrigation was applied to all 12 lysimeters in February, March and April. The cumulative total applied was 91.4mm equivalent to 12.4 litres per lysimeter.

3.4.2 Degradation

Samples (112) of each biomix type (25 g) were weighed out into clear glass bottles (125 mL) fitted with bakelite screw cap lids. Samples (84) of each biomix type were then treated either with isoproturon, chlorothalonil, mecoprop-P or metsulfuron-methyl in water to give final dry weight concentration of 100, 60, 48 and 1.2 mg kg^{-1} of isoproturon, chlorothalonil, mecoprop-P and metsulfuron methyl respectively. A further 21 samples were treated with a mixture containing all 4 pesticides. Tap water was applied to the remaining untreated samples (7). The moisture content of all samples was 50% w/w. Immediately after treatment, three treated replicates and one untreated control for each biomix type and pesticide treatment were taken 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 treated, with a single sample from the untreated controls. The samples were stored at –20 °C prior to analysis.

3.5 "Real World" use

Three lysimeters were prepared using PVC-u piping (22.5 cm internal diameter), cut to 165 cm length. Each pipe section was filled with 5 cm of washed gravel (10-15mm diameter) followed by 150 cm of biomix made using the sandy loam topsoil (Table 2). The base of each core drained via Teflon tubing to a 2.5 litre amber glass collection vessel located in a central collection pit. All 3 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 off the sides of the slabs.

The three lysimeters were treated on 7 occasions at 3 – 4 day intervals in January 2003 with 350 mL of a mixture containing 80 mg L^{-1} isoproturon, 10.9 mg L^{-1} dimethoate and 38.6 mg L-1 mecoprop-P in order to achieve a final treatment rate of 196 mg (isoproturon), 27 mg (dimethoate) and 95 mg (mecoprop-P). Treatment rates were again based on findings of the Cherwell study and are described in detail in (Appendix I). At the same time as the first pesticide treatment was made, potassium bromide (KBr) was applied (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 recorded. Volumes in excess of 200 mL were collected and frozen prior to analysis. Where possible, a 60 mL sub-sample was also taken for KBr analysis.

Artificial irrigation was applied to all 3 lysimeters in February, March and April. The cumulative total applied was 91.4 mm equivalent to 124 litres per lysimeter.

3.6 Shock water Loadings

The three lysimeters used to investigate "real world" use (section 3.5) were re-treated in May 2003 with 50 mL of a mixture containing 3200 mg litre^{-1} isoproturon and 1536 mg litre^{-1} mecoprop-P in order to achieve a final treatment rate of 298 mg, and 143 mg respectively. Prior to treatment, each lysimeter was irrigated with 500 mL (12.6mm) of tap water to increase the soil moisture status to approximately -5 kPa (field capacity). One day after application of the pesticide mixture, each lysimeter was irrigated with 2.6 litres (~20 mm) of tap water over a 1 hour period, equivalent to a 1 in 5 year rainfall event. Six days after treatment each lysimeter was again artificially irrigated with a further 1 litre (~7.4 mm).

Leachate collection vessels were monitored after all rainfall and irrigation events and the total volume of leachate recorded. Volumes in excess of 200 mL were collected and frozen prior to analysis

3.7 Application rate and Volume

Forty five lysimeters were prepared using PVC-u piping (6.3 cm internal diameter), cut to 155 cm length. One end of each pipe was closed off with nylon mesh voile held in place with an adjustable pipe clip. Each pipe section was filled with 150 cm of biomix made using the sand loam topsoil (Table 2). The base of each core drained through a 300 mL HDPE conical funnel into a 1 litre clear glass collection vessel. All lysimeters were irrigated (650 mL or 209 mm) prior to treatment to, a) provide pre-treatment water and b) to increase the soil moisture status to approximately -5 kPa (field capacity).

Fifteen lysimeters were treated with a range of volumes (10, 30, 60, 100 and 150 ml) of different pesticide mixtures containing isoproturon and mecoprop-P to give treatment rates of 23.4 mg isoproturon and 11.2 mg mecoprop-P. A further fifteen lysimeters were treated with

the same mixtures and the same volumes but the application was performed over a 4 hour period (i.e. either 2, 6, 12. 20 or 30 mL was applied hourly). The remaining fifteen lysimeters were treated in the same way but over 9 hours. All lysimeters were artificially irrigated following treatment. Irrigation (150 mL or 48 mm every 24 hours) commenced approximately 12 hours after the last pesticide application.

Leachate collection vessels were monitored after all irrigation events and the total volume of leachate recorded. Volumes in excess of 100 mL were collected and frozen prior to analysis

3.8 Analysis

3.8.1 Water extraction

Pesticides were extracted from water samples into dichloromethane (DCM) using a glass separating funnel (250 mL). The amount of solvent used depended on the sample volume. For most studies, the sample volume was 200 ml and these were extracted into 3 x 40 ml DCM. For the application rate and volume studies, only 100 ml of sample was available so 2 x 30 ml DCM was used. 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 re-dissolved into either 1 ml (application rate and column experiment) or 2 mL (all other samples) of methanol. Concentrations of isoproturon and mecoprop-P were then determined by HPLC, dimethoate concentrations were determined by GC and metsulfuron-methyl concentrations were determined by LC/MS. Recoveries for all of the extraction methods were > 94 %.

3.8.2 Biomix extraction

Samples (40 g) of biomix from the semi-field experiments were placed into glass 250 ml bottles and extracted into 80 ml of methanol for 1 hour 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 isoproturon, mecoprop-P and metsulfuron-methyl determination by HPLC. A further aliquot was taken for dimethoate determination by GC.

Laboratory samples (25 g) treated with isoproturon, chlorothalonil, mecoprop-P and metsulfuron-methyl were shaken for 1 hour 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.

3.8.3 HPLC analysis

Concentrations of isoproturon, mecoprop and metsulfuron-methyl were determined by HPLC using a Spectra Physics SP8810 pump linked to a Kontron 430 UV detector. Samples (20 Pl) were injected using a Spectra Physics SP8775 autosampler. Separation was achieved using a Genesis C8 column (250 x 4.6 mm). The mobile phase used was acetonitrile:methanol:0.05M acetic acid (27:28:45) with a flow rate of 1.7 ml min^{-1} 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^{-1} for metsulfuron-methyl and mecoprop and 0.03 µg L^{-1} for isoproturon.

3.8.4 GC analysis

Concentrations of dimethoate were determined on a Hewlett Packard HP5890 gas chromatograph fitted with a split/splitless injector, 12m x 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). Oven temperature was raised from 90 ^{o}C to 190 ^{o}C (40 ^{o}C min^{-1}) and then to 220 ^{o}C (10 ^{o}C min^{-1}) and finally to 245 ^{o}C (15 ^{o}C min^{-1}). Samples (2 Pl) were injected using a Hewlett Packard HP7673 autosampler. Under these conditions dimethoate had a retention time of 3.1 minutes. Quantification was achieved by comparison of peak areas with results from external standards. The limit of quantification was 0.01 µg L^{-1}.

3.8.5 LC/MS analysis

Concentrations of metsulfuron-methyl were determined by liquid chromatography / mass spectrometry, operated in positive electrospray reaction monitoring mode (ES +MRM). Separation was achieved using a Spherisorb C8 3µ ODS2 column (150 x 1.0 mm). The mobile phase used was 47.5% methanol, 47.5% 10 mN ammonium formate and 5 % acetonitrile with a flow rate of 50 ml min^{-1} 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 ng mL^{-1}.

3.8.6 Bromide

Water samples (11 mL) were filtered to 0.45 µm (Whatman 13mm polysulphone syringe) prior to loading into the proprietary autosampler cartridges. A Metrohm (Herisau, Switzerland) 790 Personal ion chromatograph and 813 compact autosampler were used for all bromide determinations. Analytical columns used were Metrohms', Metrosep RP guard, Metrosep A Supp 4/5 guard, and Metrosep A Supp 4 (250 x 4.0 mm). A 20 µL injection loop and isocratic eluent of composition 1.8 mM sodium carbonate / 1.7mM sodium hydrogen carbonate were utilised, with a typical retention time of 8.5 minutes ± 30 seconds. The limit of quantification was 0.5 mg L^{-1}, with a limit of detection at 0.1 mg L^{-1}.

3.8.7 Biomass

Total microbial biomass was determined by fumigation extraction, (Mele and Carter 1996). 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 dessicator to remove the chloroform and then shaken for 50 minutes with 50 mL of 2 M potassium chloride. Samples were then centrifuged, 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 minutes. After cooling, samples were made up to 10 mL using 50:50 mixture of ethanol and water, transferred to plastic cuvettes and the absorbance 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) calculated.

3.8.8 Data

3.8.8.1 Pesticide degradation

Where possible the first order rate equation was fitted to the observed concentrations, (Equation 1),

$$\frac{dC}{dt} = -kC \qquad \text{(Equation 1)}$$

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

$$C_{(t)} = C_0 \exp(-kt) \qquad \text{(Equation 2)}$$

However, the first order rate equation is often considered unacceptable if the determination coefficient (r^2) falls below 0.7 (Beulke et al., 2001). Where data indicated increasing rates of degradation with time, DT_{50} and DT_{90} values were calculated using an empirical two-parameter relationship,

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

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 summarised by calculating the times to 50% degradation (DT_{50}) and the time to 90% degradation (DT_{90}) from the calculated degradation curves using the relationship;

$$DT_{50} = \ln(1-\ln(0.5)/k_1)/k_2 \qquad \text{(Equation 4)}$$

$$DT_{90} = \ln(1-\ln(0.1)/k_1)/k_2 \qquad \text{(Equation 5)}$$

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

$$C_{(t)} = A\exp(-k_1 t)+B\exp(-k_2 t) \qquad \text{(Equation 6)}$$

where $C_{(t)}$ (mg kg^{-1} soil) is the concentration at time *t*, A (mg kg^{-1} soil) and B (mg kg^{-1} soil) are constants, k_1 ($days^{-1}$) and k_2 ($days^{-1}$) determine the decline of the first and second component of the curve, respectively. (Beulke et al., 2001)

4 Results

4.1 Determine optimum dimensions of biobed

4.1.1 Rainfall and leachate volumes

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

4.1.2 Bromide in leachate

Breakthrough of bromide from all lysimeters receiving high (i.e. connected to 0.32 m^2 slabs) and medium (i.e. connected to 0.16 m^2 slabs) water loads generally occurred 13 –16 days after treatment (Figure 1). In contrast breakthrough from the 1.0 and 1.5 m lysimeters receiving only direct water inputs occurred much later (41-55 DAT). No bromide leached from the 0.5 m lysimeters that received only direct rainfall inputs. In all 1.5 m columns and the 1.0 m column receiving only direct rainfall inputs, peak bromide concentrations were observed 80 DAT. Peak concentrations were observed 41 DAT in the 0.5 and 1.0 m columns receiving a medium water loading. Highest concentrations from the 0.5 m 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, highest amounts of bromide leached from columns receiving a high water loading whereas lowest amounts 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.

4.1.3 Pesticide residues in leachate

Maximum concentrations of pesticide were measured in leachate collected from lysimeters with a high water loading (Figure 2). By increasing the depth of the lysimeter and controlling water inputs the concentrations of pesticide in leachate were reduced significantly (Figure 3).

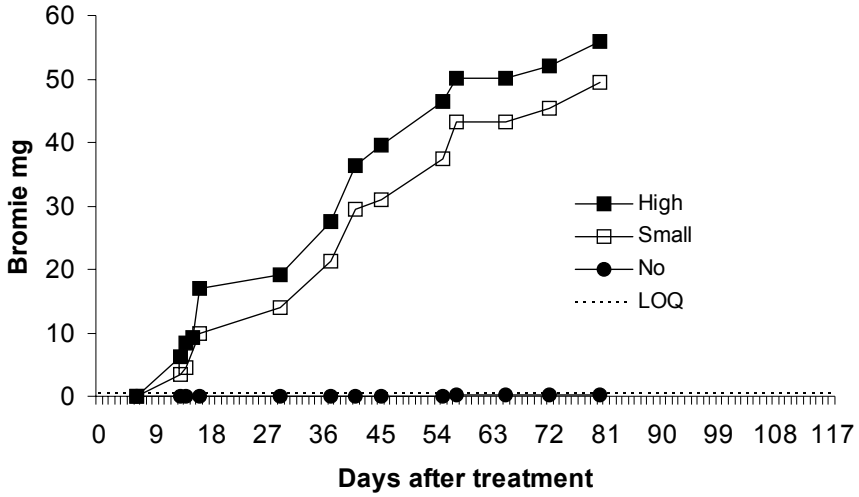
4.1.3.1 High water loading

Peak concentrations of isoproturon were 310.87 µg L^{-1} from 0.5m lysimeters, 14.92 µg L^{-1} from 1.0 m lysimeters and 17.31µg L^{-1} from the 1.5 m lysimeters. Breakthrough from the 0.5 m lysimeters was measured 13 DAT with peak concentrations measured 1 day later. Breakthrough from the 1.0 and 1.5 m lysimeters was measured 16 DAT. Peak concentrations were measured 55 DAT from the 1.0m lysimeters and 65 DAT from the 1.5 m lysimeters. Cumulative losses of isoproturon were 0.4 %, 0.04 % and 0.06 % for the 0.5 m, 1.0 m and 1.5 m deep lysimeters respectively.

