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Leaching and degradation of 21 pesticides in a full-scale model biobed

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Abstract

Filling and cleaning of pesticide sprayers presents a potential risk of pollution of soil and water. Three different solutions for handling sprayers have been suggested: Filling and cleaning in the field, filling and cleaning on hard surfaces with collection of the waste water, and filling and cleaning on a biobed, which is an excavation lined with clay and filled with a mixture of chopped straw, sphagnum and soil with turf on top, and with increased sorption capacity and microbial activity for degradation of the pesticides. In the present study the degradation and leaching of 21 pesticides (5 g of each) was followed in an established full-scale model biobed. Percolate was collected and analysed for pesticide residues, and the biobed material was sampled at three different depths and analysed by liquid chromatography double mass spectrometry (LC-MSMS). During the total study period of 563 days, no traces of 10 out of 21 applied pesticides were detected in the percolate (detection limits between 0.02 and 0.9 $\mu g\,l^{-1}$) and three pesticides were only detected once and at concentrations below 2 $\mu g\,l^{-1}$. During the first 198 days before second application, 14% of the applied herbicide bentazone was detected in the leachate with maximum and mean concentrations of 445 and 172 $\mu g\,l^{-1}$, respectively. About 2% of the initial mecoprop and fluazifop dose was detected in the percolate, with mean concentrations of 23 $\mu g\,l^{-1}$, while MCPA and dimethoate had mean concentrations of 3.5 and 4.7 $\mu g\,l^{-1}$, respectively. Leachate concentrations for the remaining pesticides were generally below the detection limit (0.02–0.9 $\mu g\,l^{-1}$, below 1% of applied). Sorption studies of five pesticides showed that compounds with a low K_d value appeared in the leachate. After 169 days, all pesticides in the biobed profile were degraded to a level below 50% of the calculated initial dose. Pesticides with K_{oc} values above 100 were primarily found in the uppermost 10 cm and degraded slowest due to the low bioavailability. The 11 most degradable pesticides were all degraded such that less than 3% remained in the biobed after 169 days.

Following second pesticide application of the biobed, leachate was sampled 215 and 365 days after the treatment. This showed the same pesticides to be leached out and at concentrations comparable to those of the first treatment. The same pesticides as after the first treatment were retained in the biobed.

Keywords: Biobed; Bioavailability; Degradation; Leaching; Pesticides; Point sources; Pollution; Sprayer

1. Introduction

Much attention has been given to the use of pesticides in the field and the risk of pollution of ground and surface water. Approval of new pesticides is based on comprehensive documentation of the risk during application. Less attention has been given to the risk of pollution from filling and cleaning of sprayers. A German study has reported that more than 90% of the pesticide load in a small watershed came from farmyards (Frede et al., 1998). A Danish study (Helweg et al., 2002) demonstrated that the pesticide content in the uppermost ground water in samples from 2–4 m beneath sites used for mixing and loading pesticides was above the European drinking water criteria (0.1 $\mu g\,l^{-1}$), and 24 different pesticides and degradation products were detected in water samples from six farmyards. A Swedish study has shown that highlighting the

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problems associated with the handling and cleaning of sprayers, and providing farmers with site-specific information, can reduce the pesticide concentration in streams (Kreuger, 1998; Kreuger and Nilsson, 2004). Different solutions have been suggested for the establishment of safe sites for handling sprayers (Rose et al., 2004; Helweg et al., 2005), for instance, a consolidated impermeable ground with collection of the wastewater in a manure tank, where the wastewater is diluted before it is spread on the field, or another kind of collection tank so the wastewater is unable to reach the bare soil in a concentrated spot. Filling and cleaning sprayers on vegetation is another acceptable solution. Torstensson and Castillo (1997) and Torstensson (2000) suggested a so-called biobed where the soil on the filling and cleaning site is replaced by an excavation with a 10 cm clay lining at the bottom, and filled with 50 cm of a mixture of 50% chopped straw, 25% peat moss and 25% top soil with turf on top. The straw promotes microorganisms with the ability to degrade those pesticides characterised by an aromatic ring structure. The peat moss will enhance the sorption capacity and the topsoil will supply microorganisms, which are often scarce in farmyards covered with gravel or pebbles.

Several studies have shed light on the influence of different conditions on the fate of pesticides in the biobed. Torstensson and Castillo (1997) investigated the composition of the biobed material and concluded that the optimum composition was 50% straw, 25% peat and 25% top soil. Henriksen et al. (2003) showed decreasing degradation rate with increasing load of pesticides on the biobed and that autumn application resulted in leaching of mecoprop (3.6% of applied dose) and isoproturon (12.2% of applied dose). Fogg et al. (2003a,b, 2004, 2004a,b) have investigated the influence of pesticide concentration, biobed depth, water loading and soil texture. It was reported that increasing the concentration of isoproturon and chlorothalonil resulted in increasing DT_{50} values. In topsoil, chlorothalonil had an antagonistic effect on the degradation of isoproturon, while biomix (a mixture of topsoil, compost and wheat straw) increased the degradation rate and reduced the antagonistic effect. Fogg et al. (2004a) suggested that a biobed should have a minimum depth of 1.0–1.5 m and that a biobed with a depth of 1.5 m and a surface area of about 30–40 m^2 would be able to treat up to 44 000 l of pesticide wastewater, such that average concentrations of all but the pesticides classified as very mobile were less than 5 $\mu g\, l^{-1}$ in the treated water. Fogg and Boxall (2004) concluded that the topsoil texture was of minor importance and that local topsoils could be used for the biomix.

