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

By

P Fogg, ABA Boxall and A Walker

Final Report

September 2001

MAFF Project: PL0543

Cranfield Contract: JA3754E

Cranfield Centre for EcoChemistry
Cranfield University, Shardlow Hall, Shardlow, Derby. DE72 2GN
Tel: 01332 799000 Fax: 01332 799161
E-mail: ecochemistry@cranfield.ac.uk Web: http://cranfield.ac.uk/ecochemisty/

SUMMARY

When used correctly, according to label instructions and with the appropriate precautions, pesticides present minimal risk to the environment. However, even when pesticides are used by trained operators using well maintained equipment small drips and spillages can result in a significant amount of surface water contamination. Similarly tank and equipment washings should be disposed of in accordance with the Code of Practice for the Safe use of Pesticides on Farms and Holdings (1998, currently under review) and the Groundwater regulations (1998). However, due to the practicalities and costs associated with the recommended procedures and lack of awareness of the legislation, it is possible that many users do not comply with these requirements. A system is therefore required that is able to treat the small drips and spills which occur as part of the normal mixing procedure as well as the larger volumes of tank and equipment washings which can lead to significant water contamination if not disposed of correctly. The system must be robust, simple to construct and manage and require a low technical input. Biobeds appear to offer an alternative to current methods of treating pesticide waste and washings.

Any pesticide treatment process needs to be able to treat a complex mixture of pesticides, applied repeatedly often at high concentrations. The degradability and leaching potential of a range of commonly used pesticides was investigated using a series of laboratory and semi-field experiments. Previous laboratory experiments, (Fogg et al. 2000) measured degradation rates in biomix and topsoil at concentrations up to 20 times the maximum field application rate. Whilst pesticides degraded more slowly at high concentrations the effects were less significant in biomix than in topsoil. The effects of combining more than one pesticide were also investigated. Degradation in biomix was unaffected whereas in topsoil isoproturon DT50 values increased from 17.4 to >97 days. Six pesticides were subsequently mixed together and added to biomix and topsoil. Results indicated that interactions between pesticides were possible, however the effects were generally less significant in biomix than in soil. With one exception calculated DT50 values for all pesticides in biomix were similar to values for individual pesticides applied to soil at normal application rates. The same pesticide mixture was applied repeatedly to biomix at approximately 30 days intervals. There was no evidence of enhanced biodegradation due to the repeated exposure however with one exception <30% of the maximum nominal application rate remained after 200 days. Ammonia based tank cleaning products, e.g "All-Clear Extra" were tested and found to have no detrimental effect on pesticide degradation within the biobed. Experiments comparing degradation in sterile and non-sterile biomix confirmed that pesticides were degraded.

Semi-field studies investigated the degradability and leaching potential of the same commonly used pesticides in lined and unlined systems. Lined biobeds (Fogg et al. 2000) had to be covered to prevent waterlogging. However, once covered the top 10cm dried out to form a cap on top of the biobed. Hydrologically connectivity was interrupted severely restricting evaporation from the system. Minimal water loss resulted in saturated conditions below 10cm within 12 months. Microbial biomass was used to access levels of biological activity within the biobed. Over a 12 month period biomass decreased in the 0-10cm layer a function of low moisture content but also inhibition brought about by the high levels of pesticide retained in the top 5cm. Although pesticides were effectively retained in the lined system residue levels of 52% were still recovered after 12 months.

Studies using unlined biobeds confirmed that the biomix could retain and subsequently degrade high concentrations of pesticide. Only the most mobile pesticides (Koc 16-100) leached and for these >99% was retained / degraded in the biobed. Biobed performance in terms of leaching potential was affected by hydraulic load but even then <0.61% of the pesticide applied leached from biobeds receiving a medium water loading. In terms of the amount of pesticide retained by the biobed performance was similar to that of other commercially available treatment systems. Analysis of the biomix material after ten months showed that a significant proportion of the non-leached pesticide had been degraded.

Studies to date have demonstrated that a biobed can treat high concentrations of complex mixtures of pesticide applied repeatedly. Water management is crucial in terms of performance, construction cost and management. Using unlined biobeds >99.3% of the applied pesticide was retained with a significant proportion of the retained pesticide degraded within ten months. Whilst a small proportion of the applied pesticide may leach optimisation of the biobed design should results in pesticide concentrations of <0.1µg L-1. Biobeds appear to offer a simple, low cost system for treating accidental spills and drips as well as tank and equipment washings.

ACKNOWLEDGEMENTS

The authors acknowledge the support of the funding organisations listed below:

Ministry of Agriculture Fisheries and Food

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

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

1 INTRODUCTION

Pesticides play an important role in the success of modern farming and food production. When used according to label instructions and with the appropriate precautions, pesticides present minimal risk to the environment. Research over recent years (Gatzweiller et al. 1999, Reese-Stähler et al. 1999, Brown et al. 1995, Fogg et al. 1994) has focused on the fate of non-point sources of pesticide residues in water resulting from the application of approved pesticides to agricultural land. Contamination arising from non-approved use, poor practice, illegal operations or misuse is however increasingly recognised as contributing to water contamination (Carter 1999, Jones et al. 1999). Table 1 summarises the different diffuse and point sources which have been identified.

Table 1 Sources of water contamination by pesticides (Carter 1999)

Diffuse	Point
Spray drift	tankfilling
volatilisation	spillages
surface runoff / overland flow	faulty equipment
leaching	washings and waste disposal
throughflow / interflow	sump, soakaways and drainage
drainflow	direct contamination including overspray
base flow seepage	consented discharges

Until relatively recently the importance of point sources with respect to their contribution to pesticide load in raw water had not been fully recognised. Recent work (Mason et al. 1999, Higginbotham et al. 1999) demonstrated that even when pesticides were handled and mixed following best agricultural practices a number of activities resulted in contamination of the farmyard. Calculations showed that losses from the farmyard contributed approximately 40% of the total IPU load in the small catchment despite 'good practice' being followed (Carter 2001).

In order to minimise the environmental impact of using pesticides in the UK the Code of Practice for the Safe use of Pesticide on Farms and Holdings 1998 (currently under review) makes recommendations as to how pesticides should be used and any associated waste disposed of. The Code of practice recommends that all filling, washing and disposal activities should be performed on an area so that accidental spillages and waste cannot escape from the area and contaminate either soil, surface water or ground waters. Any dilute pesticide should

be disposed of in an environmentally acceptable manner and in accordance with the Groundwater regulations 1998. 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;

Other ways, that need prior approval from the Environment Agency or the Local Water Services Company (WSC) include;

- use of equipment to treat the waste;
- application to an area of uncropped land that is not stubble or fallow and which has minimal wildlife value and minimal risk to Groundwater;
- disposal into the public sewer.

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 resulting in contamination of raw water (Breach 2001). Alternative methods are therefore required that are not only cheap to implement but also easy to manage.

A study (PL0527) recently completed by the Cranfield Centre for EcoChemistry investigated the degradability and leaching potential of 6 commonly used pesticides with a range of sorption coefficients and degradation rates using lined and unlined small scale biobeds. The lined system quickly became waterlogged after construction and consequently had to be covered to exclude rainfall. Once covered the top 10cm became hydrophobic, restricting moisture loss from the system. Little downward movement of the applied pesticides was observed, however degradation was slow as a result of low moisture content in the upper layers as well as decreasing levels of microbiological activity.

Studies using unlined biobeds confirmed that the biomix material 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% from biomix compared with 0 to 8% for soil. Continuous rainfall inputs helped maintain moisture status and microbiological activity of the biomix and prevented the formation of the impermeable layer observed in the lined systems. Moreover, because the mini-biobeds were unlined, excess water was able to drain away thus preventing the system from becoming water logged. Analysis of the solid material from within the biobed indicated that there was little downward

movement of the 6 pesticides studied and that a significant proportion of each active substance was degraded.

On a farm, the actual volumes of liquid that will enter the biobed are likely to be significantly higher than investigated in the unlined systems. Studies are therefore being performed to investigate the leaching behaviour of pesticides from unlined biobeds when subjected to high and medium water loadings.

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 whereas in topsoil isoproturon DT50 values increased from 17.4 to >97 days. One possible explanation for the difference in isoproturon degradation between soil and biomix is microbial adaptation and thus 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 as well as pesticide mixtures on degradation rate are therefore currently being studied.

In summary therefore Biobeds appear to offer an alternative to current methods of treating pesticide waste and washings. Laboratory and semi-field studies carried out in the UK, (Fogg et al. 2000) indicated that biomix can degrade high concentrations of a range of active substances when applied individually and in combination with another pesticide. Moreover the leaching of pesticides from the biobed mixture is significantly slower than from topsoil. Studies have demonstrated that for a lined biobed to function correctly the amounts of water entering the biobed need to be managed.

A workshop held in April 2000 involving representatives from MAFF, the Environment Agency, industry and the farming community identified a number of issues that needed to be addressed before prototype biobeds could be developed. These issues included: the legal restraints on the use and operation of biobeds; the implications of bound residues; the effects of spray tank cleaning agents; a determination of actual volumes of waste that need to be

treated; and the cost of constructing and operating a biobed system. Further studies are therefore required to address these issues.

The specific objectives of this study were:

1). Complete ongoing laboratory and semi field experiments
2). Review alternative approaches for treating pesticide waste on the farm
3). Review regulation covering the use of on farm waste treatment systems
4). Assess the implications (if any) of bound residues and the use of tank cleaning agents.
5). Develop one or more designs for a working biobed

This report describes results of the study. In Chapter 2 alternative treatment methodologies and regulations covering the use of biobeds in the UK are described. In Chapter 3, the results of the laboratory studies are reported. Chapter 4 details studies at the semi-field scale investigating the leaching potential of a range of pesticides at different hydraulic loadings. Chapter 5 reports on various biobed design options. The results are summarised in Chapter 6 and recommendations provided for future work.

2 ALTERNATIVE CONTROL AND TREATMENT METHODS

2.1 Introduction

Pesticide inputs to the environment can be reduced by either implementing measures to reduce the potential sources of pesticide contamination, or by treatment. A number of treatment systems are available for example:

- Sentinel
- Evaporation beds
- Reedbeds
- Biofilm reactors
- Biobeds

Each system is discussed in more detail below.

2.2 Control Measures

Results from the Cherwell project (Carter 2001) showed that pesticides losses from the farmyard resulting from accidental spills and drips could be reduced by 95% when practices to minimise pesticide loss were adopted. These include;

- transfer of tank mixing from concrete area to permeable hard core area;
- prevent any surface water from the mixing area moving into the yard sump;
- wash down away from the farmyard;
- do not invert empty containers;
- put seal and lids in cardboard packaging;
- incinerate containers and packaging as soon as possible;
- avoid spraying when the soil is cohesive;
- spray headlands last and
- store sprayer under cover

Whilst moving the tank mixing area from concrete to permeable hardcore will result in reduced surface water contamination the risk to groundwater is likely to increase significantly. The suggested practice would therefore fail to comply with the Groundwater Regulations and as such should not be encouraged.

Washing equipment in the field is an effective way of removing pesticide residues from the farmyard. The amounts of 17 different pesticides retained on the outside surfaces of the sprayer as well as inside the spray tank were measured (Ganzelmeir 1998). Total pesticide loads were calculated and converted to an equivalent area treated at the maximum recommended rate. For outside cleaning a maximum treatment area of 18m2 was calculated and could therefore be achieved in the field without overdosing the crop. Residues for inside the spray tank were thirty times higher. However if sufficient water could be made available, in field cleaning would be possible.

Many modern sprayers are fitted with a 100 - 200 litre clean water tank. In tank washers can effectively wash the inside of the tank and waste sprayed out in the field. However sufficient water is only available to rinse the tank once which may be insufficient if the tank needs to washed more thoroughly (3 rinses with 10% of the sprayer volume) to allow for following crop sensitivity. Under these circumstance up to two additional journeys would be necessary travelling between a clean water supply, normally the farmyard, and the intended disposal site. If the outside of the sprayer is also to be washed in the field a further 100 - 150 litres (Fogg 1999, Mason et al. 2000) will be required.

Modern equipment can result in less pesticide waste being generated and thus requiring disposal. The use of injection metering systems reduces the amount of waste generated as the spray tank itself contains only clean water and therefore the requirements for decontamination and the disposal of an associated waste are substantially reduced (Handbury 1998). As formulated pesticide is metered into the spray line whilst the application process is carried out, no mixture remains at the end of the job regardless whether the field size is known or not. By switching off the metering system pump clean water purges the spray boom of any pesticide. Such equipment undoubtedly reduces the amount of pesticide waste generated. However the cost of such systems is significant and therefore is unlikely to be adopted by the vast majority of users.

2.3 Sentinel

Environmental protection equipment, for example the Sentinel can be used to effectively treated pesticide waste. The Sentinel system incorporates the 'Carbo-flo' treatment system which is a process of chemical treatment and filtration which removes organic substances from waste water prior to its re-use or disposal (WMEC Limited). The 'Carbo-flo' process is intended to treat dilute waste (concentration of all organic ingredients in effluent must not exceed 0.3%) and not concentrated products. The Sentinel should be installed onto a bunded

concrete base capable of retaining at least 1000 litres of liquid in the event of spillage. The bunded area should drain back into a holding tank in preparation for treatment, with arrangements made to exclude rain water.

The treatment procedure is as follows:

- Collect effluent and transfer to Sentinel;
- Add treatment chemicals and agitate for 20 minutes. (Treatment chemicals are pre-packed, with one pack used to treated one batch of 1000 litres);
- The solids settle at bottom of tank;
- Clear liquid is pumped through a sand filter and then through two carbon filters which are connected in series, (a carbon filter will treat 20 000 litres);
- Liquid waste either re-used or disposed of.

It takes 3 hours for 1000 litres to pass through the filters with complete treatment achieved in approximately 4 hours. Every 3000 litres it is necessary to consolidate the sludge, which accumulates during settlement. Disposal of sludge, waste liquid and exhausted carbon filters should be done through a licensed disposal contractor. Performance of the system consistently removed > 99.9% of all pesticides tested and subject to the best available analytical methods residues were frequently found below the detection limit, Table 2 (Harris et al. 1991).

Table 2 Peformance of Sentinel treatment system

Product	Effluent Initial loading µg L-1	Residue in Treated water µg L-1	% Reduction	Limit of Detection µg L-1
atrazine	5100000	4.0	>99.9	0.4
alachlor	795000	N.D	>99.9	0.4
bentazon	480000	<4.8	>99.9	0.075
permethrin	237500	N.D	>99.9	0.4
cypermethrin	50000	N.D	>99.9	0.02 - 0.4
pirimicarb	225000	N.D	>99.9	0.02 - 0.4
carbaryl	225000	N.D	>99.9	0.02 - 0.4
dicamba	35000	N.D	>99.9	0.02 - 0.4
2,4-D	200000	N.D	>99.9	0.02 - 0.4
paraquat	200000	N.D	>99.9	0.02 - 0.4

Even though the Sentinel treatment system has been commercially available for 20 years or more (Harris et al. 1991), uptake has been limited (Wise 1994). Cost has probably been the most limiting factor with regards to uptake, with an initial purchase price of £12500.00 for a

standard 1000 litre unit, running costs of £25 / 1000 litres (including sludge disposal), £300 - £400 for an annual service and labour of 1 hour per 1000 litres. The Sentinel is therefore unlikely to be a viable way of treating pesticide waste and washing on the majority of farms.

2.4 Evaporation Beds

In the United States lined evaporation beds have been evaluated (Winterlin et al. 1984). Evaporation beds were typically 6 m x 12m x 0.9m, lined with butyl rubber membrane and back filled with 0.3 - 0.45 m of sand loam soil. Bed size was calculated on a site by site basis and was based on the regions pan evaporation rate (inches / month) and the pesticide waste application rate (gallons / month).

$$\text{area of evaporation bed ft2} = \frac{\text{volume of waste (gallon /month)}}{0.8 \times \text{pan evaporation (inches / month} \times 0.625}$$

0.8 = reduced evaporation from soil relative to open water

0.625 = conversion between gallons and inches / ft2

A safety factor of 100 % (twice the calculated bed size) is recommended.

Pesticide application equipment was washed on an adjacent concrete slab with the washings draining into a collection tank. Waste was then pumped into the evaporation bed via a series of 20cm diameter perforated plastic pipes installed below the soil layer. The system was designed such that water moved through the soil layer and evaporated off the surface. In order to prevent water logging and the unnecessary treatment of rainwater the beds were covered. At some of the sites the concrete wash down area was also covered. General observations from the evaporation beds under investigation were that during winter and spring months many of the beds became water logged, a result of heavy use, high rainfall and low temperatures. Poor pesticide records had been maintained throughout the duration of the study and it was therefore unclear as to exactly what actives had been applied. Sampling indicated that the pesticides tended to concentrate in the 0 - 2.5cm layer with a non-uniform distribution due to the method of application. Total residue levels for one year in the 6 most heavily used beds are summarised (Table 3).

Table 3 Average soil surface residues (0 - 2.5cm) exceeding 1 mg kg-1 in evaporation beds sampled throughout California in 1982

	Spring		Summer	
	Concentration mg kg-1	S.D	Concentration mg kg-1	S.D
Westside	289.2	439.7	398.5	663.3
Kearney	100.8	122.2	141.4	225.8
Lindcove	2031	5490	7465	14666
Tuelake	40.66	87.51	270.4	454.8
Davis	88.85	160.8	50.60	74.01

Rate of pesticide loss from evaporation beds was dependent on several factors;

- Type of pesticide formulation
- Presence of oils
- Amount of water in bed
- Pesticide solubility
- Biological activity of the soil

In order to estimate the loss of pesticides over a one year period the beds were sampled. Table 4 summarises the pesticides found in each bed which had an average concentration in excess of 5 mg kg-1 during the 2 year sampling period.

Table 4 Major pesticides found in evaporation beds sampled during 1981 and 1982. Levels shown are average residues (>5.0 mg kg-1) for a 0 - 30 cm depth.

	West side		Kearney		Lindcove		Tulelake		Davis	
	1981	1982	1981	1982	1981*	1982	1981	1982	1981	1982
Atrazine	n.d	n.d	<5.0	<5.0	<5.0	113	n.d	n.d	28	11
Carbaryl	<5.0	<5.0	n.d	n.d	167600	<5.0	n.d	n.d	n.d	n.d
Chlorpyrifos	134	43	<5.0	<5.0	339	15	<5.0	<5.0	n.d	n.d
Dacthal	243	206	6.3	5.4	n.d	n.d	n.d	n.d	n.d	n.d
Devrinol	81	74	27	13	**	1346	n.d	<5.0	n.d	n.d
Endosulgan	<5.0	5.8	8.8	9.4	n.d	n.d	13.6	136	n.d	n.d
Parathion	n.d	n.d	n.d	n.d	56	508	7.6	30	n.d	n.d
Simazine	129	26	40	46	16820	300	11.8	n.d	n.d	2.3
Trifluralin	489	192	<5.0	22	n.d	114	9.8	50	n.d	<5.0

* The bed was approximately 90% flooded, allowing only one sample to be collected
* GLC response was masked by other peaks, preventing quantitation

Generally all pesticides degraded within the system. Winterlin (1984) concluded that evaporation beds provided an economical method for disposing of dilute pesticide waste and washings. Large volumes of waste were concentrated down to more manageable levels and

under the conditions of this experiment pesticides did not appear to accumulate after 6 - 10 years of use. However even when subjected to California weather the evaporation beds became water logged during the winter and early spring months. It is therefore extremely unlikely that such a system would be viable in the UK.

2.5 Reedbeds

Reedbeds have shown to be very effective waste water treatment systems (Watson et al. 1989, cited in Revitt et al. 1997) and have been used to control pollution arising from industrial, farm waste, municiple wastes and urban runoff (Bastin and Hammer, 1993 cited in Revitt et al. 1997). Reedbed technology is based on same fundamental process as constructed wetlands, but is isolated from natural water systems and uses a single plant species. The most common type of reed planted for water treatment is the common reed, Phragmites australis. This is a rapidly growing species, which is able to cope with a range of climatic conditions and many types of wastewater. Conventional reedbed systems work by the wastewater being passed over or through a substrate (sand, gravel or soil) in to which reeds have been planted. The choice of substrate material has a significant impact on the efficacy of the reedbed. Clay and organic matter content affect porosity. As porosity decreases so does the available surface area for microflora to attach to resulting in reduced efficacy of the reedbed. Substrates which provide a high surface area and cation exchange capacity are best, as they allow maximum sorption during periods of excessive loading and then slow release as concentrations in the waste fall (Cobban et al. 1998).

Until recently the use of reedbeds to treat pesticide waste had not been investigated. McKinlay et al. 1999 selected four different species of macrophyte, Common Club-rush, Schoenoplectus lacustris; Bulrush, Typha latifolia; Yellow iris, Iris pseudacorus and the Common Reed, Phragmites australis and tested their ability to decontaminate water polluted with atrazine. Gravel filled, sub-surface flow reedbeds were constructed in the laboratory. An atrazine solution, 6 - 7 mg L-1, (approximately one thousandth of the manufactures recommended field application rate) was prepared and applied to the reedbeds in June 1992, March 1993 and twice in April 1993. Following each application the liquid was circulated through the reedbeds and the time taken to reach the analytical limit of detection LOD (0.01 µg L-1) for each reed species was measured. After application 1 the LOD was reached 32 days after application in the Common Club Rush system and with 53 days in the other plant systems. Following the second application the LOD was reached within 25 -30 days in all plant systems and after application 3 and 4 the detection limit was reached with 7 days. The plants tested varied in their ability to tolerate atrazine. All Common Reed Plants died

following the first application in contrast to the other species, which were able to tolerate the four applications of herbicide. In spite of the fact that the Common Reed died following the first application subsequent applications continued to decline to the LOD at a similar rate to the unaffected species. The authors concluded that this pattern of decline was therefore associated with the plant root zone. They also suggest that microbial degradation was the main mechanism accounting for the decline in atrazine concentrations although they do not exclude the possibility that the plants are capable of directly assimilating the herbicide and/or its breakdown products into their tissue. The use of marsh plants is a simple inexpensive technique that could be developed and eventually transferred to individual farms (MacKinlay et al. 2000).