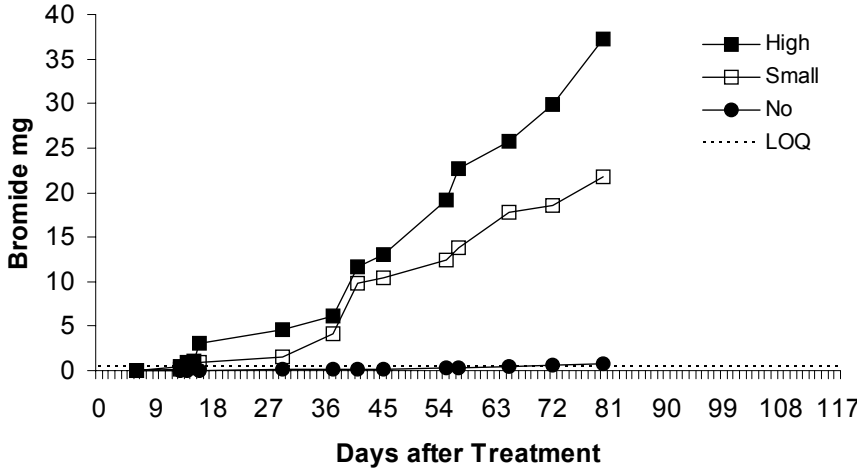
Maximum concentrations of mecoprop-P were 1687.16 µg L^{-1} from the 0.5 m lysimeters, 88.40 µg L^{-1} from the 1.0 lysimeters and 423.07 µg L^{-1} from the 1.5 m lysimeters and were measured 14, 41 and 101 DAT respectively. Breakthrough was measured 6, 13 and 16 DAT from the 0.5, 1.0 and 1.5m lysimeters respectively. Cumulative losses were 3.4 %, 1.0 % and 2.1 % for the 1.5 m, 1.0 m and 0.5 m lysimeters respectively.

Breakthrough of dimethoate for all depths was measured 6 DAT. Maximum concentrations of 253.37 µg L^{-1}, 1.77 µg L^{-1} and 18.16 µg 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.

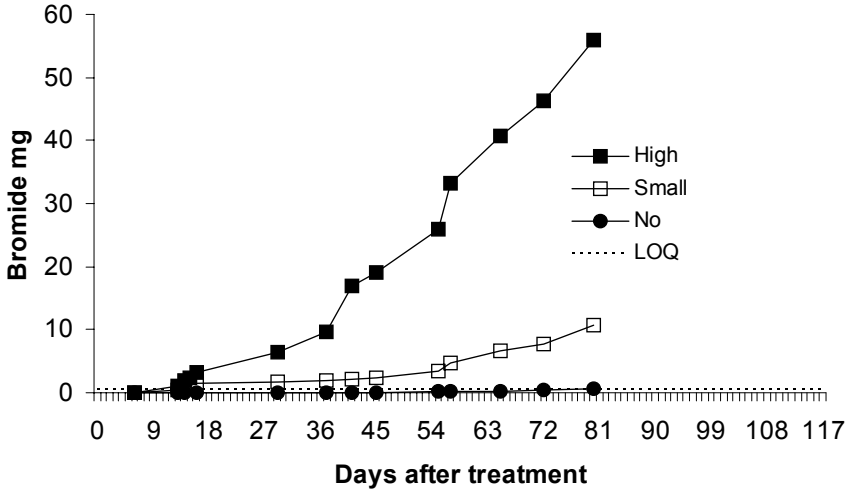
Metsulfuron-methyl peak concentrations were 183.0 µg L^{-1}, 28.6 µg L^{-1} and 29.9 µg L^{-1} from the 0.5, 1.0 and 1.5m lysimeters respectively, with breakthrough measured 13, 14 and 16 DAT respectively. Peak concentrations from the 0.5m lysimeters were measured 14 DAT and 101 DAT from the 1.0 and 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.



(a)



(b)



(c)

Figure 1 Cumulative amounts of bromide leached from (a) 0.5m, (b) 1.0m and (c) 1.5m deep biobed lysimeters when subjected to No (direct input of rainfall)), low (0.16m2) and high (0.32m2) water loadings

4.1.3.2 Low water loading

Peak concentrations of isoproturon from lysimeters subjected to a low water loading were 33.35 µg L^{-1} from the 0.5 m lysimeters, 3.34 µg L^{-1} from the 1.0 m lysimeters and 2.96 µg L^{-1} from the 1.5 m lysimeters and were measured 41, 45 and 37 DAT respectively. 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 877.89 µg L-1 from the 0.5 m lysimeters, 70.39 µg L^{-1} from the 1.0 m lysimeters and 24.79 µg L^{-1} from the 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.

Breakthrough of dimethoate occurred 6 DAT from the 1.0 and 1.5 m lysimeters and 6 DAT from the 0.5m depth. Maximum concentrations of 7.74, 5.93 and 2.20 µg L^{-1} were measured from 0.5 m, 1.0 m and 1.5 m depth, 37, 41 and 87 DAT respectively. Cumulative losses from the 0.5 m 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 deep lysimeters and 57 DAT from the 1.5 m deep lysimeters. Maximum concentrations for each depth (0.5 m to 1.5 m) were measured 16, 41 and 101 DAT and were 75.3, 54.2 and 16.6 µg L^{-1} respectively. Cumulative losses were 48 %, 18 % and 6 % for the 0.5, 1.0 and 1.5 m lysimeters respectively.

4.1.3.3 Direct inputs of rainfall only

For isoproturon no concentrations were measured above the LOQ of 0.03 µg L^{-1}. Cumulative losses were estimated to be ≤ 0.0002 % of the applied dose for all depths.

Maximum concentrations of mecoprop-P were 1.96 µg L^{-1} at 0.5 m depth, 0.98 µg L^{-1} at 1.0 m depth and 4.98 µg L^{-1} at 1.5 m depth. Breakthrough and maximum concentrations coincided and were measured 41 DAT at 0.5 m and 1.5 m depth and 126 DAT at 1.0 m depth.

Cumulative losses were ≤ 0.0007 % for all depths. At 0.5 m depth concentrations of dimethoate were all below the LOQ. Breakthrough at 1.0 m and 1.5 m was measured 41 DAT with maximum concentration of 1.23 µg L^{-1} measured at 1.0 m depth, 87 DAT and at 1.5 m depth 0.13 µg L^{-1}, 41 DAT.

As for mecoprop-P losses of dimethoate from the biobed lysimeters receiving only direct inputs of rainfall losses were all ≤ 0.0007 %.

Concentrations of metsulfuron-methyl were below the LOQ in leachate collected form 1.0 and 1.5 m depth. At 0.5 m maximum concentrations coincided with breakthrough and were measured 101 DAT at 4.51 µg L^{-1}. Cumulative losses of 0.2 % were measured for the 0.5 m lysimeters and ≤ 0.0003 % for the 1.0 and 1.5 m deep lysimeters.

4.1.4 Pesticide residues in biomix

No mecoprop-P or metsulfuron-methyl was measured in the biomix at the end of the study (197 DAT). No isoproturon or dimethoate was measured below 10cm depth under either of the water loading scenarios investigated with between 92 and 100 % retained in the top 5cm. 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 %.

4.1.5 Mass balance

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^2 concrete slabs (high water loading) between 100 % (metsulfuron methyl) and 0.39 % (isoproturon) leached from the 0.5m 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 3).

For the lysimeters connected to the 0.16 m^2 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 4).

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 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 5).

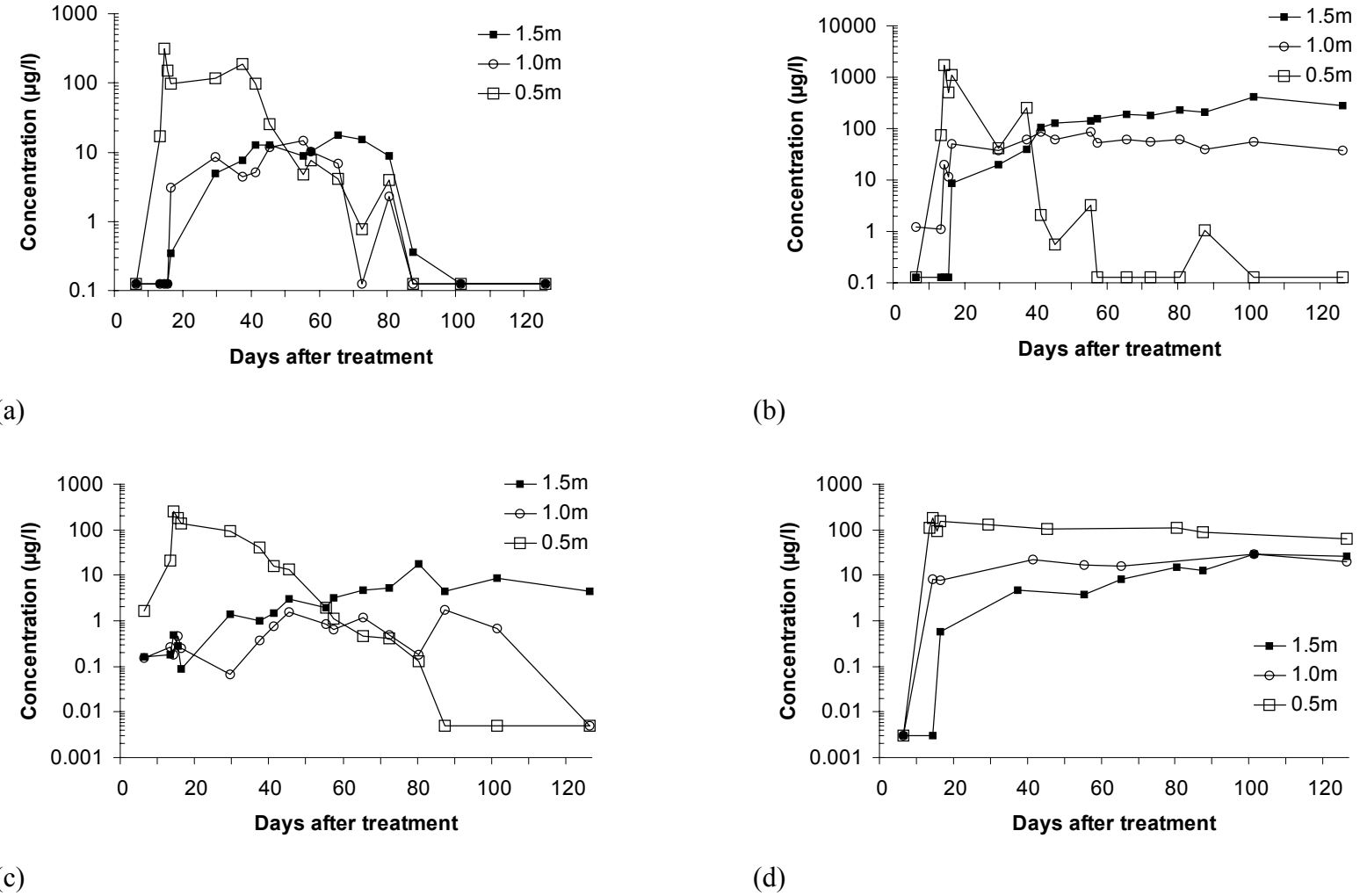


Figure 2 Mean concentrations of (a) isoproturon, (b) mecoprop-P, (c) dimethoate and (d) metsulfuron-methyl from different length lysimeters connected to 0.32 m^2 concrete slabs

