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

By

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Final Report August 2000

MAFF Project: PLO527 Environment Agency: R&D Technical report P415 DETR: EPG 1/5/104

SSLRC Contracts JF4107V, JF4225E AND JF3740E



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SUMMARY

Pesticide waste and washings should be disposed of in accordance with the Code of Practice for the Safe use of Pesticides on Farms and Holdings (1998) and the Ground water Regulations (1999). Under these Regulations a site authorisation is required for the disposal of pesticides to land. Due to the practicalities associated with the recommended procedures and a lack of awareness of the legislation, many users do not comply with the Code guidelines. An alternative method is therefore required which is easy to use and cheap to run. One possible approach is to use an artificial degradation system such as a biobed.

A biobed is a composted mixture of straw, peat (or peat substitute) and topsoil. Studies in Sweden have demonstrated that biobeds can effectively treat pesticide waste arising from accidental spillages of concentrate and prepared pesticide. In order to be used for UK farming operations a biobed would need to cope with much larger volumes of waste arising from tank and machinery washings in addition to accidental spillages. This study was therefore performed to determine the degradability of a range of pesticides in a biobed under conditions that are likely in the UK. The study involved a combination of laboratory, semi-field and field studies.

Field biobeds were established on three arable farms within the UK. Temperature measurements from within the biobeds indicated a rapid increase in biological activity soon after installation. However, above average rainfall following construction resulted in the biobeds becoming waterlogged. Covers were therefore erected over the biobeds to minimise water inputs. The top 10cm dried rapidly to form an impermeable layer and this combined with an inability for grass cover to establish and higher volumes of waste being generated than anticipated resulted in low evapotranspiration and prolonged waterlogging. The studies demonstrated that water management is a key factor in the successful operation of a biobed and that the design used is probably unsuitable for use on UK farms.

Semi-field studies investigated the degradability and leaching potential of a number of pesticides commonly used in the UK. Studies using closed biobed columns (i.e. columns with an impermeable lining at the base) demonstrated that pesticides readily sorb to the upper layer of the biobed. However, even when covered, the columns quickly became waterlogged below 10cm depth. Whilst pesticide residues were retained in the top 10 cm low moisture content and a decrease in levels of microbial activity in the top 10 cm resulted in slow degradation.

Studies using open biobed columns confirmed that the biomix could retain and subsequently degrade high concentrations of pesticide. Only the most mobile compounds (K_{oc} 16-100) leached and even for these compounds the proportion of applied pesticide that leached was very small. Pesticide leaching

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did increase with water loading but even then <6% of the pesticides applied leached from a column receiving high water loading compared with <0.2% from a column receiving medium loading. The performance of the columns receiving medium water loading was similar to currently available commercial treatment systems such as the Sentinel. Analysis of solid material at the end of one study indicated that a significant proportion of the non-leached pesticide had been degraded.

Degradation in biomix and topsoil of concentrations up to 20 times the maximum field application rate of widely used pesticides was investigated in the laboratory. Generally pesticide degradation was faster in the biomix than in a sandy loam topsoil, the exception being isoproturon at high application rates. This may have been due to microbial adaptation in the soil used to make the biomix following previous treatments with isoproturon in the field. Combinations of isoproturon and chlorothalonil had no effect on degradation rates of either pesticide in biomix whereas in topsoil DT50 values for isoproturon in the presence of chlorothalonil increased from 17.4 days to >97 days. Experiments investigating the effect of up to 6 pesticides in combination on degradation rates are continuing as are repeat application experiments to determine whether the biobed microbial community will adapt to repeated treatments of pesticides resulting in enhanced biogegradation.

Studies to date have therefore demonstrated that a biobed can treat high concentrations of pesticide. Even at high water loadings, the amount of pesticide released from the system will be less than 0.2 %. Mixture studies indicate that the performance of the biobed is not as sensitive to pesticide mixtures as soil. Field and semi-field studies indicate that water input to the biobed has to be managed and that of the two simple systems investigated to date an open system is the most appropriate. Very high temperatures were measured in the field biobeds, however these could not be maintained in the laboratory or semi-field studies. It is therefore likely that degradation and hence removal in a full scale working system will be even greater than observed in the laboratory and semi-field studies.

ACKNOWLEDGEMENTS

The authors acknowledge the support of the funding organisations and analytical laboratories listed below:

Department of the Environment, Transport and the Regions

Environment Agency

Ministry of Agriculture Fisheries and Food

Crop Protection Association (formally British Agrochemical Association)

Monsanto

Aventis (formally Rhône-Poulenc Agriculture Ltd)

Opinions expressed within this report are those of the authors and do not necessarily reflect the opinion of the sponsoring organisations. No comment within this report should be taken as an endorsement or criticism of any herbicide compound or product.

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1 INTRODUCTION

Pesticides play an important role in the success of modern farming and food production. When used according to the label instructions and with appropriate precautions, pesticides present a minimal risk to the environment. The Food and Environment Protection Act 1985 (FEPA) places a special obligation on users "to safeguard the environment and in particular avoid the pollution of water" and under the Water Resources Act 1991, it is an offence to cause or knowingly permit a discharge of poisonous, noxious or polluting matter into any controlled waters without the proper authority. More recently the European Directive on Groundwater (80/68/EEC) has specified specific measures to protect ground water from, chemicals which should be either prevented (List I) from entering groundwater or those for releases to groundwater should be minimised (List II). Pesticides are classified as either List I or List II substances. The Code of Practice for the Safe use of Pesticides on Farms and Holdings 1998 forms Part III of the Food and Environment Protection Act 1985 (FEPA) and the Health and Safety at Work Act 1974 (HWSA). The Code of Practice provides practical guidance to farmers and growers engaged in commercial crop production in Great Britain.

There are a number of potential sources of pesticide waste, these include:

- pesticide spillages resulting from the filling operation;
- unused pesticide in the tank, pump and booms (Harris et al., 1991);
- tank washings resulting from the need to clean the sprayer when moving to a new product; and
- washings resulting from the external cleaning of spray equipment.

The Code of Practice recommends that all filling, washing and disposal activities should be performed on an area so that accidental spillage's and waste cannot escape from the area and contaminate either soils, surface waters or ground waters. Any dilute pesticide should be disposed of in an environmentally acceptable manner and in accordance with the Groundwater Regulations. A number of approaches are approved, these include:

- application of the waste to untreated or under-dosed parts of the field;
- storage of the waste pending collection by a licensed disposal contractor;
- use of equipment to treat the waste; and
- with appropriate Environment Agency approval application to an area of uncropped land that is not stubble or fallow and which has minimal wildlife value and minimal risk to Groundwater.

These disposal methods can be either costly or time consuming. For example, even when self-flushing systems are fitted to a sprayer, enabling the tank washings to be sprayed out onto the intended target, availability of clean water often means that the second and third washings involve a return to the farmyard. Collection of pesticide waste for disposal is extremely costly. Currently available treatment systems, such as the Sentinel system can remove more than 99.9% of the pesticide waste, however they are expensive to install and have high operating costs often resulting in the illegal disposal of waste pesticide and washings in the farmyard.

Recent research suggests that some of the monitored contamination of surface waters by pesticides results from inputs from the farmyard rather than from treated land (Mason *et al* 1999). Work in one catchment suggests that as much as 40% of isoproturon pollution can be attributed to farmyard activities (Carter 2000). These localised contamination incidents may cause undesirable toxicological effects on non-target organisms as well as potentially contributing to pesticides levels of greater than $0.1 \mu g L^{-1}$ in surface water. Alternative treatment methodologies are therefore required to reduce these localised contamination incidents. These methodologies need to be cheap to use and require low labour and time inputs.

Biobeds may offer a cost-effective, low maintenance alternative to current treatment methodologies. A biobed, which is a composted mixture of straw, peat substitute and topsoil, readily sorbs pesticide whilst maintaining bioavailabiliity and optimising microbial breakdown (Torstennson and Castillo, 1996). The technology has been successfully applied in Sweden to retain accidental spills associated with filling sprayers. The Swedish system comprises an unlined hole filled with volumetric proportions of straw, topsoil and peat mould (50:25:25%) with grass either laid or sown on the surface. A frame is constructed over the bed to enable the sprayer to be parked on top of the biobed whilst being filled. The size of the biobed is dependent on the intensity of spraying activity and also on the size of the application equipment. Monitoring of the biobeds indicated that degradation of all 40 pesticides monitored was achieved.

Whilst the Swedish system can treat accidental spillages of low volumes of pesticide the design is probably not suitable for disposal of tank washings due to the large volumes of relatively low concentration waste that could be generated. An alternative design is therefore required if biobeds are to be used as a treatment method on UK farms. The Soil Survey and Land Research Centre were therefore commissioned by a consortium comprising Aventis, the Crop Protection Association, the Department of Environment Transport and the Regions, the Environment Agency, the Ministry of Agriculture Fisheries and Food and Monsanto to perform a study involving the development of biobeds for use on farms in the UK. The specific objectives of the study were to:

- 1. establish three trial biobeds on high profile, commercially significant farms where the pesticide use pattern is in line with normal agricultural practices;
- 2. to monitor the performance of the biobeds under representative use conditions
- 3. to investigate factors and processes controlling the overall dynamics of pesticides in the biobed system in order to ensure long-term viability
- 4. to develop a biobed construction and management strategy
- 5. to perform cost benefit analyses of the biobed system relative to other disposal options
- 6. to maintain communication with interested parties on research progress and future applicability

This report describes the results of the study. In Chapter 2, the results of the field-scale studies are described. Chapters 3 and 4 detail studies performed at the semi-field scale into the leaching behaviour and degradability of a range of pesticides in biobeds under natural conditions. Chapter 5, describes laboratory studies into the degradation of a range of pesticides and the effects of mixtures on biobed performance. The results are summarised in Chapter 6 and recommendations provided for future work.

2 FIELD STUDIES

2.1 Introduction

A full-scale biobed was established on each of three UK farms in October, 1998 (Table 1). The farms chosen were high profile to facilitate technology transfer. The biobeds were established adjacent to the concrete washing area at each farm, the washing areas draining to one point with the resulting waste being pumped onto the biobed.

Location	Area/Type	Other information
Yokefleet Farms Ltd, East	490 ha, arable	LEAF demonstration farm
Yorkshire		
Morley Research Centre,	360 ha, arable	Farmer members and LEAF
Norwich		farm
Velcourt Farms Ltd, Suffolk	462 ha, arable	Velcourt farms have 42500 ha
		in UK

Table 1 Locations of field biobeds and characteristics of the farms

2.2 Materials and methods

2.2.1 Development and construction of field biobed design

The field biobeds were designed to treat waste arising from a typical arable farm scenario. The volume of dilute pesticide waste and washings generated is primarily dependent on the number of times in a given season the spray application equipment is cleaned and the volume of water used to clean the equipment. It was assumed that a sprayer, of 2000 L capacity, is typically cleaned 20 times a year. The first tank washings being sprayed out in the field and the 2nd and 3rd tank washing disposed of on the biobed. Assuming that 10% of the sprayer's capacity was used for each wash the total volume of waste generated was calculated to be 8000 L.

Holes (1.5 m deep x 39 m²) were excavated using a mechanical digger and lined with sand followed by a geotextile membrane and a waterproof liner (Plate 1). A 40cm layer of sand was then placed in the bottom of each pit to act as a sump followed by 42 m^3 of biomix consisting of 50% straw, 25%

topsoil and 25% peat substitute. The biobed surface was then seeded with grass. An access tube was installed into the centre of each biobed to enable the water table depth to be measured and water pumped out if necessary. The biobeds were instrumented with suction samplers at 3 different depths (25 cm, 50 cm, 100 cm). Temperature probes and equitensiometers were installed to allow the measurement of temperature and pore water pressures at different depths. Water meters were installed to measure the volume of liquid pumped onto the biobed. Initially the biobeds were to be uncovered however the initial theoretical water balance calculations for the uncovered design underestimated the volume of water intercepted by the biobed resulting in the need for a covered design. Covers were therefore placed over the biobeds 107 to 166 days after construction.