2.6 Biofilm Reactors

Sequencing batch biofilm reactors (SBBR) have also been used to treat pesticide waste. Protzman et al. 1999 carried out a study to develop an SBBR capable of treating liquid waste of variable pesticide load whilst maintaining a high biomass population. The SBBR consisted of a 3.5 L glass reactor filled with 12.5mm polypropylene balls to act as the biofilm support medium. The reactor was then inoculated with Agrobacterium radiabacter strain J14A, which had been shown to degrade atrazine (Struther et al. 1998 cited in Protzman et al. 1999). The reactor was treated on a batch system, with 2 L of an atrazine solution (30 mg L-1) being added at a time. The solution was circulated at 100 ml min-1 for a range of hydraulic retention times HRT (0.5, 2 and 7 days) and the temperature maintained at 22°C. The reactor was completely drained before the next batch was added. The study showed that J14A could be used in a biofilm type reactor and that atrazine was degraded. The atrazine degradation rate was enhanced when a supplementary carbon source was added. With an initial concentration of 30 mg L-1 of atrazine and supplementary carbon the atrazine was degraded to 1 mg L-1 within 12 hours for the 2 day HRT. For a 7 day HRT more than 90% of atrazine was degraded within 45 hours (Protzman et al. 1999).

2.7 Biobeds

Biobeds based on the design by Torstensson (1994, 2000), Stenberg et al. (1994) Torstensson and Castillo (1996a, 1996b, 1997, 1998) have been used in Sweden since 1993, with more than a 1000 in practical use on farms today. Similar systems are also being tested in Denmark and Norway (Torstensson 2000), France (Jones et al. 1999, Helen Legrand pers. Comm.), Belgium (Pussemier et al. 1998a, 1998b) and England (Fogg et al. 1998, 2000). In its simplest form the Swedish biobed is a clay lined hole in the ground filled with a mixture of

topsoil, peat and straw in the ratios 25%:25%:50% respectively. The biobeds are covered with grass and have a ramp installed over the top to allow the sprayer to be parked on top of the biobed. The size of the biobed is dependent on the anticipated amount of use as well as the size of the sprayer. The biobeds were sampled at three times throughout a year with analysis for more than 40 different actives carried out (Table 5).

Table 5 Examples of pesticide residues found in Swedish biobeds during 1993 - 1996

Pesticide	Pesticide residue range (µg g-1 biobed sample)		
	Spraying season	Late autumn	Next spring
Bentazone	0.1-60	<0.03-14	<0.03
Clopyralid	0.1-0.4	<0.03-0.2	<0.03
Cyanazine	0.01-1	<0.01-0.5	<0.01
Cyfluthrin	0.1-1	<0.05-0.6	<0.05
Deltamethrin	0.08-2	<0.05-1.2	<0.05-1
Dichlorprop	1-15	<0.03-2	<0.03
Esfenvalerate	4-7	<0.05-0.8	<0.05-4
Ethofumesate	0.1-4	<0.05-2	<0.05
Fenpropimorph	0.3-2	<0.05-1	<0.01-1
Fluroxypyr	0.04-0.3	<0.03-0.3	<0.03
Isoproturon	0.7-10	<0.02-24	<0.02-1
Lambda-cyhalothrin	0.1-5	<0.1-2	<0.01-0.8
Linuron	0.1-4	<0.03-0.3	<0.03-0.1
MCPA	0.08-40	<0.03-6	<0.03
Mecoprop	0.03-2	<0.03-0.06	<0.03
Methabenzthiazuron	0.2-0.4	<0.1-0.16	<0.1-0.1
Metazachlor	0.2-12	<0.01-3	<0.01-0.1
Primicarb	0.3-4	<0.02-2.6	<0.02-1
Propiconazole	0.2-40	<0.05-4	<0.05-2
Terbuthylazine	0.4-1	<0.02-0.6	<0.02-0.04
Terbutryn	0.1-30	<0.03-10	<0.03
Tolyfluanid	0.2-16	<0.1-6	*

* Only used during 1996. Sample not yet analysed.

From these initial studies it was concluded that biobeds effectively collect, retain and degrade pesticide spills.

Pesticide mobility within the biobed was also considered. Samples were collected from the most contaminated part of the biobed. Data suggests (Table 6) that the majority of the pesticides were retained within the biomix with only a single detection made within the top 5cm of the clay layer. Leaching potential was however based on concentrations of pesticide found in the biobed matrix and not in leachate. Detection limits in water can be 1000 times more sensitive are necessary in order to fully assess the risk to ground water.

Table 6 Pesticide residues measured in a biobed which had been used for 6 years

	Residues found ug g-1 (dry weight)				
	Biomix 0 - 20cm	Biomix 20 - clay layer	Clay layer 0 - 5 cm	Clay layer 5 - 10cm	Limit of detection
Diflufenican	0.70	0.08	<0.05	<0.05	0.05
Esfenvalerate	0.40	0.01	<0.01	<0.01	0.01
Fenpropimorph	0.24	0.04	<0.04	<0.04	0.04
Fluroxypyr	0.01	<0.01	<0.01	<0.01	0.01
Isoproturon	0.45	0.25	0.05	<0.01	0.01
Metazachlor	0.13	0.04	<0.04	<0.04	0.04
Metabenzthiazuron	0.22	<0.05	<0.05	<0.05	0.05
Primicarb	0.23	0.04	<0.02	<0.02	0.02
Propiconazole	0.25	0.05	<0.05	<0.05	0.05
Teruthylazine	0.30	<0.04	<0.04	<0.04	0.04

Long term use of biobeds was investigated. Using microbial activity as an indicator as to the performance of the biobed Torstensson 2000 suggests that biobed material needs to be completely replaced between 5 and 8 years depending on climate and the number of times the biobeds has had fresh material added. It is recommended that the biobeds have fresh material added every spring, prior to the start of the spraying season. Four biobeds were excavated and biomix samples taken for residue analysis over a 12 month period. Excavated material was placed onto an impermeable membrane with the biomix covered during period of heavy rainfall. In 3 of the 4 biobeds pesticide levels were below the limit of detection within 8 months and for the fourth biobed residue levels were close to limit of detection within 12 months.

In Belgium a lysimeter type experiment was set up to look at the leaching potential of the herbicides atrazine, bentazone, chloridazon, chlortoluron, cyanazine, isoproturon, lenacil and quinmerac and the insecticide carbofuran in biobeds (Pussimier et al. 1998). Some of the lysimeters had granulated active carbon introduced into the drain outlet. The lysimeters were treated 3 times, autumn 1996 and spring and autumn 1997 with 0.5 L aqueous mixture containing approximately 200 mg L-1 of each major herbicide active ingredient and 1000 mg L-1 of the insecticide carbofuran. Following the first application the authors reported that as much as 20% of the most mobile pesticides leached in the first 50 mm of rainfall, which occurred within 14 days of application. Following the second application (spring 1997) 3.27% of the applied carbofuran leached and 0.45% of the herbicides. The effects of evapotranspiration had a clear effect on leaching potential throughout this period as in excess of 400 mm of rainfall was required in order for the most readily available pesticides to leach.

This compared to losses of 6.71% of the applied carbofuran and 1.13% of the applied herbicides following the third application. The majority of the leaching occurred within 1 month compared to 80 days following the second application. In biofilters fitted with an activated carbon filter no significant leaching was detected.

In France Aventis are sponsoring a system called 'Phytobac'. This is a system based on that designed by Torstennson et al. 1997 and has been designed to retain and degrade pesticide waste and washings. The system consists of a concrete lined hole filled with a mixture of soil and chopped straw. The system is still in the early stages of development however initial assessments indicate the system has the potential to achieve high rates of degradation whilst representing minimal risk to the environment. In spite of the systems potential French regulation considers the contents as hazardous waste and would therefore require licensed disposal once the contents of the 'Phytobac' require replacement.

In Denmark biobed experiments have been operating for 3 years (Heniksen et al. 1999 cited in Rose et al. 2000). The biobeds (2m x 1m) were treated on two occasions with 8 g of MCPP and IPU and exposed to a controlled amount of rainfall. Drainage water was collected from the bottom of each system. Mean concentrations were 0.08 mg L-1 (IPU) and 0.5 mg L-1 (MCPP). Even though the biobed system was able to retain a significant amount of the applied pesticide concentrations in leachate were not acceptable to the Danish EPA, in addition the content of the biobed was classified as hazardous waste.

Many of the treatment systems discussed may be too expensive to become widely used on UK farms or the technology inappropriate for use in the UK. There is potential for the use of reedbeds and batch biofilm reactors in treating pesticide waste and washings. However until further research has been carried out looking at their effectiveness at treating a complex mixture of pesticides and full scale field systems have been tested they are unlikely to provide a system for treating pesticide waste on the farm. Biobeds however appear to offer an alternative to the current disposal options described in the Code of Practice. Biobeds appear to effectively retain and degrade pesticide spills thus reducing the environmental risk form point sources of pesticide.

2.8 Regulation of Biobeds in the UK

Biobeds have been evaluated in the UK (Fogg et al. 2000 and this report) and have been demonstrated to retain / degrade pesticide waste and equipment washings. However

regulation with respect to their use is unclear. Several options have been highlighted by the Environment Agency (Barnden pers.com., Jones pers.com.) and are described below;

1). Adopt best practice procedures. This would involve the operator building and operating the biobed in accordance with the best available advice. It is an uncontrolled approach, which relies on the end user adhering to the recommended procedures.

2). Adopt best practice procedures and notify the Environment Agency of your intentions to build and operate a biobed in accordance with best available advice.

3). Notification and approval. Notify Environment Agency that you would like to build a biobed. The Environment Agency then would have to approve the site with respect to possible ground and / or surface water contamination. A biobed could then be built subject to the site being approved.

4). Conditional Prohibition Notice. This is issued to a named individual who is responsible for the construction and safe operation of the biobed. Conditional Prohibition Notices apply to Sentinel treatment systems. Currently no cost is attached to a Conditional Prohibition Notice.

5). Formal permission. This takes the form of a Ground Water Regulations authorisation. Any deliberate discharges of listed substances, onto or into land requires a Ground Water Regulations authorisation. The regulation's state that List I substances must be prevented from entering ground water. Therefore in theory concentrations of pesticide discharged from the bottom of a biobed can be > 0.1 µg L-1 provided there is potential for further attenuation. The potential for further attenuation would be dependent on the biobed design. At present there is a £92 charge associated with an application for a Ground Water Regulations Authorisation. This may however change whereby annual applications have to be made.

6). Discharge Consent. This can be either surface water or ground water. Again a one off application charge of £92 applies. In addition Environmental Quality Standards (EQS's) would have to be met which would involve monitoring and analysis (£100 / sample). Annual charges for a discharge consent licence could extend to several £1000's.

Under the current legislation biobeds would require a Ground Water Regulations authorisation. However once waste management controls are extended to cover agricultural

waste, a waste management licence will be required by anyone who proposes to deposit, recover or dispose of waste. Additionally pesticides are likely to be classified as special waste under the Special waste Regulation 1996, with special wastes subject to additional, more stringent controls to safeguard the environment.

It is seems neither, practical or desirable to issue an authorisation to every individual farm that may want to build and operate a biobed. Similarly there is a need to avoid additional regulation for farmers who try to do the "right thing" with regards to environmental protection.

3 LABORATORY STUDIES

3.1 Introduction

Any system designed to treat pesticide waste arising from accidental spillages, drips or washings needs to treat high concentrations of pesticide, applied repeatedly, often as part of a complex mixture. Previous work (Fogg et al. 2000) investigated the potential for biomix to degraded 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 biomix at high application rates. Isoproturon and chlorothalonil were applied as a mixture at 100 and 60 mg kg-1 (respectively). Degradation in biomix was unaffected by combining the two pesticides whereas in topsoil isoproturon DT50 values increased from 17.4 to > 97 days.

One possibly explanation for the difference in isoproturon degradation between soil and biomix is that fact that the topsoil used for the experiment had previously been treated with isoproturon as part of normal agricultural practice. These previous treatments may have resulted in microbial adaptation of the soil microbial community resulting in enhance biodegradation of isoproturon, a theory supported by Cox et al. 1996. It is possible that repeated exposure of biomix to a pesticide could result in similar microbial adaptation. Laboratory studies were therefore performed to investigate the degradability of pesticides when applied repeatedly.

Isoproturon has been shown to degrade at a similar rate in both topsoil and biomix (DT50 values of 21.1 and 19.1 days respectively) when applied on its own at 100 mg kg-1 concentration. However when applied to topsoil as a mixture with chlorothalonil, the time to 50% of the initial concentration increased indicating interaction between the two pesticides. As a biobed would need to be able to treat more than one pesticide, laboratory studies were performed to investigate the degradability of pesticides when applied as part of a relatively complex mixture.

Sulfonylurea herbicides can unintentionally be retained in sprayers if not properly washed out and subsequently cause crop damage (Read et al. 1998). One method of removing residues which may have bound onto the internal surfaces of the spray tank is to use an ammonia based cleaning product for example "All Clear Extra". Standard clean out procedures involve completely filling the spray tank with a solution of "All-Clear Extra" followed by a soaking period of 15 minutes and can generate high volumes of waste depending on the size of the

application equipment. Reduced volume clean out procedures can decrease the volume of wash solution required by as much as 66% however as "All-Clear Extra" has no effect on the efficacy of the pesticide (Neil Baldwin pers. comm.), sensitive crops would still be damaged by the wash solution. It is therefore highly likely that such washings would be disposed of onto a biobed. Laboratory studies were therefore performed to investigate the degradability of pesticides following pre-treatment of the biomix with "All-Clear Extra".

The assumption for all laboratory studies has been that the applied pesticides degraded with time. Alternatively the pesticides may have become irreversibly bound, a function of increased contact time between the pesticide and the test material resulting in the chemical becoming less extractable and maybe less bioavailable (Gevao et al. 2000). It is vital then any system designed to receive pesticide waste and washings must degrade the pesticides it receives. Experiments were therefore performed to address the issue of bound residues in biomix.

3.2 Materials and methods

3.2.1 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, air dried to approximately 30-40% w/w and then refrigerated at approximately 4°C prior to use.

Field moist topsoil (Characteristics are given in Table 7) 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.

Table 7 Physical characteristic of topsoil used in both the biomix and on its own

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

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.

3.2.2 Studies with a mixture of 6 pesticides

The degradability of a combination of the six pesticides was investigated (Table 8).

Table 8 Properties and field application information for each of the study compounds.

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

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

Samples (25 g) of topsoil and biomix were treated with formulated product, with the pesticides applied individually or 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 - 8m3 biobed 6 times a year, (Table 9). Samples were taken 0, 3, 10, 20 30, 60, 90 and 120 DAT and stored prior to analysis. Three treated soil and biomix samples were collected at each time point with a single sample from both acting as a control.

Table 9 Concentrations of pesticides used in laboratory study investigating the degradation of 6 pesticides individually and in combination

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

3.2.3 Repeat application study

Topsoil and biomix samples (25g) were treated with a mixture of the six study compounds (Table 8). With the exception of epoxiconazole, the application rates used were the same as used in the laboratory mixture study (Table 9). 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.

With the exception of epoxiconazole DT50 values were calculated by fitting first-order kinetics to the observed patterns of degradation. The first order fit for epoxiconazole gave r2 values of < 0.7 which are considered unacceptable, (Beulke and Brown, in press). DT50 values for epoxiconazole were therefore calculated by interpolating between two points.

3.2.4 Tank cleaning agents

"All-Clear Extra" is a liquid formulation containing 6% w/w ammonia, sequestrants and surfactants. Standard and reduced clean out procedures following the use of "All-Clear Extra" can result in up to 600g of ammonia being deposited, resulting in concentrations of ammonia between 1 and 500 mg kg-1 depending on the size of biobed.

Biomix samples (25g) were pre-treated with "All-Clear Extra" at 1, 5, 35, 50, 100 and 500 mg kg-1 concentration with a number of samples left as untreated controls. Chlorothalonil and isoproturon were applied separately as formulated product at 60 and 100 mg kg-1 respectively. The moisture content was made up to 50% w/w (40% of the MWHC) with the samples then incubated at 20°C. Samples were taken 0, 3, 10, 20 30 and 60 DAT and stored at -15 °C prior to analysis. Three treated samples from each treatment were collected at each time point with a single sample for each pesticide acting as a control. A further three samples from each "All-Clear Extra" treatments were taken for pH determination.

3.2.5 Bound residues

Again biomix samples (25g) were weighed out into 125 mL clear glass bottles. Half the samples were treated with chloroform (2 mL). Both treated and untreated samples had lids attached and sealed, with all samples then incubated at 30°C for 7 days. Treated samples were evacuated 6 - 8 times to remove the chloroform and then treated either with chlorothalonil or pendimethalin. The pesticides were applied as formulated product at 60 and 80 mg kg-1 concentrations respectively. Moisture content was made up to 50 % w/w and the samples incubated at 20°C. Samples were subsequently collected at 0, 3, 10, 20, 30, 60, 90 and 120 DAT. Three treated samples from each pesticide and for both the sterile and non-sterile treatments were collected at each time point. A single sample for each pesticide and treatment was taken as a control.

3.2.6 Bound residues (repeat study)

Biomix samples (19g and 20g) were weighed out into 100 mL Duran glass bottles. Samples were then autoclaved at 121 °C for 1 hour. Bacterial and fungal sterility was confirmed by spreading a 0.1 g (fresh weight) sub-sample of the autoclaved material over plates of R2A and malt extract agar MEA. Plates were maintained at 20°C and checked regularly over a 20 day period for growth of bacterial colonies on R2A and fungal hyphae on MEA. A single sample of the autoclaved biomix was extracted with 50 mL acetonitrile and was analysed using HPLC to check for background interference. Half the samples (19g) were re-inoculated with 1 g of non-autoclaved biomix. A 400 µg mL-1 solution of chlorothalonil was prepared in sterile distilled water. Samples were treated with 3 mL of the prepared solution in order to achieve a final concentration of 60 mg kg-1 and a moisture content of 50% w/w. Both sterile and non-sterile samples were incubated at 20°C with three treated and one untreated sample from each collected at 0, 5, 10, 20 and 30 DAT.

3.2.7 Analysis

Methods of analysis are given in Appendix A.

3.3 Results

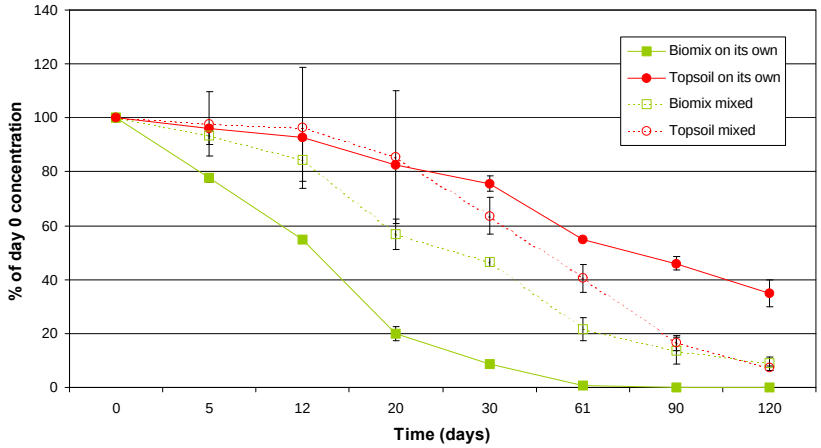
3.3.1 Studies with a mixture of 6 pesticides

Rates of degradation of each pesticide were studied individually and in combination, in both topsoil and biomix (Figure 1 and Figure 2). Degradation was generally faster in the biomix than in topsoil (Table 10). The exception to this being chlorpyrifos in both the individual and mixture treatments and epoxiconazole in the mixture treatment.