In the present study a full-scale model biobed was established and a sprayer wash was simulated to follow the leaching and degradation of pesticides under realistic conditions, and thereby evaluate the efficiency of a biobed as a cleaning site for sprayers. During the study, percolate samples were analysed as well as biobed material at different depths to follow the movement and degradation of the pesticides. A bromide tracer was applied with the pesticides, precipitation and temperature were recorded, and the percolate was collected so it was possible to calculate the water balance. The straw promotes microorganisms with the ability to degrade those pesticides characterised by an aromatic ring structure.

2. Materials and methods

2.1. The biobed

The biobed was built with concrete elements from Perstrup Beton Industri (Kolind, Denmark). The dimensions were 4×3.8 m. The bottom was filled with gravel (10 cm deep) and a drainage tube leading to a collection well was inserted for sampling the percolate. The gravel was covered by a 10 cm layer of rammed clay taken from the subsurface of a nearby field. The biobed was filled 27th September 2001 (Table 1) with 50 cm of biobed with 50% chopped wheat straw, 25% sphagnum and 25% soil from the A-horizon. The material was mixed in a fodder blender and the biobed was covered with a thin pre-established turf to increase microbial activity and evaporation. After one year the level of the biobed was reduced by 10–15 cm; the turf was removed and fresh biobed material was applied before the turf was replaced (Table 1).

2.2. Chemicals

Acetonitrile and methanol, gradient grade, acetic acid (100%), acetone, dichloromethane and 2-propanol were purchased from Merck (Darmstadt, Germany). Ammonium acetate was from Fluka (Buchs, Switzerland), while 25% ammonia, anhydrous sodium sulphate, incinerated for 4 h

Table 1
Time schedule

Date	Event
27th September 2001	Biobed filling
13th May 2002	First application of 21 pesticides in 100 l of water
14th May 2002	First percolate sampling. Sampling during the next 198 days
26th June 2002 (44 days after treatment)	Biobed material samples from a depth of 0–10 cm, 10–25 cm and 25–40 cm
29th October 2002 (169 days after treatment)	Biobed material samples from a depth of 0–10 cm, 10–25 cm and 25–40 cm
27th November 2002	Second application of 21 pesticides in 100 l of water
27th November to 17th June 2003	Outflow from biobed to reservoir closed
28th November to 28th March 2003	Biobed covered to reduce leaching
2nd May 2003	10–15 cm fresh biobed material applied
30th June 2003	Percolate sampling
21st November 2003	Percolate sampling

at 400 °C, 9- fluorenylmethyl chloroformate (FMOCl), disodium tetraborate, decahydrate, pro analysis and sulphuric acid (96%) were from Merck (Darmstadt, Germany). All pesticide reference standards were purchased from Dr. Ehrensdorfer (Augsburg, Germany).

Internal standard: 2-^{13}C, ^{15}N-glyphosate was from Cambridge Isotope Laboratories (Andover, Massachusetts, US).

2.3. Application of pesticides

Table 2 displays the 21 pesticides and formulated products used in the study. The products were divided into three groups of seven pesticides, and an amount corresponding to 5 g pesticide of each product was dissolved in water and transferred to a watering can. Each group of seven pesticides was applied with 20 l of water on two 1.25 m^2 plots of the biobed, simulating hot spots directly beneath the sprayer. Finally, 40 l of water was applied to achieve a total water volume of 100 l, simulating a typical sprayer cleaning. The two applications were done in exactly the same way. The amount of pesticide and cleaning water used for the study was based on observations of the amount of pesticides deposited on the external surfaces of sprayers determined in Jensen and Spliid (2004).

2.4. Time schedule

The time schedule for the study is shown in Table 1. The biobed was established in the autumn of 2001, 6 months before the pesticides were applied 13th May 2002, so that the biobed material had time to settle and the microbial activity could be established. Percolate samples were collected before pesticide application and the day after application, and, in total, 15 times during the study period, with the last sampling 21st November 2003 (Table 3). Samples of biobed material were taken after 44 and 169 days at three depths, 0–10 cm, 10–25 cm and 25–40 cm, and analysed for the applied pesticides. The biobed was covered with a plastic roof from 28th November 2002 to 28th March 2003 to reduce the surplus precipitation. From 27th November 2002 to 17th June 2003 a valve sitting on the drainage tube was closed to stop the outflow from the biobed. Even with coverage of the biobed in the winter period it was not possible to achieve a neutral water balance in the biobed and it was necessary to open the valve to avoid water saturation.

2.5. Meteorological registration

Precipitation, as shown in Fig. 1, was determined at the local climatological station with hourly registrations. The biobed was drip irrigated as a supplement to precipitation to achieve average monthly precipitation for the locality. Fig. 1 includes precipitation as well as irrigation, which was applied using a frame with small tubes covering the biobed to secure an even application on the biobed surface. The irrigation was applied with up to 20 mm at a rate of 20 mm per hour. The biobed was equipped with TDR probes (Tektronix Metallic cable tester 1502c, Beaverton, Oregon, US) for indication of water content at 10 and 40–50 cm. Furthermore, the leachate from the

Table 2
Pesticides and formulated products used for the study and parent/daughter ions for the LC-MSMS analysis