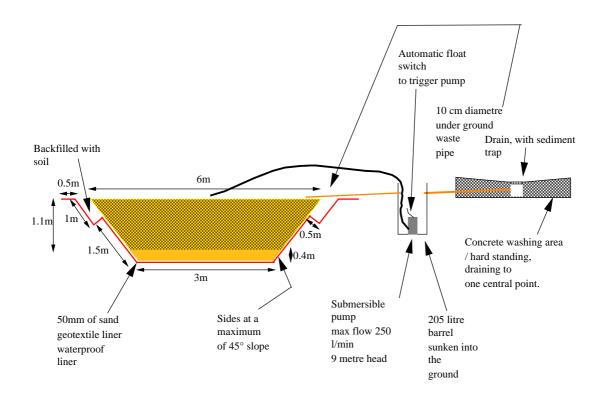


Figure 1 Field biobed design



Plate 1 Field biobed under construction

2.2.2 Treatment

Operation of the biobeds was unrestricted with the volumes of waste and active substances applied being controlled by the farms. All pesticide waste and washings were deposited onto the disposal area and then pumped onto the biobed. After, each disposal, cumulative rainfall of 10 mm was intercepted and directed into the biobed. Any further rainfall was then diverted to surface water drains. Generally, no pesticides were applied to the biobeds until the covers were in place.

2.2.3 Sampling

Samples of each biobed were collected (16 - 45 days) following construction for determination of microbial biomass.

2.3 Results

2.3.1 Water balance and temperature

A derived water retention value for the biomix of 9010 L at 5 kPa was calculated with a theoretical evapotranspiration value from the bed of approximately 19500 L. With the biobeds covered and the biobeds managed as described, theoretical annual water balance ranged from -7710 to -3650 L (Table 2). No allowance for the initial moisture status of the construction materials was made which would approximately cancel out the calculated negative balance (Table 2).

	Velcourt Farms	Morley research	Yokefleet farms
	Ltd	Centre	Ltd
Area of biobed m ²	39	39	39
Disposal area m ²	79.9	84.3	64.0
Average annual rainfall (mm)	592	636	667
Pesticide waste (litres)	8000	8000	8000
Evapotranspiration (litres)	19500	19500	19500
Inputs from disposal area (litres)			
10mm rainfall after disposal	15972	16860	12800
Biomix retention at 5 kPa (litres	9010	9010	9010
Water balance (litres)	-4538	-3650	-7710

Table 2 Theoretical water balance for field biobeds

Initial rainfall at each site, prior to addition of covers to the biobeds, was 21 - 60% above the annual average for each site (Table 3). This high rainfall resulted in the field capacity of the biomix being exceeded in all three biobeds (e.g. Figure 2). After this time the biobeds remained water logged.

Significant increases in temperature were observed in all field biobeds 7-10 days after being established (Morley 55°C, Yokefleet, 48°C and Velcourt 25°C (e.g. Figure 3). This temperature drop coincided with water logging in each of the biobeds.

Total biomass in the samples of the biobed material was generally higher than total biomass measurements for soil (Figure 4). Microbial activity of the biobeds appeared to be dependent on the activity of the soil used to construct the biobed, i.e. highest biomass levels were observed in the biobed constructed using the most microbially active soil. Change in total biomass with time was not measured due to the overriding effect caused by the saturated conditions observed soon after construction.

Table 3 Measured and average rainfall at each of the study sites, for the period November 1998 to
January 1999

Site	Actual rainfall (mm)	Average rainfall	% of average rainfall	
		(mm)		
Morley research centre	294	184	160	
Velcourt	224.8	166	135	
Yokefleet	257.4	213	121	

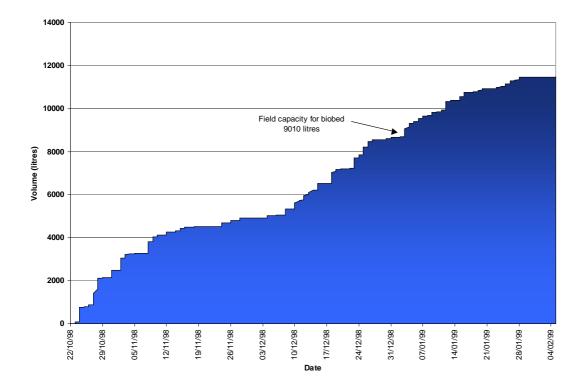


Figure 2 Volume of water intercepted by the Morley biobed prior to being covered

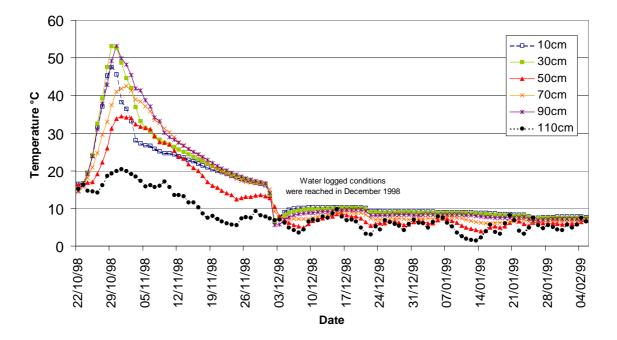


Figure 3 Average temperatures recorded at different depths in the biobeds situated at Morley

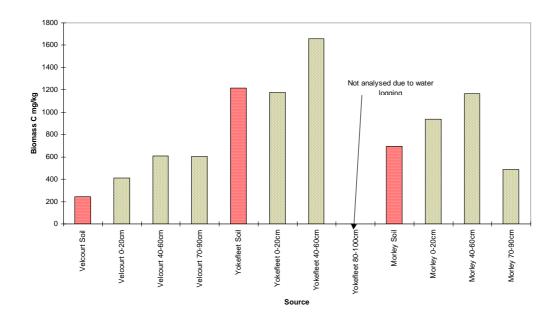


Figure 4 Total biomass measured in samples taken from the three biobeds as well as the soil component of the biomix, 16 - 45 days after construction

2.3.2 Pesticide waste application to field biobeds

Data was provided on the volumes of pesticide disposed of onto the biobeds at the Yokefleet and Velcourt study sites (Table 4). Between March and June 1999, a total of 1650 l of waste was disposed of onto the Yokefleet biobed and 2900 l to the Velcourt biobed. A total of 24 active substances were contained in the waste at the Yokefleet site and 10 in the waste at the Velcourt site. Whilst actual data was not supplied for the Morley site, records were available for disposal over the previous year and these indicated that greater than 90,000 l of waste was disposed of.

Product	Active substance	Sprayer type	Total volume (I)
Yokefleet site			
Topik	clodinafop-propargyl	Direct injection	60
Chlormequat	chlormequat	Direct injection	150
Folicur	tebuconazole	Direct injection	30
Reflex	fomesafen + terbutryn	Direct injection	60
Landmark	epoxiconazole +kresoxim-methyl	Direct injection	30
Opus	epoxiconazole	Direct injection	90
CMPP	mecoprop	Direct injection	60
Ally	metsulfuron-methyl	Direct injection	180
Moddus	trinexapac-ethyl	Direct injection	30
Oxytril	bromoxynil + ioxynil	Direct injection	30
Compass	iprodione + thiophanate-methyl	Direct injection	30
Falcon	propaquizafop	Direct injection	30
Debut	triflusulfuron-methyl	Direct injection	120
Venzar	lenacil	Direct injection	60
Adsi oil	-	Direct injection	60
PDQ	diquat + paraquat	Direct injection	70
Retain	adjuvant	Direct injection	30
Grasp	tralkoxydim	Direct injection	30
Starane	fluroxypyr	Direct injection	60
Terpal	2-chloroethylphosphonic acid +	Direct injection	60
	mepiquat chloride		
Amistar	azoxystrobin	Direct injection	30
Shield	-	Direct injection	30
Nortron	ethofumesate	Direct injection	30
Betanal	phenmedipham	Direct injection	60
Magnum	chloridazon + lenacil	Direct injection	30
General sprayer			
wash		Direct injection	200
		TOTAL	1650
Velcourt farm			
PDQ	diquat + paraquat	Bulk mix	400
Herbicides (4)		Bulk mix	600
Totril ioxynil		Bulk mix	100
Falcon	propaquizafop	Bulk mix	300
Nortron + Betanal E	ethofumesate + phenmedipham	Bulk mix	300
Betosip combi	ethofumesate + phenmedipham	Bulk mix	400
Laser	cycloxydim	Bulk mix	300
Thiovit	Sulfur	Bulk mix	200
Dosaflo	metoxuron	Bulk mix	300
		TOTAL	2900

Table 4 Tank washings disposed of onto the field biobeds at the Velcourt and Yokefleet sites

Pesticide disposed March to June 1999

2.4 Summary and Conclusions

Biobeds have been established on three high profile farms in the UK. Shortly after construction, the temperature of all biobeds rapidly increased indicating high levels of biological activity. These results were supported by a limited number of biomass measurements that indicated that the microbial activity of the biobed mixture is generally higher than observed in soil. The microbial activity of the soil used in the biobed construction appeared to effect the activity of the biobed.

Two to three months after construction, all of the biobeds became waterlogged.

Covers were therefore erected to minimise the amounts of clean rainwater entering the biobeds and the excess water in the biobeds was pumped out. However the water content of the biobed remained very high, the water level being only a few centimetres below the surface of the biobed for much of the monitoring period.

Once covered, the surface (0-10cm) of the biobed dried rapidly producing a hard layer that restricted both evaporation of water from the biobed and growth of the shallow rooting grass. The current design therefore appears to be unable to receive the quantities of liquid that are likely to be discharged from a farm.

The field studies did however yield some useful information:

- 1) in order to successfully treat pesticide waste and washings, water management will be crucial to prevent a) waterlogging and b) formation of a surface crust that limits evapotranspiration;
- after construction, the temperature of the biobed rapidly rises, if these temperatures can be maintained then it is likely that degradation rates in the biobed will be more rapid than corresponding rates in soil;
- the volume of tank washings that will need to be treated by the biobed will typically range from 1650 to 2900 L during a spraying period with the total volume of waste generated on a large farm potentially exceeding 90,000 L;
- 4) typically, up to 25 active substances may need to be treated;
- 5) the microbial activity of a field biobed appears to be dependent on the activity of the soil used in the construction of the biobed.

In order to keep the volumes of waste entering the biobed to a minimum the field biobeds were operated so that such that after each disposal event only 10mm of cumulative rainfall was intercepted and directed onto the biobed. Results from a monitoring study in the Cherwell catchment (Mason et al 1999) suggest that a significant proportion of a spill is retained on the farmyard surface and released over a prolonged period of time. Biobeds may therefore need to treat all waste water draining from the disposal site.

3 SEMI-FIELD STUDIES 1: LINED SYSTEMS

3.1 Introduction

The nature and size of the biobeds used in the field investigations meant that inputs to the systems could not be controlled and hence the generation of information on the degradation of the pesticides released to the biobeds would be problematic. Semi-field investigations were therefore performed using small scale biobeds. The objectives of these studies were to:

- 1. measure the dissipation of commonly used pesticides in a biobed under natural conditions; and
- 2. assess the movement of pesticides through the biobed system

3.2 Materials and methods

3.2.1 Study compounds

The degradability in biobed material of a range of pesticides was investigated. The pesticides, had a range of properties (Table 5) and were those that would normally be applied to a winter cereal crop. Pesticides were applied as product formulations each containing the active substance under investigation.