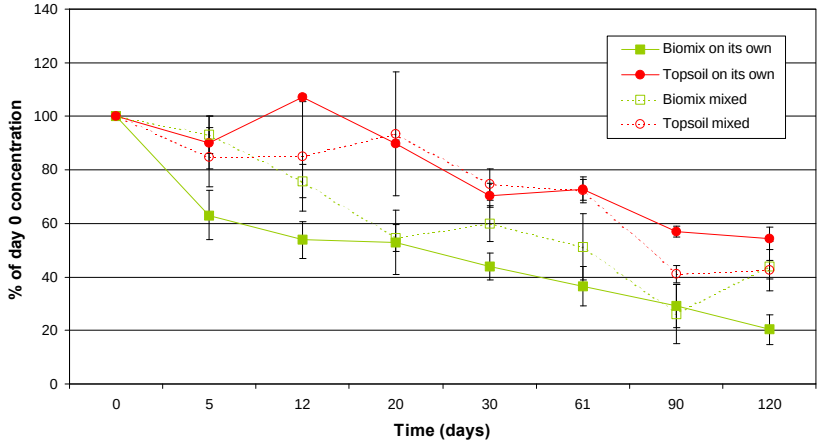
Table 10 DT50 values for isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate in topsoil and biomix when applied individually and in a mixture

	Individual				Mixed			
	Topsoil		Biomix		Topsoil		Biomix	
Isoproturon	76.3	r2 1	10.3	r2 0.98	40.2	r2 0.97	28	r2 0.99
Pendimethalin	122.9	r2 0.83	50.2	r2 0.79	98.0	r2 0.88	67.2	r2 0.78
Chlorpyrifos	31.8	r2 0.98	49.1	r2 0.88	66.0	r2 0.92	106.0	r2 0.67
Chlorothalonil	225.0	r2 0.80	12.2	r2 0.99	55.1	r2 0.74	10.6	r2 0.80
Epoxiconazole	>120	*	>120	*	63.7	*	84.7	*
Dimethoate	8.6	r2 0.99	5	r2 0.99	42.0	r2 0.96	17.1	r2 0.99

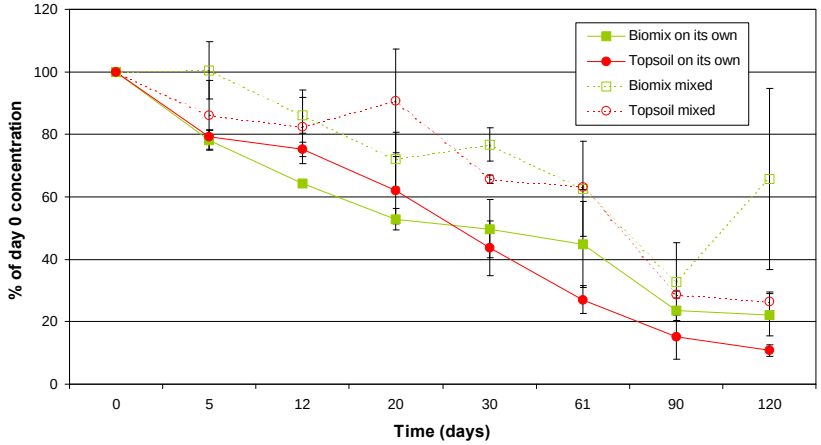
* Not possible to calculate



(a)

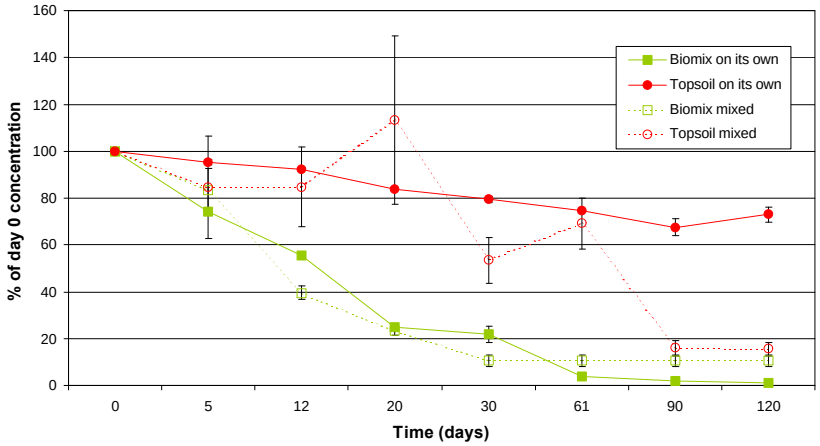


(b)

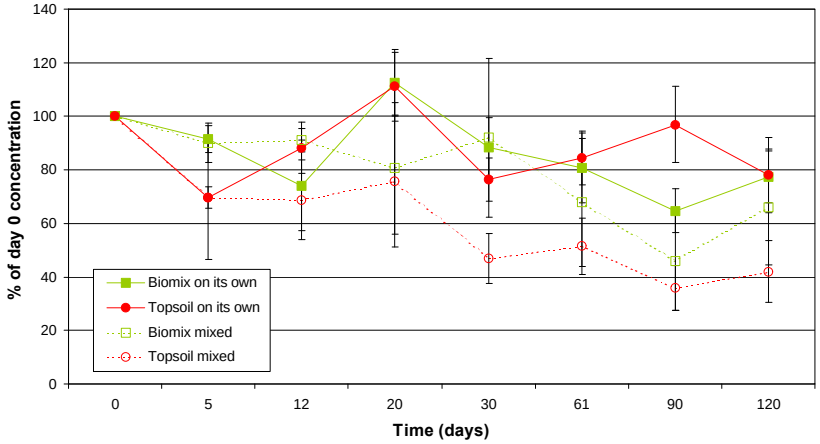


(c)

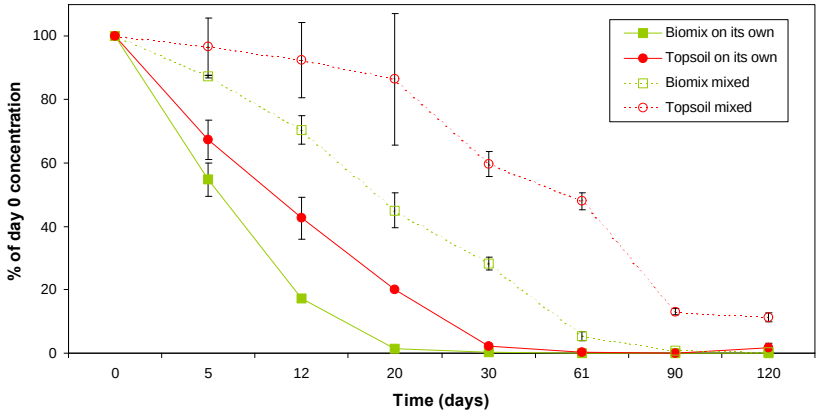
Figure 1 Mean amounts (±SE) of (a) isoproturon, (b) pendimethalin and (c) chlorpyrifos in topsoil and biomix both individually and when mixed the 5 remaining pesticides being investigated



(a)



(b)



(c)

Figure 2 Mean amounts (±SE) of (a) chlorothalonil, (b) epoxiconazole and (c) dimethoate in topsoil and biomix both individually and when mixed with the 5 remaining pesticides being investigated

For epoxiconazole applied individually to biomix and topsoil the time to 50% of the initial concentration was > 120 days. At the end of the study the amount of the initial epoxiconazole remaining in biomix and topsoil was 77.4% and 78.1% respectively.

3.3.2 Repeat application study

The degradation of 6 pesticides applied repeatedly to topsoil and biomix, at high concentrations and as a mixture was measured. With the exception of chlorpyrifos pesticide degradation was faster in biomix than in topsoil (Figure 3 and Figure 4). With the exception of epoxiconazole, degradation in biomix was such that < 30% of the total amount applied remained after 200 days (Table 11).

Table 11 Amounts of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate (as % of applied) remaining in biomix and topsoil following 3 applications of a mixture containing each pesticide

	Nominal application rate			% remaining	
	Application 1	Application 2	Application 3	BIOMIX	Topsoil
Isoproturon	100	100	100	1.5	47.6
Pendimethalin	80	80	80	28.3	51.8
Chlorpyrifos	28.8	28.8	28.8	26.6	19.7
Chlorothalonil	60	60	60	0.1	17.5
Epoxiconazole	5	5	5	78.5	86.8
Dimethoate	13.6	13.6	13.6	0	11.4

Results for biomix indicate that concentrations of pendimethalin, chlorpyrifos and epoxiconazole increase 30 days after the second application. Concentrations are approximately double that measured 20 DAT and are attributed to a double application of the pesticide mixture. Similarly soil concentrations of all pesticide with the exception of chlorothalonil increase 30 days after application number 3 and remain higher than anticipated in samples collected 60 and 90 DAT. Over application is again considered the most feasible explanation.

DT50 and DT90 values are summarised for each of the 3 applications in Table 12, Table 13 and Table 14. Following the first application DT50 values for biomix were all lower than reported values in soil. Following the second application a slight decrease in the time taken to reach 50% of the day 0 (application 2) concentrations was observed with the exception of chlorpyrifos for which the DT50 value was approximately the same as that following application 1 and dimethoate for which the DT50 value increased. After the third application DT50 values for all 6 pesticides increased. DT90 values for isoproturon, dimethoate and

chlorothalonil were 188, 86 and 45 days respectively after 3 applications at 4 times the maximum recommended field application rate indicating that carryover from of these pesticides from one year to the next should not be a problem. It was not possible to calculate a DT90 for epoxiconazole from the data available however for pendimethalin and chlorpyrifos values of 498 and 1044 days respectively were calculated.

Table 12 DT50 and DT90 values for each pesticide in biomix following a single application of a mixture of all 6 pesticides

	Application 1			
	Reported DT50	Measured DT50	Measured DT90	r2
Isoproturon	25	14.5	48.1	0.98
Pendimethalin	90	23.5	78.1	0.94
Chlorpyrifos	30	26.5	115.3	0.99
Chlorothalonil	30	2.9	9.8	1
Epoxiconazole	60-90	90.3	>120	*
Dimethoate	7-16	8.6	28.4	1

* calculated by interpolation between two points and not by fitting a curve

Table 13 DT50 and DT90 values for each pesticide in biomix following two applications of a mixture of all 6 pesticides

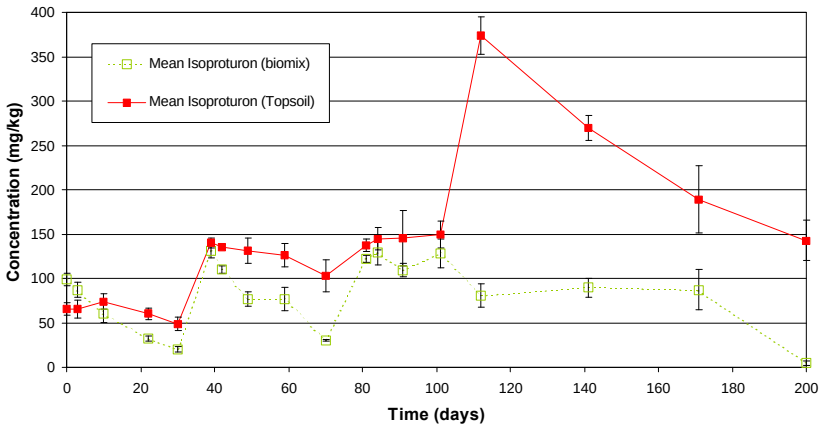
	Application 2			
	Reported DT50	Measured DT50	Measured DT90	r2
Isoproturon	25	13.9	77.5	0.86
Pendimethalin	90	33.4	198.8	0.84
Chlorpyrifos	30	25.9	66.7	0.91
Chlorothalonil	30	2.7	9.1	0.99
Epoxiconazole	60-90	36.8	>120-	*
Dimethoate	7-16	13.6	45.2	0.92

* not calculated as rates of degradation calculated by interpolation between two points and not by fitting a curve

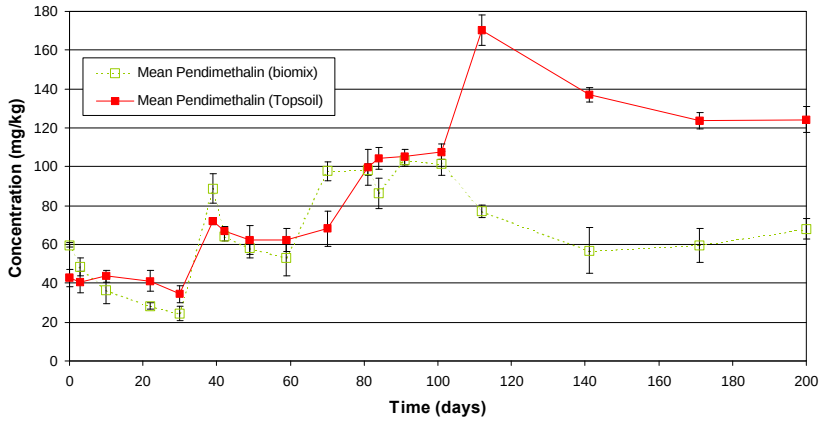
Table 14 DT50 and DT90 values for each pesticide in biomix following three applications of a mixture of all 6 pesticides

	Application 3			
	Reported DT50	Measured DT50	Measured DT90	r2
Isoproturon	25	101.7	118.5	0.97
Pendimethalin	90	149.8	497.6	0.64
Chlorpyrifos	30	314.3	1044.0	0.80
Chlorothalonil	30	17.9	45.5	0.94
Epoxiconazole	60-90	*	*	*
Dimethoate	7-16	25.9	86.0	0.95

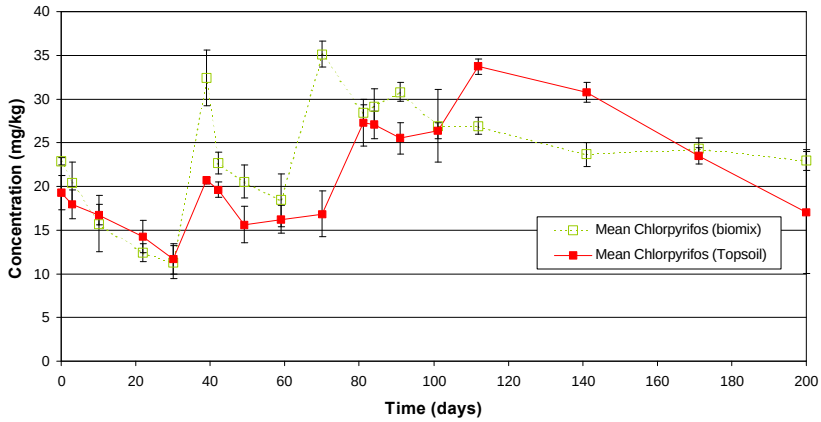
* not possible to calculate from the data available



(a)

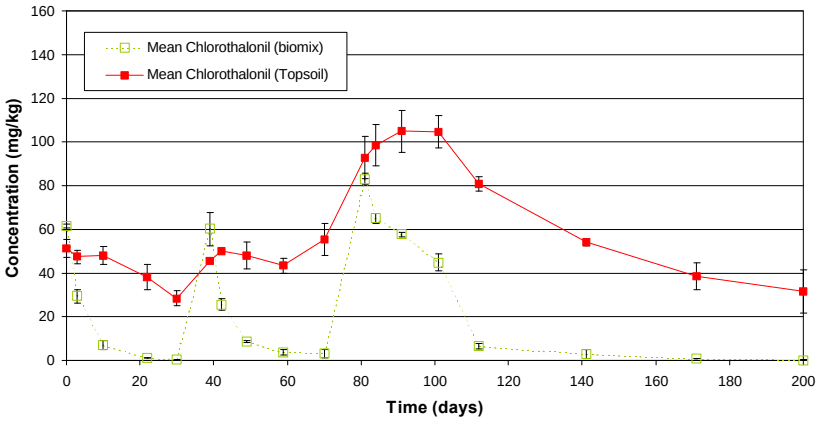


(b)

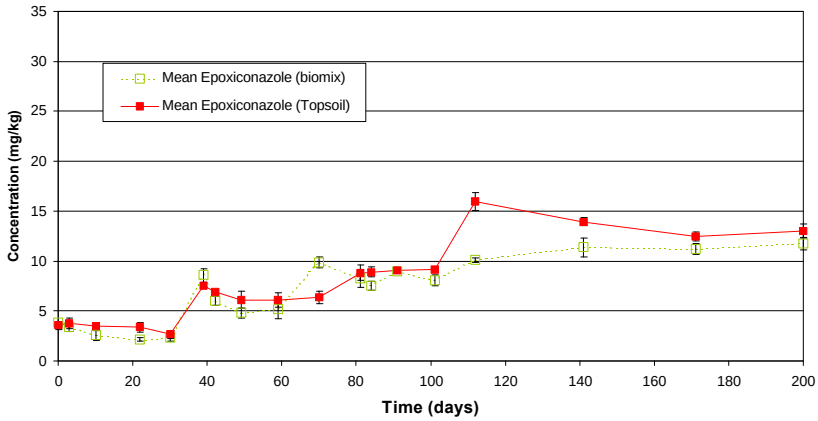


(c)

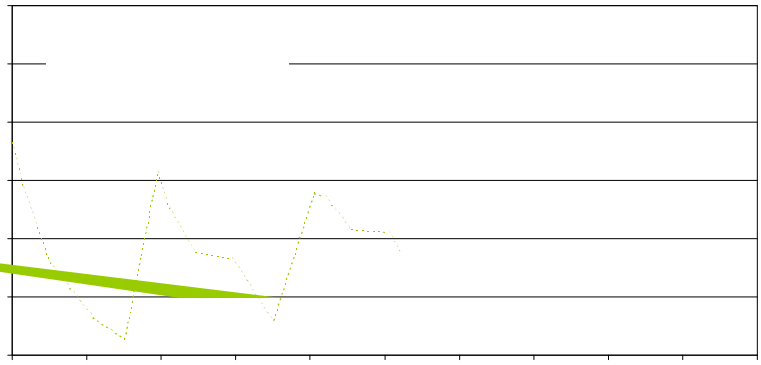
Figure 3 Degradation of; (a) isoproturon, (b) pendimethalin and (c) chlorpyrifos following repeated applications of a pesticide mixture containing isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate


Mean Chlorothalonil (biomix)
Mean Chlorothalonil (Topsoil)
Concentration (mg/kg)
Time (days)
0
20
40
60
80
100
120
140
160
180
200

(a)


Mean Epoxiconazole (biomix)
Mean Epoxiconazole (Topsoil)
Concentration (mg/kg)
Time (days)
0
5
10
15
20
25
30
35
0
20
40
60
80
100
120
140
160
180
200

(b)



3.3.3 Tank cleaning agents

Rates of isoproturon and chlorothalonil degradation in biomix were measured following pre-treatment of the biomix with the "All-Clear Extra" at a range of concentrations. Chlorothalonil degradation was faster in biomix treated with "All-Clear Extra" than in untreated biomix. Degradation rate increased with increasing concentration of "All-Clear Extra" up to a maximum concentration of 25 mg kg-1 with a subsequent decrease observed in biomix pre-treated at 100 and 500 mg kg-1 concentration (Figure 5).

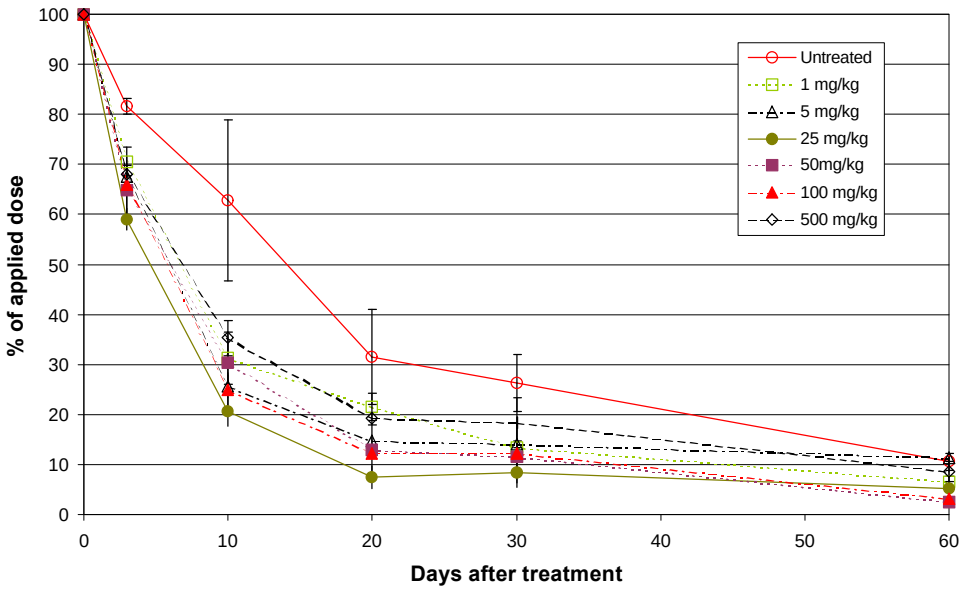


Figure 5 Chlorothalonil degradation in biomix treated with "All-Clear Extra" at a range of concentrations

A similar pattern of degradation was observed for isoproturon (Figure 6). Degradation rates were higher in biomix treated with "All-Clear Extra" up to a maximum concentration of 100 mg kg-1. However isoproturon degradation in biomix pre-treated at 500 mg kg-1 was slower than in untreated biomix, (DT50 values 15.4 (R2 0.99) and 8.6 (R2 0.99) respectively).

Biomix pH ranged from 6.51 to 6.99 for "All-Clear Extra" treatments 0 - 100 mg kg-1 but increased to 7.8 for the biomix spiked at 500 mg kg-1, indicating an inability for the biomix to completely buffer the high dose rate. Correlation between biomix pH following pre-treatment with "All-Clear Extra" and time to 50% loss show a strong positive relationship (R2 = 0.96) and may account for the slower degradation observed for isoproturon in biomix pre-treated with "All-Clear Extra" at the maximum dose.