Active ingredient	Product	Company	Parent/daughter ions (*m*/*z*/*m*/*z*) (collision energy, V)
Azoxystrobin, 250 g l^{-1}	Amistar	Syngenta	+404/372 (20 V)
Bentazone, 480 g l^{-1}	Basagran 480	BASF	−239/132 (−50 V)
Bromoxynil, 200 g l^{-1}	Oxitril CM	Aventis	−276/79 (−55 V)
Ioxynil, 200 g l^{-1}			−370/127 (−60 V)
Dimethoate, 500 g l^{-1}	Perfekthion 500 S	BASF	+230/125 (35 V)
Diuron, 800 g kg^{-1}	Karmex	Griffen	+233/72 (55 V)
Fenpropimorph, 750 g l^{-1}	Corbel	BASF	+304/147 (40 V)
			+34/107 (acid) (55 V)
Fluazifop-P-butyl, 250 g l^{-1}	Fusilade X-tra	Zeneca	−326/254 (−30 V) (free acid)
Glyphosate, 360 g l^{-1}	Roundup BIO	Monsanto	−390/168 (−30 V)
			−332/110 (AMPA) (−30 V)
Kresoxim-methyl, 500 g kg^{-1}	Candit	BASF	+314/131 (35 V)
Linuron, 450 g l^{-1}	Afalon disp.	Aventis	+249/160 (30 V)
MCPA, 750 g l^{-1}	M-750	Klarsø & Co.	−199/141 (−20 V)
Mecoprop-P, 600 g l^{-1}	Duplosan MP	BASF	−213/141 (−30 V)
Metamitron, 700 g kg^{-1}	Goltix WG	Bayer	+203/104 (45 V)
Methabenzthiazuron, 700 g kg^{-1}	Tribunil WP	Bayer	+222/165 (35 V)
Metribuzin, 700 g kg^{-1}	Sencor WG	Bayer	+215/187 (30 V)
Pirimicarb, 500 g kg^{-1}	Pirimor G	Syngenta	+239/72 (29 V)
Propiconazole, 250 g l^{-1}	TILT 250 EC	Syngenta	+342/159 (55 V)
Propyzamide, 500 g l^{-1}	Kerb 500 SC	BASF	+256/173 (40 V)
Prosulfocarb, 800 g l^{-1}	Boxer EC	Syngenta	+252/91 (35 V)
Terbuthylazine, 500 g l^{-1}	Inter-terbuthylazin	Inter Trade	+230/174 (24 V)

Table 3
Concentration of pesticides in the leachate during the study period

	Sampling date														
	13.5.02	14.5.02	16.5.02	21.5.02	27.5.02	7.6.02	21.6.02	17.7.02	14.8.02	12.9.02	15.10.02	14.11.02	27.11.02	30.06.03	21.11.03
Day after treatment	0	1	3	8	14	25	39	65	93	122	155	185	198[a]	413	563
Percolate (l)[b]	–[a]	27	34	51	68	92	331	412	347	120	728	1262	582	973	873
Bromide (mg l^{-1})	0.49	0.56	0.63	0.66	0.57	0.65	1.4	1.2	1.6	2.2	1.2	0.07	0.07	1.1	1.5
AMPA	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02				
Azoxystrobin	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Bentazone	<0.4	5.6	48	30.2	42	4.7	445	262	262	373	243	65	71	124	154
Bromoxynil	<0.8	<0.8	1.7	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
Dimethoate	<0.3	<0.3	3.6	1.7	2	<0.3	29	7.4	7.3	10	2.3	0.3	0.4	1.4	<0.3
Diuron	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Fenprop. acid	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fenpropimorph	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Fluazifop	<0.2	0.65	4.5	2.4	3	0.18	71	31	32	46	22	13	12	28	5.9
Glyphosate	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02				
Ioxynil	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Kresoxim-methyl	<0.8	1.5	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Linuron	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
MCPA	<0.4	1.1	12	8.5	8.6	<0.4	29	6	1.8	<0.4	<0.4	<0.4	<0.4	0.5	<0.4
Mecoprop	<0.5	4.6	40	25	33	1.2	178	51	19	<0.5	<0.5	<0.5	1.4	33	0.73
Methabenzthiazuron	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Metamitron	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Metribuzin	<0.7	<0.7	1.2	<0.7	<0.7	<0.7	18	7	7	3.6	<0.7	0.7	0.4	8.6	4.1
Pirimicarb	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	2	1	2	<0.3	<0.3	0.4	<0.3	1.8	0.5
Propiconazole	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Propyzamide	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	0.1	<0.4	0.8	0.5
Prosulfocarb	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
Terbuthylazine	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.4	<0.3

Pesticide content as $\mu g\ l^{-1}$.

[a] Sampling before application of pesticides.

[b] Amount of percolate collected (l) since previous sampling date.

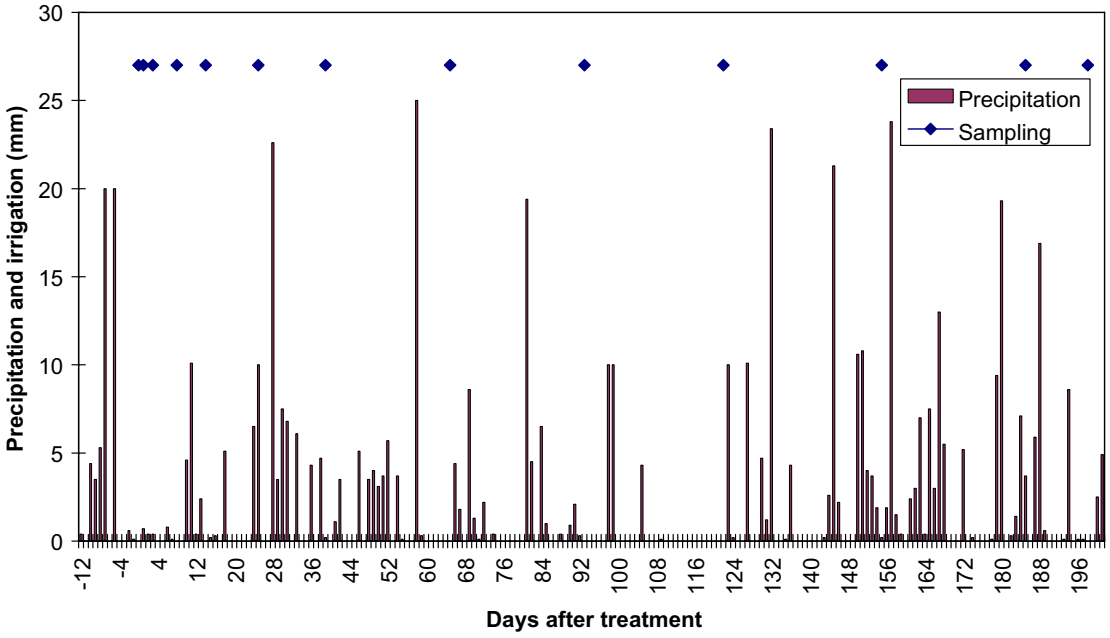

Fig. 1. Precipitation and irrigation (mm) as daily values during the first application period. Sampling dates indicated.