Active	Koc	DT50	Product	Concentration	Application	Application
substance		(d)		of active	rate (l/ha)	volume (l/ha)
				substance (g/l)		
Isoproturon	100	25	Alpha	500	5	200
			Isoproturon			
			500			
Pendimethalin	5000	90	Stomp	400	5	200
			400 SC			
			100.20			
Chlorpyrifos	6000	30	Dursban 4	480	1.5	200
emorpymos	0000	50	Dursoun 4	-00	1.5	200
Chlorthalonil	1400	30	Cronsord	500	3	220
Chlorulaionn	1400	30	Cropgard	300	3	220
			- 10			
Dimethoate	16-51	7-16	Rogor 40	400	0.85	220
epoxiconazole	957-	60-	Opus	125	1	200
	2647	90				

Table 5 Properties and field application information for each of the study compounds.

 K_{oc} and DT_{50} values taken from Wauchop et al (1992) and Tomiln (1997)

3.2.2 Test system

Forty five cores were prepared using underground piping (20 cm diameter x 75 cm length) with one end of the cut pipe sealed using a socket. A 15 cm layer of washed sand was placed in the base of each core followed by a 50 cm layer of biobed mix (i.e. 25% topsoil, 25% Levington Peat Free Universal and 50% chopped straw).

Forty of the prepared cores were placed, in 5 groups of 8, into the ground at Horticulture Research International (HRI) Wellesbourne (Plate 2). A further three cores, containing tensiometers, were also placed into the ground. The remaining cores were used as pre-treatment controls.



Plate 2 Semi-field residue experiment

3.2.3 Treatment

Pesticide mixtures were applied to four groups of cores, the remaining group was left untreated and acted as a control. Treated cores received applications of a mixture of isoproturon, pendimethalin and chlorpyrifos in December 1998 and January 1999; and chlorthalonil, epoxiconazole and dimethoate in April 1999, and June 1999. Application rates (Table 6) were based on theoretical worst case disposal rates (i.e. 2 applications of 100 litres of full strength dilute pesticide).

Active substance	Application rate (mg/kg)	Total quantity of active	
		applied (mg)	
Isoproturon	77.4	1114	
Pendimethalin	55.6	800	
Chlorpyrifos	40.5	583	
Chlorothalonil	45.3	653	
Epoxiconazole	5.3	76	
Dimethoate	16.9	244	

Table 6	Application	rates of the study	compounds to	semi-field d	egradation experiment
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Following the first herbicide application all of the columns were covered to exclude rainfall. Artificial irrigation was then applied in February, May, July, August and September 1999 at a rate of 10 mm equivalent rainfall to simulate the 10 mm of rainfall allowed to enter the field biobeds from the concrete wash down areas.

3.2.4 Sampling

The 2 pre-treatment control cores were taken and sectioned into 3 approximately equal sections. Subsamples were obtained from each section for total microbial biomass determination.

Cores were collected from the treated and untreated groups on 8 occasions over a 12 month period (Table 7).

Time point	Days after	Days after	Days after	Days after
	Application 1	Application 2	Application 3	Application 4
T=0	1			
T=1	36			
T=2	105	68		
T=3	123	86	1	
T=4	165	128	43	
T=5	260	223	138	89
T=6	322	285	200	151
T=7	365	328	343	194
T=8				

 Table 7 Sampling time points for treated and untreated cores.

Applications 1 and 2 (isoproturon, pendimethalin and chlorpyrifos)

Applications 3 and 4 (chlorothalonil, epoxiconazole and dimethoate).

On each sampling occasion, 3 treated cores and one untreated core were removed. The cores were sectioned into 5 sections (0-5 cm, 5-10 cm, 10-20 cm, 20-30 cm and 30-50 cm). With the exception of the samples taken at T=0 and T=3, samples were sub-sampled (0-10, 10-30 and 30-50 cm) for biomass and moisture content determinations. Sections down to 20 cm depth were homogenised in a food processor and stored at -20° C prior to chemical analysis.

A complete weather station was located next to the lysimeter station at Horticulture Research International (Wellesbourne). Data, including temperature, rainfall, wind direction, wind speed and soil temperature, was recorded at daily resolution.

3.2.5 Analysis

Methods of analysis are given in Appendix A.

3.3 Results

3.3.1 Rainfall and moisture content

Following construction, 156 mm of rainfall was intercepted by each core. An additional 1.5 L of water was applied to each core by irrigation. Sixty two days after construction, covers were placed over the cores to exclude water inputs from further rainfall.

The measured maximum water holding capacity for the Biomix material was 127%. Moisture content in the top 10 cm remained static (average 52%) throughout the study period. Moisture content in the deeper layers in the closed system increased over the study period and saturated conditions were observed below 10 cm by the end of the study (Figure 5).

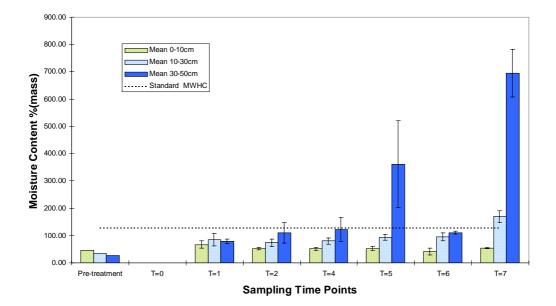


Figure 5 Measured water content within the biobed cores

3.3.2 Microbiological activity

Total biomass in the untreated and treated sealed columns ranged from 141 to 3164 mg kg⁻¹ carbon. Despite considerable variation in measurements in the upper section, biomass in the treated cores columns declined over the study, whereas the biomass measurements in the untreated cores remained constant (Figure 6).

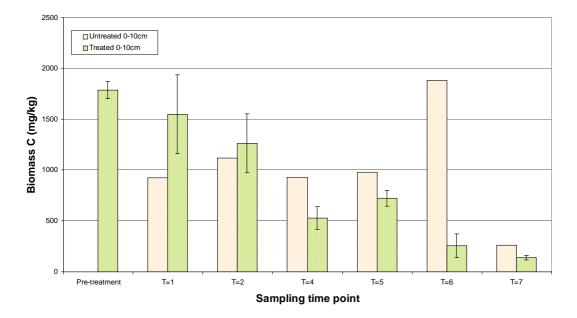


Figure 6 Mean biomass in the 0-10 cm layer of the closed biobed columns

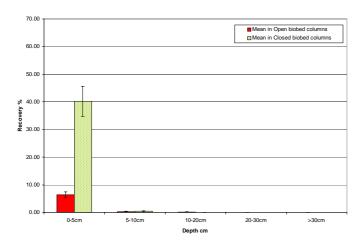
3.3.3 Residues in the closed biobeds

At the end of the study, highest concentrations of pesticide were measured in the 0-5cm layer. Concentrations in the deeper layers were significantly lower indicating little downward movement of the study compounds (Figure 7 and Figure 8). With the exception of chlorothalonil and epoxiconazole, total amounts of pesticide declined throughout the study (Table 8)

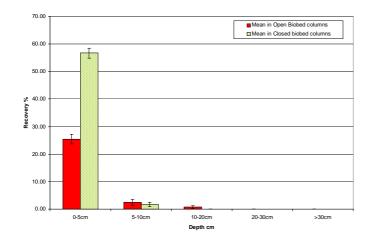
Time	Isoproturon	Pendimethalin	Chlorpyrifos	Chlorothalonil	Epoxiconazole	Dimethoate
T=0	81	81	58			
T=1	81	87	66			
T=2	72	82	62			
T=3	43.	40	22	41	52	65
T=4	31	47	25	53	40	41
T=5	40	57	20	63	42	25
T=6	59	81	31	119	74	23
T=7	48	52	22	50	51	18

 Table 8 Amounts (expressed as a % of the applied) of isoproturon, pendimethalin, chlorpyrifos,

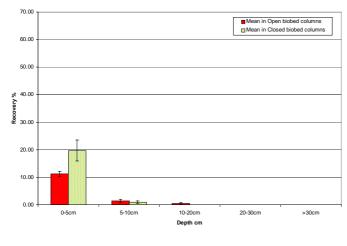
 chlorothalonil, epoxiconazole and dimethoate determined at each sampling time point



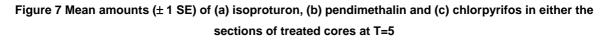


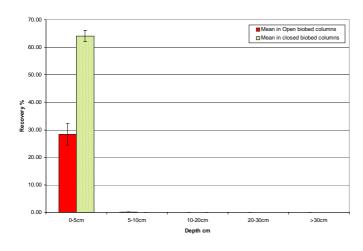




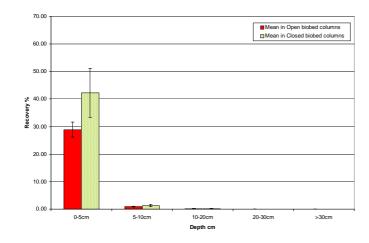


(c)

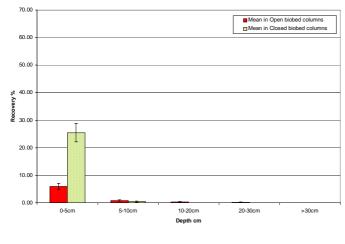












(c)

Figure 8 Mean amounts (\pm 1 SE) of (a) chlorothalonil, (b) epoxiconazole and (c) dimethoate in sections of treated cores at T=5

3.4 Summary and Conclusions

Studies using lined cores demonstrated that pesticides, with a range of properties, accumulate in the upper layer of the cores. With the exception of chlorothalonil and epoxiconazole, the pesticides degraded in the system.

Monitoring of moisture content quickly indicated that the lined cores needed to be covered in order to prevent water logging. Once covered the surface layer 0-10 cm rapidly dried forming an impermeable layer which restricted rates of evaporation. This resulted in saturated conditions below 10 cm depth within 12 months of construction.

Once the cores were covered, an impermeable layer formed preventing evaporation of water. If the system could be uncovered and unlined, it is unlikely that this layer would be formed and hence the performance of the system could be enhanced.

The drying out of the 0-10 cm was also associated with a decrease in microbial biomass in the treated cores. However, no decrease was observed in the untreated columns (Figure 6) indicating that the retained pesticide residues may have an inhibitory effect on the biomix microbial community.

4 SEMI-FIELD STUDIES 2: UNLINED SYSTEMS

4.1 Introduction

Studies using lined cores demonstrated that pesticides are likely to be retained in the upper layer of a biobed system and will degrade over time. However, the development of an impermeable layer on the top of the cores meant that the cores became waterlogged. Therefore, further studies were performed to assess the feasibility of using an uncovered and unlined biobed system for the treatment of pesticide waste. The objectives of these studies were to:

- 1. determine the leaching potential of a range of pesticides from a biobed and to compare this with soil
- 2. measure the dissipation of pesticides applied to an unlined biobed system
- 3. determine the effects of water loading on the leaching, from a biobed, of a range of commonly used pesticides

4.2 Materials and Methods

Two sets of four cores were prepared containing either biomix or topsoil. The cores were constructed in plastic tubing and contained a 2-3 cm layer of course gravel followed by a layer of nylon voile, a 15 cm layer of sand and a 50 cm layer of either biomix or topsoil. All cores were sited in the lysimeter facility at the Horticulture Research International Wellesbourne (Plate 3). The base of each core drained via teflon tubing into 2.5 L amber glass collection vessels.

4.2.1 Leaching studies

4.2.1.1 Treatment

Three of the biomix filled cores and 3 of the topsoil filled cores were treated with the study pesticides. The remaining cores acted as untreated controls. Isoproturon, pendimethalin and chlorpyrifos were applied to the cores in December 1998 and January 1999; and chlorothalonil, epoxiconazole and dimethoate were applied in April and June 1999. A bromide tracer was also applied in December 1998 at a rate of 222 kg ha⁻¹ (628 mg core⁻¹). The application rates were the same as used in the lined columns (Table 6).