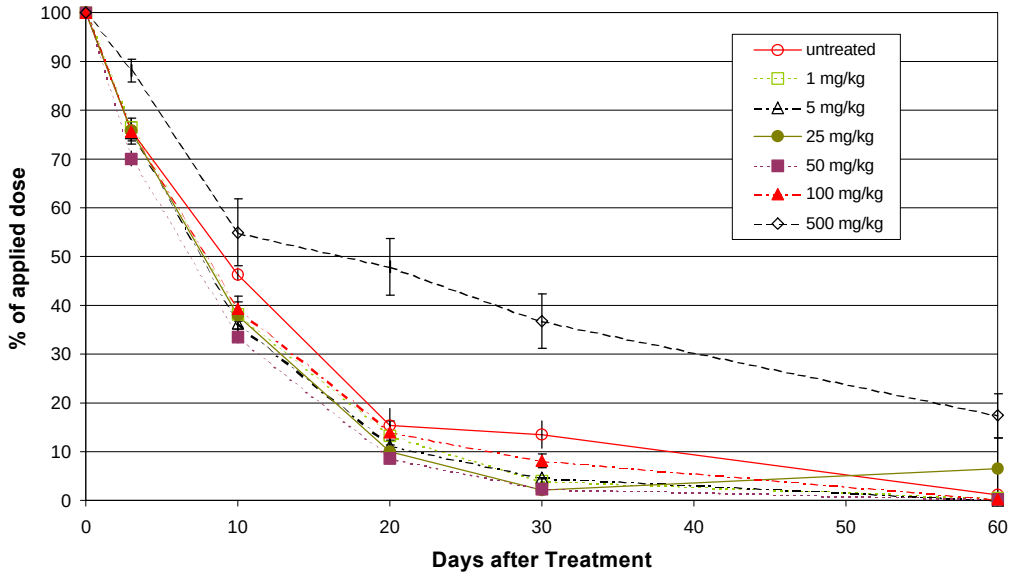


Figure 6 Isoproturon degradation in biomix treated with "All-Clear Extra" at a range of concentrations

3.3.4 Bound residues

The degradation of chlorothalonil and pendimethalin was measured in sterile and non-sterile biomix (Figure 7 and Figure 8). Degradation rates of the two pesticides in non-sterile biomix were 25.3 (r2 = 0.94) and 81.4 (r2 = 0.99) days respectively whereas in sterile material DT50 values of 41 (r2 = 0.96) and 124.5 (r2 = 0.97) were measured. Comparison between pendimethalin degradation rates in sterile and non-sterile biomix indicate that the biomix remained sterile for 20 - 30 days. After 20 days 99.5% of the applied pendimethalin could still be recovered from the sterile biomix whereas 83% was recovered from non-sterile material. Data for chlorothalonil however suggest incomplete sterilisation may have been achieved resulting in rapid re-establishment of micro-biological communities. The experiment was therefore repeated using a more rigorous sterilisation technique.

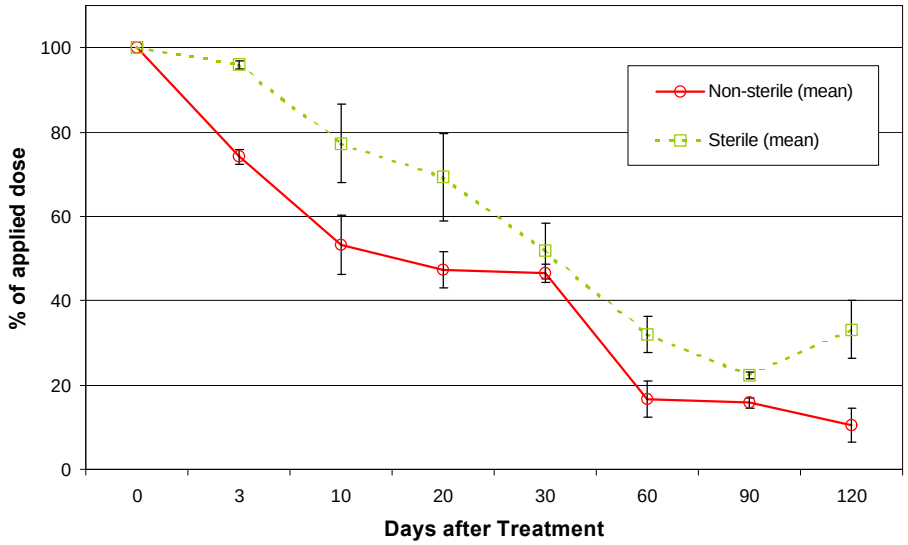


Figure 7 Chlorothalonil degradation in non-sterile biomix and biomix sterilised using chloroform

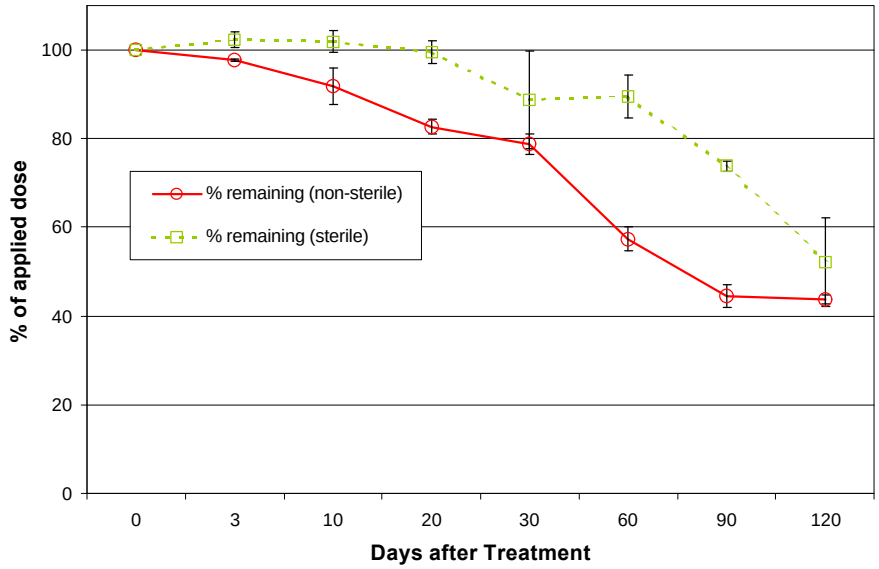


Figure 8 Pendimethalin degradation in non-sterile biomix and biomix sterilised using chloroform

3.3.5 Bound residues (repeat study)

Chlorothalonil degradation was again measured in sterile and non-sterile biomix. Sterilisation was achieved through autoclaving, with half the samples re-inoculated with non-sterile biomix (Figure 9). RA2 and malt extract agar (MEA) plates were checked regularly over a 20 day period for growth of bacterial colonies on RA2 and fungal hyphae on MEA. No growth was observed on either agar type demonstrating that the autoclave treatment had brought

about complete sterilisation. At the end of the study <50% of the applied dose was measured in non-sterile biomix compared to 84% in sterile material.

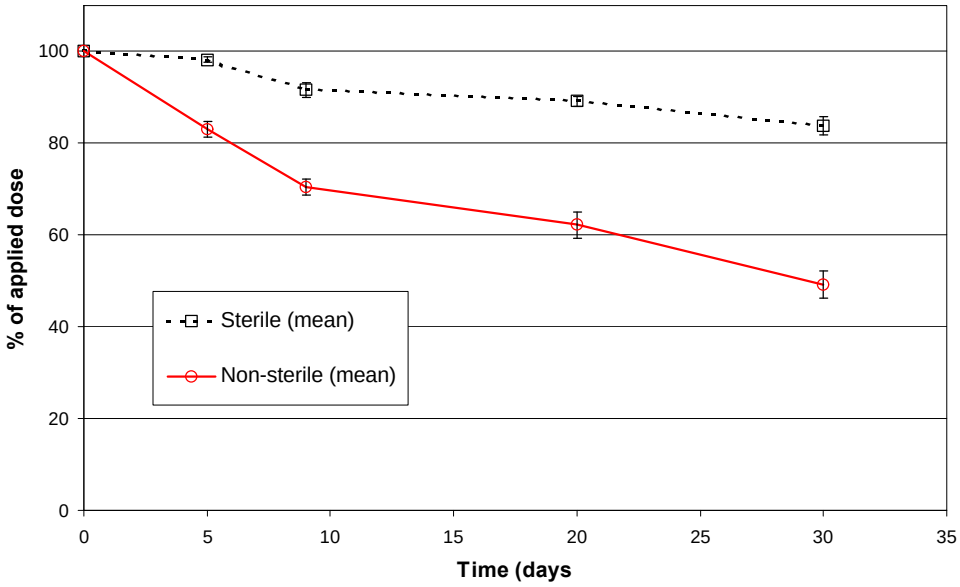


Figure 9 Chlorothalonil degradation in non-sterile biomix and biomix sterilised by autoclaving

3.4 Summary and Conclusions

Studies into the effects of pesticide mixtures indicated that interactions between pesticides were possible, however the effects were generally less significant in biomix than in soil. With the exception of chlorpyrifos, degradation rates were similar in biomix treated with a mixture of pesticides at 4 times the maximum field application rate to reported DT50 values for each compound applied individually to soil (Table 15).

Table 15 DT50 values for pesticides applied at 4 times the maximum field application rate and as part of a mixture to biobed mixture compared to reported DT50 rates in soil

	Reported DT50 for soil *	DT50 in biomix when applied in a mixture
Isoproturon	25	28
Pendimethalin	90	67
Chlorpyrifos	30	106
Chlorothalonil	30	11
Epoxiconazole	60 - 90	85
Dimethoate	7 - 16	17

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

Repeated applications of pesticide to agricultural soil can results in enhanced biodegradation, (Cox et al. 1996). A biobed would need to a treat complex mixtures of pesticide applied repeatedly at high concentrations. The effect of applying a mixture containing 2 herbicides, 2 fungicides and 2 insecticides, at 4 times the maximum field application rate to biomix was therefore investigated. Overall the biobed mixture was able to cope with a relative complex mixture of pesticides, applied repeatedly at high concentrations. Degradation rates were faster in biomix than in soil, for example dimethoate (Table 16).

Table 16 Dimethoate degradations in topsoil and biomix following 2 applications of a mixture containing, isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate.

	Topsoil			Biomix		
	DT50	DT90	r2	DT50	DT90	r2
Application 1	40.3	133.8	0.97	8.6	28.4	1
Application 2	62.7	208.4	0.96	13.6	45.2	0.92
Application 3	*	*		25.9	86.0	0.95

* Could not be calculated due to over application at the time of treatment

In biomix degradation rates (DT50) for all six pesticides generally decreased following the second application of the pesticide mixture with an increase observed for all six pesticides following the third treatment. With the exception of pendimethalin and chlorpyrifos DT90 values were >365 days. A poor first order fit (r2 = 0.64) for pendimethalin may explain a DT90 value of 498 days, however for chlorpyrifos a DT90 of 1044 days (r2 = 0.80) was calculated. Under normal circumstances aerobic degradation studies should not exceed 120 days unless necessary to characterise the decline curve. Where studies do extend for periods >120 days as was the case for this study results should be interpreted with caution (Lynch 1995). Under semi-field conditions both pesticides degraded.

Pesticide degradation is influenced by the chemical properties, nutrient status and environmental conditions (Walker et al. 2001) and also by the availability of the compound(s) to the degrading micro-organisms (Gevao et al. 2000). Gevao et al. 2000 suggests that at high application rates only a fraction of the applied pesticide would typically be in solution (depending the solubility of the compound) and available to the micro-organisms. A moisture content of 40% of the maximum water holding capacity (50% w/w) was maintained throughout the duration of the study. Torstensson (2000) suggests that a moisture content between 95 - 100% is optimum in field biobeds to allow adequate aeration of plant roots and is also the range for optimal activities of micro-organisms. Below 75% moisture content would be limiting with respect to microbial activity. There was no evidence of enhanced biodegradation within the biobed systems following the 3 applications of the pesticide

mixture possibly as a result of high concentration, low moisture content and the fact the pesticide mixture was relatively insoluble. However with the exception of epoxiconazole < 30% of the nominal application rate was recovered after 200 days.

Pesticide degradation in biomix pre-treated with the ammonia based tank cleaning agent 'All-Clear Extra' was generally faster than in untreated biomix. At very high concentrations of ammonia (500 mg kg-1) the biomix was unable to completely buffer the effects of ammonia resulting in an increase in pH from 6.5 to 7.8. Isoproturon degradation at this 'All-Clear Extra' concentration was effected DT50 15.4 (r2 0.99) compared to 8.6 days (r2 0.99) in untreated biomix. However degradation was still similar to that reported for soil, DT50 6 - 28 days, (Tomlin 1997).

The significance of bound residues in the context of the biobed was whether the observed % losses were as a result of degradation or 'Ageing'. 'Ageing' refers to the increased contact time between the chemical and the material to which it was applied. The longer the contact time the more strongly associated the pesticide and the material to which it was applied become. Whenever a pesticide is applied there is always a degree of binding for which adsorption is probably the most important mode of interaction. The degree of adsorption is largely controlled by the physico-chemical properties of the pesticides and also the material to which it is being applied. The more tightly sorbed a pesticide is the more difficult it will be to extract. However, it is the not ease of extractability under laboratory conditions which is of significance but the bioavailabiliity (Gevao et al. 2000).

The degradation of chlorothalonil, a fungicide known to readily degrade in biomix and pendimethalin, a strongly sorbed, persistent herbicide was measured in sterile and non-sterile biomix. Biomix was initially sterilised using liquid chloroform. Comparison of pendimethalin degradation rates in sterilised and non-sterile material indicated that the biomix remained sterile for 20 days with 99.5% of the applied recovered from the sterile biomix compared to 83% from the non-sterile. Comparison between the two recoveries indicate that the herbicide was degraded. Chlorothalonil recoveries indicate that the biomix remained sterile for approximately 3 days after which the rate of degradation was similar to that observed in non-sterile material. Sterility checks were not performed for this experiment, however investigations looking at the performance chloroform fumigation as a means of sterilising soil (Toyota et al 1996) suggest that only 10% of bacterial and 0.5% of fungal colony-forming units survived chloroform fumigation. Data for pendimethalin and chlorothalonil suggest that different populations of micro-organisms are responsible for their breakdown in the biomix.

The experiment was repeated using a more rigorous sterilisation technique. Biomix was autoclaved, with half material re-inoculated to enable comparison between sterile and non-sterile biomix. Bacterial and fungal sterility was confirmed, and the rate of chlorothalonil degradation measured. After 30 days < 50% of the applied dose was recovered from non-sterile material compared to 84% in sterile material. These data suggest that chlorothalonil is degraded. Degradation rates were however slower then previously measured, DT50 23.4 (r2 1) compared to 2.9 days (r2 1) following the first application in the repeat application experiment. It is suggested that the 1g of non-autoclaved material used to re-inoculate may have been insufficient to allow microbial populations to re-establish to pre-autoclaving levels prior to the addition of chlorothalonil.

4 SEMI-FIELD STUDIES: EFFECT OF WATER LOADING

4.1 Introduction

Previous studies demonstrated that concentrations of pesticide leaching from biomix were significantly lower than from soil columns. Only the most mobile pesticides investigated leached to any great extent and even for these pesticides the system appeared to retain / degrade more than 99% of the applied pesticide (Fogg et al. 2000). Degradation rates were higher in unlined biobeds than in lined systems and combined with the fact that the need to manage water inputs was removed an unlined system appeared the most practical. Further studies were therefore performed to assess the feasibility of using and uncovered and unlined biobed for the treatment of pesticide waste.

4.2 Materials and Methods

The effects of water loading on pesticide leaching behaviour were investigated. Twelve cores containing pre-composted biomix (97 days) were prepared. The cores were constructed using plastic tubing (19cm internal diameter) 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 either 10 litre high density polyethylene (HDPE) bottles or 2.5 L amber glass collection vessels depending on the hydraulic loading.

Three water loading scenarios were investigated (Table 17). Four cores were connected using plastic guttering to 0.54 m2 concrete slabs (Scenario 1). A further four cores were connected to 0.135 m2 concrete slabs (Scenario 2). The remaining cores received only direct inputs of rainfall (Scenario 3), (Plate 1). Silicon sealant was placed on three sides of each slab to prevent water loss.

Table 17 Water loading scenarios used in the semi-field studies

Scenario	Water inputs	Biobed size
1	Rainfall to approximately a 24m x 17m washing area + direct rainfall inputs to biobed	7.5 m3
2	Rainfall to approximately a 12m x 9m washing area + direct rainfall inputs to biobed	7.5 m3
3	Direct rainfall inputs to biobed only	7.5 m3

Plate 1 Water loading experiment at Horticulture Research International

4.2.1.1 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 spray tank washings (Fogg 1999) (Table 18). Three of the four replicates received pesticide and the remaining core in each set acted as a control. At the same time as the pesticides were applied a bromide tracer was also applied at a rate of 100 kg ha-1 (314 mg core-1). Bromide is a conservative, non-sorbed tracer. Such tracers are a useful tool for tracking water movement. For the purpose of this study the tracer was applied to check the hydrological integrity of the lysimeters, as well as looking at the breakthrough timing of infiltrating water and hence provide additional information on the leaching potential of the pesticides.

Table 18 Application details for water loading studies

Pesticide	Amount (mg)	Concentration 0-5cm (mg/kg)
Isoproturon	255	150
Pendimethalin	204	120
Chlorpyrifos	73.4	43.2
Chlorothalonil	153	90
Epoxiconazole	51	30
Dimethoate	34.7	20.4

4.2.1.2 Sampling

Leachate 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. Samples for pesticide residue analysis were frozen prior to analysis whilst bromide sub-samples were stored at 0 - 10 °C.

At the end of the study period (299 DAT) each of the 12 lysimeters was excavated and cut in the following sections: 0-5, 5-10, 10-20, 20-30 and 30-50cm. Each section was macerated and then frozen prior to analysis.

4.2.2 Analysis

Methods of analysis are given in Appendix A.

4.3 Results

4.3.1 Rainfall and leachate volumes

Rainfall throughout the study period January to September 2000 was 17 % above average (1951 - 1970, Whitfield 1974) and totalled 581.7mm. Below average rainfall was recorded for the remainder of the sampling period. Leachate samples were collected on 28 occasions (Figure 10) providing 265 water samples for analysis.

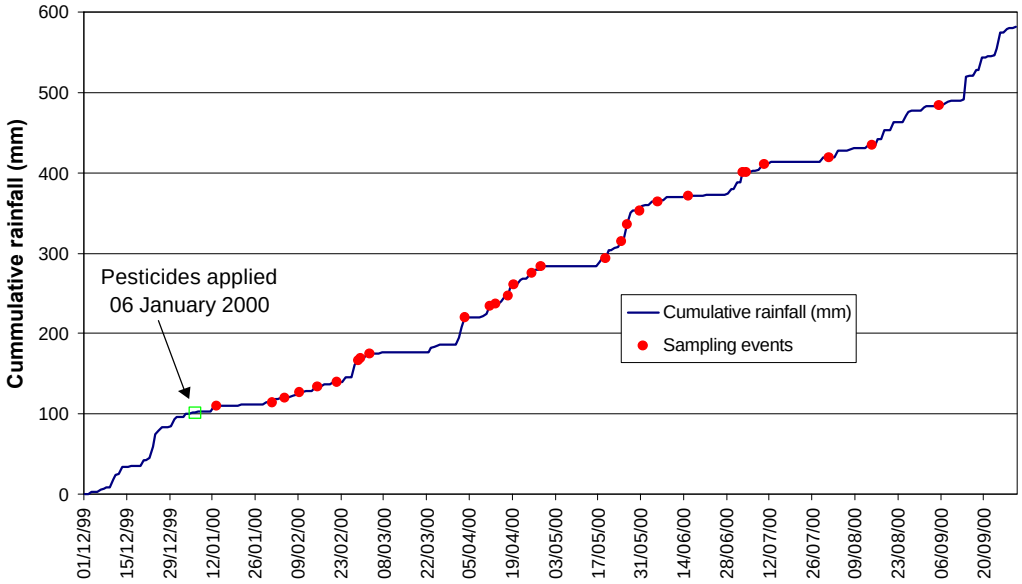


Figure 10 Cumulative rainfall at the Horticulture Research International lysimeter station

4.3.2 Leachate volumes

Cumulative leachate volumes from lysimeters with no hydraulic loading ranged from 3.4 to 5.1 litres (Figure 11). The lysimeters receiving a medium loading recorded between 45.2 and 56.4 litres of leachate, whilst the large loading resulted in volumes of 103.7 to 177.6 litres.

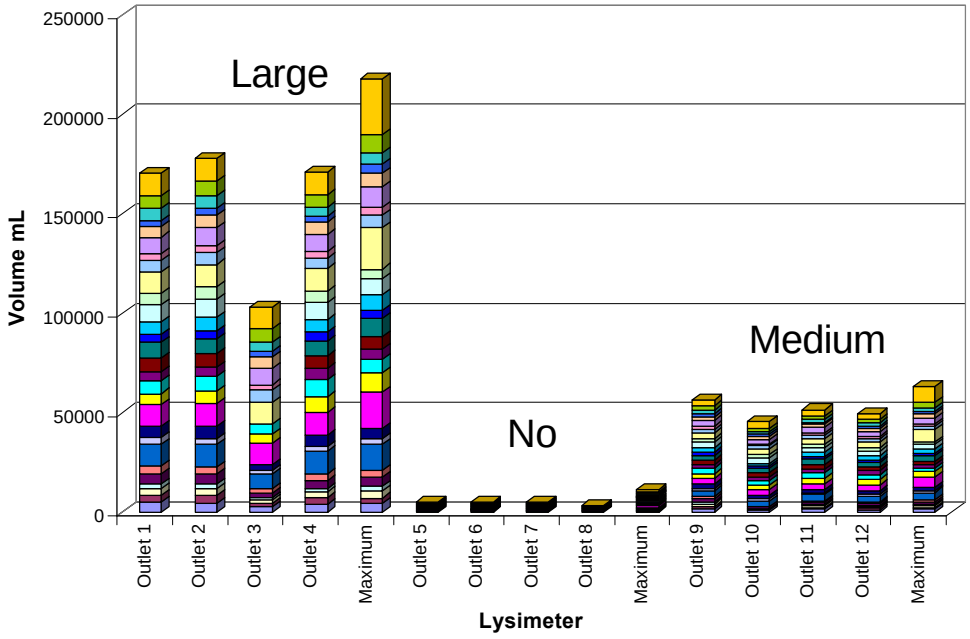


Figure 11 Leachate volumes from lysimeters with (a) a large hydraulic loading (b) a medium hydraulic loading and (c) no additional hydraulic loading

4.3.3 Bromide in leachate

Bromide breakthrough in lysimeters with a high and medium hydraulic loading occurred 7 DAT and in lysimeters with no additional loading 57 DAT (Figure 12). Mean maximum concentrations from lysimeters with a high loading were measured in the first sample collected after application. Bromide concentrations subsequently fell to just above the 1.1 mg L-1 LOQ 57 DAT. From lysimeters with a medium loading mean maximum bromide concentrations were reached 29 DAT. Bromide concentrations subsequently fell to c.a. 7 mg L-1 57 DAT. No further analyses were carried out. For lysimeters with no additional loading maximum concentrations were reached close to the end of the study 221 DAT. The last water samples were collected 22 days later at which time average concentrations of bromide started to fall.