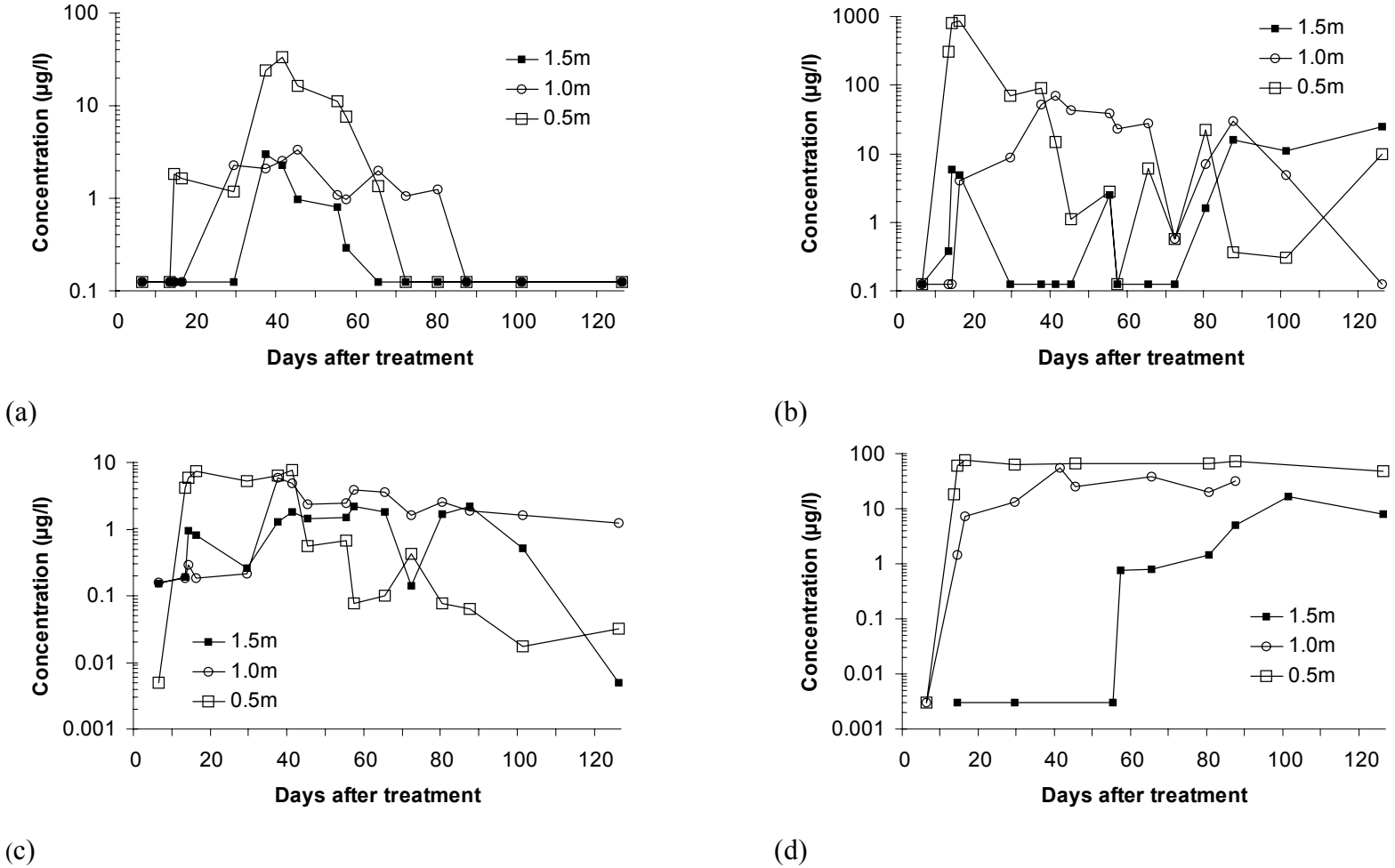


Figure 3 Mean concentrations of (a) isoproturon, (b) mecoprop-P, (c) dimethoate and (d) metsulfuron-methyl from different length lysimeters connected to 0.16 m^2 concrete slabs

Table 3 Mass balance for 0.5 m, 1.0 m and 1.5 m deep biobed lysimeters subjected to a high water loading (0.32 m^2 concrete slabs)

	% leached			% retained			% degraded			Maximum Concentration (µg L^{-1})			Average concentration (µg L^{-1})		
Pesticide	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**
Isoproturon	0.06	0.04	0.39	0.13	3.51	0.41	99.81	96.45	99.20	17.31	14.92	310.87	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	253.37	3.46	0.58	44.47
Mecoprop-P	3.37	1.02	2.07	0	0	0	96.63	98.98	97.93	423.07	88.40	1687.16	123.70	45.78	216.12
Metsulfuron-methyl	15.29	19.34	100	0	0	0	84.71	80.66	0	29.90	28.60	183.00	10.09	14.90	103.09

Maximum concentrations are based on the mean from duplicate lysimeters

Table 4 Mass balance for 0.5 m, 1.0 m and 1.5 m deep biobed lysimeters subjected to a small water loading (0.16 m^2 concrete slabs)

	% leached			% retained			% degraded			Maximum Concentration (µg L^{-1})			Average concentration (µg L^{-1})		
Pesticide	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**
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	877.89	4.27	19.45	137.22
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

Maximum concentrations are based on the mean from duplicate lysimeters

Table 5 Mass balance for 0.5 m, 1.0 m and 1.5 m deep biobed lysimeters receiving only direct inputs for rainfall

	% leached			% retained			% degraded			Maximum Concentration (µg L^{-1})			Average concentration (µg L^{-1})		
Pesticide	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**	**1.5m**	**1.0m**	**0.5m**
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

Maximum concentrations are based on the mean from duplicate lysimeters

4.2 Effect of soil type

4.2.1 Microbial biomass

The microbial biomass was measured to give an indication of microbial activity. Values of 83.47, 229.4 and 185.47 mg kg^{-1} carbon were measured for the sand, silt and clay topsoils respectively. By mixing the three topsoils with straw and compost a significant ($P<0.05$) increase in microbial biomass was measured with values of 255.43, 416.7 and 388.16 mg kg^{-1} carbon being obtained for the sand, silt and clay biomix respectively (Figure 4).

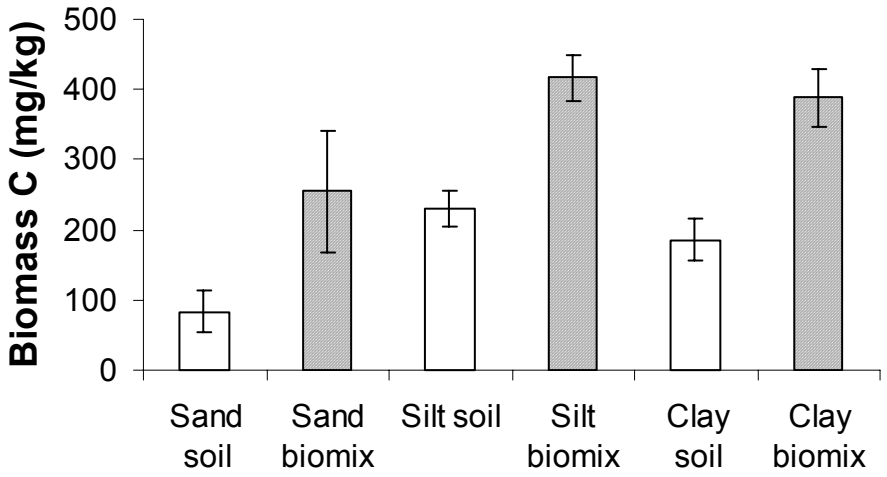


Figure 4 Microbial biomass measured in the sand, silt and clay topsoil and biomix

4.2.2 Leaching

4.2.2.1 Rainfall and leachate volumes

With artificial irrigation (91.4 mm) the rainfall total for the period 14/01/03 (pesticides applied) to 02/05/03 (last set of water samples collected) was 201.5 mm and was 53 % above the long term average for period January to April inclusive. Leachate samples were collected on 19 occasions providing 228 water samples for analysis. Cumulative leachate volumes ranged from 26.2 – 30.6 litres from the silt biomix lysimeters, from 30.4 – 33.7 litres from the clay biomix lysimeters and from 27.4 – 34.2 litres from the sand biomix lysimeters.

4.2.2.2 Bromide in leachate

Bromide breakthrough curves from three different biobed mixtures were similar (Figure 5). 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 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}. Cumulative losses from the sand, silt and clay biomix lysimeters were 17, 13 and 12 % respectively.

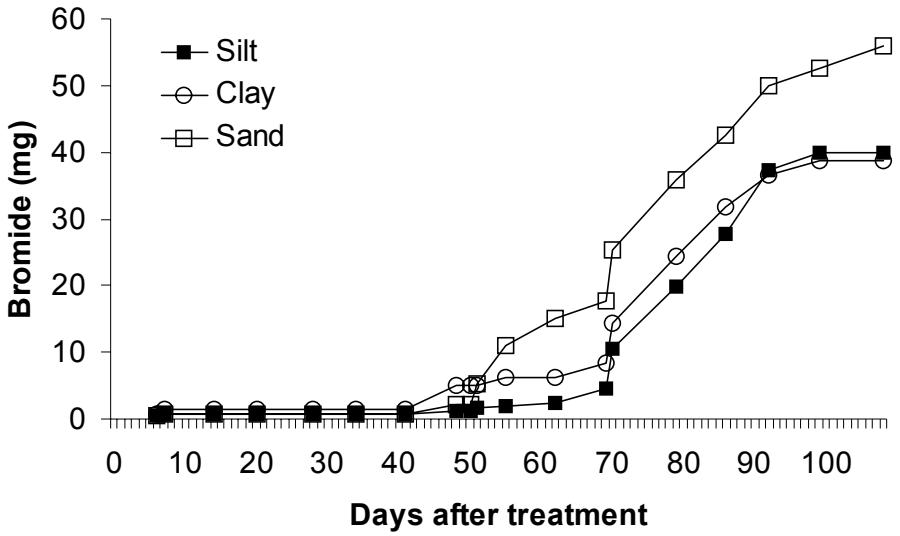


Figure 5 Bromide leaching from lysimeters filled with different biobed mixtures made using sand, silt and clay textured topsoil

4.2.2.3 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 6).. Breakthrough from the silt biomix lysimeters occurred 7 DAT. Whereas in the clay and sand biomix it occurred much later, i.e. 34 and 50 DAT respectively.

Mecoprop-P breakthrough from the silt and clay biomix was measured 6 DAT and from the sand biomix 14 DAT. Peak concentrations were measured 62 DAT from the silt biomix and

108 DAT from the sand and clay biomix. The maximum measured concentrations were 45.22, 117.72 and 145.33 μg L^{-1} from the silt, clay and sand biomix respectively.

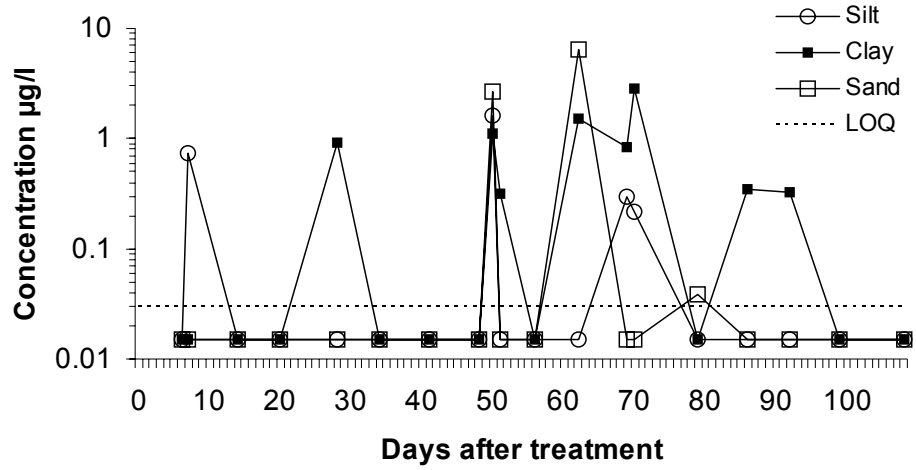
Maximum concentrations of dimethoate were measured 50, 70 and 108 DAT from the silt, clay and sand biomix with values of 0.53, 1.06 and 6.27 μg L^{-1} respectively. Breakthrough of dimethoate was measured 34 DAT from the silt biomix, 41 DAT from the clay biomix and 48 DAT from the sand biomix.

4.2.2.4 Pesticide residues in biomix

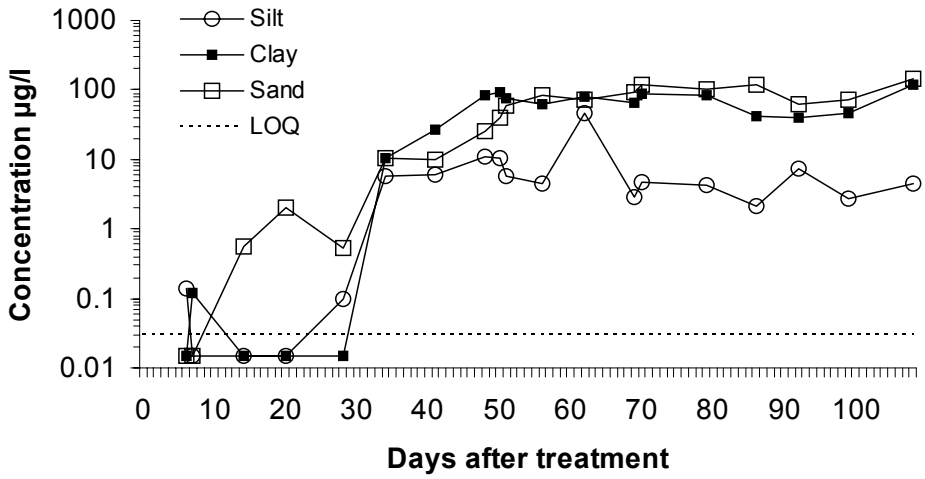
No mecoprop-P was measured in either the sand, silt or clay biomix lysimeters at the end of the study (115 DAT), and no isoproturon or dimethoate was measured below 10 cm depth. For isoproturon, the measured residues (expressed as percentage of the applied dose) remaining in the sand silt and clay biomix 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 the sand biomix and 0.25 % from the silt biomix.

4.2.2.5 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 biomix made using either sand, silt or clay topsoil (Table 6). 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 99.61 % (clay) and 99.49 % (silt) was degraded. 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) degraded. For dimethoate between 0.11 % (clay) and 0.004 % (silt) leached, between 0.61 % (silt) and 0 % (clay) was retained in the biobed matrix with between 99.89 % (clay) and 99.38 % (silt) was degraded.