Plate 3 Year 1 lysimeter cores at Horticulture Research International

4.2.1.2 Sampling

Collection vessels were monitored after all rainfall events and the total volume of leachate recorded. If the volume exceeded 500 mL, the sample was taken and stored between 0 and 10°C prior to analysis. Where possible, a 60 ml sub-sample was also taken for bromide analysis.

At the end of the study (i.e. 217 days after the last application of isoproturon, pendimethalin and 83 days after application of chlorothalonil, epoxiconazole and dimethoate) all cores were removed and sectioned (i.e. 0-5, 5-10, 10-20, 20-30 and >30 cm). Sections were macerated and then stored at -20° C prior to analysis.

4.2.2 Effects of water loading

The effects of water loading on pesticide leaching behaviour were also investigated. Twelve cores containing biomix were prepared. The cores were constructed using plastic tubing and consisted of a

50 cm layer of composted biomix on a 5 cm layer of course gravel. The cores were sited at the HRI lysimeter station and drained into 2.5 L amber glass collection vessels.

Three water loading scenarios were investigated (Table 9). Four cores were connected using plastic guttering to 0.54 m^2 concrete slabs (Scenario 1). A further four cores were connected to 0.135 m^2 concrete slabs (Scenario 2). The remaining cores received only direct inputs of rainfall (Scenario 3). Silicon sealant was placed on three sides of each slab to prevent water loss (Plate 4).

Scenario	Water inputs	Surface area ratio (yard : biobed)	Biobed size
1	Rainfall to approximately a 20 m x 20 m washing area + direct rainfall inputs	19:1 (high)	7.5 m ³
2	Rainfall to approximately a 10 m x 10 m washing area + direct rainfall inputs	5:1 (medium)	7.5 m ³
3	Direct rainfall inputs	no additional loading	7.5 m^3

Table 9 Water loading scenarios used in the semi-field studies



Plate 4 water loading experiment at Horticulture Research International

4.2.2.1 Treatment

Isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate were applied to cores in January 2000. Application rates were based on concentrations of pesticide measured in a second tank washings (Fogg 1999) (Table 10). Three of the four replicates received pesticide and the remaining core in each set acted as a control. A bromide tracer was also applied at a rate of 100 kg ha⁻¹ (314mg core⁻¹).

Pesticide	Amount (mg)	Concentration (mg/kg)
Isoproturon	255	150
Pendimethalin	204	120
Chlorpyrifos	73.4	43.2
Chlorothalonil	153	90
Epoxiconazole	51	30
Dimethoate	34.7	20.4

Table 10 Application details for water loading studies

4.2.2.2 Sampling

Collection vessels were observed after all rainfall events and the total volume of leachate recorded. If the volume exceeded 200 mL, then the collected sample was removed and taken for analysis. Where available, a 60 mL sub-sample was also taken for bromide analysis. All samples were frozen prior to analysis.

4.2.3 Analysis

Methods of analysis are given in Appendix A.

4.3 Results

4.3.1 Leaching from topsoil vs biomix

4.3.1.1 Rainfall and leachate volume

Topsoil and biomix lysimeter cores received above average rainfall and 13 samples of leachate were obtained (Figure 9).

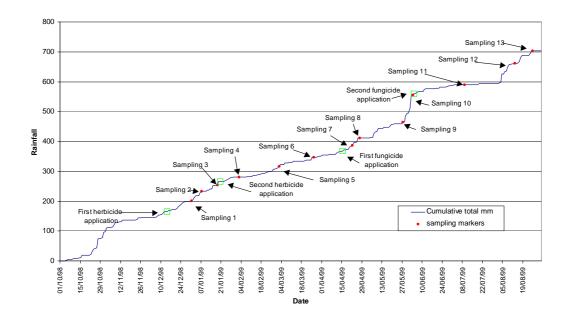


Figure 9 Cumulative rainfall at the Horticulture Research International lysimeter station measured over the duration of the study

Cumulative leachate volumes from both biomix and topsoil were similar, (Figure 10) with approximately 10 litres (353 mm equivalent rainfall) of leachate being collected from the treated replicates. The exception to this was core B3 (biomix treated replicate 3) which produced around 2 litres of leachate, probably a result of leaking around the base of the lysimeter.

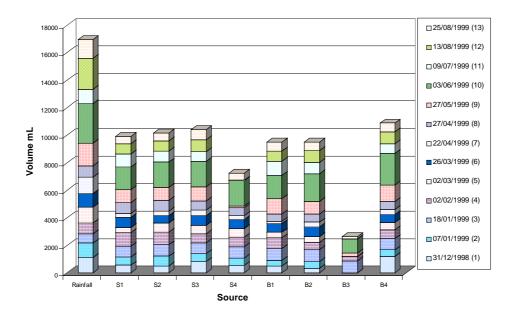
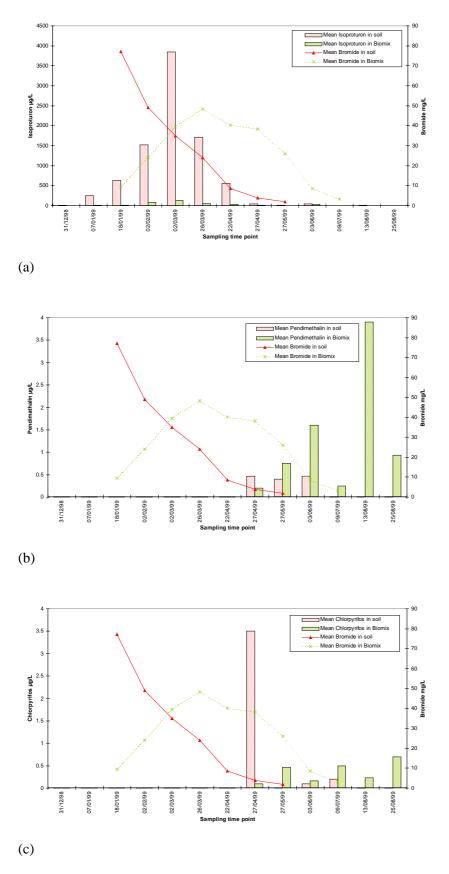
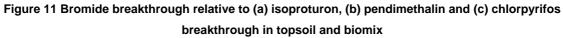


Figure 10 Leachate volumes measured in soil cores (S1 - S4) and biobed cores (B1 - B4)

4.3.1.2 Bromide concentrations

Very rapid breakthrough of bromide was observed for the topsoil with highest concentrations observed on 18 January 1999, 35 days after treatment (DAT) (Figure 11). Movement through the biomix was slower, with maximum concentrations not being observed until 26 March 1999, 102 DAT.





4.3.1.3 Residues in leachate

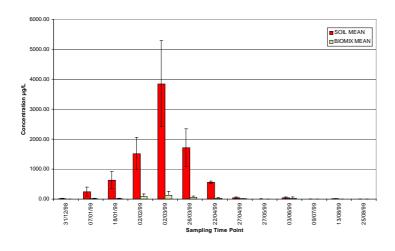
With the exception of pendimethalin, concentrations of pesticide in leachate from the biomix lysimeters were significantly lower than in leachate from the soil lysimeters (Figure 12 and Figure 13). Considering the physico-chemical properties of pendimethalin (k_{oc} 5000, solubility 0.3 mg L⁻¹) the results were unexpected and without further experimental work cannot be confirmed. Peak concentrations of active ingredient in leachate from the biomix cores ranged from 0.15µg L⁻¹ (epoxiconazole) to 127 µg L⁻¹ (isoproturon) whereas concentrations in leachate from the topsoil cores ranged from 0.47µg L⁻¹ (pendimethalin) to 3845µg L⁻¹ (isoproturon).

Isoproturon, chlorpyrifos and pendimethalin were first measured in samples taken on 31 December 1998 (17 DAT) and maximum concentrations of pesticide in leachate from both substrates were observed in samples taken on 02 March 1999 (50 DAT application 1, 13 DAT application 2). Concentrations had dropped below $1\mu g L^{-1}$ by the end of the study (254 DAT).

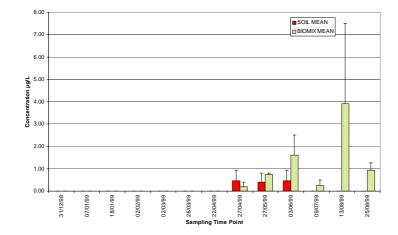
Maximum concentrations of chlorothalonil, epoxiconazole and dimethoate were measured in soil leachate obtained on the 13 August 1999 (119 DAT). After this time, concentrations of all three pesticides dropped. Dimethoate and chlorothalonil were detected in biomix leachate but were at or close to the limit of detection by 25 August 1999, 131 days after the first spring application.

4.3.1.4 Residues in biomix

With the exception of dimethoate in soil, no pesticide was detected below 30 cm depth (Figure 14 and Figure 15), the majority being retained in the top 10cm. By the end of the study between 7% (isoproturon) and 30% (epoxiconazole) remained in the biomix.



(a)



(b)

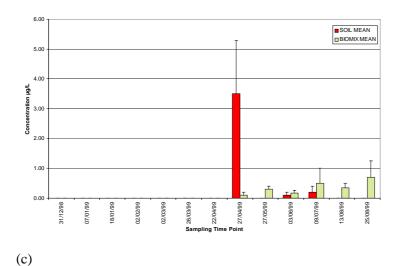
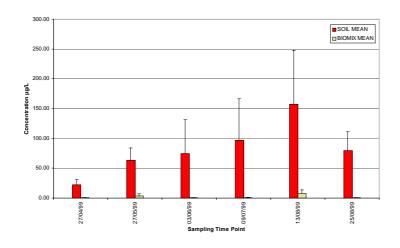
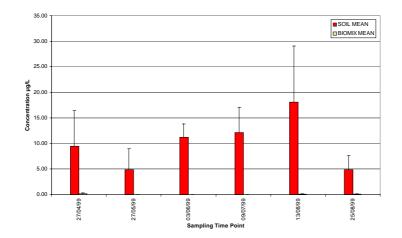


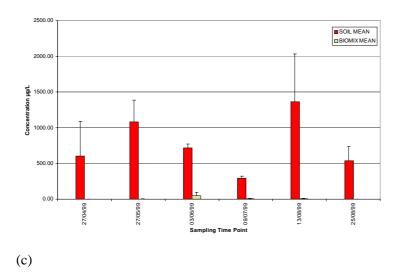
Figure 12 Mean concentrations (\pm 1 SE) of (a)isoproturon, (b) pendimethalin and (c) chlorpyrifos in leachate from topsoil and biomix cores

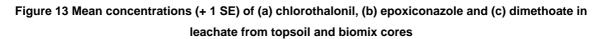


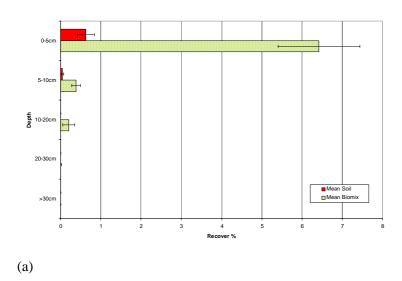


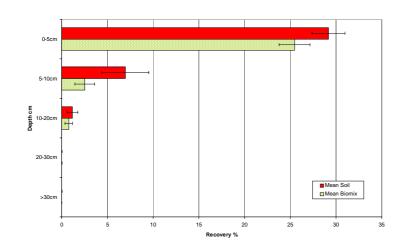












(b)