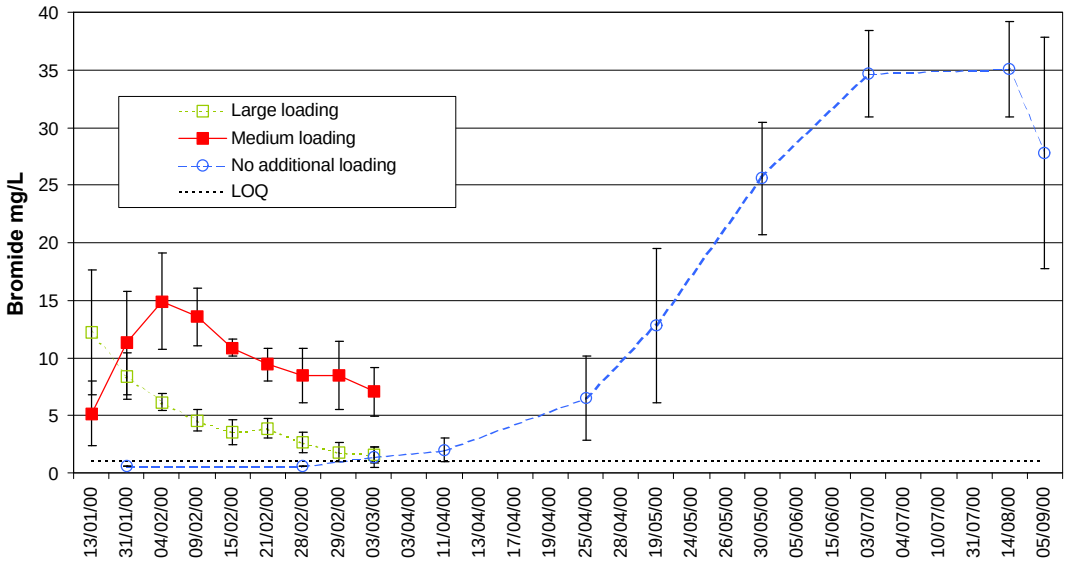
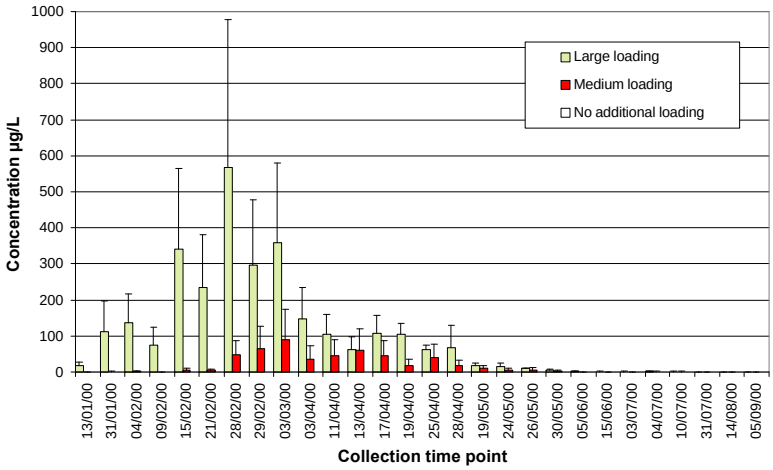


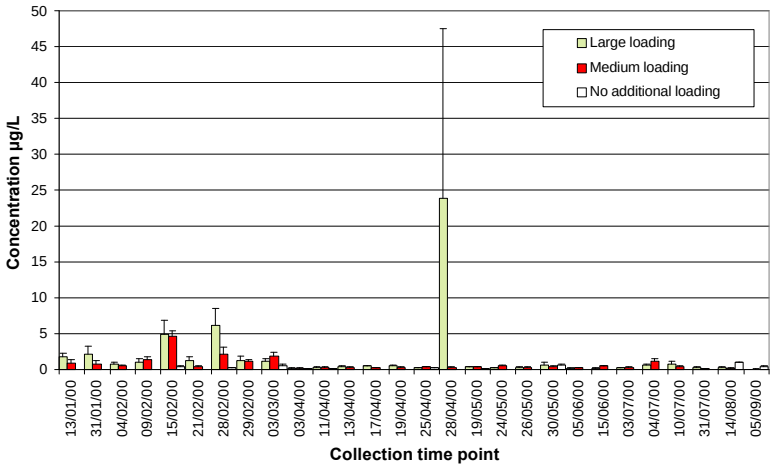
Figure 12 Bromide breakthrough from lysimeters subjected to (a) high hydraulic loading, (b) medium hydraulic loading and (c) no additional hydraulic loading

4.3.4 Residues in leachate

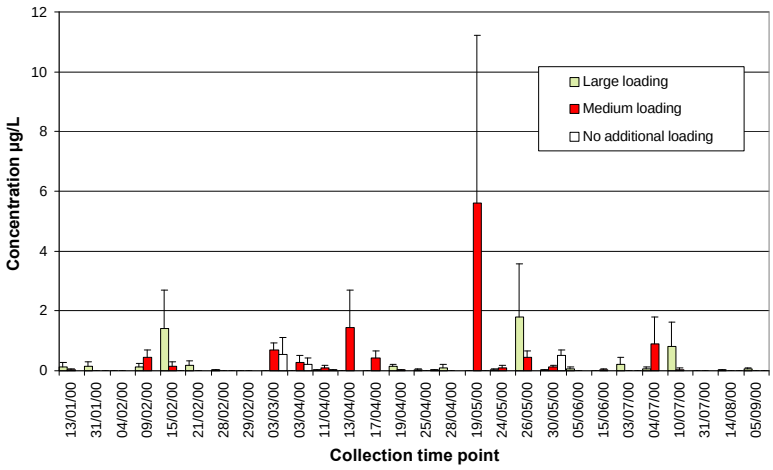
Maximum pesticide concentrations were measured in leachate collected from lysimeters with a high hydraulic loading. These were an order of magnitude higher than the columns receiving a medium water loading and 3 orders higher than columns receiving no additional water loading (Figure 13 and Figure 14).



(a)

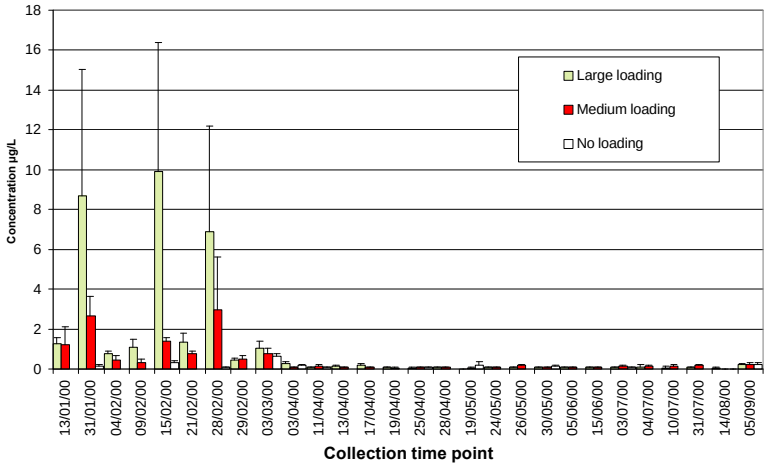


(b)

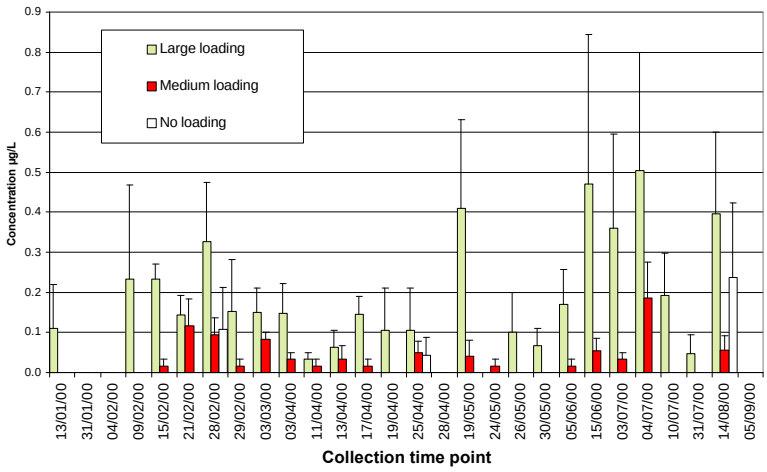


(c)

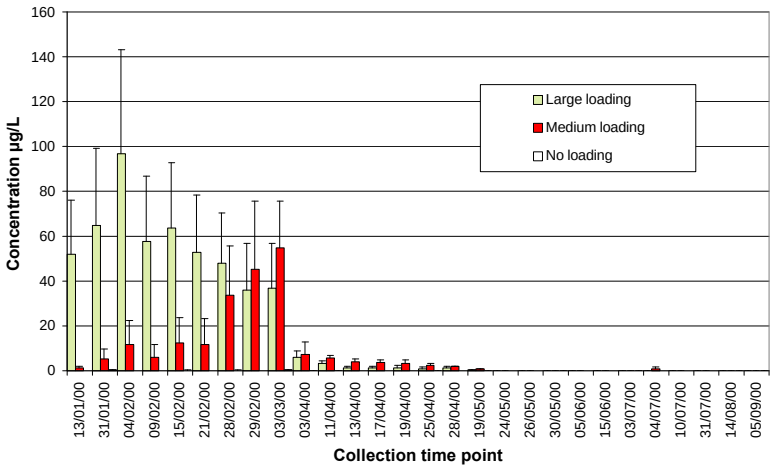
Figure 13 Mean concentrations (+1 SE) of (a) isoproturon, (b) pendimethalin and (c) chlorpyrifos in leachate from lysimeters subjected to a high, medium and no additional hydraulic loadings



(a)



(b)



(c)

Figure 14 Mean concentrations (+1 SE) of (a) chlorothalonil, (b) epoxiconazole and (c) dimethoate in leachate from lysimeters subjected to a high, medium and no additional hydraulic loadings

Generally highest concentrations were observed for the most mobile compounds (isoproturon and dimethoate), whereas chlorpyrifos was measured at the highest concentration in leachate from lysimeters with no additional water loading. Breakthrough of all pesticides from lysimeters with a medium and high water loading occurred 7 DAT with the exception of epoxiconazole in the medium loading lysimeters, which occurred 40 DAT.

Peak concentrations ranged from 1367 µg L-1 (isoproturon) to 1.21 µg L-1 (epoxiconazole) in samples from the lysimeters with a high water loading and from 258 µg L-1 (isoproturon) to 0.35 µg l-L (epoxiconazole) in leachate from the medium loading experiment. Leachate collected from lysimeters with no additional water loading concentrations of pesticide ranging from 1.65 µg L-1 (chlorpyrifos) to 0.57 µg L-1 (dimethoate).

Cumulative losses of isoproturon and dimethoate from lysimeters with a high loading were 6.37 % and 6.08 % respectively with losses of each of the remaining pesticides less than 0.2% (Figure 15). Isoproturon and dimethoate losses from lysimeters with a medium loading were 0.2% and 0.61% respectively. Maximum cumulative losses were measured 57 DAT with cumulative losses of each of the remaining pesticides < 0.02%. Cumulative pesticide residues in leachate from lysimeters with no additional hydraulic loading were all < 0.005%.

4.3.5 Residue in biomix

In biomix from lysimeters exposed to a high hydraulic loading no concentrations of pesticide were measured below 30cm depth. Between 95 and 100% of the retained pesticides was held within the top 10cm. By the end of the study (299 DAT) between 34% (epoxiconazole) and 0.02% (dimethoate) remained in the biomix (Figure 16).

From lysimeters with a medium water loading no concentrations of pesticides were measured below 20cm depth with the majority (97 - 100%) retained in the top 10cm. Total residues retained in the biomix at the end of the study ranged from 0.02% (dimethoate) to 34% (epoxiconazole).

Pesticide residues in biomix from lysimeters with no additional water loading ranged from 0.11% (dimethoate) to 33% (epoxiconazole). No concentrations or pesticide were measured below 10cm depth.

4.3.6 Mass balance

A mass balance calculation was performed to determine the fate of each of the study compounds under each of the three hydraulic scenarios investigated. For lysimeters with a high hydraulic loading between 0.04% (chlorpyrifos) and 6.37 % (isoproturon) leached, between 0.02% (dimethoate) and 34% (epoxiconazole) was associated with the biomix matrix and 87 % (pendimethalin), to > 99.5% (chlorpyrifos) was degraded (Table 19). The total amount of pesticide either retained or degraded by the system was > 93%.

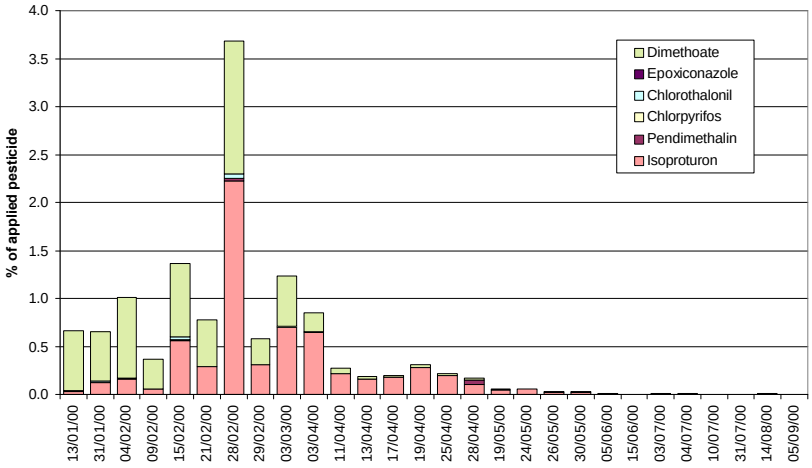
Table 19 Mass balance for lysimeters with a high additional hydraulic loading

	Leached %	Recovered %	Degraded %	Maximum mean concentration µg L-1
Isoproturon	6.37	0.10	93.53	568.03
Pendimethalin	0.12	12.80	87.08	23.82
Chlorpyrifos	0.04	0.44	99.52	1.79
Chlorothalonil	0.11	1.85	98.04	9.90
Epoxiconazole	0.05	33.54	66.41	0.50
Dimethoate	6.08	0.02	93.90	96.84

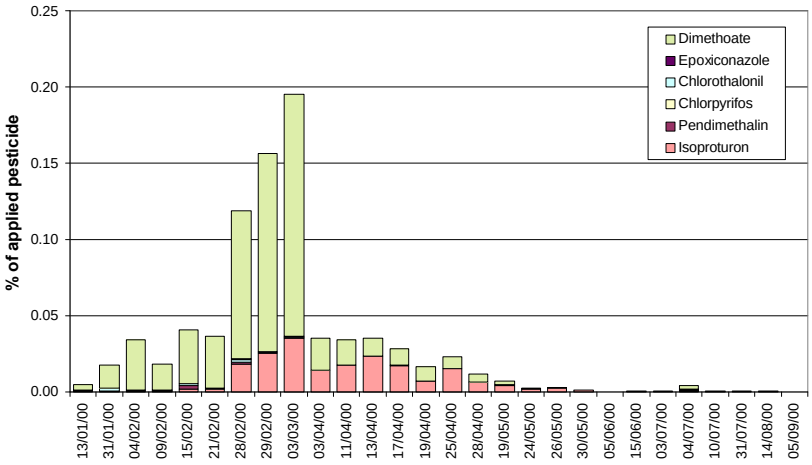
For lysimeters with a medium hydraulic loading between 0.002% (epoxiconazole) and 0.61 % (dimethoate) leached, 0.02% (dimethoate) and 34% (epoxiconazole) was associated with the biomix matrix and 85 % (pendimethalin), to > 99.7% (isoproturon) was degraded (Table 20). The total amount of pesticide either retained or degraded by the system was > 99.3%.

Table 20 Mass balance for lysimeters with a medium additional hydraulic loading

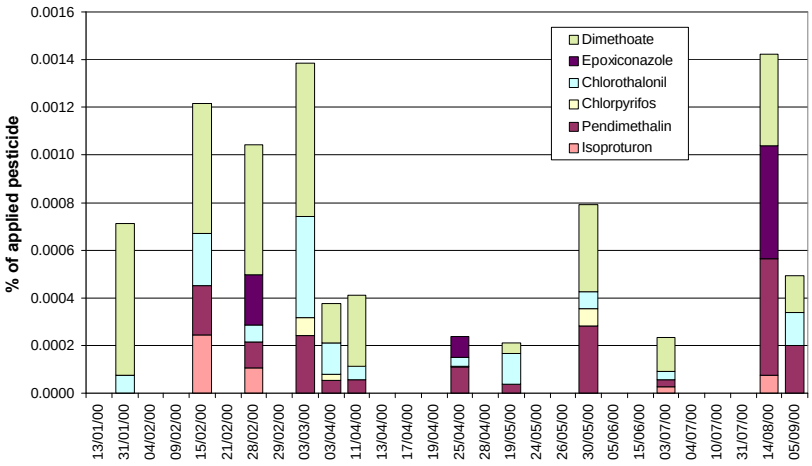
	Leached %	Recovered %	Degraded %	Maximum mean concentration µg L-1
Isoproturon	0.20	0.09	99.71	89.38
Pendimethalin	0.01	14.93	85.06	4.58
Chlorpyrifos	0.01	0.71	99.27	5.61
Chlorothalonil	0.01	1.70	98.30	2.99
Epoxiconazole	0.002	33.92	66.08	0.20
Dimethoate	0.61	0.02	99.37	55.00



(a)

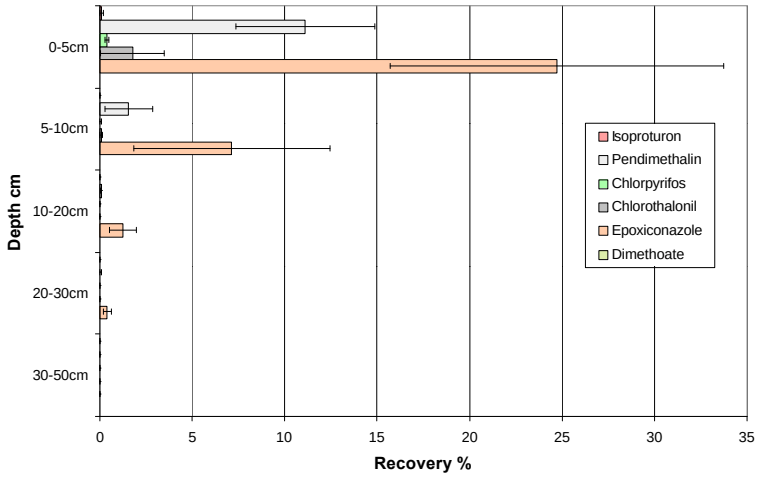


(b)

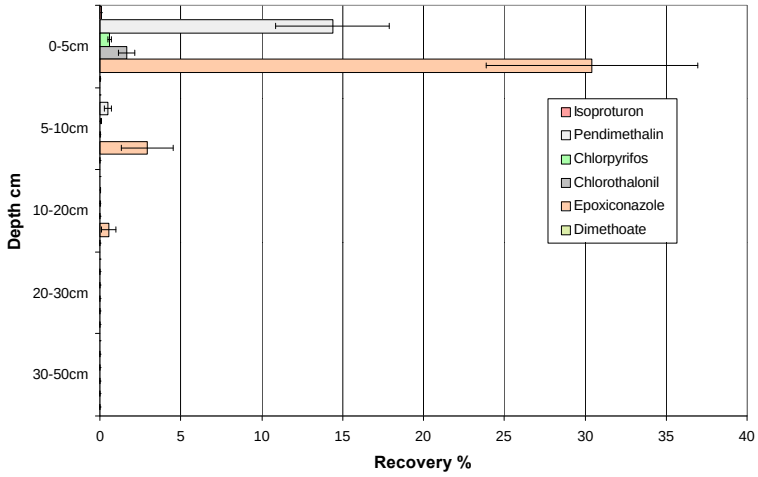


(c)

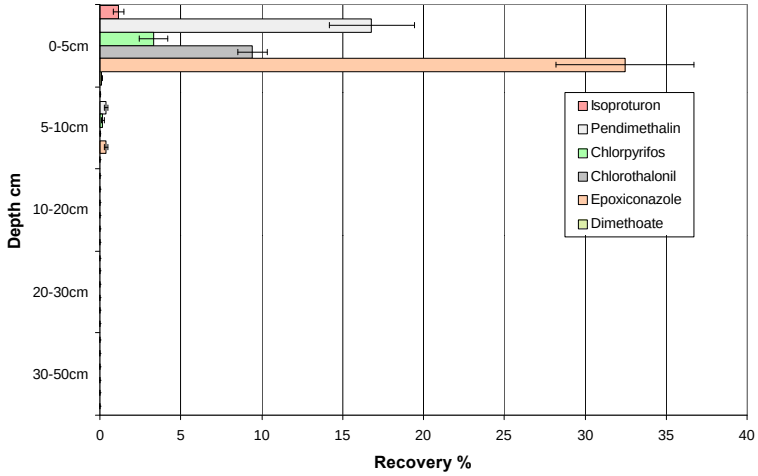
Figure 15 Pesticide residues in leachate (as % of the applied) from lysimeters with (a) a high hydraulic loading, (b) a medium hydraulic loading and (c) no additional hydraulic loading



(a)



(b)



(c)

Figure 16 Mean amounts (±SE) of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate in biomix sections taken from lysimeter exposed to (a) high water loading, (b) medium water loading and (c) no additional water loading

For lysimeters with no additional hydraulic loading < 0.004% of each chemical applied leached, between 0.11 % (dimethoate) and 33 % (epoxiconazole) was retained within the biomix and 67 %- 99.9% was degraded (Table 21). More than 99.99% of the applied pesticide was either retained or degraded by the biobed.