(a)



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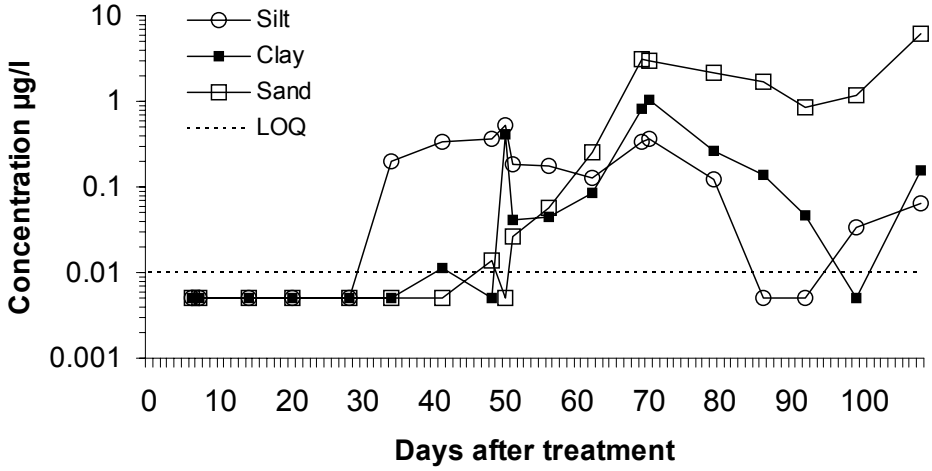


(c)

Figure 6 Mean concentrations of (a) isoproturon, (b) mecoprop-P and (c) dimethoate from 1.5m deep lysimeters connected to 0.16m^2 concrete slabs and filled with biomix made from either sand, silt or clay topsoil

Table 6 Mass balance for lysimeters filled with biomix made using either sand, silt or clay topsoil

Soil Type	% leached	% retained	% degraded	Maximum Concentration ($\mu g\ L^{-1}$)	Average Concentration ($\mu g\ L^{-1}$)
Isoproturon					
Sand	0.006	0.50	99.50	6.49	0.50
Silt	0.002	0.51	99.49	1.62	0.16
Clay	0.007	0.38	99.61	2.84	0.44
Mecoprop-P					
Sand	1.36	0	98.64	145.33	53.28
Silt	0.04	0	99.96	45.22	6.15
Clay	1.64	0	98.36	117.72	48.06
Dimethoate					
Sand	0.02	0.48	99.50	6.27	0.98
Silt	0.004	0.61	99.38	0.53	0.15
Clay	0.112	0	99.89	1.06	0.16

4.2.3 Degradation in sand, silt and clay biomix

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 biomix 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 7a), however, <16% was recovered after 60 days. DT_{50} values of 6.3, 13.4 and 5.9 days were calculated for the sand, silt and clay biomix soils respectively, (Table 7). Degradation of chlorothalonil was bi-phasic (equation 6) in all 3 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 biomix < 13% of the applied dose was recovered at the end of the end of the experiment (Figure 7b) with a DT_{90} values of 49.5 days calculated for both matrices. In the silt biomix a DT_{90} of 71.3 days was calculated which accounts for the fact that 23% of the applied dose was recovered after 60 days (Table 7). Mecoprop-P degraded rapidly in all 3 biomix types (Figure 7c). The data indicated increasing rates of degradation with time (equation 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 3 biomix types (Table 7). 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 7d). 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 (Table 7). Recovered residues at the end of the study were 1.9, 12.7 and 28.3 % for the sand, silt and clay biomix soils respectively.

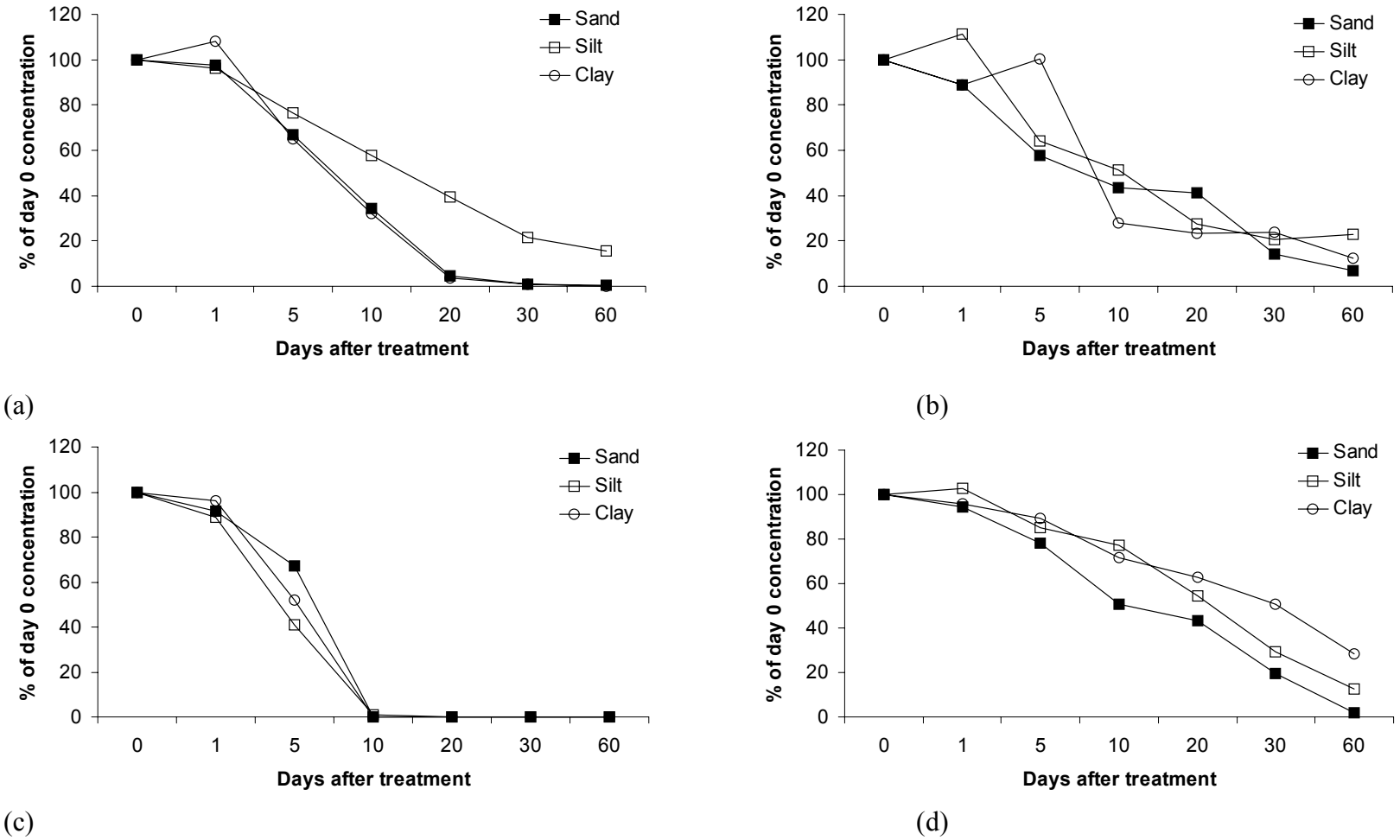


Figure 7 Degradation of (a) isoproturon, (b) chlorothalonil, (c) mecoprop-P and (d) metsulfuron-methyl when applied to biomix made from either sand, silt or clay textured topsoil

Table 7 DT50 and DT90 degradation rates, degradation rate constants (*k*) and determination coefficients (r^2) for isoproturon, chlorothalonil, mecoprop-P and metsulfuron-methyl when applied individually to biomix 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	0.1106	0.99	13.4	52.9	*k*1 1.5887 *k*2 0.0542	1	5.9	19.5	0.1180	0.98
Chlorothalonil	8.0	49.5	*k*1 0.0382 *k*2 0.43	0.98	8.2	71.3	*k*1 0.0001 k2 0.10	0.95	9.4	49.5	*k*1 1.9532 *k*2 0.0822	0.85
Mecoprop-P	6.2	8.6	*a* 0.0381 *b* 0.4773	1	4.3	8.0	*a* 0.3429 *b* 0.2560	1	5.1	7.5	*a* 0.0668 *b* 0.4759	1
Metsulfuron-methyl	13.4	44.4	0.0518	0.98	19.5	64.8	0.0355	0.99	31.4	104.3	0.022	0.99

Table 8 DT50 and DT90 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 biomix 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* 0.9177 *b* 0.0263	0.99	34.7	115.4	0.0199	0.98	16.1	30.7	*a* 0.3985 *b* 0.0624	1
Chlorothalonil	15.6	82.0	*k*1 0.0240 *k*2 0.23	1	19.6	167.0	*k*1 0.0106 *k*2 0.15	1	14.2	101.9	*k*1 0.0174 *k*2 0.17	1
Mecoprop-P	6.5	7.6	*a* 0.0008 *b* 1.0342	1	5.6	8.6	*a* 0.1047 *b* 0.3653	1	6.8	8.8	*a* 0.0115 *b* 0.5998	1
Metsulfuron-methyl	37.4	124.3	0.0185	0.99	43.5	66.5	*a* 0.0971 *b* 0.0482	0.88	58.6	64.7	*a* 0.0000076 *b* 0.1950	0.96

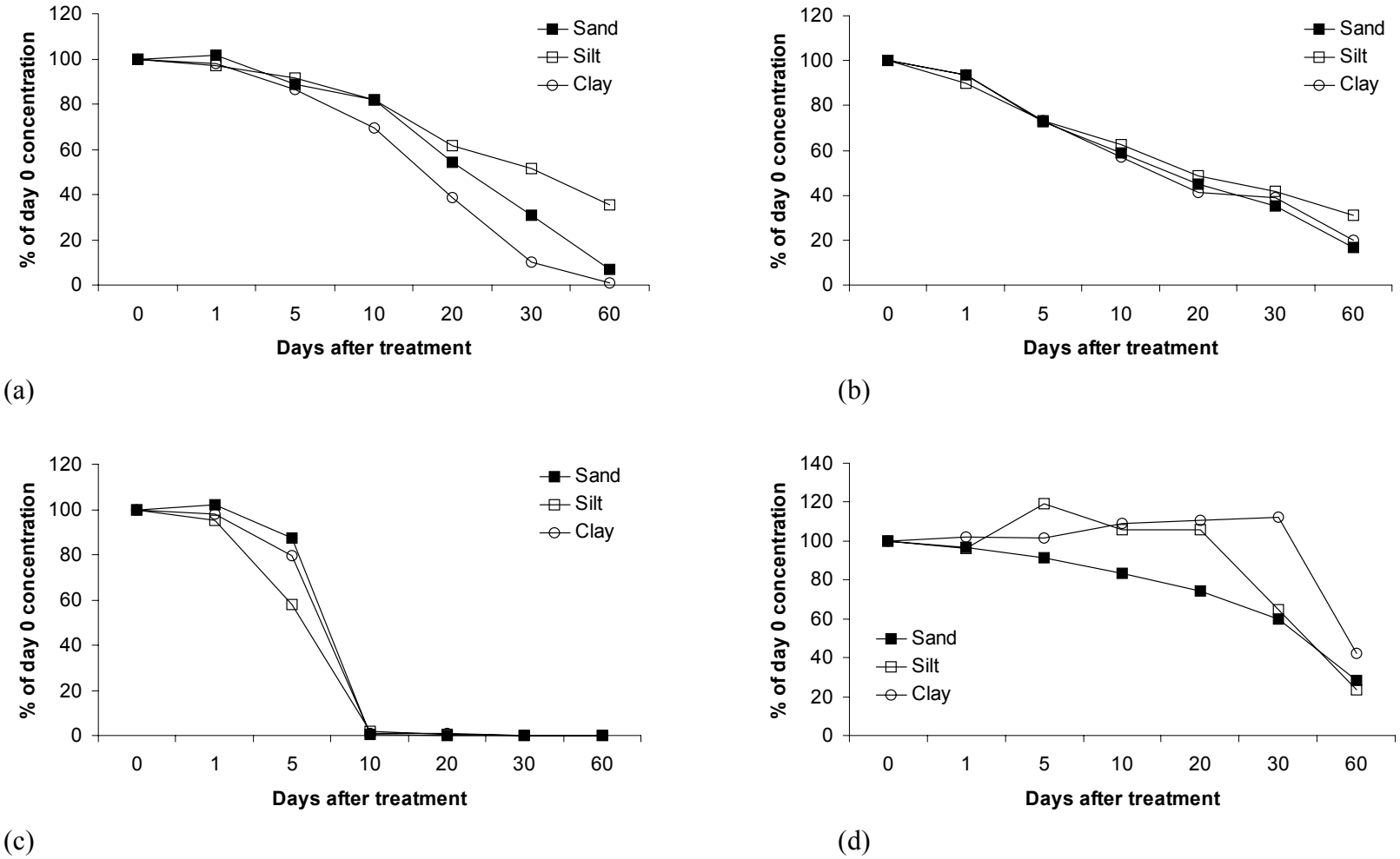


Figure 8 Degradation of (a) isoproturon, (b) chlorothalonil, (c) mecoprop-P and (d) metsulfuron-methyl when applied as a mixture with each of the remaining pesticides to biomix made from either sand, silt or clay textured topsoil

4.2.3.1 Effect of pesticide mixture on degradation

Degradation was slower for all 4 pesticides in each of the biomix soils when applied as a mixture. The pattern of isoproturon degradation in the sand and clay biomix was bi-phasic showing increasing rates of degradation with time (Figure 8a). 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 (Table 8). At the end of the experiment < 7% of the applied pesticide was recovered. The pattern of isoproturon degradation in the silt biomix was linear and was fitted to first order kinetics. 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 rate of degradation was similar in all 3 biomix types. After an initial period of rapid degradation residue levels persisted at relatively low levels until the end of the study, (Figure 8b). 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 8). 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 the individual treatments. The pattern of degradation was the same for all three biomix types showing increasing rates of degradation with time (Figure 8c). DT_{50} values ranged from 5.6 day 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 8d). DT_{50} values of 43.5 days and 58.6 days were calculated for the silt and clay biomix soil respectively. At the end of the study 23% of the applied dose was recovered from the silt biomix compared to 42 % from the clay. Degradation in the sand biomix soil was fitted to first order kinetics. 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.