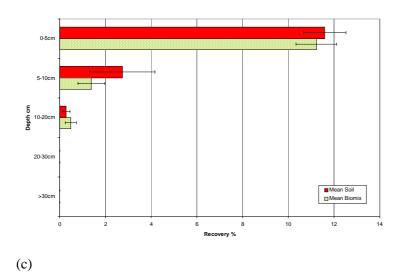


Figure 14 Mean amounts(± 1 SE) of (a) isoproturon, (b) pendimethalin and (c) chlorpyrifos in sections of the treated open lysimeter columns

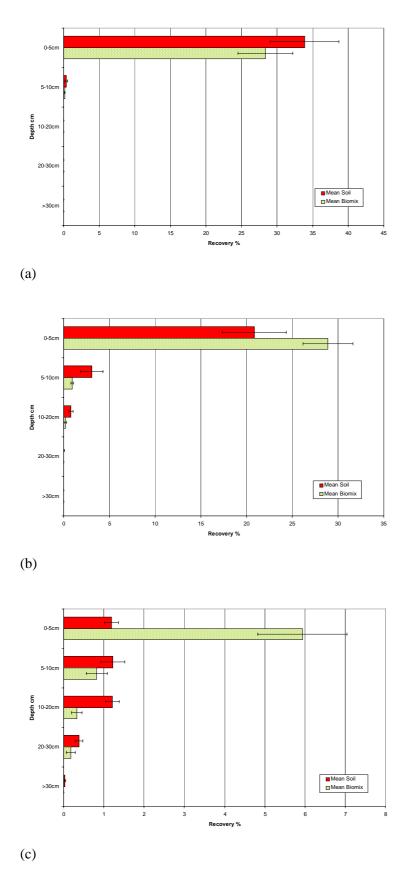


Figure 15 Mean amounts(± 1 SE) of (a) chlorothalonil, (b) epoxiconazole and (c) dimethoate in sections of the treated open lysimeter columns

4.3.1.5 Mass balance

A mass balance calculation was performed to determine the fate of each of the study compounds in topsoil and biomix. For topsoil, between 0 and 8% of the applied pesticides had leached - 0.7 - 37% was associated with the soil matrix; and 66 - 98% was either degraded or unextractable (Table 11). For biomix between 0 and 0.05% of the applied pesticide had leached - 7 - 30% was associated with the biomix matrix; and 71 - 93% was either degraded or unextractable (Table 12).

Pesticide	Koc	DT ₅₀ for soil	Leached %	Recovered %	"Degraded"
		(published) days			%
Isoproturon	100	25	1.53	0.67	97.8
Pendimethalin	5000	90	0	37.38	62.62
Chlorpyrifos	6000	30	0	14.62	85.38
Chlorothalonil	1400	30	0.2	34.25	65.55
Epoxiconazole	957-	60-90	0.27	24.74	74.99
	2647				
Dimethoate	16-51	7-16	8.42	4.04	87.54

Table 11 Mass balance for topsoil lysimeters

Table 12 Mass balance for biomix lysimeters

Pesticide	Koc	DT ₅₀ for soil	Leached %	Recovered %	"Degraded"
		(published)			%
Isoproturon	100	25	0.05	7.01	92.94
Pendimethalin	5000	90	0	28.8	71.2
Chlorpyrifos	6000	30	0	13.11	86.89
Chlorothalonil	1400	30	0	25.56	71.44
Epoxiconazole	957-	60-90	0	30.01	69.99
	2647				
Dimethoate	16-51	7-16	0.01	7.26	92.73

4.3.2 Effects of water loading

4.3.2.1 Rainfall and leachate volumes

Following application of the pesticides to the columns, rainfall in January was only 35% of the long term average, whilst above average rainfall was recorded for February. Eight samples of leachate were obtained (Figure 16).

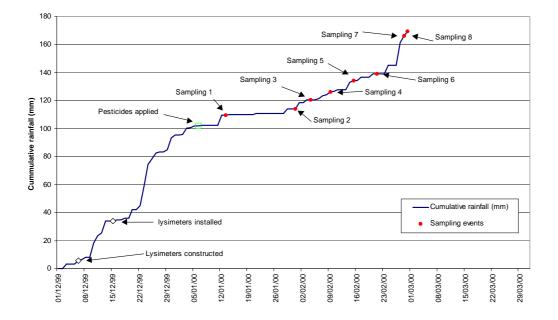


Figure 16 Cumulative rainfall at the Horticluture Research Intenational lysimeter station measured during the year 2 leaching experiment

4.3.2.2 Leachate Volumes

Cumulative leachate volumes from the lysimeters with no loading were similar for all columns (Figure 17). With one exception, in excess of 22 L leached from the high loading columns. The columns receiving a medium loading leached between 2.7 and 7.7 L.

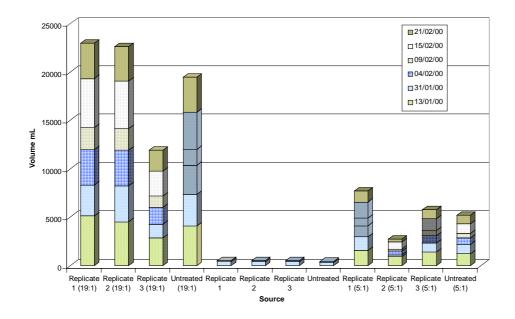


Figure 17 Leachate volumes measured from lysimeters with (a) a 19:1 loading, (b) no loading and (c) a 5:1 loading

4.3.2.3 Bromide in leachate

Bromide breakthrough in lysimeters with a high and a medium loading occurred 7 DAT (Figure 18) with bromide concentrations to date below the analytical limit of detection in lysimeters with no loading. Peak concentrations were observed 7 and 29 DAT for the high and medium loading columns respectively.

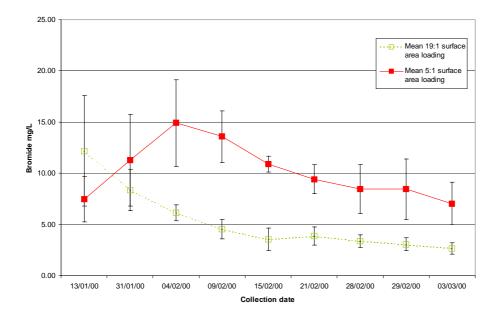
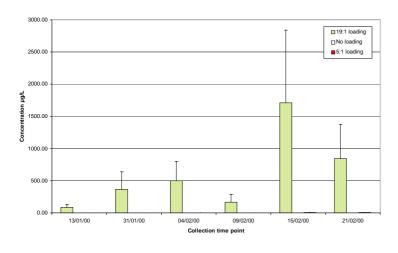


Figure 18 Bromide breakthrough in lysimeters with a 19:1 and 5:1 surface area loading

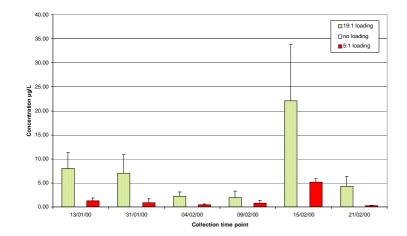
4.3.2.4 Residue in leachate

Maximum pesticide concentrations were observed in leachate from the high loading columns. Concentrations in leachate from the lysimeters with no water loading were below the analytical limit of detection in all samples collected (Figure 19 and Figure 20). Highest concentrations of pesticide were observed for the most mobile compounds (isoproturon and dimethoate). Breakthrough of all pesticides from columns with medium and high water loadings occurred 7 DAT with the exception of epoxiconazole in the medium loading lysimeters which occurred 40 DAT.

Peak concentrations ranged from 1711 μ g L⁻¹ (isoproturon) to 1.04 μ g L⁻¹ (epoxiconazole) in samples from the high loading and from 20 μ g L-1 (dimethoate) to 0.07 μ g L-1 (epoxiconazole) in the medium loading columns. Maximum concentration were generally observed 40 DAT with concentrations of all pesticide falling in subsequent samples.









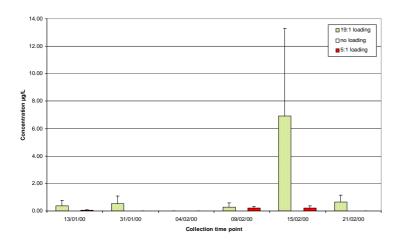
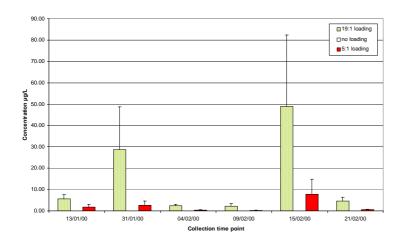
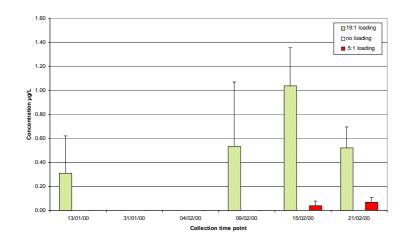




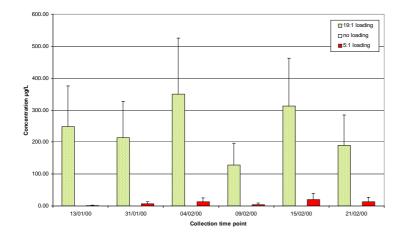
Figure 19 Concentrations of (a) isoproturon, (b) pendimethalin and (c) chlorpyrifos in leachate from the year 2 lysimeter experiment (Effects of water loading)



(a)



(b)



(c)

Figure 20 Concentrations of (a) chlorothalonil, (b) epoxiconazole and (c) dimethoate in leachate from the year 2 leaching experiment (Effects of water loading)

Losses of each pesticide for each event (Figure 21 and Figure 22) were at 1% or less for the high loading columns and below 0.06% for cores with a medium loading. Total losses of isoproturon were 1.44% and 0.01% and of dimethoate 4.16 and 0.17% at high and medium water loading respectively.

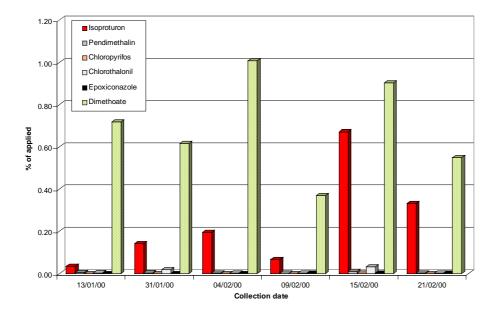


Figure 21 Pesticide residues in leachate (as a % of the applied) from lysimeters with a 19:1 loading

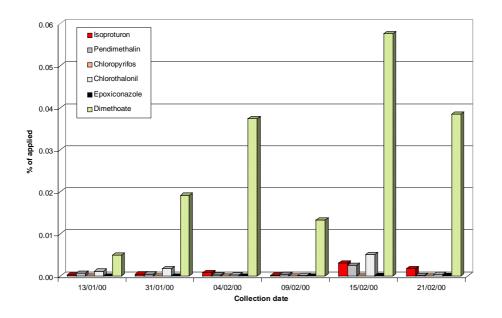


Figure 22 Pesticide residues in leachate (as a % of the applied) from lysimeters with a 5:1 loading

4.4 Summary and Conclusions

The studies using unlined systems clearly demonstrated that the concentrations leaching from the system were significantly lower than from soil columns. As the compounds tested covered a wide range of hydrophobicities and degradation rates it is likely that similar results would be obtained for other pesticides. Only the most mobile compounds leached to any great extent and even for these compounds the system appeared to retain/degrade more than 99% of the applied pesticide. The performance of the biobed is therefore likely to be similar to other treatment systems such as a Sentinel. All pesticides were degraded in the open system with <35% of the applied dose remaining after nine months.