Table 21 Mass balance for lysimeters with no additional hydraulic loading

	Leached %	Recovered %	Degraded %	Maximum mean concentration µg L-1
Isoproturon	0.000	1.19	98.81	0.62
Pendimethalin	0.002	17.20	82.80	1.00
Chlorpyrifos	0.002	3.49	96.51	0.55
Chlorothalonil	0.001	9.45	90.55	0.65
Epoxiconazole	0.001	32.85	67.15	0.24
Dimethoate	0.004	0.11	99.88	0.22

4.4 Summary and Conclusions

Pesticide leaching potential is clearly effected by hydraulic loading. Amounts of pesticide leaching from lysimeters receiving a high water loading were < 6.5% of the applied whereas amounts from lysimeters with a medium water loading were < 1% of the applied. Only the most mobile compounds leached to any great extent and even for these compounds > 99.3% was retained / degraded in lysimeters with a medium water loading. All pesticides degraded with < 35% of the applied dose remaining after 10 months.

Performance of the biobed lysimeters exposed to a medium water loading was similar to that of other treatment systems such as the Sentinel with respect to the total amount of pesticide retained / degraded. However mean maximum concentrations, for example 89.38 µg L-1 (isoproturon), 55 µg L-1 (dimethoate) currently fail acceptable limits.

The water loading scenarios used were based on surface areas likely to be required on farms using large (24 meter spray boom) and small / medium (12 metre spray boom) application equipment. The volume of biobed however was fixed and was selected on the basis as to what appeared practical (7 - 8 m3 field scale) and was restricted to 50cm depth for this experiment. If the area / biobed ratio were optimised biobed performance would likely improve.

5 BIOBED DESIGN OPTIONS

5.1 Introduction

The aim of the biobed is to provide a low cost system for treating pesticide waste and washings arising from the normal use of pesticides. The system must be simple to construct and manage, require a low technical input and satisfy all relevant regulations.

Lined and unlined biobeds have been tested at the semi-field scale. The lined system relied on evapotranspiration to remove water, however once covered the top 10cm of the biobed became hydrophobic, restricting moisture loss from the system. Within 12 months the biobed was saturated below 10cm depth. The highest concentrations of pesticide were measured in the 0-5cm layer with concentrations in deeper layers significantly lower indicating little downward movement of the pesticides tested. However after 12 months 52% of each pesticide was recovered. Microbial biomass was measured and used to assess biological activity within the biobed. Biomass in the top10cm decreased over the 12 month monitoring period, with the decrease attributed not only to the fact that the surface layer became hydrophobic but also inhibition brought about by the high concentrations of pesticide.

The open biobeds were uncovered with the need to manage water inputs removed. Pesticide concentrations from biomix were significantly lower than from topsoil. Only the most mobile pesticides leached and for these >99% was retained / degraded.

Swedish biobeds were constructed such that the sprayer is parked on top of the biobed. In the UK it is highly likely that pesticides will be handled on an area adjacent to the biobed and the waste then pumped / diverted onto the biobed. This area will be typically be uncovered and as such represent an additional hydraulic load. The effects of water loading on pesticide leaching behaviour were therefore investigated. With a medium water loading performance with respect to the amount of pesticide retained / degraded was similar to more expensive treatment systems. Again only the most mobile compounds leached with mean maximum concentration of 89 µg L-1 for isoproturon and 55 µg L-1 for dimethoate.

5.2 Design criteria

In order for biobeds to offer an alternative to current pesticide treatment systems they must be:

- Low cost
- Simple to construct
- Easy to manage
- Require a low technical input
- Must work

In order to gain a better understanding as to what farmers required, what they are prepared to invest and how they envisaged a biobed being incorporated into the farmyard the Crop protection Association arranged a visit to four farms in Cambridgeshire. Details from the visit are reported in Appendix (B) with the key points summarised below:

- Typical volumes of waste requiring treatment were between 2000 and 10,000 litres per annum
- Biobeds are an attractive low cost system which appeal to farmers
- Farmers are prepared to invest between £2000 - £5000
- Environment Agency endorsement would be preferred
- Farmers would support a modest Environment Agency licensing arrangement

On all of the farms visited it was agreed that the biobed needed to be able to treat small drips and spills as well as tank and equipment washings of which equipment washing are the most significant with regards to potential environmental contamination. It was explained that farmers generally sought to organise their spray programme in order to avoid the need for a thorough cleaning of the sprayer thus keeping the volume of washings generated to an absolute minimum. The mixing and handling of pesticides was generally carried out in the farmyard near to the pesticide store and a clean water supply. Farmers preferred the idea of having a standalone biobed with waste and washings diverted onto it.

The dimensions and design of the biobed depends on several factors:

- Size of the sprayer
- Size of pesticide mixing / handling area
- Volume of washings requiring treatment
- Rainfall
- Management of the biobed (permanent or temporary connection to pesticide handling area)
- Required performance

The biobed must achieve acceptable levels of treatment, with the pesticides residues retained in the biobed subsequently degraded to avoid any additional disposal costs. Ground water regulations stipulate that concentrations of pesticide reaching ground water must be < 0.1µg L-1. However, provided further attenuation of any pesticide residues discharged from an unlined biobed is possible concentrations of pesticide in leachate could be > 0.1µg L-1. Regulations covering the disposal of exhausted biobed mix are still unclear. However it is hoped that disposal to land will be approved provided pesticide residues levels are acceptable.

Unlined biobeds appear to provide a system for treating pesticide waste and washings.

5.3 Biobed designs

Concentrations of pesticide in leachate are largely controlled by the concentration of pesticide in the waste liquid, the volume of waste to be treated, the rate at which waste is applied to the biobed, the volume of the biobed and the physico-chemical properties of the pesticide(s). Hydraulic loading is likely to be one of the most significant factors effecting the performance of the system. Three hypothetical hydraulic scenarios were therefore tested as described in Chapter 4. Data from this experiment have been used to develop a theoretical unlined biobed.

Each lysimeter contained 0.014m3 of biomix and was treated with a fixed pesticide load (Table 18). Rainfall totalled 382.8mm throughout the duration of the study resulting in hydraulic loadings of 348 - 11662 L m-3 (Table 22).

Table 22 Hydraulic loadings used to develop unlined biobed

	Catchment area m2	Volume of leachate collected (litres)	Litres per m3 of biobed
Large	0.568	165	11662.03
Medium	0.163	51	3599.12
No	0.028	5	348.06

Mean maximum pesticide concentrations measured in leachate were calculated (Table 23). The highest concentrations of pesticide were measured for isoproturon. If pesticide waste containing isoproturon can be treated down to 0.1µg L-1 then concentrations of the other pesticides should be < 0.1µg L-1. A single biobed (0.014m3) removed between 93.63% and 99.99% of the applied isoproturon depending on hydraulic loading. Passing the leachate through a second biobed should result in similar reduction in pesticide load and also in leachate concentrations. Theoretical maximum concentrations were calculated (Table 24) and correlated against hydraulic load, expressed in litres per m3 of biobed (Figure 17).

Table 23 Mean maximum concentration of pesticide measured in leachate collected from biobed lysimeters subjected to three different hydraulic loadings

	Mean maximum concentration of pesticide measured in leachate µg L-1		
	Large loading	Medium loading	No loading
Isoproturon	568.03	89	0.62
Pendimethalin	23.82	5	1
Chlorpyrifos	1.79	6	0.55
Chlorothalonil	9.90	3	0.65
Epoxiconazole	0.50	0.20	024
Dimethoate	96.84	55	0.22

Table 24 Theoretical concentrations of isoproturon in leachate following treatment through two biobeds of the same volume

		Hydraulic load		
		Large	Medium	No
Pesticide load Biobed 1 (µg)	A	255000	255000	255000
Mean maximum concentration (µg l-1)	B	568.03	89	0.62
(A / B)	C	2.228 x 10-3	3.51 x 10-4	2.43 x 10-6
% retained / degraded biobed 1	D	93.63	99.8	99.99
Pesticide load biobed 2 (A - D)	E	16243.5	510	1.275
Theoretical maximum concentration Biobed 2 µg L-1 (E x C)		36.18	0.18	0.000003

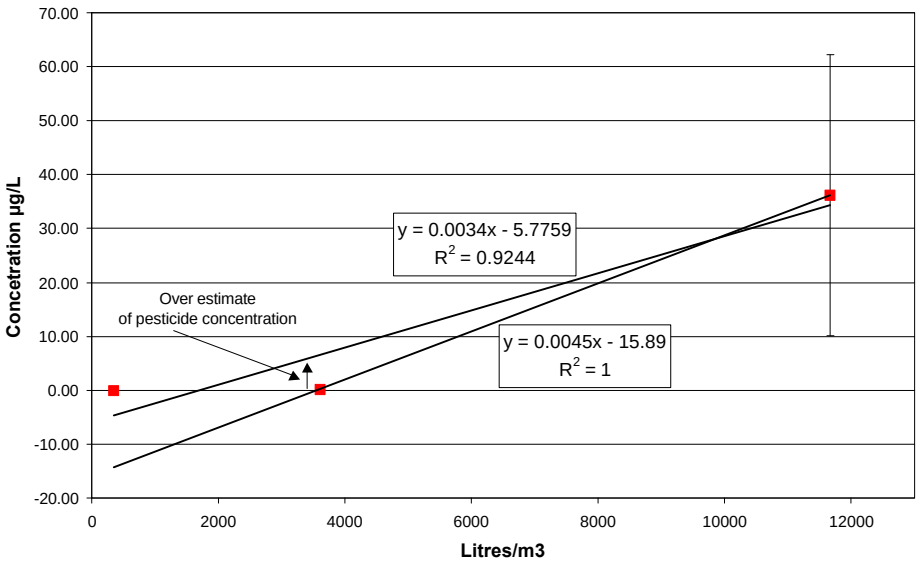


Figure 17 Theoretical isoproturon concentrations in leachate after passing through two biobeds

By fitting a standard linear trend line through all three data points there is an over estimation of the likely concentrations in leachate from biobeds subjected to medium water loading. The true breakthrough pattern is more likely to follow an exponential fit however insufficient data are available to confirm this. By fitting a trend line through the medium and large hydraulic loading data points a safety margin is incorporated whilst at the same time not over estimating pesticide concentration at low hydraulic loadings. A large standard error is associated with pesticide concentrations in leachate from lysimeters with a high hydraulic loading. Bromide breakthrough curves suggest possible preferential water movement through lysimeter 1 whilst leachate volumes for lysimeter 3 indicated a reduced hydraulic loading. Data for lysimeter 2 are considered realistic with the mean maximum concentration measured in leachate similar to the mean from all 3 lysimeters. All 3 data points have therefore been included.

The equation y = 0.0045x - 15.89 (Figure 17) was used calculate the hydraulic loading per m3 of biobed in order to achieve a range of maximum isoproturon concentrations in leachate.

Maximum concentration	Hydraulic loading
10µg L-1	5753 L m-3
1µg L-1	3753 L m-3
0.5µg L-1	3642 L m-3
0.1µg L-1	3553 L m-3

These data were then used to calculate the size of the two biobeds required, to treat a range of waste volumes (Table 25). A schematic diagram of the proposed system is illustrated (Figure 18).

Table 25 Volume of biobed required to treat pesticide waste down to concentrations of between 10 and 0.1µg -1

	Volume of biobed m3 in each biobed			
Volume of waste (litres)	10 µg L-1	1 µg L-1	0.5 µg L-1	0.1 µg L-1
90000	16	24	25	25
80000	14	21	22	23
70000	12	19	19	20
60000	10	16	16	17
50000	9	13	14	14
40000	7	11	11	11
30000	5	8	8	8
20000	3	5	5	6
10000	2	3	3	3
5000	1	1	1	1

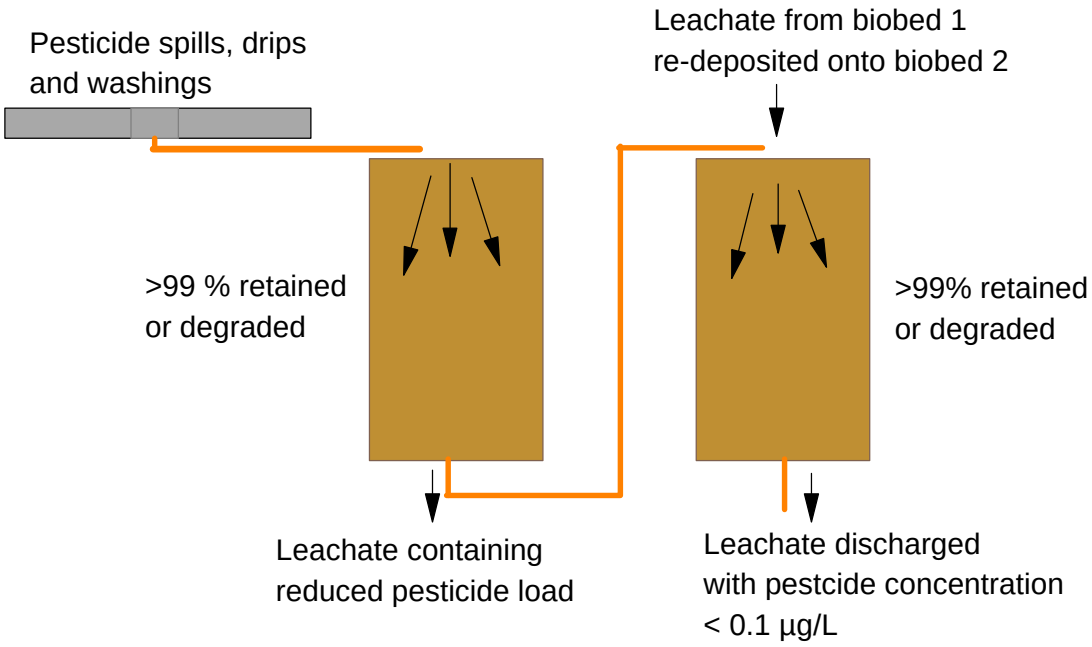


Figure 18 Schematic diagram of unlined biobed system

Experimental data used in the development of this system were collected under natural conditions. The effects of one off extreme rainfall events have therefore been incorporated into the calculations. The largest single event recorded over a 24 hour period during the hydraulic loading experiment was 19.2mm. An event of this magnitude would result in a total hydraulic load of 2880 litres, equivalent to a surface area wetting rate of 57.6 L m-2 day-1.

For a normal wash down and disposal procedure, e.g. 2 internal rinses of the spray tank and booms using 10% of the sprayer volume approximately 400 litres of washings would be created. If this were combined with an external wash then another 100- 200 litres of waste would be generated. The total volume of liquid is significantly less than that created by one off large rainfall events. However unless controlled the waste and washings would be added to the biobed over a very short period of time (1 hour) resulting in a surface wetting rate of 288 L m-2 day-1. The effects of such an application rate are still to be investigated. Surface wetting rate is closely correlated to hydraulic retention time (HRT), (Figure 19). A calculated HRT for the theoretical 288 L m-2 day-1 disposal rate is 1.5 days compared to 8.2 days for the 19.2 mm rainfall event discussed. The calculated HRT values are based on water movement through 50cm long column of biomix and a surface area / depth ratio of 5.6 : 1. Provided this ratio is maintained increasing the depth the biobed should increase the HRT.

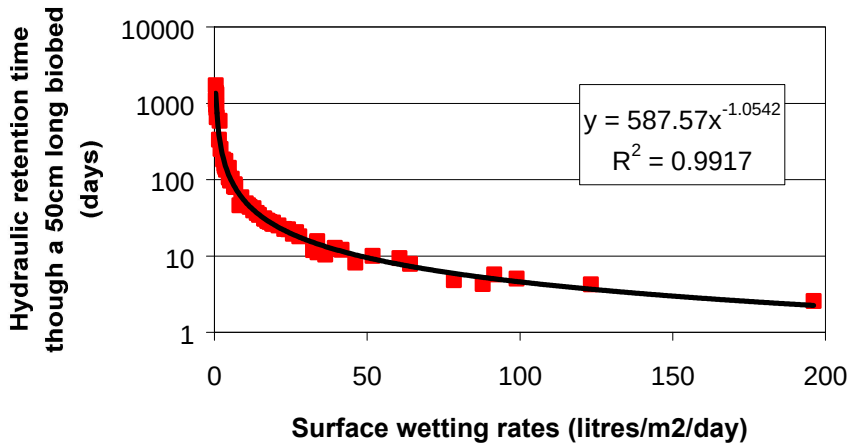


Figure 19 Relationship between surface wetting rate and hydraulic retention time

The amount of pesticide available for transport is determined by its distribution between adsorbed and solution phases (Cox et al. 1999) and is controlled by the physico-chemical properties of the pesticides as well as the material to which it is applied. Laboratory studies have demonstrated an increase in the strength of adsorption with increased residence time. Similarly adsorption in static systems is slower than in standard shaken experiments (Walker et al. 1995). Standard adsorption experiments suggest equilibrium between the liquid and solid phase is achieved within 24 hours, however under natural soil conditions equilibrium can take 2 - 3 weeks (Walker et al. 1996). Under field conditions during periods of heavy rainfall water will move through the soil rapidly. As the mobile soil water leaches through the soil, rainwater will re-wet the upper soil layers. The rate at which the water moves will effect the contact time between the liquid and matrix material thus changing the equilibrium between the sorbed and solution phases. Data suggest that the adsorption distribution

coefficient for isoproturon in a structured soil with just 5 to 10 minutes contact time may be less than 30% of that observed after 4 to 8 hours (Walker et al. 1995). In the case of biobeds the greater the HRT the greater the opportunity is for sorption and therefore a reduced risk of leaching. If low HRT's are anticipated then passing the waste liquid through multiple columns of biobed material will enable maximum sorption to be achieved.

5.3.1 Operational considerations

In order to keep the dimensions of the biobed to a minimum the amount of uncontaminated material entering the biobed must be controlled. Assuming that a 100m2 of concrete was designated as the handling / disposal area and rainfall was in the region of 600mm, 60000 litres of initially clean water would enter the biobed. If the catchment area of the biobed itself is included then depending on surface area dimensions up to a further 30000 litres of clean rainwater could need to be treated. Based on these data and assuming that 10000 litres of washings were generated each year a cumulative total of 100000 litres of dilute pesticide waste would need treatment requiring in excess of 50m3 of biobed in order to achieve to 0.1µg L-1 pesticide concentration (Table 25). By either reducing the surface area of the pesticide handling area or not maintaining a permanent connection between the biobed and the handling area the volume of liquid requiring treatment could be significantly reduced.

The size of the handling area is restricted by the size of the sprayer and 50 - 100m2 is not considered unrealistic. The only way therefore to reduce the amount of rainwater entering the biobed from the handling area is to not maintain a permanent connection. Results from the Cherwell study (Higginbotham et al. 1999) demonstrated that even after 6 months small amounts of isoproturon (2.5 mg kg-1) were recorded in mud collected from the mixing area. If after use the pesticide handling area was pressure washed to remove all mud and associated pesticide residues than it may not be necessary to maintain a permanent link. It is anticipated that you would generate 100 - 200 litres of washings whilst cleaning a 100m2 area, creating an additional 1000 - 2000 litres of liquid requiring treatment in the biobed if as suggested a thorough washdown was carried out 10 times a year. This procedure however does not take into account the accidental spills and drips created whilst filling the sprayer. Results again from the Cherwell study (Mason et al. 1999) showed that even after pressure washing the yard where spills of pesticide had been observed decreasing concentrations in drainwater from the farmyard where still being measured 4 months later. The handling area may therefore need to be washed down more frequently, however this would still result in a significant reduction in the volume of clean water entering the biobed.

5.4 Biobeds on the farm

The pesticide handling area is an integral part of any system in trying to reduce the environmental impact of pesticides through normal operations carried out in the farmyard. The handling area (Figure 20) based on that seen at the Morley Research Centre and Greenwell Farms is such that the sprayer can be filled on a level concrete surface with any spills draining into the biobed. When necessary the booms can be unfolded and lowered into walled area at the back of the handling area and washing discharged without the fear of drift. The size and shape of the area may be further reduced if the sprayer is equipment with a full internal circulation system. This system enables the spray booms to washed without the need to discharge through the spray nozzles. Clean water passes through the spray lines and is returned to the spray tank. Tank washing can then be discharged be opening the sump.