4.3 "Real World" use

4.3.1 Rainfall and leachate volumes

Rainfall and irrigation inputs were the same as those for experiments investigating the effect of different soil types on pesticide leaching, (section 4.2.2.1). Leachate samples were collected on 19 occasions providing 57 water samples for analysis. Cumulative leachate volumes ranged from 32.8 – 34.03 litres.

4.3.2 Bromide breakthrough

Bromide breakthrough and maximum concentrations in leachate were measured 48 DAT (Figure 9). Concentrations subsequently fell to 1.8 mg L^{-1} (LOQ 0.5mg L^{-1}) by the end of the study (108 DAT). Cumulative losses were 23 %.

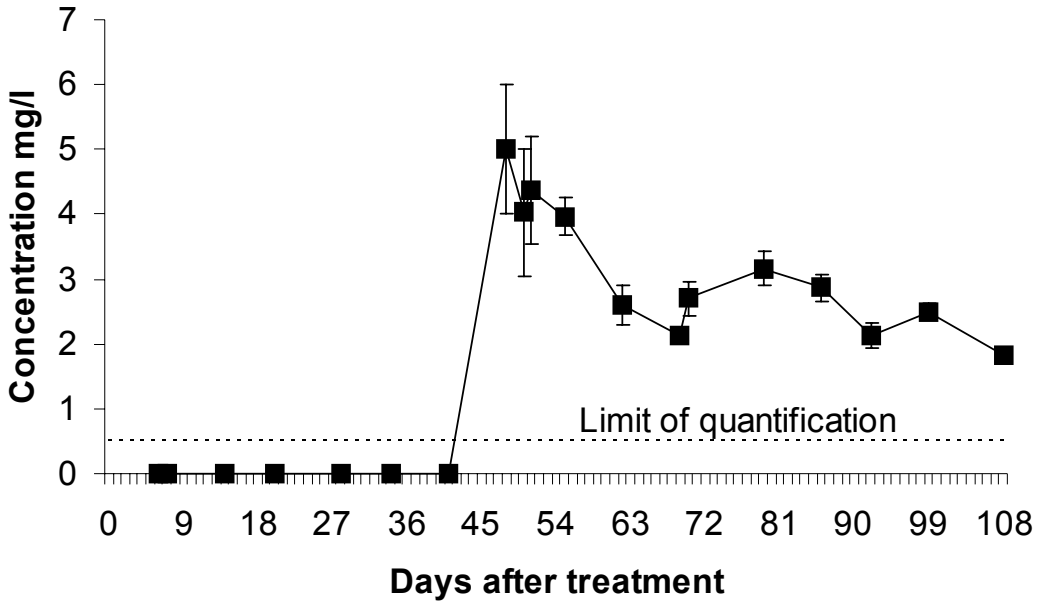


Figure 9 Bromide leaching from lysimeters receiving multiple applications of a pesticide mixture, " Real world use"

4.3.3 Pesticide residues in leachate

Initial breaktrough of isoproturon in leachate collected from lysimeters treated with a single application of isoproturon, mecoprop-P and metsulfuron-methyl was measured 50 DAT, with peak concentrations of 6.5 µg L^{-1} measured 62 DAT (Figure 10a). Cumulative losses were 21.0 µg, equivalent to 0.007 % of the applied dose. For the lysimeters receiving split applications isoproturon breakthrough was measured 28 DAT (first application), with a maximum concentration of 5.6 µg L-1 measured 62 DAT. Cumulative losses were 29.41 µg, equivalent to 0.01 % of the applied.

The first concentrations of mecoprop-P were measured 6 and 14 DAT for the multiple and single treatments respectively (Figure 10b). For the single treatment maximum concentrations in leachate were measured 108 DAT at 145.33 µg L^{-1}. Cumulative losses were 2342.78 µg equivalent to 1.64 % of the applied dose. For the lysimeters receiving multiple

treatments a maximum concentration in leachate of 261.73 µg L^{-1} was measured 51 DAT. Cumulative losses for the multiple treatment experiment were 4765.85 µg equivalent to 3.33 % of the applied.

Breakthrough of dimethoate following single and multiple application was measured 41 and 34 DAT respectively. Highest concentrations were measured 69 DAT for the multiple treatment experiment and 108 DAT for the single treatment with values of 34.15 µg L-1 and 6.27 µg L-1 respectively. Cumulative losses from the lysimeters receiving a single treatment were 45.20 µg equivalent to 0.112 % of the applied dose. For the multiple treatment experiment cumulative losses were an order of magnitude higher at 438.6 µg, equivalent to 1.08% of the applied pesticide.

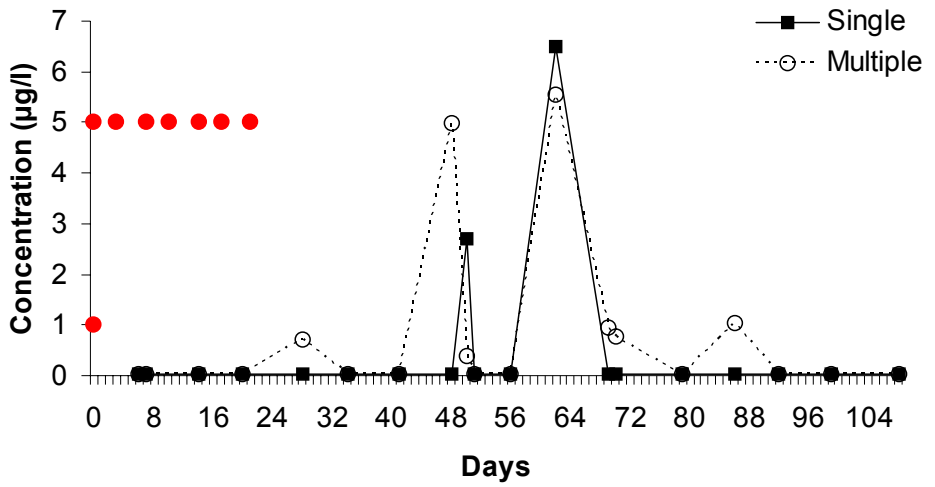
4.4 Shock water Loadings

4.4.1 Rainfall and leachate volumes

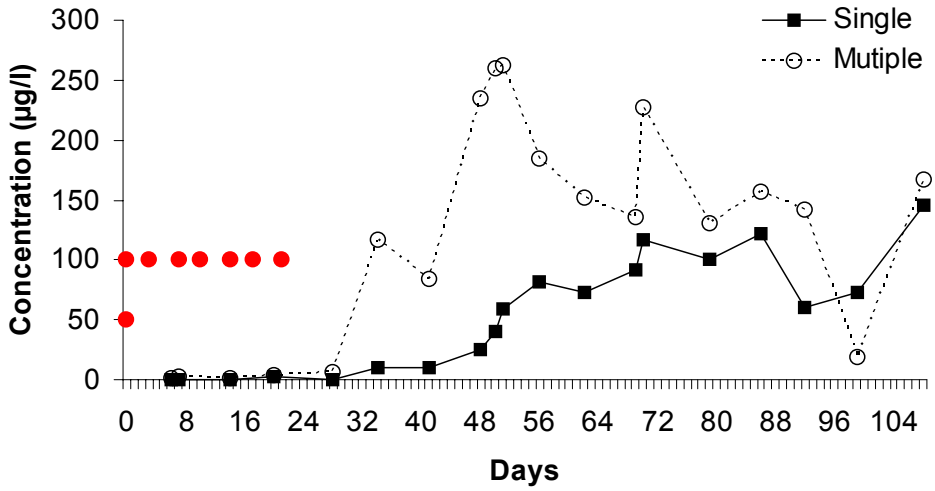
Including irrigation, rainfall for the 28 day period 13/05/03 (pesticides applied) through until 09/06/03 (last water samples collected) totalled 64.3mm. Cumulative leachate volumes ranged from 5.37 – 5.40 litres with water samples collected on 3 occasions providing 9 water samples for analysis.

4.4.2 Pesticide residues in leachate

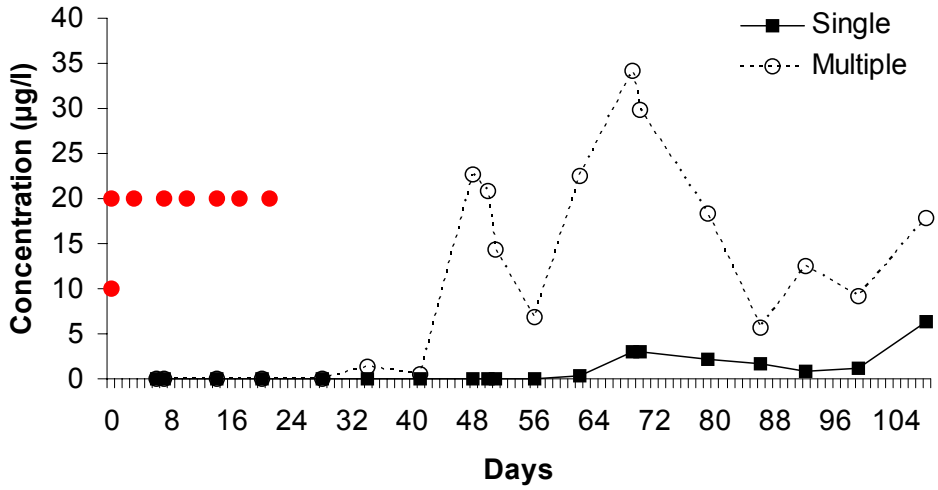
Breakthrough of both isoproturon and mecoprop-P was measured 2 DAT (Figure 11). Concentrations of isoproturon ranged from 4.16 – 21.0 µg L^{-1}, 2 DAT, from 1.27 – 7.01 µg L^{-1}, 7 DAT and from 0.51 – 1.74 µg L^{-1}, 27 DAT. Cumulative losses totalled 40.3 µg equivalent to 0.014 % of the applied dose. For mecoprop-P, measured concentrations ranged from 96.46 – 285.31 µg L^{-1}, 2 DAT, from 73.31 – 149.26 µg L^{-1}, 7 DAT and from < LOQ – 4.80 µg L^{-1}, 27 DAT. Cumulative losses of mecoprop-P totalled 646.4 µg, equivalent to 0.45 % of the applied dose.



(a)



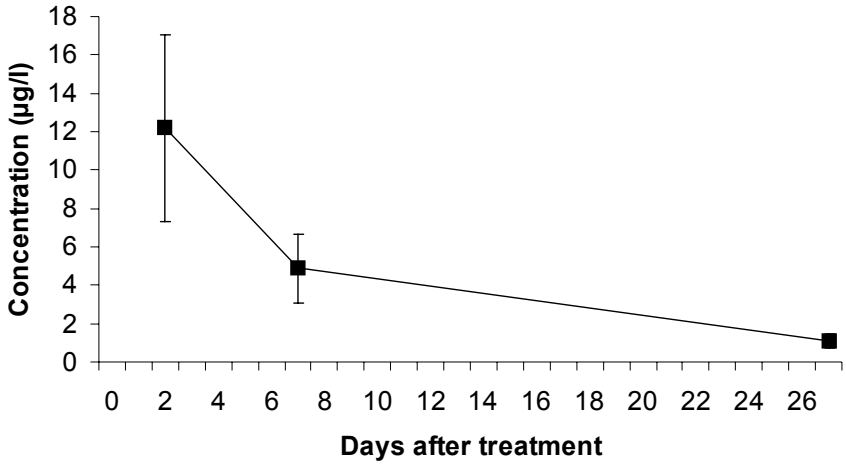
(b)



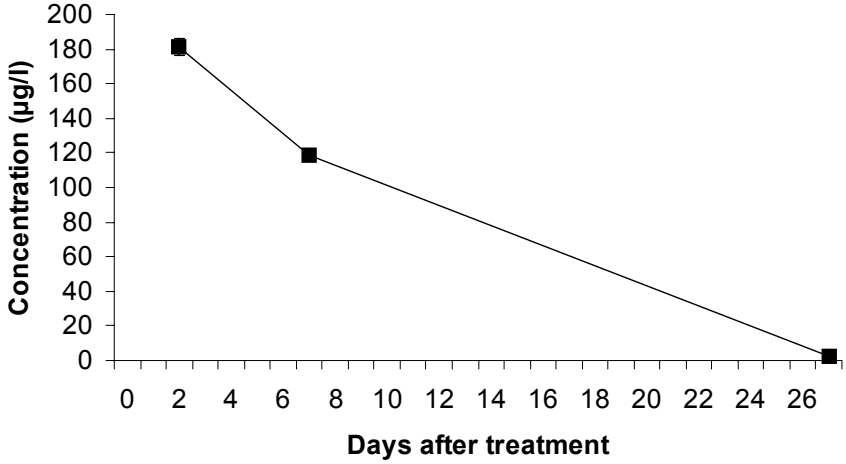
(c)

Figure 10 Mean concentrations of (a) isoproturon, (b) mecoprop-P and (c) dimethoate from lysimeters treated either single or multiple applications of a mixture containing all 3 pesticides

The filled circles adjacent to the y axis indicate the timing of the pesticide treatments



(a)



(b)

Figure 11 Mean concentrations(±1 SE) of (a) isoproturon and (b) mecoprop-P in leachate collected from lysimeters subjected to a 1 in 5 year rainfall event 1 day after treatment

4.5 Application rate and Volume

4.5.1 Irrigation and leachate volumes

A total of 1650 mL of artificial irrigation was applied to all 45 lysimeters. Leachate volumes ranged from 1345 mL to 1650 mL. Post treatment leachate samples were collected on 8 occasions from the lysimeters treated with a single application and those treated over a 4 hour period and on 7 occasions from those treated over a 9 hour period, providing 345 water samples for analysis.