biobed was measured for calculation of the water balance. Leachate was collected in a 100 l plastic barrel in a well beside the biobed. In the event of heavy rainfall and overflow of the barrel, the leachate was collected from the concrete well. Both barrel and well were equipped with a submerged pump so it was possible to take samples from barrel and well, and the water volume could be recorded. The temperature was recorded at a depth of 10 and 30 cm in the biobed and in the soil adjacent to the biobed during the study period with thermo probes and data loggers (Gemini Data loggers equipped with Tinytag Plus, Chichester, United Kingdom). Temperatures are shown in Fig. 2.

2.6. Sorption studies

Sorption of bentazone, dimethoate, glyphosate, MCPA and metribuzin was determined with material from the biobed profile sampled 7, 13 and 18 months after the biobed had been established. Samples were taken at the same depths as samples for residue analysis but outside the application area. Material from the biobed was irradiated (11 kGy) to reduce microbial activity and degradation of the tested pesticides, and 5 g was shaken for 24 h in a "batch equilibrium test" with 25 ml of 0.001 M $CaCl_2$ before centrifugation, analysis and calculation of K_d (OECD, 2000).

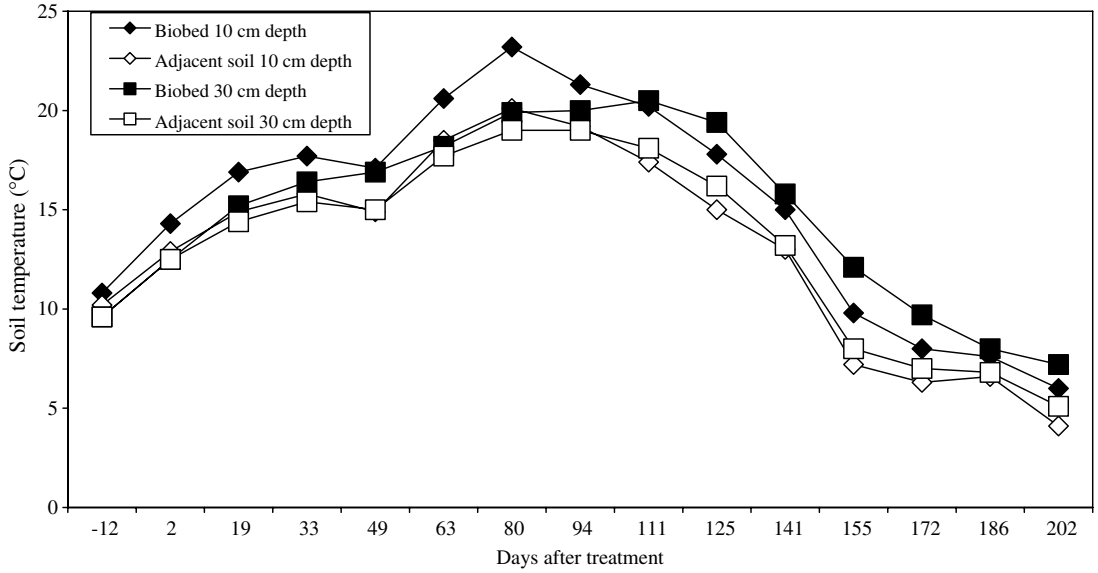

Fig. 2. Temperatures at a depth of 10 cm and 30 cm in the biobed and in the adjacent soil.

2.7. Chemical analysis—pesticides except glyphosate and AMPA

All percolate and biobed material samples were kept below −18 °C until analysis.

2.7.1. Water preparation

Percolate was filtered through a 0.45 μm Minisart SRP 15 filter from Sartorius (Goettingen, Germany) and was ready for analysis without further preparation. The simple pre-treatment resulted in recovery rates of around 100%.

2.7.2. Biobed material extraction

Fifty grams of biobed material (dry weight) was extracted with 100 ml of methanol, sonicated in an ultrasonic bath for 10 min, shaken at 25 rpm on a Comfort Heto Master Mix type MMV 15 (Heto Holten, Allerød, Denmark) for 1 h, and then centrifuged at 3200 rpm for 12 min using a Sorwall RT7 centrifuge (Newton, USA). The supernatant was decanted into a 200 ml graduated flask. The extraction procedure was repeated with 80 ml methanol for the second extraction. The two methanol supernatants were pooled and the graduated flask was adjusted to 200 ml with methanol. The extract was transferred to a Duran bottle and stored below 5 °C until chemical analysis. Recovery rates were from 73% to 100%, with the exception of fenpropimorph and fenpropimorphic acid, which gave recovery rates of about 43%.