Rainfall during the study using open and closed systems was 15% above average with leachate volumes equivalent to 353mm.

The effects of water loading on the leaching behaviour of pesticides was also investigated. Amounts of pesticide leaching from columns receiving a high water loading were below 6 % of the applied whereas amounts leaching from columns with a medium loading were less than 1% of the applied. As the leaching of pesticide had ceased by the end of the study it appears that the biobed system can effectively remove pesticide and if it receives a medium loading its performance will be equivalent to other systems such as the Sentinel system.

The lysimeters used for this experiment contained only 50 cm of biomix. Assuming equivalent inputs increasing the length of the lysimeter would increase the residence time within the biomix and thus further reduce concentrations in leachate. In addition, the high temperatures observed at the field scale were not observed in the columns so it is possible that greater microbial activity and hence faster degradation rates could be expected in a larger scale system.

Degradation rates in the unlined system were higher than in the lined system. In addition, continuous inputs of moisture combined with the ability for excess liquid to drain away meant that the unlined system did not become waterlogged.

5 LABORATORY STUDIES

5.1 Introduction

The initial concentration of a given pesticide may affect the rate at which it degrades. It is possible that a farm scale biobed will be treated with a range of pesticides at a range of concentrations, depending on (a) the volume of pesticide waste being disposed of; (b) the concentration of the pesticide in the waste; and (c) the quantity of water used during the washing down procedure. Consequently, the system will probably receive a complex mixture containing a number of active substances and co-formulants. Laboratory studies were therefore performed to investigate 1) the degradability of the pesticides investigated in the semi-field studies at a range of concentrations; and 2) the degradability of pesticides in mixtures.

5.2 Materials and methods

5.2.1 Study system

For all laboratory studies, biomix was prepared using volumetric proportions of topsoil, straw and peat free compost. The mixture was composted outside for 80 - 100 days after which time it was macerated using a food processor and refrigerated at approximately 4°C prior to use. Field moist topsoil (Characteristics are given in Table 13) was used in the mixture and this was collected from Little Cherry field next to the Horticulture Research International lysimeter facility, air dried and sieved to <5.4mm.

	Little Cherry (field)
Sand %	69
Silt %	13
Clay %	18
Organic matter %	1.95
рН	6.15

Table 13 Physical characteristic of topsoil used in both the biomix and on its own

The maximum water holding capacity (MWHC) was determined by capillary rise for both the topsoil and biomix using the techniques described in Section 8.1.1.2.

5.2.2 Concentration studies

Samples (25 g) of topsoil or composted biomix were treated with a range of concentrations ranging from half to 20 times the maximum field application rate of either isoproturon or chlorothalonil as formulated products (Table 14). Application rates of up to 20 times the field rate were tested to establish whether the biobed could treat a worst case scenario. There were three replicate samples per concentrations and one control sample for each sampling time point. Following application, three replicate samples were taken for each concentration and frozen prior to analysis. The remaining samples were allowed to stand for approximately 30 minutes, they were then gently shaken, lids attached and weighed before being incubated at 20°C. Periodically samples were re-weighed and the moisture content corrected where necessary to maintain constant conditions. Samples were sampled at each time point. Samples were then frozen prior to analysis.

Pesticide	K _{oc}	DT ₅₀ (days)	Concentration mg/kg
Isoproturon	100	25	12.5
Isoproturon	100	25	25 (field rate)
Isoproturon	100	25	50
Isoproturon	100	25	100
Isoproturon	100	25	250
Isoproturon	100	25	500
Chlorothalonil	1400	30	7.5
Chlorothalonil	1400	30	15 (field rate)
Chlorothalonil	1400	30	30
Chlorothalonil	1400	30	60
Chlorothalonil	1400	30	150
Chlorothalonil	1400	30	300

Table 14 Application details for concentration experiment

5.2.3 Mixture studies

5.2.3.1 Studies with isoproturon and chlorothalonil

Samples (25 g) of either topsoil or biomix were treated with a mixture of isoproturon and chlorothalonil to give concentrations of 100 mg kg⁻¹ and 60 mg kg⁻¹ for isoproturon and chlorothalonil respectively. Individual samples were weighed before incubation at 20°C to enable moisture losses to be corrected if necessary. The samples were then incubated for either 0, 3, 10, 20, 31, 60 and 97 d after which time they were taken and stored prior to analysis.

5.2.3.2 Studies with a mixture of 6 pesticides

The degradability of a combination of the six pesticides used in the semi-field experiments (Table 5) was investigated. Samples (25 g) of topsoil and biomix were treated with formulated product, with the pesticides applied individually and as a mixture. A treatment rate of 4 times the maximum field application rate was selected which approximately equates to second rinse tank washings being disposed of onto a 7.5m³ biobed 6 times a year, (Table 15). Samples were taken 0, 3, 10, 20 and 30 DAT and stored prior to analysis (further samples are scheduled to be collected at 60, 90 and 120 DAT). Three treated soil and biomix samples were collected at each time point with a single sample from both acting as a control.

Table 15 Concentrations of pesticides used in laboratory study investigating the degradation of 6pesticides individually and in combination

Pesticide	Concentration (mg/kg)
Isoproturon	100
Pendimethalin	60
Chlorpyrifos	28.8
Chlorothalonil	13.6
Epoxiconazole	20
Dimethoate	80

5.2.4 Repeat application study

Topsoil and biomix samples were treated with a mixture of the six study compounds (Table 5). With the exception of epoxiconazole, the application rates used were the same as used in the laboratory mixture study (Table 15). Due to experimental error epoxiconazole was only applied at the maximum field application rate, equivalent to 5 mg kg⁻¹ instead of 20 mg kg⁻¹. One application (application 1) of the pesticide mix was made to three replicated batches (1-3) of topsoil and biomix. After 39 days batches 2 and 3 were retreated, and after a further 37 days batch 3 was treated again.

Following the first application, individual samples were left for approximately 30 minutes before being weighed, gently shaken, lids attached and placed into incubators set at 20°C. Day 0 samples were frozen. Due to the fact that the pesticide was applied as formulated product and to enable constant moisture conditions to be maintained the sample lids were removed from the batch 2 and batch 3 samples 3 and 2 days respectively prior to the second application. This allowed evaporation to occur so that the minimum possible volume of pesticide mix could be applied without exceeding the moisture status following application 1. Prior to application 2 batch 2 and 3 samples were weighed and the weight lost since the first application calculated. A standard volume of prepared chemical was added to all samples with tap water used to make up the balance. Untreated samples were treated with water. Following the second application, samples were again allowed to stand before being gently shaken, weighed and return to the incubator, with the exception of the day 0 samples which were frozen.

Sample lids were removed 1 day before the third application. As before moisture loss since the second application was calculated. A standard volume of pesticide was applied with the balance again made up with water. After 30 minutes the samples were gently shaken as before and returned to the incubator with the exception of day 0 samples. Samples were taken 0, 3, 10, 20, 30, 60, 90 and 120 days after each treatment. To date samples have been collected as follows:

Application 1	up to 90 DAT
Application 2	up to 60 DAT
Application 3	up to 20 DAT

5.2.5 Analysis

Methods of analysis are given in Appendix A.

5.3 Results

5.3.1 Concentrations studies

 DT_{50} values for isoproturon in biomix were similar to DT50s for soils and ranged from 9.5 to 53 d (Table 16). DT50s for isoproturon in both soil and biomix increased with isoproturon concentration (Table 16). A similar concentration relationship was obtained for chlorothalonil (Figure 23) however degradation of chlorothalonil in biomix was faster than for soil, DT50s ranging from 1.6 to 20 d (Table 16). Generally results indicated that degradation in biomix was similar to or faster than degradation in topsoil.

Isoproturon (mg/kg)	DT50 (days)		Chlorothalonil	DT50 (days	5)
			(mg/kg)		
	Soil	Biomix		Soil	Biomix
12.5	10.3	9.5	7.5	13.2	1.6
25	14.1	13.1	15	12.5	1.7
50	19.5	18.9	30	23.3	2.5
100	21.1	19.1	60	44.4	4.0
250	28.4	36.7	150	55.0	19.5
500	34.9	52.5	300	59.0	9.2

Table 16 DT50 values for isoproturon and chlorothalonil at a range of concentrations

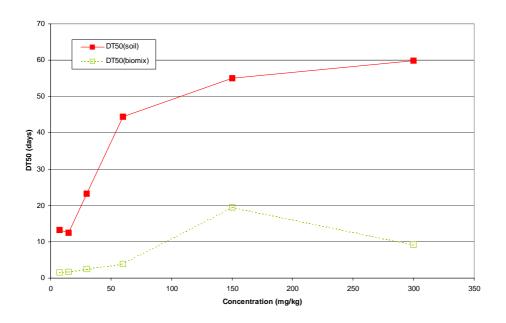


Figure 23 Chlorthalonil degradation in topsoil and biomix at a range of concentrations

5.3.2 Mixture studies

5.3.2.1 Isoproturon and chlorothalonil

Rates of isoproturon and chlorothalonil degradation individually and in combination, in both topsoil and biomix were monitored. Degradation rates of the two substances in biomix spiked with the mixture were similar to degradation rates for biomix spiked with single substances (Figure 24). However, whilst degradation rates of chlorothalonil in topsoil on its own and in combination with isoproturon were similar, degradation of isoproturon was reduced in the presence of chlorothalonil (Figure 25). Results for both topsoil and biomix indicate that concentrations of isoproturon increase after day 60. The reason for this cannot be accounted for scientifically and is therefore considered as an experimental anomaly.

 DT_{50} values for both pesticides (Table 17 and Table 18) indicate an increased ability for biomix to cope with high concentrations of more than one pesticide relative to topsoil. DT_{50} values for isoproturon in soil increased from 17.4 days to > 97 days when chlorothalonil was added whereas in biomix the increase was only 6.7 days. Chlorothalonil degradation was more rapid in the biomix than in topsoil with the addition of isoproturon having no effect of the rate of chlorothalonil degradation.

Table 17 DT50 values for isoproturon in topsoil and biomix on its own and mixed with chlorothalonil

	Isoproturo	n on it own	Isoproturon +	Chlorothalonil
	Soil	Biomix	Soil	Biomix
DT ₅₀ (days)	17.4	14.9	>97	21.6

Table 18 DT50 values for chlorothalonil in topsoil and biomix on its own and mixed with isoproturon

	Chlorothalonil on it own		Chlorothalonil	+ Isoproturon
	Soil	Biomix	Soil	Biomix
DT ₅₀ (days)	41.1	2.3	26.3	2.4

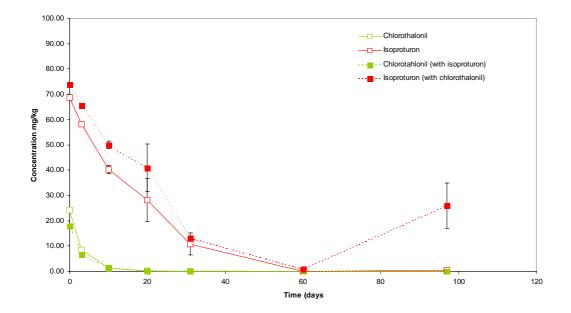


Figure 24 Isoproturon and chlorothalonil degradation individually and in combination in biomix

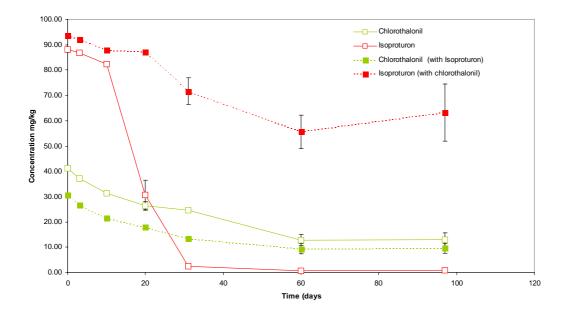


Figure 25 Isoproturon and chlorothalonil degradation individually and in combination in topsoil

5.4 Summary and Conclusions

Studies into the effects of pesticide concentration generally indicated that degradation in biomix was similar to or faster than degradation in topsoil. The exception being isoproturon at high application rates (i.e. at 500 mg kg⁻¹ DT₅₀ values in soil were 35 days and in biomix 52 days). This enhanced degradation in soil may be explained by the fact that the topsoil used for the experiment was collected from a field where adaptation of the soil microbial community is thought to have occurred due to repeated applications of isoproturon. This is supported by the results from previous studies (Cox *et al* 1996) that have indicated that the topsoil used in the study degrades isoproturon faster than typical soils, this being due to an adaptation of the microbial community in the field.

