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Degradation of Pesticides in Biobeds: The Effect of Concentration and Pesticide Mixtures

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Biobeds aim to create an environment whereby any pesticide spills are retained and then degraded, thus reducing the potential for surface or groundwater contamination. Biobeds may receive high concentrations of relatively complex mixtures of pesticides. The effects of concentration and pesticide interaction on degradation rate were therefore investigated. At concentrations up to 20 times the maximum recommended application rate for isoproturon and chlorothalonil, the rate of degradation in topsoil and biomix decreased with increasing concentration. With the exception of isoproturon at concentrations above 11 mg kg^{-1}, degradation was quicker in biomix (a composted mixture of topsoil, compost, and wheat straw) than in topsoil. One possible explanation for faster isoproturon degradation in topsoil as compared to biomix may be that previous treatments of isoproturon applied to the field soil as part of normal agricultural practices had resulted in proliferation of microbial communities specifically adapted to use isoproturon as an energy source. Such microbial adaptation could enhance the performance of a biobed. Studies with a mixture of isoproturon and chlorothalonil showed that interactions between pesticides are possible. In biomix, the degradation of either isoproturon or chlorothalonil was unaffected by the presence of the other pesticide, whereas in topsoil, isoproturon DT_{50} values increased from 18.5 to 71.5 days in the presence of chlorothalonil. These studies suggest that biobeds appear capable of treating high concentrations of more than one pesticide.

KEYWORDS: Biobeds; pesticide; waste treatment; degradation; concentration; mixtures

1. INTRODUCTION

The filling and cleaning of agricultural spray equipment is often performed at the same site in the farmyard year after year due to the availability of a clean water supply (*1*, *2*). The small drips and spills that can occur at these sites as part of normal agricultural practices (*3*) can result in high concentrations of pesticide being measured in both adjacent water courses and underlying groundwaters (*1*, *2*, *4*). Biobeds aim to trap these drips and spills and create an environment whereby maximum sorption is achieved while maintaining bioavailability and optimum conditions for microbial decomposition (*5*). In its simplest form, a biobed is a hole in the ground filled with a mixture of topsoil, peat, and straw (*5*, *6*). The biobed is covered with grass and equipped with a ramp enabling the tractor and sprayer to be parked over the bed while being filled. Studies in Sweden have demonstrated that biobeds can effectively retain and degrade pesticide waste arising from accidental spillages of concentrate and prepared pesticides (e.g., ureas, triazoles, trazines, and carbamates) (*7*). Generally, persistence increases with increasing concentration (*2*, *4*, *8*, *9*), and at high concentrations, pesticides have been shown to depress microbial biomass and bioactivity; consequently, degradation may be inhibited (*9*). In many agricultural situations, the use of tank mixes and complex spray programs is common practice (*1*, *10*, *12*). There is evidence that the persistence of a number of pesticides may be changed when used in combination with other pesticides (*10*, *12*−*14*). The objectives of the experiments reported here were (i) to determine whether biobeds are able to degrade the high concentrations of pesticide that have been measured at spray fill sites and (ii) to study the effects of a binary pesticide mixture on degradation rates of individual compounds.

2. MATERIALS AND METHODS

Biomix was prepared by mixing topsoil (69% sand, 13% silt, 18% clay, 1.95% organic mater, pH 6.15, maximum water holding capacity 37% w/w), peat free compost (Levington Peat Free Universal), and winter wheat straw in the volumetric proportions of 1:1:2, respectively. The mixture (organic matter 12.36%, pH 7.5, maximum water holding capacity 121% w/w) was composted outside for 80−100 days and then macerated using a food processor, air-dried to approximately 30−40% w/w, and refrigerated at 0−10 °C prior to use. A sample of topsoil, used in the preparation of the biomix, was air-dried, passed through a

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Table 1. Study Compounds and Their Reported Physicochemical Characterisistics[a]

active substance	k_{oc} (mL g^{-1})	DT_{50} (days)	water solubility (mg L^{-1})
isoproturon (SC*)	100	6–28	65
chlorothalonil (SC*)	1600–14 000	6–43	0.81

[a] Values taken from refs *27* and *28*. *, Suspension concentrate.

5.4 mm mesh sieve, and refrigerated with the biomix prior to use. Disturbed subsamples of topsoil and biomix were repacked into 222 cm^3 volumetric tins, and the maximum water holding capacity was determined by capillary rise (*15*). The test chemicals were isoproturon and chlorothalonil, which were selected on the basis of their physicochemical properties, in particular their sorption potential, water solubility, and reported degradation rates (**Table 1**), and represent compounds that are of relatively high annual usage (*16*).

2.1. Effect of Concentration on Degradation Rates. Samples (25 g) of moist topsoil or biomix were weighed into clear glass bottles (125 mL) fitted with Bakelite screw cap lids to provide three treated replicates and one untreated control per sampling time point. Subsamples of each matrix were taken, and moisture contents were determined by oven drying at 105 ± 2 °C for 24 h. Formulated isoproturon (Alpha Isoproturon 500, 43.6%w/w) and chlorothalonil (Cropgard, 41.57% w/w) were used to make up stock suspensions in tap water of 5190 and 3118 mg a.i. L^{-1}. Serial dilutions of the stock samples were made in order to achieve final fresh weight concentrations of 11, 23, 46, 91, 228, and 456 mg kg^{-1} of isoproturon and 7, 14, 29, 57, 143, and 287 mg kg^{-1} of chlorothalonil in topsoil and biomix. Topsoil and biomix were treated with either 2.2 (isoproturon) or 2.3 mL (chlorothalonil) of the appropriate pesticide suspension in order to achieve a final moisture content of 15% w/w in topsoil and 105% w/w in biomix (40 and 87% of the respective maximum water-holding capacities). Tap water was used to adjust the moisture content in untreated samples. Immediately after treatment, three treated replicates and one untreated control were taken for each concentration and frozen (−20 °C). The remaining samples were loosely capped and incubated in the dark at 20 °C. At intervals of 3, 10, 20, 30, 46, 60, and 90 days after treatment (DAT), three soil and three biomix samples were collected for each chemical treatment, with a single sample from the untreated controls. The samples were stored at −20 °C prior to analysis.