2.7.3. Analytical methods

The chromatographic separation was performed using a Hewlett-Packard 1100 system with gradient elution; 50 μl was injected on a 250 × 2.1 mm BDS Hypersil C 18, 5 μm column from the Thermo Electron Corporation (Waltham, Massachusetts, US). For negative ions the following gradient was used: A-eluent 90% 20 mM of acetic acid in water, 10% methanol and B-eluent 20 mM acetic acid in methanol, gradient from 20% to 90% B for 15 min, back to 20% B for 1 min and restabilisation with 20% B for 8 min. Gradient elution of positive ions was performed with A-eluent 99% 10 mM of ammonium acetate, 1% methanol and B-eluent 10% 10 mM of ammonium acetate in water and 90% methanol, gradient from 40% to 100% B for 10 min, 100% B for 15 min, back to 40% B for 1 min, and restabilisation with 40% B for 8 min. The column was kept at 30 °C in a column oven, eluent flow 0.2 ml min^{-1}. MSMS detection was performed using an Applied Biosystems Sciex API 2000 instrument in electrospray-positive and -negative multiple reaction (MRM) ionisation mode. Table 1 gives further details for the MSMS parent/daughter ions and the collision energy.

2.8. Chemical analysis—glyphosate and AMPA

2.8.1. Water extraction

Sixteen milligrams of fluorenyl methyl chloroformate (FMOCl) in 100 ml of acetone was added to 16 ml of 5% borate buffer and a 100 ml water sample in a separatory funnel. The mixture stood for 30 min after manual shaking. One hundred millilitres of dichloromethane/2-propanol (3/1) was added and after vigorous manual shaking for 3 min the lower organic phase was discarded. The extraction was repeated with 50 ml of dichloromethane/2-propanol.

The water phase was acidified with 8 ml of 2.5 M sulphuric acid and the extraction was repeated twice each time with 100 ml of dichloromethane/2-propanol. The lower organic phases were dried through anhydrous sodium sulphate and cotton wool in a glass funnel, transferred to a round-bottom flask, and 20 drops of 25% ammonia were added.

The organic solvents were evaporated to dryness on a rotavapor at 60 °C. The flask was rinsed twice with 2 ml of dichloromethane, which was removed with a Pasteur pipette, and the sample was redissolved after swirling the flask with 1 ml of 50% methanol/water.

The sample was then ready for instrumental analysis.

2.8.2. Analytical method

Gradient HPLC was performed with a binary gradient composed of LC solvent A (99% 10 mM ammonium acetate, 1% acetonitrile or methanol), LC solvent B (10% 10 mM ammonium acetate, 90% acetonitrile) according to the following programme: 0–2 min 10% B, from 2 to 12 min linear gradient to 100% B, 100% B to 18 min and linear gradient back to 10% B for 1 min, followed by from 19 to 30 min restabilisation with 10% B. The flow rate of the mobile phase was 0.2 ml min^{-1} and 100 μl of standard/sample solution was injected into the HPLC system, where the column was kept at 40 °C in a column oven. MSMS detection was performed using an Applied Biosystems Sciex API2000 instrument in electrospray-negative multiple reaction (MRM) ionisation mode. In Table 2 further details are given for the MSMS parent/daughter ions of derivatised glyphosate and AMPA and the collision energy.

3. Results and discussion

3.1. Water balance

TDR probes showed that the mean water content in the biobed was 16% higher at a depth of 40–50 cm than at a depth of 20–30 cm. The clay liner at the bottom retained the water to some extent, but over time the water percolated through the membrane and was collected as leachate. Before the first application, 3663 l of leachate was collected from 16th October 2001 to 11th March 2002, corresponding to 262 mm of precipitation or 90% of the actual 290 mm precipitation in the period. In the summer period, 145 mm of leachate was collected, or 46% of the actual 318 mm precipitation from 12th March 2002 to 14th August 2002 (Fig. 1). So even during the summer period the grass cover was not able to remove water by root

uptake and evaporation to avoid a net downward water movement in the biobed. The grass was pre-grown and of the type normally used for laying out lawns; it had difficulty establishing itself on biobed material. A more appropriate type or a thicker turf might have increased the growth and evaporation rate.

The temperature of the biobed at 10 and 30 cm was 1–4 deg higher than the temperature of natural soil (see Fig. 2). The higher temperature could mainly be explained by increased microbial activity in the biobed soil.

3.2. Leaching of pesticides

During the first 198-day study period, 4054 l of water had penetrated through the 15.2 m^2 biobed, corresponding to 267 mm precipitation. The bromide tracer and bentazone (5.6 $\mu g\,l^{-1}$), fluazifop (0.65 $\mu g\,l^{-1}$), kresoxim-methyl (1.5 $\mu g\,l^{-1}$), MCPA (1.1 $\mu g\,l^{-1}$) and mecoprop (4.6 $\mu g\,l^{-1}$) were detected in the leachate one day after treatment. A more massive breakthrough was seen at 39 days after treatment (Fig. 3 and Table 3) when the biobed had received 54 mm of precipitation during the previous 2 weeks (Fig. 1). The maximum concentrations were measured and the pesticide concentrations continued to decline for the duration of the study; at the end of the study only bentazone, fluazifop and metribuzin still remained in the leachate at considerable concentrations: 154 $\mu g\,l^{-1}$, 5.9 $\mu g\,l^{-1}$ and 4.1 $\mu g\,l^{-1}$, respectively. The individual pesticide leachate results are shown in Table 3. Bentazone was the most mobile of the investigated pesticides. During the study period, 14% of the applied bentazone was collected in the leachate. The maximum concentration measured was 445 $\mu g\,l^{-1}$ and the mean concentration in the leachate was 172 $\mu g\,l^{-1}$. Table 4 shows the maximum and mean concentrations for the detected pesticides as well as the total amount of pesticide collected in the leachate. The 0.1 $\mu g\,l^{-1}$ limit of the EU drinking water directive was exceeded up to 230 and 1720 times (mecoprop and bentazone), but it should be taken into consideration that 5 g of each pesticide was applied on the 2.5 m^2 biobed, corresponding to 20 $kg\,ha^{-1}$ of each, and the contaminated water volume was limited. Application on bare soil would most likely have given worse results. MCPA, mecoprop, fluazifop and dimethoate gave maximum concentrations of 29, 178, 71 and 29 $\mu g\,l^{-1}$, and the mean concentrations during the first 198-day study period were 3.5 $\mu g\,l^{-1}$, 23 $\mu g\,l^{-1}$, 23 $\mu g\,l^{-1}$ and 4.7 $\mu g\,l^{-1}$, respectively. Bromoxynil, kresoxim-methyl and terbuthylazine were only detected once and at low concentrations, and no traces of 10 out of the 21 applied pesticides were detected in the leachate. About 2% of the applied mecoprop and fluazifop was collected in the leachate, while the rest of the detected pesticides comprised well below 1% (see Fig. 3 and Table 4). With a biobed depth of about 50 cm or less it is not surprising to find mobile pesticides in the leachate, as Fogg et al. (2004a) also have reported from column studies, where column lengths of 50, 100 and 150 cm were tested. Fogg recommended column lengths of 100–150 cm. A deeper layer may retain the pesticides for a longer period, giving time for more pesticide degradation before they reach the bottom of the biobed.