Even at very high application rates, chlorothalonil degradation in biomix was much faster than degradation in the soil investigated in this study and previous studies. Reported DT_{50} values for soil being around 30 days, compared with 1.6 - 20 d measured in the biomix. If this increased degradation rate occurs for other classes of pesticide, then it is likely that the biomix will be a good substrate for treatment in the field situation.

Pesticide waste and washings are likely to contain a range of active substances and co-formulants. The effects of mixtures of isoproturon and chlorothalonil were therefore investigated. Degradation rates of both isoproturon and chlorothalonil in biomix on their own and in combination were similar. However, in topsoil isoproturon degradation was significantly slower when combined with chlorothalonil with a DT_{50} exceeding 97 days. Experimental studies investigating the effect of combining a mixture of up to 6 pesticides are continuing.

The concentrations studies indicate that degradation rates in biomix are faster or similar to degradation rates in soil. The exception to this was for high concentrations of isoproturon in soil, possibly due to previous microbial adaptation. Over time, similar adaptation could be expected in a biobed resulting from repeated exposure to a pesticide, and experiments to investigate this possibility are in progress.

6 GENERAL DISCUSSION

Pesticide waste and washings should be disposed of in accordance with the Code of Practice for the Safe use of Pesticides on Farms and Holdings (1998) and the Groundwater regulations (1999). As part of the Code it is necessary for pesticide users to carry out all filling, washing and disposal activities on an area such that accidental spillages and waste cannot escape from the area and contaminate (a) soil, (b) surface water or (c) ground water. However, due to the practicalities and costs associated with recommended procedures and lack of awareness of the legislation, it is possible that many users do not comply with this requirement. Alternative methods of waste disposal are therefore required that are easy to use and cheap to operate. One possible approach is to use an artificial degradation system such as a biobed.

The biobed is effectively a pit containing a mixture of straw, topsoil and peat (peat substitute) on which all filling activities were carried out. Biobeds are cheaper to build and run than alternative systems (Table 19) and have been successfully applied to the treatment of low volumes of pesticide waste and spillages in Sweden. For the same technology to be applied to the UK the ability to cope with much larger volumes and amounts of pesticide had to be considered.

System	Set-up Costs	Operating costs
Sentinel	£12500.00 (1000 litre standard plant) does not included	£25 / 1000 litres (includes sludge disposal) Annual service £300 - £400 Labour input approximately 1 hour / 1000 litres
	installation	(Morley Research Centre treat approximately 90000 litres per annum)
Storage and disposal	£1280 for one 5000 litre double skinned UV resistant tank	£70-80 per 1000 litres (no OP compounds) £300-400 per 1000 litres (if OP compounds included) + £550.00 per collection
Biobed (UK)	£2000.00 - £2500.00 (construction of field biobeds discussed in report, includes labour)	as yet unknown

Table 10 Compartive as	ste of the Richard relative t	a storage and disposal	or treatment using a Sentingl
Table 19 Compartive Co	SIS OF THE DIODED FEIGURE L	o storaye and disposal	or treatment using a Sentinal

Figures base on personal communication with operators and/or suppliers

Three field biobeds were established, each with a 42m³ capacity designed to process approximately 8000 L of pesticide waste and washings per annum. Temperature measurements from within the biobeds indicated a rapid increase in biological activity soon after installation. Above average rainfall in the three months after construction resulted in the biobeds becoming waterlogged. Covers were therefore placed over all three biobeds and the disposal site managed with respect to rainfall to keep volumes of dilute pesticide to a minimum. Once covered the top 10 cm dried rapidly to form a hard layer. This, combined with an inability for grass cover to establish and higher volumes of waste being generated than anticipated, resulted in the systems becoming waterlogged. The management of the water entering a biobed system is therefore likely to be a key factor in the development of a working system.

Semi-field experiments investigated the degradability and leaching potential of 6 commonly used pesticides with a range of sorption coefficients and degradation rates. Both open and closed minibiobeds were studied. The closed system quickly became waterlogged after construction and consequently the cores were covered. After construction of the covers the upper layer of the material dried out, and an impermeable layer was formed. Most of the applied pesticide was retained in the top 10cm. However and degradation was slow as a result of low moisture content and decreasing levels of microbiological activity.

Studies using open systems confirmed that the biomix could retain and subsequently degrade high concentrations of pesticide. Only the most mobile compounds leached to any great extent with leaching losses of between 0 and 0.05% for biomix compared with 0 - 8% for soil. Continuous rainfall inputs helped maintain moisture status of the biomix and prevented the formation of the impermeable layer observed in the closed system. Moreover, because the columns were open, excess water was able to drain away and the systems did not become waterlogged. Analysis of the solid material in the column indicated that there was little downward movement of all 6 pesticides studied and that a significant proportion had been degraded by the end of the study.

On a farm, the actual volumes of water that will enter the biobed are likely to be significantly higher than investigated in the open system studies. Studies were therefore performed to investigate the leaching behaviour of pesticides from open columns receiving a high water loading and a medium water loading. The results showed that <6% of the applied pesticide would leach under high loading and <0.2% would leach under medium loading. The performance of the system receiving a medium loading is similar to established treatment methodologies such as the Sentinel.

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Any disposal system needs to be able to cope with high concentrations of individual as well as groups of pesticides. Laboratory studies therefore investigated the potential for biomix to degrade isoproturon and chlorothalonil at concentrations ranging from half to 20 times the maximum field application rate. Chlorothalonil degraded more quickly in biomix than in soil at all concentrations. Isoproturon however degraded more quickly in soil than in biomix at higher application rates. Isoproturon and chlorothalonil were combined at four times the maximum field application rate (100 and 60 mg kg⁻¹) respectively. Degradation in biomix was unaffected by combining isoproturon and chlorothalonil isoproturon DT₅₀ values increased from 17.4 to >97 days. One possible explanation for the difference in isoproturon degradation between soil and biomix is that fact that the topsoil used for the experiments was collected from a field previously treated with isoproturon. This previous treatment may have resulted in microbial adaptation resulting in enhanced degradation of isoproturon in the soil as a function of repeated exposure to the herbicide. It is possible that repeated exposure of biomix to a pesticide could result in similar microbial adaptation. The effects of repeated applications on degradation rate are therefore currently being studied.

In summary therefore, the results to date indicate that biobeds can adsorb high concentrations of pesticide and subsequently degrade them even at high water loadings. Whilst a small proportion of the applied pesticide may leach, the amounts leached are likely to be small and similar to leachate from currently available systems. The field studies and semi-field studies demonstrated that the management of water in a biobed is an important factor in the working of a biobed and that the current design for a closed field system is inadequate for the high volumes of waste generated on UK farms. Further studies are therefore required to refine the current design and to test it at the pilot scale.

6.1 Future work

In order to design a working biobed information is now required on the likely volumes of waste that will need to be treated by the biobed as well as information on the concentrations of commonly used pesticides in the waste. Whilst some of this data has been produced in previous studies (e.g. The Cherwell study, The MAFF pesticide survey), the available information has been either generated a long time ago or only addresses selected active ingredients (e.g. isoproturon). There is therefore a need to obtain up-to-date data for a wide range of active ingredients.

SSLRC are currently performing a study for the Health and Safety Executive that aims to determine operator exposure to pesticide residues on tractors and sprayers and in washings once the application of the pesticides is complete. The project involves a questionnaire survey that will identify current practices for pesticide handling, disposal and equipment washing. The survey will provide useful information for this study. The survey will provide an up-to-date and detailed synopsis of pesticide handling and disposal procedures in the UK and combined with existing literature, an extensive and complete review will be obtained.

A project to develop a design for pesticide handling and washdown areas is being led by the Environment Agency with support from DETR, Scotland and Northern Ireland Forum for Environmental Research (SNIFFER, representing SEPA and EHSNI), Pesticides Safety Directorate, Crop Protection Association, Aventis and other farming and agrochemical interests. The contractor for the project is ADAS. Experiments are being carried out to investigate the surface run-off and infiltration of pesticides following the simulated losses from tank filling on six different surfaces, including a biobed mix. Six pesticides are being investigated which are the same as those in this biobeds study adding confidence to both projects. The data generated in this study may provide some information about the concentrations of commonly used pesticides that will need to be treated by the biobed system as well as an indication of how these concentrations vary over time.

By combining the information from the survey with the experimental data obtained by ADAS, information could be obtained on the quantities of waste that will need to be treated by a biobed system along with information on concentrations of major pesticides in the waste.

In addition to information on volumes of waste, the design of a biobed will also be influenced by a number of other factors, including:

- a. what component of the waste and washing needs to be treated;
- b. whether or not treatment is required of residual pesticide that is sorbed to the yard surface which may desorb during periods of rainfall;
- c. whether or not the system needs to be closed;
- d. if the system is open, the concentrations of pesticide in leachate from biobeds which are acceptable to the Environment Agency;
- e. acceptable disposal routes for biobed leachate; and
- f. the practicality and costs of using a particular system for the farming community.

Results obtained to date indicate that pesticides adsorb to the biobed material and are subsequently degraded. Whilst previous observation using soil support this conclusion, it is possible that the observations are caused by the pesticides being irreversibly bound to the solid material and therefore unextractable. If this is the case, it has major implications for the long-term performance of the biobed. Studies are therefore required to determine whether observations to date are due to degradation or adsorption. Similarly for many pesticides, cleaning agents are used to remove residual pesticide in the sprayer tank. These agents include bleaches, which by their nature will be toxic to microorganisms. The effects of these substances on biobed performance will therefore be investigated to determine the implications of tank washings containing cleaning agents being discharged to the biobed.

Once the required information is obtained, 2-3 prototype designs for field biobeds should be developed. Two types of design may be investigated, namely an unlined system where the biobed will be unlined allowing water to filter through the system; and a lined system where the biobed will be lined and the amount of water in the system will be closely monitored. The likely costs of establishing each of the systems and the maintenance regime should be determined to ensure that the final designs are both cheap to construct and easy to maintain.

The developed designs should then be constructed at a pilot scale (1/4 of the full scale) and pesticide waste applied to each pilot biobed in such a way as to mimic waste disposal operations on a working farm. The leaching behaviour and dissipation of the pesticides from the biobeds should then be investigated.

On the basis of the results of the pilot studies, a suitable design should be selected for use on working farms. This should be established on a high profile farm and monitored over time. The possibility of longer term monitoring (e.g. up to 5 years) should also be considered to ensure that future biobeds do not pose a risk to the environment.

A design manual should be developed for distribution to farmers. The manual should describe the construction and operation of a working biobed.