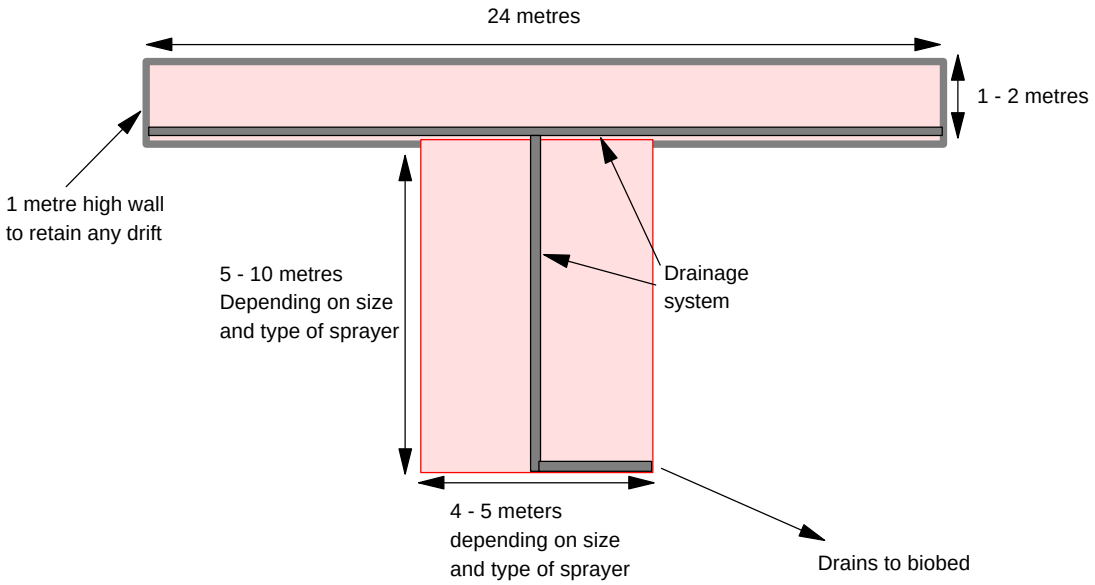


Figure 20 Possible design of pesticide handling area

Two biobeds may have to operate in series in order to provide sufficient volume of biobed to treat large volumes of liquid down to 0.1µg L-1 pesticide concentration. One possible scenario is illustrated (Figure 21 and Figure 22) where waste and washing are discharge onto biobed 1. Liquid drains through the biobed until it reaches the bottom where it is then pumped onto the top of biobed 2. Biobed 2 is either unlined or lined depending whether the leachate is to be discharge to groundwater or surface water.

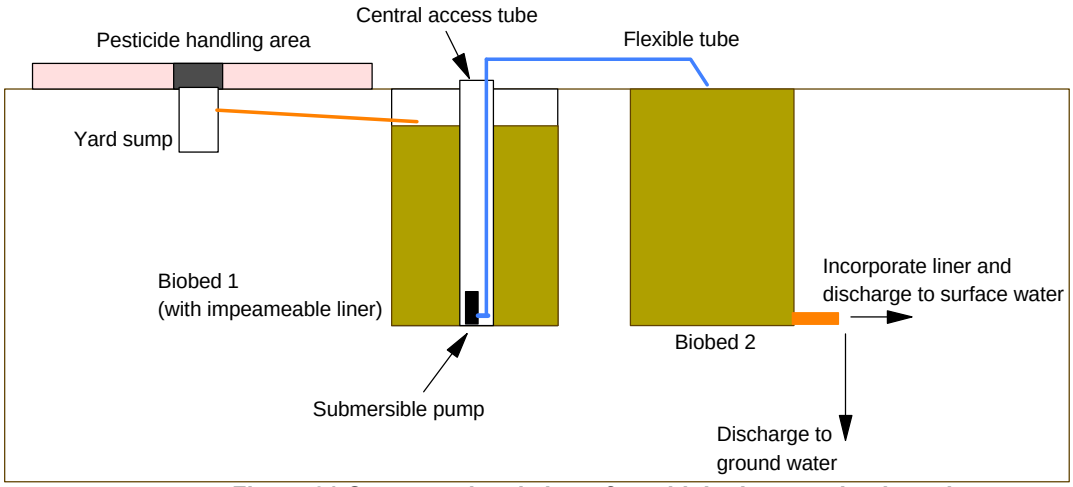


Figure 21 Cross sectional view of two biobeds operating in series

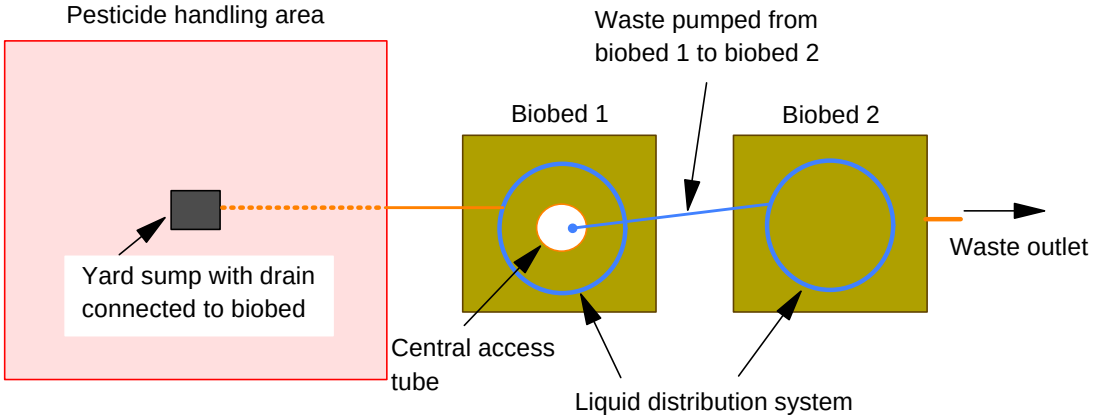


Figure 22 Plan view of two biobeds operating in series

If leachate is discharge to ground water the potential for further attenuation may be limited as the biobeds will typically be 1 - 1.5 meters long thus bypassing the more biologically active soil layers. If biobeds were constructed above ground (Figure 23) the leachate could be discharged to the soil surface thus increasing the potential for further attenuation. Construction costs of such a system may become too expensive when compared to excavating a hole in the ground.

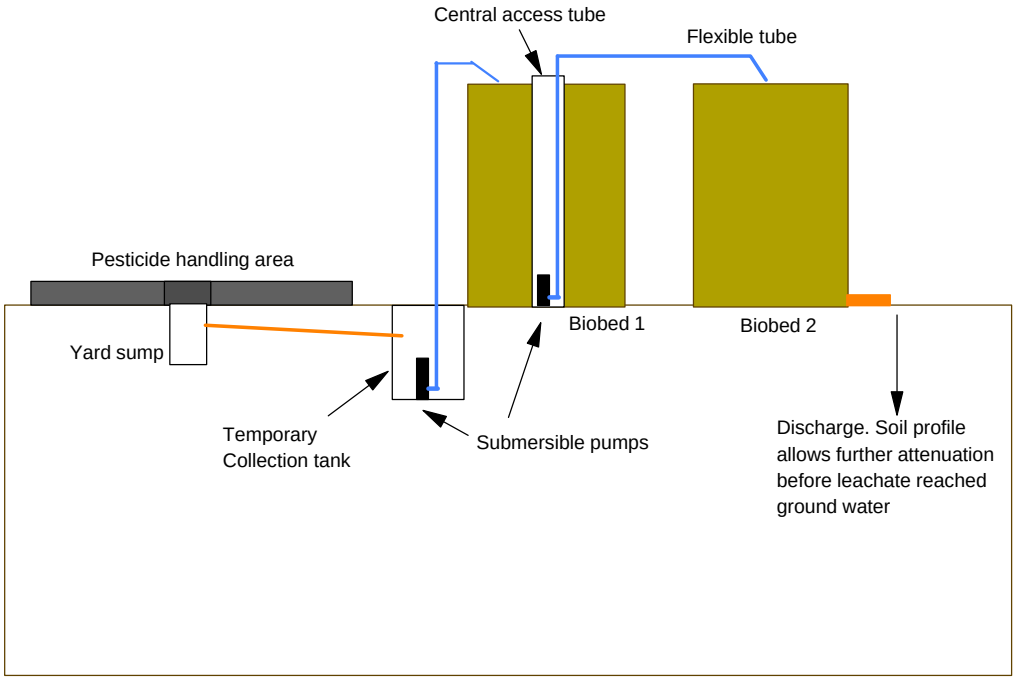


Figure 23 Above ground biobeds enabling leachate to be discharge to the soil surface

Discharge to surface waters would be subject to a discharge consent licence. The additional costs associated with this approach would probably result in the system being two expensive to be viable on most farms. However depending on the layout of the farmyard there are potential advantages (Figure 24).

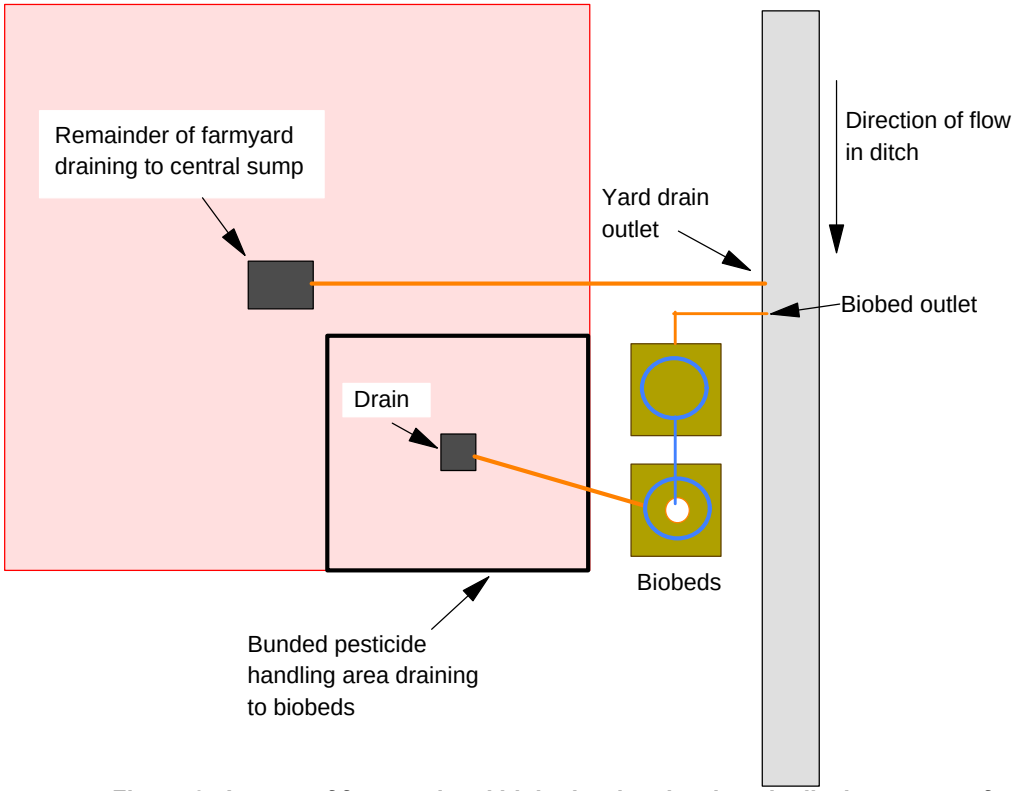


Figure 24 Layout of farmyard and biobeds when leachate is discharge to surface water

If current pesticide handling area forms part of the whole farmyard it will be necessary to build a bund to prevent large volumes of clean rainwater entering the biobed. Waste and washings from the bunded pesticide handling area would then be diverted onto the biobed(s) and the leachate discharge to an adjacent ditch. With biobed dimensions based on the calculations described (5.3) concentrations of pesticide should be <0.1 µg L-1. If surface water from the remainder of the farmyard is discharge into the ditch at the same point as the biobed outlet there is the potential for a 4 fold dilution (in the example illustrated Figure 24) of any pesticide residues leaving the biobed. This approach incorporates a significant safety margin into the system.

6 GENERAL DISCUSSION

When used correctly according the label instructions and with the appropriate precautions pesticides present minimal risk to the environment. However even when pesticides are used by trained operators, using well maintained equipment small drips and spillages can result in a significant amount of surface water contamination (Carter 2001). Similarly tank and equipment washings should be disposed of in accordance with the Code of Practice for the Safe use of Pesticides on Farms and Holdings (1998, currently under review) and the Groundwater regulations (1998). However, due the practicalities and costs associated with the recommended procedures and lack of awareness of the legislation, it is possible that many users do not comply with these requirements. A system is required that is able to treat the small drips and spills which occur as part of the normal mixing procedure as well as the larger volumes of tank and equipment washings which can lead to significant water contamination if not disposed of correctly. The system must be robust, simple to construct and manage and require a low technical input. Biobeds appear to offer an alternative to current methods of treating pesticide waste and washings.

Laboratory investigations have demonstrated that a biobed is capable of degrading a complex mixture of pesticides, applied repeatedly at high concentrations. At concentrations up to 20 times the maximum field application rate pesticides degraded more slowly however the effects were less significant in biomix than in soil. Interactions between pesticides are possible. Initial studies investigated the effect of combining isoproturon and chlorothalonil. Degradation in biomix was unaffected whereas in topsoil isoproturon DT50 values increased from 17.4 to >97 days. Six pesticides were subsequently applied as a complex mixture at 4 times the maximum recommended field application rate. Generally degradation was faster when the pesticides were applied individually than when applied as a mixture, however with one exception DT50 values for pesticides applied as a mixture to biomix were similar to those reported for the individual compounds in soil applied at the normal field rate. Repeated applications of the same pesticide mixture were made to biomix. There was generally no observed increase in the rate of biodegradation of the pesticides tested as anticipated however with one exception <30% of the maximum nominal application rate remained after 200 days.

Previous experiments (Fogg et al. 2000) carried out at the semi-field scale investigated the degradability and leaching potential of 6 commonly used pesticides with a range or sorption coefficients and degradation rates. Both lined and unlined systems were tested. Lined biobeds had to be covered to prevent waterlogging however once covered the top 10cm dried

out to form a cap on top of the biobed. Hydrologically connectivity was interrupted severely restricting evaporation from the system. Minimal water loss resulted in saturated conditions below 10cm within 12 months. Microbial biomass was used to access levels of biological activity within the biobed. Over a 12 month period biomass decreased in the 0-10cm layer a function of low moisture content but also inhibition brought by the high levels of pesticide retained in the top 5cm. Although pesticides were effectively retained in the lined system residues levels of 52% were still recovered after 12 months.

Unlined biobeds were uncovered with the need to manage water inputs removed. The performance of biomix was compared to sandy loam topsoil in a lysimeter type experiment. Pesticide concentrations were significantly lower in leachate collected from biomix than from soil. Of the 6 pesticides test only the two most mobile leached and for these >99% was retained / degraded. Biobed performance measured in terms of leaching potential was clearly effect by hydraulic load. However when subjected to a medium water loading, equivalent to a catchment area of 113m2 at the field scale, performance with respect to the amount of pesticide retained and degraded was similar to other commercially available treatment systems. Mean maximum concentrations of the two most mobile compounds, isoproturon (89.38µg L-1) and dimethoate (55 µg L-1) are still unacceptable, however optimising the design and dimensions of the biobed should improve performance. In order to prevent the contents of the biobed being classified as hazardous waste it was essential that residues retained in the biobed were degraded. After 9 months <30% of the applied dose was recovered from the unlined system. Laboratory investigations compared pesticide behaviour in sterile and non-sterile biomix and concluded that degradation was the principal mechanism responsible for the reduction in measured concentrations.

Under controlled conditions unlined biobeds appear able to treat small drips and spills as well as the dilute tank and equipment washings. In order for biobeds to be approved by the Environment Agency performance will have to improve such that concentrations of pesticide reaching ground water are <0.1µg L-1. Theoretically biobeds can achieve this target with the size of biobed dependent on the volume of dilute waste requiring treatment. Experimental data generated as part of the Cherwell project showed that there was a slow release of isoproturon from the pesticide handling after the site had been used indicating that a permanent connection between the biobed and the handling area would have to be maintained. Better management of the pesticide handling area and implementation of some of the recommendations made in Cherwell study may allow a temporary connection and thus reduce significantly the amount of clean rain water being added to the biobed.

In summary therefore, the results to date indicate that biomix will degrade high concentrations of a complex mixture of pesticides applied repeatedly. Water management is crucial in-terms of performance, construction costs and management and whilst a small proportion of the pesticide may leach optimisation of the biobed design should results in pesticide concentrations of <0.1µg L-1.

6.1 Future Work

In order to transfer the biobed technology from a semi-field controlled environment to an uncontrolled working farm situation a prototype biobed should be constructed and operated in such a way as to mimic waste disposal operations on a working farm. Methods of treatment should be the same as those proposed for a final on farm biobed with leachate samples collected to monitor biobed performance. The prototype should be operated for more than one growing season to enable the long-term performance and management requirements of the system to be determined.

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

- Pesticide usage data
- Total volume of waste pesticide requiring treatment
  - Size of sprayer
  - Volume of water used / wash
  - Number of washes / year
- Size of pesticide handling area m2
- Annual rainfall
- Underlying soil type / geology
- Depth to groundwater

Output would be the size of biobed required to treat the total volume of waste down to the required standard whilst maintaining and acceptable risk to the environment.

Further data are required in order develop the "Expert System" and also to optimise biobed performance. Biobeds are to be constructed by the farmer using locally available materials. Experimental work carried out so far has focused on one soil type as the inoculum. The effect

of using other soil types needs to be evaluated both in terms of biobed performance but also in term of preparing the biomix.

The significance of extreme rainfall events immediately after the addition of pesticide to the biobed could have a significant effect the rate at which the chemical moves through the biobed. The amount of pesticide available for transport is determined by its distribution between adsorbed and solution phases (Cox et al 1999) and is controlled by the physico-chemical properties of the pesticides as well as the material to which it is applied. Laboratory studies have demonstrated an increase in the strength of adsorption with increased residence time. Standard adsorption experiments suggest that equilibrium between liquid and soil phases is achieved within 24 hours. Five days elapsed between treating the lysimeters used in the hydraulic loading experiment and the first significant rainfall (7.3mm in 24 hours). If this rainfall had been recorded within 12 hours of treatment equilibrium may not have been achieved and concentrations of pesticide in leachate may have been significantly higher. The effects of rainfall soon after application should therefore be investigated further.

Pesticide sorption (Kd) is normally determined using batch slurry techniques and may be obtained from a measurement made at a single concentration or alternatively at a range of concentrations with a line then fitted to the data in order to calculate the Kd. A biobed is likely to receive a complex mixture of pesticides applied at arrange of concentrations, and therefore the second approach is most applicable. If a liner relationship exists between the concentration of pesticide measured in the soil and the concentrations measured in liquid then the sorption coefficient Kd can be calculated. However a non-liner relationship is frequently observed and under these circumstances the Freundlich equation is fitted to give Kf. Under normal circumstances as the concentration the liquid phase increases the concentration in soil decreases, this has relevance with regards to biobed performance. In addition reported Kd and Koc values are for soil and not biomix. Therefore in order to optimise the biobed and further develop the "Expert System" distribution coefficients for biomix at a range of pesticide concentrations need to be determined.

Only the two most mobile compounds tested isoproturon (Koc 100) and dimethoate (Koc 16-51) leached to any great extent. In order to have complete confidence that an unlined system will not contaminate ground water the leaching risk needs to be fully characterised using a range of mobile pesticides. Acidic herbicides for example mecoprop have a low Koc 12-25 as do the sulfonylureas (Koc <100). A range of mobile compounds should therefore be applied to a biobed to mimic actual disposal activities and the concentrations in leachate measured.

The biomix used to fill the biobed will compost with time. Semi-field experiments have shown that a drop of 10 - 15cm occurs within the first 12 months of operation. The effect of composting will undoubtedly impact on leaching potential and degradation rates. Studies therefore need to be performed to determine the fate of pesticides when applied to 3 - 4 year old biomix. The rate of composting will determine how often fresh material needs to be added and also how often complete replacement is required. Generally DT90 values for the pesticides tested indicate that accumulation from one year to a next should not be a problem even when applied repeatedly. However the fate of the spent biomix need to be determined.

As part of the interview carried out during the CPA farm visits farmers were questioned with regards to fertiliser usage. Three of the four farms visited used liquid nitrogen with all four farms using granule phosphorus and potassium. At farms using liquid nitrogen the same sprayer was used to apply the nitrogen as was used for applying pesticides. Farmers suggested that after nitrogen application the sprayer would be washed down probably in the same place as when washing down after applying pesticides thus adding nitrogen to the biobed. The same cleaning site would probably used for the granule applicators thus adding potassium phosphorus to the system. Biobed performance therefore needs to be monitored after the addition of nutrients.

If performance of the prototype biobed satisfies the necessary regulations it is proposed that a full scale biobed be constructed on a commercial farm. Biobed performance will be monitored. It is also recommended that the prototype biobed be kept in operation in order that long term performance can be assessed and potential problem be identified at an early stage and under controlled conditions.

7 REFERENCES

Bach, M (1996) Non-point source loads into rivers in Germany. *Vom Wasser*, 87, 1-13.

Beulke, S and Brown, C D (in press) Evaluation of methods to derive pesticide degradation and parameters for regulatory modelling. *Biology and Fertility of Soils*.

Breach, B (2001) Working with users - The water industry view. Proceedings of a joint conference held by CIWEM and Pesticide Action Network UK, Keeping pesticides out of water, 7 February 2001.

Brown, C, Hodgkinson, R, Rose, D, Syers, J K and Wilkinson, S (1995) Movement of pesticides to surface waters from heavy clay soil. *Pesticide Science*, 43 131-140.

Carter, A D (1999) Pesticide contamination of water sources and the monitoring data across the EU. Proceedings of the XI Symposium Pesticide Chemistry, 11-15 July 1999, 11-20.

Carter, A D (2001) How do pesticides get to water - The Cherwell project. Proceedings of a joint conference held by CIWEM and Pesticide Action Network UK, Keeping pesticides out of water, 7 February 2001.

Cobban, R, Gregson, D and Phillips, P (1998) Spring Cleaning Industry. Chemistry in Britain, February 1998, 40-42.

Code of practice for the safe use of pesticides on farms and holdings (1998) Ministry of Agriculture Fisheries and Food, PB3528.

Cox, L and Walker, A (1999) Studies of time-dependent sorption of linuron and isoproturon in soils. *Chemosphere*, Vol. 38, No. 12, 2707-2718.