The results give no clear pattern of a correlation between leaching and water solubility and K_{oc}, but, in general, pesticides with K_{oc} values below 50 $l\,kg^{-1}$ were detected in the leachate. Glyphosate was the exception with respect to other inorganic sorption properties. Fluazifop, as another exception, has a calculated K_{oc} of 2010 $l\,kg^{-1}$, but is one of the most mobile compounds in the biobed.

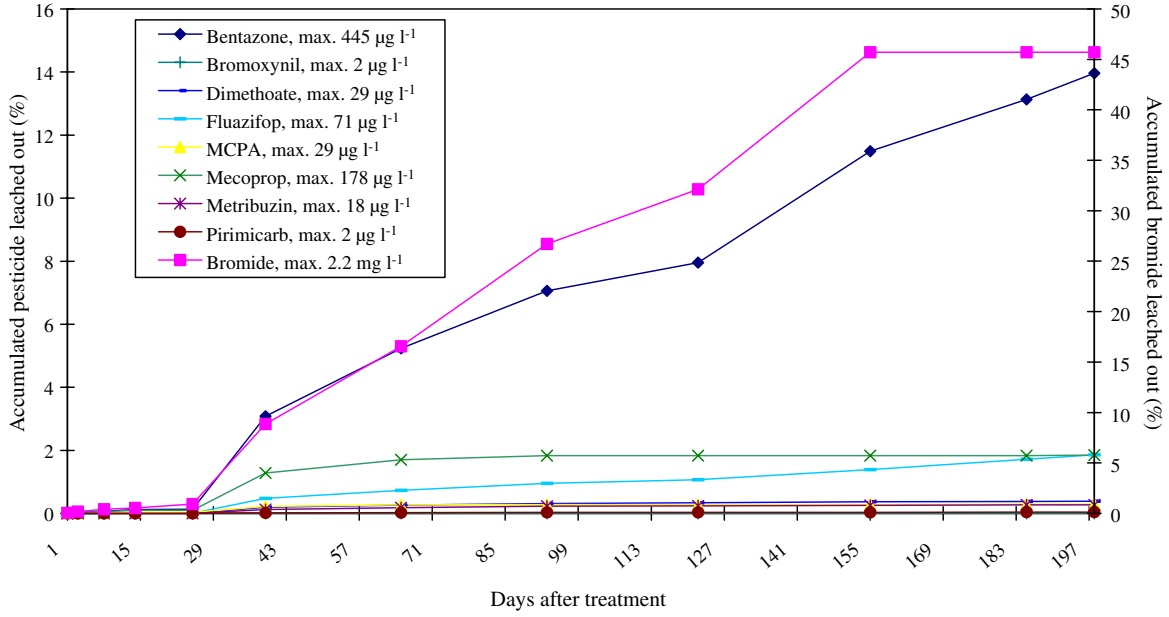

Fig. 3. Accumulated amount in the leachate as % applied dose of the added tracer bromide and the detected pesticides. The box shows maximum concentrations of the leached pesticides.

Table 4
Water solubility, % leaching, maximum and mean concentration, estimated dissipation half-lives in the biobed material, and determined K_d values

Compound	Water solubility ($mg\,l^{-1}$)[b]	K_{oc}[c] estimated	Leaching (%)	Max. conc. ($\mu g\,l^{-1}$)	Mean conc. ($\mu g\,l^{-1}$)	DT_{50}[a] (days)	K_d in biobed[d] ($kg\,l^{-1}$)
AMPA			0	<0.01	<0.01		
Azoxystrobin	10	740	0	<0.5	<0.5	38	
Bentazone	570	37.5	14	445	172	<20	<1
Bromoxynil	130	435	0.001	1.7	0.03		
Bromoxynil octanoate		4850				<20	
Dimethoate	24000	24.5	0.4	29	4.7	18	<1–1.7
Diuron	42	136	0	<0.2	<0.2	108	
Fenpropimorph	4.3	26900	0	<0.6	<0.6	84	
Fenpropimorphic acid			0	<0.5	0.04		
Fluazifop		2010	2	71	23		
Glyphosate	12000	18.8	0	<0.01	<0.01		22–82
Ioxynil	50	435	0	<0.4	<0.4		
Ioxynil octanoate		4850				18	
Kresoxim-methyl	2	40700	0.001	1.5	<0.8	<20	
Linuron	81	350	0	<0.5	<0.5	90	
MCPA	734	29.4	0.3	29	3.5	<20	<1
Mecoprop	734	48.6	2	178	23	<20	
Metamitron	1700	3280	0	<0.6	<0.6	18	
Methabenzthiazuron	59	1960	0	<0.4	<0.4	151	
Metribuzin	1050	1200	0.3	18	3.2	26	<1–3.2
Pirimicarb	3000	33	0.05	2	0.6	93	
Propiconazole	100	5560	0.005	<0.3	<0.3	160	
Propyzamide	15	1590	0.002	0.8	<0.4	91	
Prosulfocarb	13	5620	0	<0.9	<0.9	<20	
Terbuthylazine	8.5	329	0	<0.3	<0.3	60	

[a] Half-lives graphically estimated from % recovery in the biobed soil after 44 and 169 days.
[b] Tomlin (1995).
[c] Estimated using EPI Suite v. 3.11 software (US EPA, 2003).
[d] K_d determined in biobed material from 0–10, 10–25 and 25–40 cm after 7, 13 and 18 months.