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8 APPENDIX A – ANALYTICAL METHODS

8.1.1.1 Biomass

Total biomass was estimated by fumigation extraction (Mele *et al* 1996). Chloroform (2ml) was added to 20 g of each soil or biobed sample a control sample was left untreated. Treated and untreated samples were then sealed and incubated at 30°C for 7 - 10 d. Following incubation samples were evacuated 4 - 6 times in a vacuum dessicator to remove the chloroform and then shaken for 50 minutes in 50 mL of a 2 M potassium chloride solution. Samples were then centrifuged and a 1 mL extract taken and 0.5 mL of ninhydrin added. The sample was then boiled for 20 minutes. After cooling, samples were made up to 10 mL using a 50:50 mixture of ethanol and water, transferred to a plastic cuvettes and the absorbance measured using a spectrophotometer at 570 nm.. The ninhydrin reactive N was corrected for the unexposed control and calculated using a series of L-leucine and ammonium sulphate standards. Results were corrected for moisture content and the total biomass C (mg kg⁻¹) calculated.

8.1.1.2 Moisture content

The maximum water holding capacity was determined by capillary rise. Disturbed samples of biomix and topsoil were re-packed into 222 cm³ volumetric tins. Nylon voile was placed over one end of the core with the other end sealed. Samples were then placed onto saturated foam until a clear film of water was visible on the surface of the soil or biobed material. The wet weight was recorded and the sample oven dried at 105°C for a minimum of 24 hours. The gravimetric mass water content % was then calculated.

8.1.1.3 Water

Water samples were either analysed directly by using high performance liquid chromatography (HPLC) or analysed after liquid / liquid extraction by HPLC or by gas chromotography (GC). Details of the analytical methods used for individual samples are given in Table 20.

Sampling	Extraction method	Method of	Determinands
(1-13)		analysis	
1 - 7	Direct or liquid /	HPLC or GC	Isoproturon, pendimethalin and
	liquid		chlorpyrifos
8 - 13	liquid / liquid	GC	Isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate

Table 20 Analytical methods used for water samples

Water samples (500 ml) from sampling times 1-7 were extracted twice into 2 x 30 ml HPLC grade dichloromethane (DCM) in a 1 L glass separating funnel. The DCM extracts were combined and placed in brown glass bottles. Extracts were then stored at 4°C until HPLC or GC analyses. Just prior to analysis, the combined DCM extracts were evaporated to dryness using a rotary evaporator at 40°C. The resulting residue was then re-dissolved in 2 ml of a mixture containing 60% acetonitrile and 40% water. Concentrations of pendimethalin and isoproturon were then determined HPLC. For chlorpyrifos determinations, sub-samples (1 ml) of the acetonitrile/water extracts were mixed with 25 ml of water and extracted into 1 ml hexane. Hexane extracts were then analysed using GC.

Water samples (200 mL) from sampling timepoints 8-13 and from the loadings study were extracted three times into 30 mL analytical grade DCM in a 500 mL glass separating funnel. The DCM fractions were passed through anhydrous sodium sulphate and collected into a round bottom flask. The samples were then evaporated to dryness using a rotary evaporator at 40 °C. The resulting residues was re-dissolved into 2 mL of a mixture containing 10% methanol and 90% DCM. Samples not analysed immediately were stored at -15°C. Concentrations of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate were then determined using GC.

8.1.1.4 Soil and biomix

After solvent extraction soil and biomix were analysed by either HPLC or GC.

For samples T=0 to T=2, solid material (25 g) was placed in glass flasks and 50 ml methanol was added. The flasks were then shaken for 50 minutes using a wrist action shaker. After this time, the samples were left to stand until the solid material had settled. Aliquots of the clear methanol were the taken for determination of isoproturon and pendimethalin. Sub-samples (either 1 ml or 5 ml) of the methanol extract were taken for chlorpyrifos determination. The methanol extracts were mixed with 50 ml water and the methanol/water mixture was extracted into 5 ml hexane. The hexane extract was dried using 5 g anhydrous sodium sulphate prior to GC analysis.

For samples T=3 to T=7, solid material (40g) was placed into 250 mL glass bottles and 60 g anhydrous sodium sulphate added plus 160 mL of a mixture containing 90% DCM and 10% methanol. The samples were then shaken for 2 hours using an end over end shaker. The extract was filtered through 2cm of sodium sulphate. An Aliquot of the filter solution was taken for determination of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate using GC analysis.

Samples from the laboratory concentration study were extracted into methanol using the methods described for samples T=0 to T=2. Concentrations of isoproturon and chlorothalonil in the resulting extracts were then determined by HPLC using the methods described in Section 8.1.1.5

With the exception of isoproturon and chlorothalonil samples from the mixture studies were extracted into a methanol/dichloromethane mixture using the methods described in Section 8.1.1.4. Concentrations of each pesticide in the resulting extracts were then determined by GC with nitrogen phosphorous detection using the method described for samples T=3 to T=7 in Section 8.1.1.5.

Isoproturon and chlorothalonil samples were extracted using 50 mL methanol for 2 hours using and end over end shaker. The solvent was filtered through Whatman No.5 filter paper and stored at <-15°C until analysis by HPLC.

8.1.1.5 GC and HPLC analyses

Concentrations of pesticides in extracts of water or solid material were determined using four different methods, two involving HPLC, the other two methods involving GC.

Concentrations of isoproturon and pendimethalin were determined using HPLC. Samples were analysed using a Kontron Series 320 Pump linked to a Kontron Series 332 UV detector. Samples (20

µl) were injected using a Kontron Series 360 autosampler. Separation was achieved using a Lichrosorb RP18 column (250 mm x 4 mm i.d.) and a flow rate of 1 ml/minute. For isoproturon determinations, a 75:25 acetonitrile:water mobile phase was used, for pendimethalin determinations, a 90:10 acetonitrile:water mobile phase was used. The detection wavelength for both compounds was 250 nm. Quantification was achieved by comparing peak areas with results obtained from known standards.

Concentrations of chlorpyrifos in samples T=0 to T=2 were determined using gas chromatography with nitrogen/phosphorous detection. Separation was achieved using a 3% OV1 on Chromosorb WHP column (1 m x 3mm i.d.), nitrogen flow was 50 ml/min, hydrogen flow was 2 ml/min and air flow was 450 ml/min. The column temperature was 220°, the injector temperature was 225°C and the detector temperature was 230°C. Quantification was achieved by comparison of peak area with results from known standards.

Concentrations of isoproturon and chlorothalonil for the laboratory experiments were determined by HPLC using a Spectra Physics SP8810 pump was linked to a Cecil 1200 UV detector. Samples (20 μ l) were injected using a Spectra Physics SP8775 autosampler. Separation was achieved using a Spherisorb C8 column (150 x 4.6 mm). For isoproturon determinations the mobile phase used was acetonitrile:water (40:60) with a flow rate of 1.45 ml min⁻¹ to give a retention time of 4.5 min. For chlorothalonil the mobile phase used was acetonitrile:water (60:40) with a flow rate of 1.3 ml min⁻¹ to give a retention time of 3.3 min. Absorbance of both compounds was measured at 240 nm and quantification was achieved by comparison of peak areas with results from external standards.

Concentrations of pesticide in all other samples were determined on a Hewlett Packard HP5890 gas chromatograph fitted with a split/splitless injector, $12m \ge 0.53 \text{ mm BPX5}$ 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 °C to 190 °C (40 °C/min) and then to 220 °C (10 °C/min) and finally to 245 °C (15 °C/min). Samples (2 µl) were injected using a Hewlett Packard HP7673 autosampler. Under these conditions all six pesticides were baseline separated with retention times of 3.1 (dimethoate), 3.5 (chlorothalonil, 3.9 (isoproturon), 4.2 (chlorpyrifos), 4.7 (pendimethalin) and 7.2 minutes (epoxiconazole). Detector response was linear for all 6 compounds (in dicloromethane/methanol, 9:1) in the range 0.2 to 10 µg/ml. Quantification was achieved by comparison of peak areas with results from external standards with the limits of detection for each compound given in (Table 21).

Recoveries:

Untreated soil was treated with standards (in acetone) of chlorothalonil, isoproturon, pendimethalin, epoxiconazole, dimethoate and chlorpyrifos to give concentrations of 15 ppm for all 6 pesticides. The acetone was allowed to evaporate and the soil was extracted as described above. With the exception of chlorothalonil (82 %) the recovery of all the pesticides exceeded 95%.

	Isoproturon	Pendimethalin	Chlorpyrifos	Chlorothalonil	Epoxiconazole	Dimethoate
detector						
response						
limit						
(µg/mL)	0.011	0.006	0.006	0.011	0.005	0.004
Soil samples						
(mg/kg)	0.05	0.02	0.02	0.04	0.02	0.02
Water						
samples						
$(\mu g/L)$	0.23	0.12	0.11	0.22	0.10	0.08

Table 21 GC detection limits for the 6 experimental pesticides

8.1.1.6 Bromide

Water samples (0.5 mL) were filtered (0.2 μ m). Concentrations of bromide were determined using ion chromatography. Samples were analysed using a Dionex DX-100. Samples (25 μ L) were injected neat with a typical retention time of 2.3 minutes. The system was calibrated using a series of standards with known concentrations with a limit of detection set at 1.1mg L⁻¹.

9 APPENDIX B:- CONCLUSIONS FROM THE BIOBEDS WORKSHOP

A one day workshop involving representatives from a number of organisations including the Environment Agency (representatives from the National Centres for Ecotoxicolgy and Hazardous Substances and Groundwater, PSD, NFU, ADAS, and CPA was held at which work from the biobeds project was presented. The workshop forums report is included below.

There was general agreement that further research was necessary because biobeds may prove to be an essential tool for the disposal of pesticides, although they may not be required in all cases. It was clear that there will be a range of reasons for the possible installation of a biobed and the user requirement could include pesticide disposal from one, two or all of the following operations:

- Point source pollution during mixing and filling the sprayer;
- Internal decontamination of sprayers;
- Washing the exterior of the sprayer.

While it was agreed that while the current project had produced some key information, no conclusion was possible on future research requirements. Hence, it was agreed that a feasibility study is required to remove the uncertainties in order that a properly focussed research project is carried out. There was agreement that the feasibility study and the consequent research project should be seamless in time to ensure that biobeds are available to the UK farmer as soon as feasible.

The feasibility study should include:

- The implications on design and costs of the range of objectives listed above. It may be that a small and cheap biobed with no liquid output could be designed for small volumes of liquid (dependent of pesticide content?) but not for larger volumes. This may influence farmers to tackle some, but not all of their disposal problems in other ways;
- The need to minimise the amount of liquid to be treated. This should also include reduced volume tank-cleaning methods suggested by Du Pont;
- The need to manage water within both lined and open systems;
- To investigate the implications of tank cleaners on the micro-flora and the rate of breakdown of pesticides;
- The fate of sheep dips in biobeds;
- The potential for the management of temperature of the biobed;
- The implications of legislation:

- Disposal of any liquid output from a biobed, particularly where it meets the standards for the pesticide content of the drinking water directives;
- Whether unlined biobeds can be installed in the ground under the Waste Regulations. This includes the issues of the cost of approval and monitoring in addition to possible technical requirements for the removal of pesticide residues by the biobed;
- Disposal of material used to clean up spills;
- Disposal of pesticides containers;
- Possible implications of 'aerosols' that may be produced by some possible designs;
- Disposal of the 'compost' from biobeds;
- The input of information on waste disposal methods in other relevant industries using contacts provided by the Environment Agency;
- Close liaison with commercial developments and other research projects within UK and Europe.

The output of the feasibility study should be a design for a cheap to install and easy to maintain biobed for field evaluation. It may be that two or three designs may be appropriate according to volume of liquid (and concentration of pesticides?) to be treated and the possibility that unlined biobeds could be installed in some soil types and not in others.

The feasibility study needs to be managed by a committee representing the key organisations represented at the workshop, particularly the BAA, Environment Agency and NFU.

Jim Orson, 21 April 2000