Cox, L, Walker, A, Roberts, S J and Welch, S J (1996) Evidence for enhanced biodegradation of isoproturon in soils. Proceedings of COST 66 Workshop, Stratford-upon-Avon, 105-106.

Feslot, A S and Dzantor, E K (1995) Effect of alachlor concentrations and an organic amendment on soil dehydrogenase activity and pesticide degradation rate. *Environmental Toxicology and Chemistry*, Vol. 14, No. 1, 23-28.

Fischer, Von P, Hartmann, H, Bach, M, Burhenne, J, Frede, H-G and Spiteller (1998) Pesticide pollution in three watersheds. *Gesunde Pflanzen*, 50. Jahrg., Heft 5, 142-146.

Fogg, P (1999) Pesticide residues from spray equipment. *unpublished*.

Fogg, P and Carter, A D (1998) Biobeds: the development and evaluation of a biological system for pesticide waste and washings. BCPC symposium proceedings No.70, Managing pesticide waste and packaging, 49-58.

Fogg, P, Boxall, A B A and Walker, A (2000) Biobeds: The development and evaluation of a biological systems for the disposal of pesticide waste and washings. MAFF project: PLO527, Environment Agency: R&D Technical report P415, DETR: EPG 1/5/104, Soil Survey and Land Research Centre Contracts, JF4107V, JF4225E and JF3740E.

Fogg, P, Carter, A D and Brown, C D (1984) A comparison of the use and regulatory interpretation of lysimeters and field studies to determine the leaching potential of a seed dressing. BCPC Pest and Diseases, 3, 1283-1287.

Ganzelmeir, H (1998) Proper cleaning of sprayers. BCPC symposium proceedings No.70, Managing pesticide waste and packaging, 91-98.

Gatzweiler, E, Schmidt, B, Feyerabend, M, Jones, R, L and Arnold, D J (1999) Isoproturon - field studies on the behaviour in fine textured soils. Proceedings of the XI Symposium Pesticide Chemistry, 11-15 July 1999, 305-312.

Gevao, B, Semple, K T and Jones, K C (2000) Bound pesticides residues in soil: a review. *Environmental pollution*, 108, 3-14.

Handbury, J (1999) Pesticide injection metering. BCPC symposium proceedings No.70, Managing pesticide waste and packaging, 211-212.

Harries, D A, Johnson, K S and Ogilvy, J M E (1991) A system for the treatment of waste water from agrochemical production and field use. BCPC Weeds, 715-722.

Heather, A I J (1996) A simple detection frequency index for use in validating probability risk assessments. Proceedings of COST 66 Workshop, Stratford-upon-Avon, 195-196.

Helweg, A (1984) Threats to water quality from pesticides - case histories from Denmark. Pesticide Outlook, October 1994, 12-18.

Higginbotham, S, Jones, R L and Gatzweiler, E (1999) Point source contamination: quantification and practical solutions. BCPC Weeds, 681-686.

Jones, R L, Gatzeiler, E G, Guyot, C N, Hardy, I A J, Higginbotham, S, Leake, C R, Arnold, D J S, Idstien, H and Feyerabend (1999) Research and monitoring studies of isoproturon movement to surface and ground water in Europe. Proceedings of the XI Symposium Pesticide Chemistry, 11-15 July 1999, 21-27.

Lynch, M R (1995) Procedures for assessing the environmental fate and ecotoxicity of pesticides. SETAC Europe, ISBN 90-5607-002-9

Mason, P J, Foster, I D L, Carter, A D, Walker A, Higginbotham, S, Jones R L, Hardy, I A J (1999) Relative importance of point source contamination of surface waters: River Cherwell catchment monitoring study. Proceedings of the XI Symposium Pesticide Chemistry, 11-15 July 1999, 405-412.

Mcknilay, R G and Kasperek, K (1999) Observations on decontamination of herbicide-polluted waters by marsh plant systems. *Wat. Res*. Vol 33, No. 2, 505-511.

Meyer-Windel, S and Widmoser, P (1996) The influence of initial water content on herbicide transport under non-steady flow conditions. Proceedings of COST 66 Workshop, Stratford-upon-Avon, 15-16.

Protzman, R S, Pak-Hing, L, Ong, S K and Moorman, T B (1999) Treatment of formulated atrazine rinsate by *agrobacterium radiobacter* J14a in a sequencing batch biofilm reactor. *Wat. Res*. Vol 33, No. 6 1399-1404.

Pussemier, L and Elsen, Y V (1998a) Herbicide degradation and leaching potential in biobed material. Proceedings from the 9th International Congress Pesticide Chemistry. The Food-Environment Challenge, 2-7 August 1998, 6A-003.

Pussemier, L, Goux, S, Elsen, Y V and Mariage, Q (1998b) Biofilters for on-farm clean-up of pesticide wastes. Pre-print *Med. Fac. Landbouww. Univ. Gent*. 63, 1998.

Read, M A and Taylor, W A (1998) A preliminary investigation into the effectiveness of decontamination methods on the residues of amidosulfuron, used alone and in mixtures from polyethylene sprayer tanks. BCPC symposium proceedings No.70, Managing pesticide waste and packaging, 107-120.

Reese-Stähler, G and Pestmer, W (1999) Measurement of selected pesticides and their impact on surface water in a research catchment. Proceedings of the XI Symposium Pesticide Chemistry, 11-15 July 1999, 433-440.

Revitt, D M, Shutes, R B E, Llewillyn, N R and Worral, P (1997) Experimental reedbed systems for the treatment of airport runoff. *Wat. Sci. Tech*. Vol. 36 No 8-9, 385-390.

Rose, S, Carter, A and Basford, B (2000) Development of a design manual for agricultural pesticide handling and washdown areas. Environment Agency R&D project No. P2-200.

Stenberg, B, Castillo, dP and Torstensson, L (1994) Biobeds minimise environmental risks when filling agricultural spray equipment. 7th International Congress Bacteriology and Applied Microbiology, 3-8 July 1994, Abstract.

The Ground Water Regulations (1998) Statutory Instrument No. 2746, ISBN 0 11 079799 X.

The Water Code (1998) Ministry of Agriculture Fisheries and Food, PB0587.

Tomlin, C D S (1997) (eds). The Pesticide Manual eleventh edition. The British Crop protection Council, Surrey.

Torstensson, L (1984) Pesticides, the soil and the environment. 35th Swedish Crop Protection Conference, 26-27 January 1994, Uppsala, 41-52.

Torstensson, L (2000) Experiences of biobeds in practical use in Sweden. *Pesticide Outlook*, October 2000, 206-211.

Torstensson, L and Castillo, M dP (1996a) Biobeds minimise environmental risks when filling agricultural spraying equipment. Proceedings of COST 66 Workshop, Stratford-upon-Avon, 223-224.

Torstensson, L and Castillo, M dP (1996b) Bioremediation of pesticide spills when filling agricultural spray equipment. Proceedings from the 2nd International symposium on Environmental Aspects of Pesticide Microbiology, 7-11 July 1996, 196-181.

Torstensson, L and Castillo, M dP (1997) Use of biobeds in Sweden to minimise environmental spillages from agricultural spray equipment. *Pesticide Outlook*, June 1997, 24-27.

Torstensson, L and Castillo, M dP (1998) Bioprophylaxis by using biobeds. Proceedings of COST 66 Workshop, Prague, 22-25.

Toyota, K, Ritz, K and Young, I M (1996) Survival of bacterial and fungal populations following chloroform-fumigation: effects of soil matric potential and bulk density. *Soil. Biol. Biochem*. Vol 28, No. 10/11, 1545-1547.

Walker, A , Welch, S J, and Turner, I J (1995) Studies of time dependent sorption process in soils. BCPC Monograph No 62: Pesticide Movement to Water, 13-18.

Walker, A, Cox, L and Edwards, J A (1996) Changes in adsorption of isoproturon with residence time in soil. Proceedings of COST 66 Workshop, Stratford-upon-Avon, 87-88.

Walker, A, Jurado-Exposito, M, Bending, G D and Smith, V J R (2001) Spatial variability in degradation rate of isoproturon in soil. *Environmental pollution*, 111, 407-415.

Wauchop, R D, Butler, T M, Hornsby, A G, Augustjn-Beckers, P W M. and Burt, J P (1992). SCS-ARS-CES PESTICIDE PROPERTIES DATABASE FOR ENVIRONMENTAL DECISION MAKING reviews of environmental contamination and toxicology Vol 123, 1-164.

WEMEC Limited. SENTINEL A technical appraisal for dilute pesticide waste treatment. WMEC Limited, Allman Business park, Birdham Road, Chichester, West Sussex, PO20 7BE, UK.

Whitfield, W A D (1974) Soils in Warwickshire I, Sheet SP36 Leamington Spar. Soil Survey Record No. 19, Lawes Agricultural Trust, 12.

Winterlin, W L, Schoen, S R and Mourer, C R (1984) Disposal of pesticide wastes in lined evaporation beds. In: Krueger, R F and Seiber, J N *Treatment of disposal of pesticide waste*, American Chemical Society symposium series 259, 97-116.

Wise, C (1994) Reducing pesticide contamination of water: a farming view. Pesticide News, 26, 14-16.

APPENDIX A

Water

Water samples were analysed after liquid / liquid extraction using gas chromotography (GC).

Water samples (200 mL) 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 0-5°C. Concentrations of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate were then determined using GC.

Soil and biomix

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

Samples (40g) of biomix from the semi-field experiments were 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 1 hour using an end over end shaker and allowed to stand until clear. An Aliquot of the solution was taken for determination of isoproturon, pendimethalin, chlorpyrifos, chlorothalonil, epoxiconazole and dimethoate using GC analysis.

Laboratory samples treated with all 6 pesticides as well as pendimethalin, chlorpyrifos, epoxiconazole and dimethoate from the mixture experiments were extracted into a mixture containing 90% DCM and 10% methanol to which 40g of anhydrous sodium sulphate had previously been added. Soil samples were extracted with 75 mL of solvent with 100 mL used for biomix samples. For individual pesticides the volumes of solvent were reduced to 50 mL for soil and 75 mL for biomix. Concentrations of each pesticide in the resulting extracts were then determined by GC.

Isoproturon and chlorothalonil samples were extracted using 50 mL methanol for 1 hour using and end over end shaker. Aliquots of the solution were taken and analysed by HPLC. The same extraction procedure and method of analysis was used to determine concentrations of

isoproturon, chlorothalonil and pendimethalin in samples collected from the bound residues and tank cleaning agents experiments.

GC and HPLC analyses

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

GC analysis was performed using a Hewlett Packard HP5890 gas chromatograph fitted with a split/splitless injector, 12m x 0.53 mm BPX5 column (SGE) and a nitrogen-phosphorus detector. The carrier gas (helium) flow rate was 7 ml min –1 and detector –gas flow rates were 100 ml min –1 (air) and 4 ml min –1 (hydrogen). Oven temperature was raised from 90 oC to 190 oC (40 oC/min) and then to 220 oC (10 oC/min) and finally to 245 oC (15 oC/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 26).

Concentrations of isoproturon, chlorothalonil and pendimethalin for the laboratory experiments were determined by HPLC using a Spectra Physics SP8810 pump was linked to a Cecil 1200 UV detector. Samples (20 µl) 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 chlorothalonil from the repeated bound residues experiment 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.

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%.

Table 26 GC detection limits for the 6 experimental pesticides

	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 (µg/L)	0.23	0.12	0.11	0.22	0.10	0.08

Bromide

Water samples (0.5 mL) were filtered (0.2µm). Concentrations of bromide were determined using ion chromatography. Samples were analysed using a Dionex DX-100. Samples (25µL) 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.

pH

pH was measured using a 8000 pH metre fitted with a glass combination pH electrode. A 1:1 suspension of biomix/distilled water was prepared to which the electrode was placed. A stable reading was recorded after approximately 10 minutes.

APPENDIX B

Biobed - Cambridgeshire Farm Visits 8th May 2001

Background

A visit to four farms in Cambridgeshire was arranged by the Crop Protection Association (CPA). The purpose of the visits were to gain farmer feed back and to provide an opportunity for the research team to appreciate practical farm issues. The farms were predominantly arable with typical rotations including cereals, oilseed rape, sugar beet and potatoes. Mustard, dried peas and sunflowers were some of the minor crops grown. A range of crop protection products were used including IPU, sulfonyl ureas and synthetic pyrethroids. Farm size ranged from 83 to 800 hectares. Each farm was equipped with modern well-maintained pesticide application equipment (Appendix i). At each farm the current pesticide handling area was assessed, with the farmers then interviewed with respect to equipment cleaning procedures, the concept of Biobeds and their awareness of current regulations.

Pesticide handling Areas

Of the four farms visited two had a single pesticide handling area, one had two areas whilst the fourth had three areas. At the farms with more then one filling area only one was predominantly used. Data from each of the sites visited are summarised (Table 27).

Table 27 Pesticide handling areas

	Farm 1	Farm 2	Farm 3	Farm 4
Surface	concrete	1 Hardcore 2 Concrete	Concrete	concrete
Approximate size m2	133	1 Entire yard 2 300	1000	30
Bunded	yes	No	No	no
Drained	yes	No	No	no
Drains to	underground storage tank	Soakaway	Soakaway	soakaway
Water available	yes	Yes	Yes	yes
Electricity available	yes	Yes	Yes	yes
Location of pesticide store	on filling area	Farmyard	on filling area	farmyard
Relation to rest of farmyard	separate	part of main yard	part of main yard	part of main yard
Do you fill in the field	no	No	No	yes

At Farm 1 the pesticide handling area was connected to a 4500 litres underground storage tank. The tank was purchased at a cost of £400 and was installed 3 years ago. The drainage system was installed with a divert valve. Unless washing down the sprayer, surface water was discharged into the normal farm drainage systems. Since being installed the tank has not had to be emptied, although when necessary a professional waste disposal contractor would be used. At Farms 2 and 4 any drips, spills or washings deposited onto the filling area either infiltrate the hardcore standing or runoff the concrete to adjacent hardcore areas. Farm 3 was the only site installed with a proper soakaway. At Farm 2 one pesticide handling area was constructed from hardcore, (a mixture of bricks and asphalt road planings, constructed to a depth of 60cm), with another from concrete. At Farm 4 the sprayer was occasionally filled in the field. However this involved preparation of the pesticide solution at the farmyard in a trailed bowser. The dilute pesticide was subsequently transferred to the sprayer in the field.

Cleaning procedures

All farmers sought to organise and assess their spray programme to avoid unnecessary complete washdowns. All farmers were aware of the high cleaning standards required for sulfonyl-ureas. With the exception of one farm, all sprayers were installed with in-tank, full circulation wash equipment. The washing procedure was split into two categories, a general rinse and a thorough clean. At farms equipped with in-tank cleaning facilities a general rinse was usually carried out at the end of each working day, and at Farm 1 also in between different tank mixes. Generally between 150 and 250 litres of water was available on board the sprayer. The available rinse water was either used as a single rinse or split into two rinses. All rinse washings were sprayed out in the crop. At the farm without in-tank cleaning facilities the sprayer was only rinsed out when necessary or when time allowed. With regards to thorough cleaning this was carried out 2, 4, 6 and 10 times a year. Thorough cleaning generally involved a combination of using the in tank cleaning facilities as well as a pressure washer to enable exterior surfaces to be cleaned. It was estimated that between 600 and 1000 litres of dilute washings were created during a thorough clean down procedure. Reduced clean out procedures adopted for sulfonyl ureas where equipment allowed. With the exception of Farm 1, which collected and stored all dilute pesticide waste, washings were sprayed out onto designated areas approved by the Environment Agency under the Ground Water Regulations 1998. Designated areas ranged from a corner of the field with out underlying drains or adjacent ditches to soakaway systems overlying chalk or gravel.

At three farms liquid nitrogen was used and was applied using the same pesticide application equipment. All farms confirmed that after the application of fertiliser, the sprayer would be washed down at the same designated area.

When not in use all sprayers were stored under cover.

Biobeds

All farms agreed that there was a need for a cheap, effective means of treating pesticide waste and washings on the farm. They were also keen to do the "right thing". If a Biobed were seen as an acceptable solution then all four farms would be prepared to invest in the technology. All farms agreed that the biobed should be able to treat small drips and spills as well as the washings associated with thorough clean down procedures. At the 3 farms with concrete filling areas the preferred location for a biobed would be adjacent to the filling / handling area. At Farm 2, where filling operations were carried out on hardcore, location of the biobed was less important. The farmer was equally prepared to have a biobed that the sprayer parked on top of, as he was to have a biobed built adjacent to the handling area. Biobeds situated adjacent to a concrete filling area are likely to require the installation of some type of drainage systems as well as a water tight bund. All farms accepted that there would be need to link the biobed into the current pesticide handling area. The amount each farm was prepare to invest in a biobed appeared to by governed by several factors, these included the size of the farm, crop rotation (which controls the number of different actives used and thus cleaning requirements) and whether the farmer was an owner occupier, manager or tenant. Managed and tenanted farms appeared to be prepared to invest more as the costs could be split with the landowner. The level of investment varied. All farmers were aware of professional disposal costs and in that context two farms were prepared to invest between £5000 - £10000, with a third prepared to invest £2500 - £5000 and the last farm between £1000 - £2500. It was understood that the main motivation for this investment was the convenient simple method of removing an established problem ie spray washings. It was unlikely that such an investment would be made just to cater for drips and splashes at filling.

In general the major incentive for farms wanting to install a biobed was the threat of prosecution ("polluter pays") should adjacent surface waters or ground water become contaminated as a result of washing down the sprayer. Similarly all farms were of the opinion that a biobed was one way that they could be seen to be doing the right thing with respect to environmental protection. One farm also commented that he would prefer to be in control of his own waste instead of relying on a third party to collect and dispose of it with the risk of

potential operational delays. All farms agreed that it was essential for the Environment Agency to endorse the biobed technology. In addition all the farmers were prepared to pay for a licence. Licence fees of £100 - £500 / year were considered acceptable by two of the farms with a fee of £100 / year considered more reasonable by the two remaining farms. At all sites it was agreed that regular Environment Agency inspections would be beneficial and at one farm it was suggested that some license revenue could be diverted to a random monitoring program.

If biobeds are an acceptable solution it is the intention to issue a set of guidelines describing how to build and operate the system. Each farm was asked whether they thought farmers in general would follow the guidelines or whether they would try and modify them to suit their own specific requirements. All farmers agreed that if the business were prepared to invest in the technology then they would probably follow the guidance documentation. Although it was understood that there was a risk of misuse, it was concluded that prevention would be very difficult, however the threat of prosecution or further legislation would probably be the only way to prevent it. The use of incentive schemes was also suggested. One farmer asked how the biobed would cope with diesel and oil. He explained that when the sprayer and tractor were washed down a film of oil was always visible on the water surface. It was explained that this issue has not been investigated.

Operation of the biobed is going to require a degree of management. All farmers stressed the need for a very simple system and this was one reason why the idea of biobeds was so attractive. All farms agreed that the amount of time required should be kept to an absolute minimum however two farms agreed that 0.5 hour per week would be acceptable with third suggesting 2-3 days in the autumn and spring spraying periods. The issues of an annual top-up of biobed material every 12 months and complete replacement every 5 - 8 years were raised. All farms agreed that this would not be a problem.
The idea of an engineered solution, such as a Clargester, was discussed, farmers said that there was potential but in principle 3 of the four preferred the simplicity of the Biobed solution.

With respect to complete replacement all farms questioned what could be done with the contents. It was explained that in other European countries where biobeds are being tested the spent biobed material is classified as hazardous waste and as such requires disposal through the appropriate channels. Laboratory and semi-field experiments carried out in the UK have demonstrated that of the pesticides tested all appear to degrade within the biobed. It is hoped that the Environment Agency will approve disposal of the biobed contents to farmland. All

farmers agreed that this was a practical approach and were prepared to dispose to land provided it was legal and safe with respect to following crops and the environment.

All farms were very well aware of the current legislation covering the disposal of pesticide waste and washings. (All of the farmers have a BASIS Certificate). Three of the four farms already had designated disposal sites approved under the ground water regulations for which they are allowed to dispose of up to 30m3 of waste per year provide that they do not exceed 5m3 day-1. It has been suggested that one way of "licensing" Biobeds would be to use a Ground water Regulations authorisation.

Key Points

Farmers are prepared to invest probably between £2-5,000 in sorting out their spray washings problems
Biobeds are an attractive simple low cost option that appealed to farmers
EA endorsement of the concept would be a major bonus
Farmers would support a modest EA licensing arrangement for Biobeds.
For these farms, typical washing water volumes that need to be treated by biobeds were between 2,000 and 10,000 litres per annum

Paul Fogg and Patrick Goldsworthy
May 10th 2001

Appendix (i)

Farm 1

Sprayer, make and model:	JEM 2000
Mounted or trailed:	Fully mounted (Mounted to MB Trac)
Boom width:	18 metres
Tank capacity:	2000 litres
In-tank wash facilities:	Yes with fully circulation system
Clean water carrier volume:	200 litres
Age	4 years

Farm 2

Sprayer, make and model:	Berthoud Major
Mounted or trailed:	Trailed
Boom width:	28 metres
Tank capacity:	3200 litres
In-tank wash facilities:	Yes with fully circulation system
Clean water carrier volume:	150 litres
Sprayer has been subject to MOT inspection	
Age	18 months

Farm 3

Sprayer, make and model:	Chaffer T-3000
Mounted or trailed:	Trailed
Boom width:	24 metres
Tank capacity:	3000 litres
In-tank wash facilities:	no
Clean water carrier volume:	none
Age	7 years

Farm 4

Sprayer, make and model:	Knight
Mounted or trailed:	Trailed
Boom width:	24 meters
Tank capacity:	3000 litres
In-tank wash facilities:	Yes with fully circulation system
Clean water carrier volume:	250 litres
Age	4 years