4.5.2 Pesticide residues in leachate

No isoproturon was measured in any of the water samples collected. Mean concentrations of mecoprop-P from lysimeters treated with a single application ranged from < LOQ up to, 2.10µg L^{-1} for the 10 mL treatment, 11.32 µg L^{-1} for the 30 mL treatment, 12.77 µg L^{-1} for the

60 mL treatment, 3.25 µg L^{-1} for the 100 mL treatment and 276.99 µg L^{-1} for the 150 mL treatment. For lysimeters treated over a 4 hour period mean concentrations of mecoprop-P ranged from below the LOQ to 0.6 µg L^{-1}, 1.68 µg L^{-1}, 0.81µg L^{-1} and 0.55 µg L^{-1} for the 10, 30, 100 and 150 mL application volumes respectively. For the lysimeters treated over a 9 hour period the highest mean concentrations of mecoprop-P were measured in leachate from the lysimeters treated with 10 mL of the pesticide mixture and were 4.65 µg L^{-1}. For the 30, 60, 100 and 150 mL treatments maximum mean concentrations of 0.99 µg L^{-1}, <0.05 µg L^{-1}, 1.19 µg L^{-1} and 2.38 µg L^{-1} were measured. Statistical analysis show that under these experimental conditions neither application rate or volume effected the amount of mecoprop-P leaching from 1.5 m long biobed columns (Figure 12).

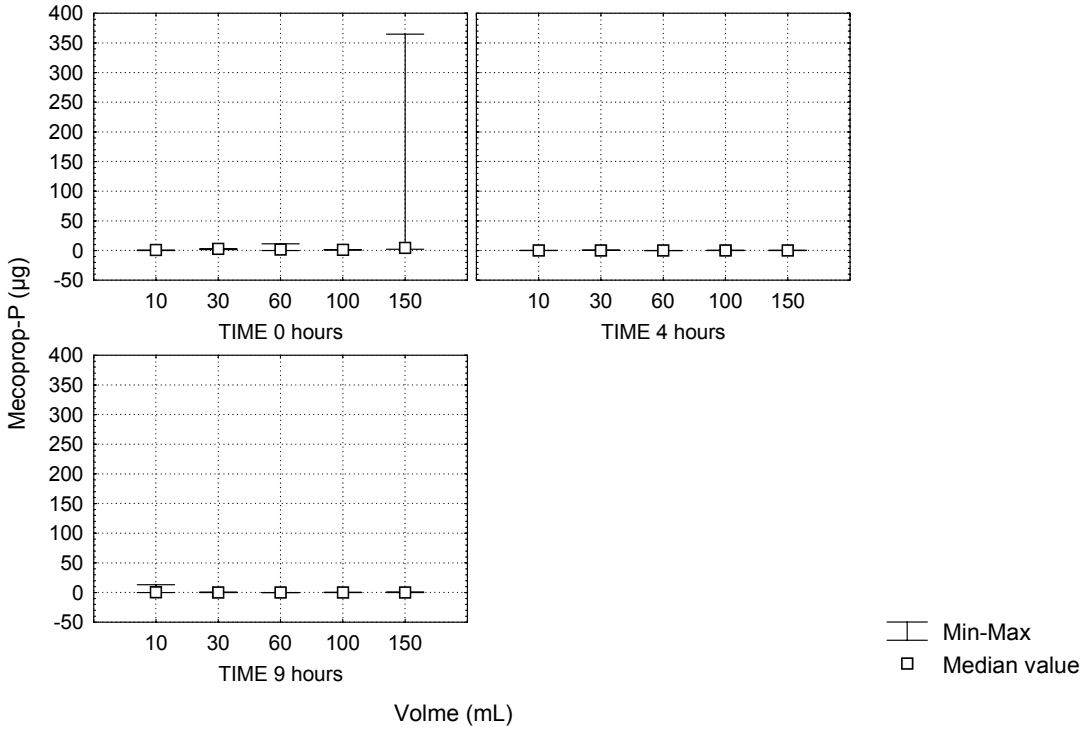


Figure 12 Median amounts of mecoprop-P leaching from lysimeters treated with a range of application volumes and three application rates

5 Discussion

Where pesticides are mixed or handled and where sprayers are parked or washed down, there is a risk of the loss of pesticide to the environment. Such losses can contribute a significant proportion of the pesticide load being released to surface waters, (Mason et al., 1999). Such 'point source' releases can be minimised by modifying handling practices in order to reduce losses. However, it is inevitable that some releases will occur. The use of additional treatment methodologies are therefore required to reduce inputs to aquatic systems. These

methodologies need to be cheap to use and require low labour 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.

Recent research indicates that biomix will degrade high concentrations of relatively complex mixtures of pesticide even when applied repeatedly (Fogg *et al*., 2003a , Fogg *et al*., 2003b). Studies at the field and semi-field scale have demonstrated that water management is crucial in terms of performance, construction cost and management and whilst a small proportion of the applied pesticide may leach improvements in biobed design should result in the biobed achieving the required level of treatment (Fogg *et al*., 2003c, Rose *et al*., 2003). Based on this research the Environment Agency has recently issued interim guidance on the use of biobeds in the UK, a copy of which is attached under Appendix II. In summary, biobeds for pesticide mixing / handling areas can be unlined and provided they are constructed and operated according to good practice they do not require authorisations under the Ground Water Regulations. Biobeds to be used as washdown areas will need to be lined and will require an authorisation under the Groundwater Regulations, including prior investigation of the site and possible monitoring of groundwater.

The experiments reported here focused on many of the uncertainties associated with our current knowledge of biobed performance.

Studies to investigate the combined effects of hydraulic loading and biobed depth showed that for mobile (Koc 74 – 15) and moderately mobile (Koc 75 – 499) pesticides <0.06 % leached from 1.5 m deep biobeds subjected to a moderate water loading with more than 99.7% of the applied pesticide being degraded within 7 months. For the two very mobile (Koc <15) pesticides tested, mecoprop-P and metsulfuron-methyl concentrations of pesticide in leachate were higher. However, only 0.11 % of the applied mecoprop-P and <6 % of the metsulfuron-methyl leached. Biobed treatment would therefore still result in a significant reduction in the amounts of these two pesticides reaching ground and surface water bodies.

Data generated in these experiments can be used to calculate the minimum depth of the biobed and the maximum hydraulic loading such annual average concentrations in leachate from the biobed do not exceed a given maximum concentration, for example 0.1 $\mu g\ L^{-1}$. The combined rainfall and irrigation for the above experiment was of 201.5mm, equivalent to a hydraulic loading of 1175, 688 and 202 L m^{-2} of biobed for the lysimeters connected to the 0.32 m^2, 0.16 m^2 slabs and those receiving only direct inputs of rainfall respectively. Three different biobed depths were exposed to the 3 hydraulic loadings. Data for isoproturon

(Figure 13) and dimethoate (Figure 14), clearly show that by controlling water inputs and increasing the depth of the biobed the concentrations of pesticide measured in leachate were reduced. The data for these two pesticides indicate that the biobeds will need to have a minimum depth of at least 1.0 m, although preferably 1.5 m. By correlating average concentrations against hydraulic loading it is possible to use the data to calculate the maximum water loading such that a given maximum concentration in leachate is not exceeded.

For example, using data for isoproturon ($y = 0.0048e^{0.004x}$, $R_2 = 0.982$) and dimethoate ($y = 0.006e^{0.006x}$, $R_2 = 0.899$) respectively and 1.5 m deep biobeds the maximum hydraulic loading in order to achieve annual average concentrations of <0.1 µg L^{-1} should not exceed 184 and 469 L m^{-2} respectively. These figures increase significantly if a higher pesticide concentration threshold is set. By using 5 µg L^{-1} the maximum hydraulic loadings for isoproturon and dimethoate are 1161 and 1121 L m^{-2} respectively. These data can subsequently be used to calculate the minimum surface area of the biobed needed to treat any given volume of pesticide waste and washings.

For example; if the farm had a bunded spray fill area of 40m^2, generated 10,000 litres of tank and equipment washings and is located in an area where the annual average rainfall is 650mm, then the total volume of liquid entering the biobed would be 36,000 litres. By dividing this figure by a maximum hydraulic loading (1121 L m^{-2}) it can be calculated that the surface area of a 1.5m deep biobed would need to be 32 m^2 in order to achieve a maximum average concentration of 5 µg L^{-1}. The surface area would need to be increased to between 76 m^2 and 196 m^2 using data for isoproturon and dimethoate respectively in order to achieve a maximum concentration of 0.1 µg L^{-1}.

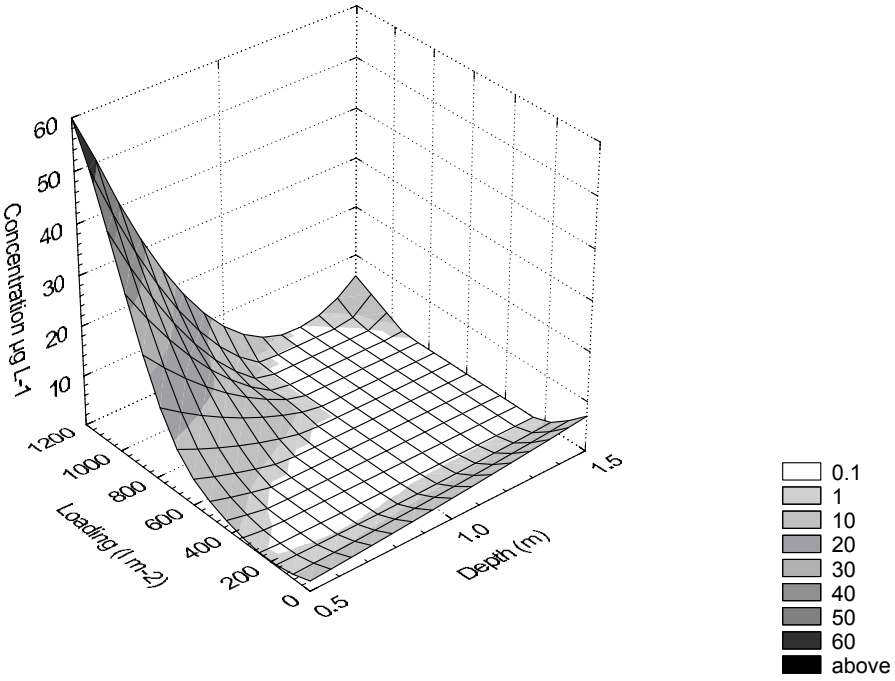


Figure 13 Annual average concentrations of isoproturon in leachate collected from 0.5, 1.0 and 1.5m deep biobeds subjected to 3 different hydraulic loadings

The fact that pesticide concentrations increase at very low hydraulic loading is considered to be an experimental artefact

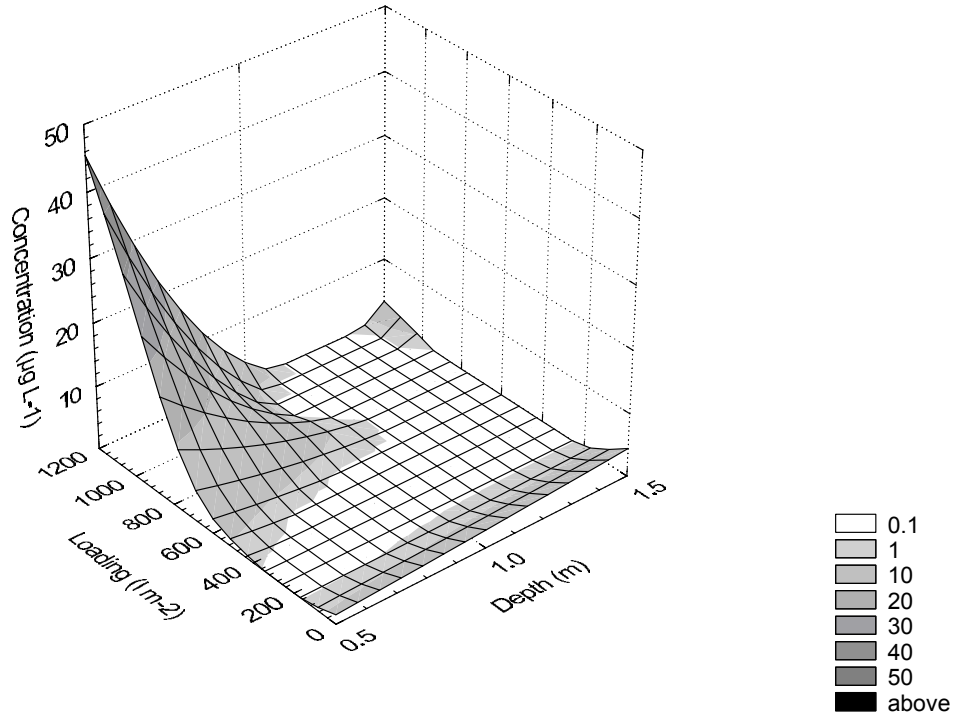


Figure 14 Annual average concentrations of dimethoate in leachate collected from 0.5, 1.0 and 1.5m deep biobeds subjected to 3 different hydraulic loadings

The fact that pesticide concentrations increase at very low hydraulic loading is considered to be an experimental artefact

The above model was evaluated for isoproturon and dimethoate as part of the experiments used to investigate the effects of different soil types. The lysimeters were treated with the same pesticide application rates and were subjected to a hydraulic loading of 688 L m^{-2}. Average annual concentrations of 0.6 µg L-1 and 0.98 µg L-1 were measured for isoproturon and dimethoate respectively (Table 6).