Pesticides with water solubilities below 81 $mg\,l^{-1}$ (linuron) were not detected in the biobed effluent, with the exception of propyzamide with a water solubility of 15 $mg\,l^{-1}$, which was detected in two samples (0.5 and 0.8 $\mu g\,l^{-1}$). From Table 4 it can be concluded that compounds with low water solubility, in general, are sorbed on the biobed material and the risk for leaching is minimal. It is therefore likely that highly ecotoxic insecticides with low water solubility not included in this study will be retained in the biobed and not reach the water environment when applied on a biobed as opposed to cleaning sites with bare soil with sinks connected to streams with drainage tubes.

It is more difficult to generalise with respect to compounds that have high water solubility. For instance, glyphosate and metamitron with solubilities of approximately 12 $g\,l^{-1}$ and 1.7 $g\,l^{-1}$, respectively, were not detected in the leachate.

Pesticide treatment was repeated on day 198 (27th November 2002). Samples were analysed in June and November 2003. After analysis of these samples, the same pattern was seen as after the first application with bentazone, dimethoate, fluazifop, MCPA, mecoprop and metribuzin at highest concentrations: 154, 1.4, 28, 0.5, 33 and 8.6 $\mu g\,l^{-1}$, respectively. The pesticides retained in the biobed after the second treatment were the same as those retained after the first treatment. In conclusion, the two treatments were in good agreement and gave similar results despite the fact that the first treatment was a spring application and the second was an autumn application. No further analyses were done for glyphosate and AMPA after the second treatment as they were not detected in the samples after the first treatment and the analysis of glyphosate and AMPA was done using another analytical method. In an attempt to limit pesticide loss during the winter when there was a surplus of precipitation, the biobed was covered from November 28th 2002 to March 28th 2003 (Table 1).

3.3. Sorption to biobed material

Sorption of bentazone, dimethoate, glyphosate, MCPA and metribuzin to biobed material supported the findings since bentazone and MCPA had K_d values <1 $l\,kg^{-1}$, dimethoate from <1 to 1.7 $l\,kg^{-1}$, and metribuzin <1 to 3.2 $l\,kg^{-1}$ (Table 4). This is in good agreement with the calculated K_{oc} values, with the exception of glyphosate, which had K_d values between 22 and 83 $l\,kg^{-1}$and not was found in the leachate. This can be explained by other inorganic sorption mechanisms. The low K_d value for metribuzin does not agree with a calculated K_{oc} value of 1200 $l\,kg^{-1}$. The measured findings indicate best agreement with the determined low K_d value. The oldest biobed material, in general, had the lowest capacity for binding (Helweg et al., 2005).

3.4. Pesticide residues

Samples of the biobed material were taken from three depths (0–10, 10–25 and 25–40 cm) after 44 and 169 days (Fig. 4a and b). Fig. 4a shows the recovery of the applied pesticides and some degradation products after 44 days. One third of the applied pesticides were recovered in amounts above 50% (57–80%) and one third of the pesticides were degraded or irreversibly sorbed, so that less than 5% (0.1–3.4%) were recovered. The most stable pesticides were all primarily sorbed on the uppermost 10 cm of the biobed, which indicates that high sorption causes low bioavailability and slow degradation. This is illustrated in the figure, where only very limited amounts of the most stable pesticides have moved below a depth of 25 cm. Pirimicarb is an exception and has a more even distribution, especially 169 days after treatment. Pirimicarb has a water solubility of 3000 mg l^{-1}, a calculated K_{oc} of 33 l kg^{-1} and an estimated DT_{50} of 93 days, so it is surprising that less than 1% has been recovered in the leachate after 169 days.

Fig. 4b shows that 169 days after treatment the total pesticide concentrations in the soil profile had decreased considerably. Forty-eight percent of propiconazole and 47% of methabenzthiazuron remained in the biobed, while the rest of the pesticides were degraded to a level below 30% of the initial applied dose. The 11 most degradable

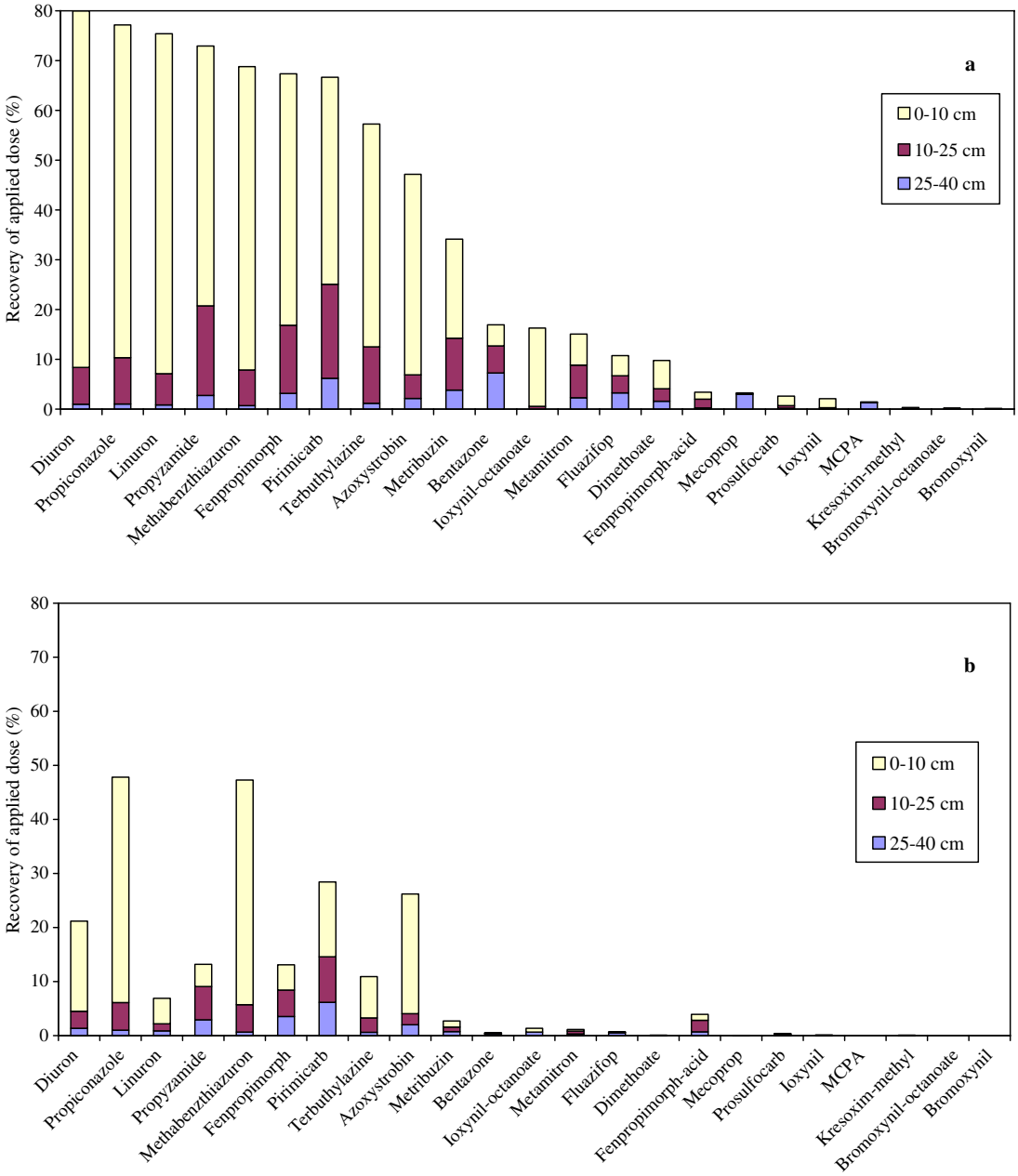

Fig. 4. Pesticide content as % applied dose in the biobed at a depth of 0–10 cm, 10–25 cm and 25–40 cm: (a) 44 days after treatment and (b) 169 days after treatment.

pesticides were all degraded so that less than 3% remained in the biobed.

Based on the results from the content in the biobed 0 days after treatment (100%), and 44 and 169 days after treatment, the dissipation half-lives DT_{50} were estimated graphically from the best curve fit. Values are shown in Table 4. Bentazone, bromoxynil octanoate, dimethoate, ioxynil octanoate, kresoxim-methyl, MCPA, mecoprop and prosulfocarb all had dissipation half-lives in the biobed material of below 20 days, while the DT_{50} values for metribuzin and terbuthylazine were 26 days and 60 days, respectively. Diuron, fenpropimorph, linuron, methabenzthiazuron, propiconazole, propyzamide and pirimicarb had DT_{50} values of about 3 months or more.

The half-lives express the conversion of the active compounds to other degradation compounds and to some extent a total mineralization, which it is not possible to quantify with the actual design of the study. Only for bentazone with 14% leached out may the leaching be important for determination of the half-life.

4. Conclusions

It was concluded from the study that—even with a turf layer on the top and a 10 cm clay membrane at the bottom of a biobed—water from precipitation and cleaning of sprayers would percolate through the biobed and reach the soil layers beneath under Danish meteorological conditions. In the leachate, 11 out of the 21 applied pesticides appeared at concentrations from 0.4 to 445 $\mu g\, l^{-1}$. Ten pesticides were not detected in the percolate. The most mobile compound in the study was bentazone, with 14% being recovered below the biobed, while the cumulated amounts of the other pesticides in the leachate were below 2%. Bentazone was detected at a maximum concentration of 445 $\mu g\, l^{-1}$ and a mean concentration of 172 $\mu g\, l^{-1}$. Dimethoate, fluazifop, MCPA, mecoprop, metribuzin and pirimicarb had mean concentrations of 4.7, 23, 3.5, 23, 3.2, and 0.6 $\mu g\, l^{-1}$, respectively, while the rest of the applied pesticides, in general, were below the detection limit.

The leaching during a year—after one further pesticide treatment but with only two samplings—supported the results from the first year.

K_d values determined in batch equilibrium studies with bentazone, dimethoate, glyphosate, MCPA and metribuzin supported the findings in the leaching studies since those with low K_d values gave most leaching.

Taking into account that, as shown by these figures, pesticide leaching contributes to ground water formation below a surface area of about 16 m^2, the potential for ground water pollution has been markedly reduced using a biobed. The biobed material contained 32% of the applied pesticides 44 days after treatment, while 169 days after treatment this was reduced to 10% of the initial amount.

Finally, it can be concluded that the present paper has demonstrated that biobeds can retain and degrade pesticides which are spilled on sites for filling and cleaning of sprayers and—with the exception of the most mobile pesticides—markedly reduce the risk of contamination of the soil and water. An increase in the thickness of the biobed would further improve the value of the biobed as a precaution against point source pollution at sites for filling and cleaning sprayers.

Acknowledgement

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