Data for mecoprop-P (Figure 15) and metsulfuron-methyl (Figure 16) show that extremely mobile pesticides 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. In order to achieve annual average concentrations of ”□5 µg 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 L m^{-2} respectively.

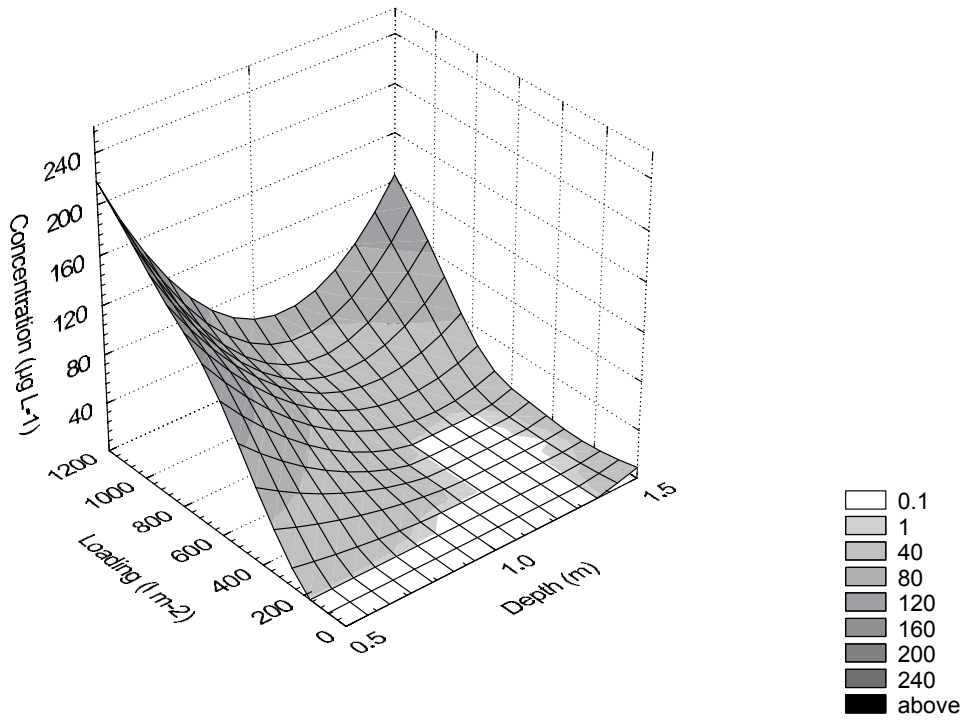


Figure 15 Annual average concentrations of mecoprop-P in leachate collected from 0.5, 1.0 and 1.5m deep biobeds subjected to 3 different hydraulic loadings

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. Microbial biomass was used as an indication as to the level of microbial activity within the 3 soils tested. Biomass was highest in the silt soil and lowest in the sand. Mixing each of the soils with straw and compost

resulted in a two fold increase in the measured biomass indicating a significant increase in the levels of microbial respiration in the biomix. Studies to investigate the leaching risk from biobeds when three different biomix soils were used, showed there to be no significant difference in amounts of isoproturon, mecoprop-P and dimethoate leaching. Degradation half lives for all pesticides applied at 4 times the maximum recommended rate were similar to the reported rates for field soils treated at approved rates. When applied as a mixture degradation rates decreased indicating that interactions between pesticides when applied as a mixture are possible. However, DT_{90} values were all < 167 days, indicating a negligible risk of accumulation from one season to the next.

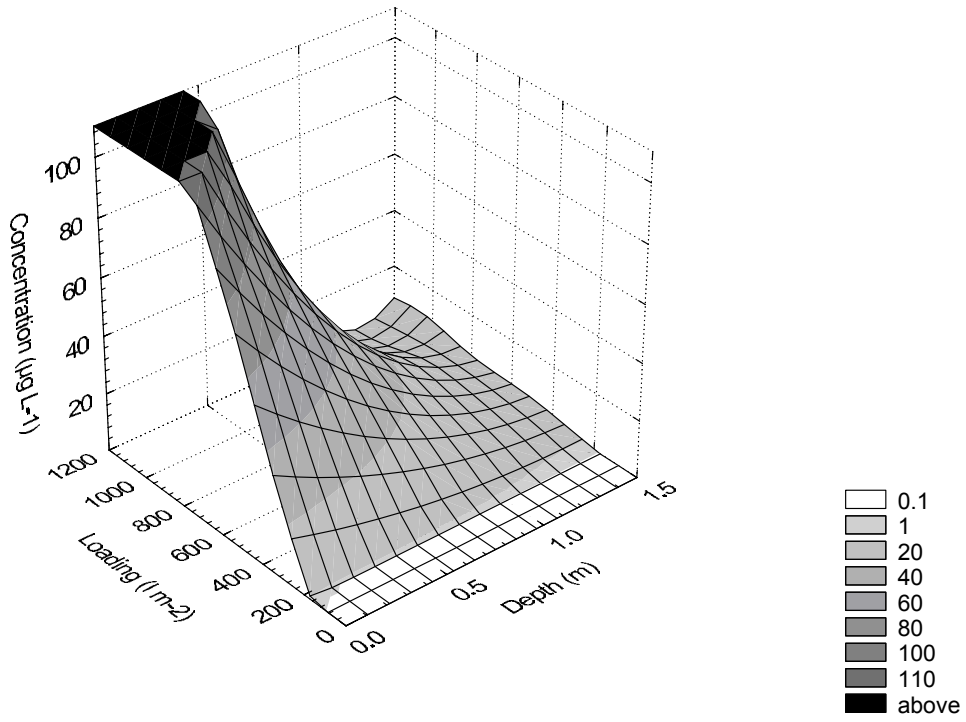


Figure 16 Annual average concentrations of metsulfuron-methyl in leachate collected from 0.5, 1.0 and 1.5m deep biobeds subjected to 3 different hydraulic loadings

Analysis of pesticide records for a number of medium to large arable farms showed that on average all of the isoproturon was applied within 7 days. Previous experiments performed at the semi-field scale were all treated with a single application of a pesticide mixture applied in a low carrier volume. "Real world" experiments described in this report compared leaching from biobeds treated with a single application applied in a low carrier volume to leaching following 7 applications made at 3 day intervals applied in a high carrier volume. Cumulative losses for isoproturon were similar for both the single and multiple treatments and were <0.01 % of the applied dose. However, for mecoprop-P and dimethoate losses were significantly higher following the multiple treatments. The additional hydraulic load to the "Real World"

lysimeters in the form the pesticide carrier was 2.4 litres, with this applied at the same time as the pesticides. It is thought that the additional volume of water applied at the same time as the pesticides resulted in increased infiltration rates, therefore faster breakthrough, reduced retention time resulting in reduced opportunity for degradation and therefore high concentrations on leachate. Shock water loadings soon after treatment were investigated further in separate experiments. A 1 in 5 year rainfall event was simulated 1 day after treatment. Breakthrough of both isoproturon and dimethoate was detected 2 days after treatment which coincided with maximum measured concentrations of both pesticides.

The volume of pesticide waste and the rate at which it is applied appears to effect the amount of pesticide measured in leachate. Laboratory experiments were performed using a range of application volumes and rates. Using a field biobed surface area of 32 m^2 the application volumes of 10 – 150 mL used in the laboratory were equivalent to 100 – 1500 litres at the field scale which applied over a period of time ranging from <1 hour to 9 hours resulting rates of between 1500 l $hour^{-1}$ to 11 litre $hour^{-1}$. However, under these experimental conditions neither application rate or volume gave statistically significant differences in the amount of pesticide measured in leachate.

6 Conclusions

Based on the results it is possible to draw a number of conclusions;

- Pesticide leaching from biobeds is to a great extent controlled by the amount of water passing through the system. By controlling these inputs and maximising the retention time within the biobed matrix losses of pesticide from the biobed should be acceptable. The data reported here suggest a minimum biobed depth of 1.0 - 1.5 m. The surface area of the biobed depends on the nature and frequency of pesticide handling activities on the farm. However, as a guide a biobed with a surface are of 30 – 40m^2 should be able to treat in excess of 33,000 litres of pesticide waste and washings such that the maximum concentrations of all but the very mobile pesticides do exceed 5 µg L^{-1}.

- Biobeds appear able to retain all pesticides other than those classified as very mobile.

- The use of different textured soils for the biobed inoculum had no significant effect of concentrations of pesticide in leachate.

- When applied at 4 times the maximum recommended rate to biomix ,the DT_{50} values for isoproturon, dimethoate, mecoprop-P and metsulfuron methyl were similar to published values for soil.

- When applied as part of a mixture DT_{50} values increase indicating that interactions between pesticides are possible. However, accumulation of the four pesticides tested here should not occur.

- At the semi-field scale repeated applications of high volumes of pesticide waste resulted in higher concentrations of pesticide leaching from biobeds, possibly due to the combined effects of increased infiltration rates, reduced retention time and therefore less opportunity of sorption and degradation.

7 Recommendations

Under optimised conditions biobed appear able to treat all but the most mobile pesticides. However, a number of issues remain unanswered, including: 1) selected substances have been shown to persist in the biobed matrix; 2) although a significant proportion of each pesticide applied to the biobed is removed, in some instances concentrations leaching from the biobed may be unacceptable; 3) the long-term operation of the biobed system has not been considered 4) disposal options for exhausted biomix require investigation; and there is a need for the development of an expert system, that uses the information generated to date, to design a biobed on a case-by-case basis. Ideally, these issues should be addressed before the biobed system is employed by farmers across the UK.

Previous laboratory and semi-field experiments (Fogg *et al*., 2003a) have shown that certain persistent active substances and, in particular, some fungicides have the potential to accumulate in a biobed over time. Further laboratory and semi-field studies are therefore required to identify the implications of this on the overall performance of the biobed. Factors to be considered should include: 1) which pesticides or groups of pesticides are likely to accumulate; 2) is there any risk of these substances becoming mobile during the lifetime of the biobed; and 3) when a biobed is dismantled, can the substances be degraded and, if so,

over what time-frame? The use of manipulation methods e.g. addition of appropriate microbial systems to enhance the degradation of these substances could also be explored.

Data suggests that concentrations in leachate of certain highly mobile pesticides (Koc <25) exceed acceptable levels. It is possible that some form of adsorbent could be included within the biobed, thus reducing the concentrations in leachate. Experiments should be performed to assess the feasibility of using such materials in the biobed.

At some stage complete replacement of the biobed matrix is likely to be necessary. The options for disposal of the spent biomix will depend on the amount of pesticide retained within the biobed matrix. Research in Sweden suggests that the biomix can be heaped in the farmyard, and left to compost for approximately 12 months prior to disposal to land. Heaping the biomix above ground on an impermeable surface may result in mobile pesticides leaching from the biomix and possible contamination of adjacent surface waters. In order to prevent this, the Swedish researchers suggest covering the heap to exclude rainfall. However, once covered the biomix is likely to dry out, inhibiting microbial activity and reducing the rate of degradation. The preferred option for the disposal of spent biomix would be a direct application to land. However, the potential impact on soil and water quality must be quantified through the use of a suitable risk assessment techniques.

Disposal options for study could include:

- Storing a covered heap.
- Storing an uncovered heap.
- Storing a covered heap with microbial inocula
- Storing an uncovered heap with microbial inocula
- Actively composted using a range of methodologies
- Direct application to soil at different application rates.

The biobed or other bioremediation system needs to be transferable from one farm to another without any compromise in performance. It is suggested that as part of any self-build guidelines an "Expert System" should be produced that will enable the biobed to be optimised on a site specific basis. The system must be simple to use with the output data easy to interpret. Input data could include:

- x Pesticide usage data
- x Total volume of waste pesticide requiring treatment
- Size of sprayer
- Volume of water used / wash
- Number of washes / year
- x Size of pesticide handling area
- x Annual rainfall
- x Underlying soil type / geology
- x Depth to groundwater

The system would operate using a series of databases containing information on pesticide physico-chemical characteristics, weather, soil type, underlying geology and depth to ground water and operate using a post code system to enable quick and accurate retrieval of the relevant environmental data. It is possible that the 'expert system' could link in with the EMA (Environmental Management for Agriculture) system. The EMA system is based on the principals and philosophy of existing environmental management systems such as ISO 14001 and EMAS. EMA is essentially a technology transfer tool integrating information on best practice, decision support, environmental models and performance assessment routines. The system already contains detailed databases on pesticides and groundwater and it is possible that a bioremediation construction and operation module could be attached. Alternatively a standalone system or a downloadable tool from the web could be produced.

8 Acknowledgements

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Appendix I

Pesticide treatment rates

Results for year 1 of the Cherwell study (Mason *et al*., 1999) were used to establish treatment rates for the biobed experiments to investigate biobed depth and water, loading, the effects of soil type on pesticide leaching and shock water loading experiments. An area of 40 ha was sprayed with isoproturon in one day with tank filling and mixing carried out on four occasions. Results were reported as follows:

	Active substance (g)	Volume (mL)
Split concentrate	0.5	100
Split spray solution	1.25	1000
Split tank rinsate	0.5	1000*
Equipment washings	0.675	150000

* 25 litres of tank rinsate was left in the sprayers sump. The concentration was 470 mg L^{-1}, equivalent to 11.75 g of active substance.

Analysis of pesticide usage data for a number of farmers (1000 – 2000 acre) showed that on average all of the farms isoproturon was applied within 7 days spaying with filling and mixing being carried out on 16 occasions. On this basis results form the Cherwell study were adjusted to calculated realistic worst case application rate.

Split spray concentrate	0.5 g
Split spray solution	1.25 g
	1.75 g

1.75 g / 4 tank filling / mixing procedures = 0.44 g / filling
0.44 g x 16 mixing and fillips = **7.1 g**

The next assumption is that that assuming worst practices the 25 litres remaining in the sump was disposed of in the farm yard at the end of each days spraying.

11.75 g x 7 days = **82.25 g**

It is possible that the spray tank may be washed out a third time in the yard. This could generate up to a further 200 litres of dilute pesticide waste. It is possible that this third rinse could contain isoproturon at concentrations as high as 40 mg L^{-1}. If this third tank rinse was carried out at the end of each days spraying then a further **56 g** of active could be disposed of into the farmyard.

Finally there are the equipment washings. 0.675 g x 7days spraying = **4.7 g**.

The theoretical worst case loading (based on the findings of the Cherwell study, and only for one active substance) to a biobed is **150.05 g**.

If this loading were to be applied the field scale biobed (concrete to biobed) built and being tested as part of the EA project P2-200 titled "Development of a design manual for agriculture pesticide handling and washdown areas" the concentration of isoproturon in the 0-5cm layer would be ~ 150 mg kg^{-1}. In the semi-field scale biobeds used in these experiments the equivalent loading is 298 mg / biobed lysimeter.

"Real world use"

Again based on finding of the Cherwell study (year 1) for 1 days spraying and 4 filling / mixing procedures.

	Active substance (g)	Volume (L)
Split concentrate	0.5	0.1
Split spray solution	1.25	1.0
Split tank rinsate*	11.75	25
Equipment washings	0.675	150
	14.175 g	176.1 litres

*The Crop Protection Association confirmed that it was not an unrealistic scenario to assume that the 25 litres of dilute tank washings would be disposed of into the farm yard at the end of each working day.

Using the concrete to biobed field scale model, 176 litres of dilute pesticide waste and washings disposed of onto a 20 m^2 biobed is equivalent to 8.8 L m^{-2}, or 350 mL on the small scale lysimeters described in section 3.5. The pesticide load of 14g isoproturon is equivalent to 27.8 mg at the semi-field scale. However this only represents 1 days spraying. On average data suggests that up to 7 days spraying would be required to apply all of the isoproturon on a 1000 – 2000 acre farm. Therefore 7 applications of 28 mg (isoproturon) applied in a carrier volume of 350 mL were made.

Appendix II

Interim guidance on agricultural pesticide handling and washdownareas in relation to the protection of controlled waters.(This guidance focuses on biobeds)

This document describes the Agency's approach to the control of pesticide handling and washdown areas in order to prevent pollution of controlled waters and ensure that the provisions of the Groundwater Directive are met.

Summary statements:

1. The Agency considers that, providing they are constructed and operated according to good practice, biobeds for pesticide mixing/handling areas do not require authorisations under the Groundwater Regulations.

2. The Agency may use its discretionary powers under the water legislation to ensure that individual biobeds are operated according to good practice so that there is no discharge of pesticides to the water table.

3. The use of biobeds for pesticide washdown areas is not encouraged. Any discharge to ground from these systems will require an authorisation under the Groundwater Regulations.

Background

Where pesticides are mixed or handled and where sprayers are parked or washed down, there is a risk of loss of the pesticide to the environment. Traditionally, such activities have taken place in the farmyard on impermeable surfaces. The run-off generated from such areas typically drains to ground (for example, via soakaways) or potentially to surface water via drains, posing a risk of pollution of controlled waters. Research has shown that emissions from these activities can be responsible for a significant proportion of the total pesticide loading in surface waters. There are little or no data on the impact on groundwater.

Mixing and handling can result in small spillages or drips of pesticides that may be regarded as unintentional losses. These drips and spills may seem small and insignificant but as they are of pesticide concentrate they can be significant sources of pollution. The pesticide can be adsorbed onto concrete and will leach with rainfall over the following weeks. **Washing down** of equipment can potentially produce a significant volume of pesticide-contaminated liquid, which, if not collected and disposed of appropriately, may discharge to ground or via drains to surface water.

In view of environmental concerns, increasing interest is being expressed in the potential of alternative designs for pesticide handling and washdown areas. In particular, biobeds or soil/grass areas have been the subjects of recent research, as have secondary containment and collection systems for spills.

Biobeds and soil/grass areas are intended to capture and retain drainage and to provide conditions where physical, chemical and/or biological attenuation and breakdown can take place. Sweden has the most experience of biobeds in Europe where they are quite common for pesticide filling and mixing areas in arable areas. They are not used for washdown areas.

UK research has included a project titled, "*Development of a Design Manual for Agricultural Pesticides Handling and Washdown Areas*" (Technical Report P2-200/TR/1 2000). This project was jointly funded by the Environment Agency (EA), the Scotland and Northern Ireland Forum For Environmental Research (SNIFFER), Defra and the Pesticides Safety Directorate (PSD). The original intention of this project was to develop a practical design manual but this has not been considered appropriate until further investigations are undertaken, particularly with respect to potential risks to groundwater.

Description of Biobeds

Typically, a biobed system is an area of ground several square metres in size which has been excavated and the excavation backfilled with the biobed material. The excavation is at least 1.0 metre in thickness and is filled with a mixture by volume of 50% straw, 25% topsoil and 25% peat-free compost, turfed over. In addition there must be at least a further 0.6 metres of soil beneath the 1 metre thick biobed material. A biobed can either be a **direct** (or "driveover") system, where liquids fall directly onto the biobed, or an **indirect** system, where all liquids are intercepted in a buffer tank, and then directed to the biobed (via gravity or a pumped system). Buffer tanks can be installed both on the route into and out of the treatment system, with a view to providing a greater degree of control on the rate of liquid transfer. The drive-over biobed option requires the installation of a metal grid capable of taking the weight of a fully loaded sprayer.

Biobeds can be **lined** or **unlined**. In lined biobeds liquid is collected at the base and must be disposed of appropriately (for example, disposed of under a Groundwater Regulations Authorisation or tankered off-site to an authorised disposal site) or recirculated into the biobed. Providing there is no discharge to ground or surface water from the system, such biobeds do not need an authorisation under existing water protection legislation. In unlined biobeds there is the likelihood of a discharge through the base of the system to ground and therefore the possibility that, depending on the presence and concentrations of listed substances in the discharge, this discharge may need to be authorised under the Groundwater Regulations.

Where suitable soil conditions exist, 'grass areas' may also provide a similar degree of groundwater protection to biobeds. A 'grass area' would need to be covered by permanent grass/vegetation, need a soil depth of at least 1.6 metres, should be free draining and should not contain tile/mole drains or similar. If such conditions are met then 'grass areas' can be considered as unlined biobeds for the purposes of this guidance.

The basic principle of operating a biobed is to contain pesticide losses at source and in a known location. The biobed is intended to retain and promote biodegradation of the pesticides. Whether the biobed can achieve this is dependent on:

- The loading (concentration and volume) of pesticides discharged to the system;
- The capability of the biobed to adsorb the pesticides and provide the conditions necessary to promote biodegradation;
- The volume of other liquid (such as rainfall run-off) discharged to the biobed;
- The continued operation and maintenance of the system according to good practice.

Agency Assessment

The Agency acknowledges that scientific uncertainties exist in relation to the design and operation of biobeds and therefore does not intend to actively promote their uptake. However, the Agency recognises the importance of promoting good practice in the handling of pesticides and in managing pesticide handling and washdown areas.

It is clear from the research undertaken to date that biobeds are several orders of magnitude better at reducing pesticide run-off to surface waters than impermeable surfaces, such as concrete. The risk to groundwater from unlined systems is uncertain.

In view of the above, the Agency intends to consider proposals for biobeds on a case-by-case basis and will not impede their construction where there is an obvious commitment on behalfof the farmer to improve pesticide handling practices.

It is not yet clear how proposals to extend controls over agricultural wastes or the implementation of the Landfill Directive will apply to the use of biobeds. Further guidance on this matter will be issued in due course. For this reason the present document must be regarded as interim guidance.

Biobeds for pesticide mixing and handling

The liquids generated through unintentional spillages during filling, mixing and handling must pass through the system so that pesticides can in principle be retained within the system. Providing that the area of the biobed itself and any associated hardstanding is small (see Annex A*)* and the system is operated according to good practice, research suggests that the discharge of listed substances such as pesticides from the base should be minimal. Interim good practice guidance is given in Annex A of this document. In due course it is possible that a formal Groundwater Regulations Code of Good Practice for pesticide mixing and handling and washdown areas may be developed.

From a regulatory perspective the Agency considers that unlined biobeds for mixing and handling of pesticides are unlikely to give rise to a discharge that would come within the scope of the Groundwater Regulations. The proviso is that the area drained into the biobed is relatively small (see Annex A) and the biobed is operated according to good practice. In such cases an authorisation under the Groundwater Regulations would not be needed. However, should the operation not be conducted to good practice the Agency may serve a notice under the Groundwater Regulations to require changes to the activity to prevent the discharge of listed substances to ground. This could include lining of the biobed or in extreme situations the prohibition of the activity.

If it becomes apparent that the biobed is resulting in a release of listed substances to ground and that this may be permitted (subject to prior investigation to determine the impact on groundwater), then an authorisation under the Groundwater Regulations will be required.

Biobeds for washdown areas

For washdown areas, significant volumes of liquid will be generated which in principle could generate a polluting discharge. Consequently, the Agency considers that biobeds intended to handle washdown waters should be effectively contained (e.g. 'lined') with all effluent collected for subsequent appropriate disposal. This disposal may take the form of application to a disposal area under the terms of an authorisation under the Groundwater Regulations.

Unlined biobeds for washdown areas would not be encouraged at present and would require an authorisation under the Groundwater Regulations, including prior investigation of the site and possibly monitoring of groundwater.

Annex A: Interim good practice for biobed construction

- The biobed should contain a mixture by volume of 50% straw, 25% topsoil and 25% peat-free compost, turfed over. Clay soils should be avoided in the biobed mixture.

- The mix of straw, topsoil and compost should be left for some 6-8 weeks, in order to promote biological action. The mix should then be loaded into an excavated pit, which should be a minimum 1 metre in depth. In addition there should be at least a further 0.6 metres of soil beneath the 1 metre thick biobed material.

- The area of the biobed should be determined on the nature and frequency of pesticide handling activities undertaken on the farm. Above all, it must be large enough to contain all of the liquids, and preferably allow the even distribution (e.g. via a sprinkler system) of these liquids across its surface. As a rule of thumb, the area of the biobed should be approximately two-thirds of the area it is accepting intercepted liquid from.

- Biobeds should also be designed to reduce the entry of clean water as this is likely to impact upon their effectiveness. The mixing and handling area should be kept as small as reasonably practicable so that the volume of run-off to the biobed is minimised. Areas that are not used for pesticide handling etc. should be separated from the area draining to the biobed by shallow ramps/bunds and so that “clean” (pesticide-free) drainage can be directed away from the biobed.

- In the event of lining being required, a type suitable for small reservoirs is recommended. This is likely to be not less than 1.5 mm thick and should be installed over a recommended geotextile mat and/or a 25 mm sand blinding layer.

- Sites for biobeds should be chosen and systems operated so that:

x Drips, spillages and leaks when filling and mixing pesticides are prevented as far as possible;

x Areas of high groundwater vulnerability are avoided;

x Unlined biobeds are located on light or medium loamy soils. There should be at least 0.6 metres soil cover beneath the biobed;

x All drains immediately beneath the biobed are removed;

x Biobeds must be located at least 10 metres from a watercourse or drain and at least 50 metres from any spring, well or borehole;

x Suitable containment measures (e.g. concrete bunds) should be installed to ensure that all spillages and liquids generated are directed to and retained within the biobed; and,

x A contingency plan should be produced to deal with spillages that pose a risk of pollution. Suitable absorbents (e.g. fine sand) should be available on-site to aid any clean-up operation.

 It should be noted that if at any point the grass/vegetation cover on top of the biobed was to die then the biobed should no longer be used and alternative arrangements must be made until the grass/vegetation has been re-established.

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