2.2. Effect of Pesticide Mixtures on Degradation Rate. Samples (25 g) of moist topsoil or biomix were weighed into clear glass bottles (125 mL). Individual stock suspensions of 925 and 555 mg a.i. L^{-1} were made up in tap water using formulated isoproturon and chlorothalonil, respectively. For mixture experiments, an appropriate isoproturon and chlorothalonil mixture was prepared. Samples were treated with 2.6 mL of the respective stock suspension in order to achieve final fresh weight concentrations of 96 mg kg^{-1} for isoproturon and 58 mg kg^{-1} for chlorothalonil and a moisture content of 15% w/w for topsoil and 105% w/w for biomix. Tap water was used to adjust the moisture content in control samples. Following treatment, three treated replicates and one untreated control sample were removed and placed immediately into freezer storage. Remaining samples were loosely capped and incubated in the dark at 20 °C. At intervals of 3, 10, 20, 31, 60, and 97 DAT, three topsoil and three biomix samples were collected from each chemical treatment, with a single sample from the untreated controls. Samples were stored at −20 °C prior to analysis.

2.3. Analysis. Isoproturon and chlorothalonil were extracted from topsoil and biomix by shaking for 1 h with 50 mL of methanol on an end over end shaker. The resulting extracts were analyzed by high-performance liquid chromatography. The extraction efficiencies for isoproturon were >90% and for chlorothalonil >82% in both topsoil and biomix. Concentrations of isoproturon and chlorothalonil were determined using a Kontron Series 320 Pump linked to a Kontron Series 332 UV detector. Samples of extract (20 μL) were injected using a Kontron Series 360 autosampler. Separation was achieved using a Lichrosorb RP18 column (250 mm × 4 mm i.d.) and a mobile phase flow rate of 1 mL/min. The mobile phase was acetonitrile:water: phosphoric acid (75:24.75:0.25 v/v). The detection wavelength for both compounds was 230 nm, and the retention times were 3.18 and 4.56 min for isoproturon and chlorothalonil, respectively.

2.4. Data Analysis. Where possible, the first-order rate equation was fitted to the observed concentrations (eq 1)

$$\frac{dC}{dt} = -kC \quad (1)$$

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

$$C_t = C_0 \exp(-kt) \quad (2)$$

However, the first-order rate equation is often considered unacceptable if the determination coefficient (r^2) falls below 0.7 (*17*). Where data indicated increasing rates of degradation with time, DT_{50} and DT_{90} values were calculated using an empirical two parameter relationship

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

where S_0 and S are the concentrations of pesticide at time 0 and time t, respectively. Microsoft Excel Solver was used to estimate parameters k_1 and k_2 using the least-squares method in order to give the best agreement between calculated and observed concentrations. The degradation data were summarized by calculating the times to 50% degradation (DT_{50}) and the time to 90% degradation (DT_{90}) from the calculated degradation curves using the relationship

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

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

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

$$C_t = A \exp(-k_1 t) + B \exp(-k_2 t) \quad (6)$$

where C_t (mg kg^{-1} soil) is the concentration at time t, A (mg kg^{-1} soil) and B (mg kg $^{-1}$ soil) are constants, and k_1 (days^{-1}) and k_2 (days^{-1}) determine the decline of the first and second component of the curve, respectively (*17*).

3. RESULTS

3.1. Effect of Concentration on Degradation Rate. Results from the experiments to investigate the effects of initial concentration are summarized in **Table 2** for isoproturon and in **Table 3** for chlorothalonil. The pattern of isoproturon degradation in topsoil and biomix is shown in **Figure 1**. At all concentrations in biomix and at concentrations below 46 mg kg^{-1} in topsoil, degradation curves were fitted to a simple first-order rate equation (eq 1). Above 23 mg kg^{-1} concentration in topsoil, the pattern of decline could not be fitted to simple first-order kinetics; data indicated increasing rates of degradation with time, with fitted curves showing a short lag phase before the onset of rapid degradation. DT_{50} values for isoproturon in biomix and topsoil ranged from 8.6 to 44.2 days and 9.4 to 34.7 days, respectively. Although a significant (P <0.001) concentration effect was observed in both topsoil and biomix, there were no significant differences in the DT_{50} values between substrates. DT_{90} values also highlighted a significant (P < 0.001) concentration effect and also a significant (P < 0.001) difference

Table 2. DT_{50} and DT_{90}, Degradation Rate Constants (k), and Determination Coefficients (r^2) for Isoproturon in Topsoil and Biomix[a]

	topsoil						biomix					
concn (mg kg^{-1})	DT_{50} (days)	±1 SE	DT_{90} (days)	EnDash± 1 SE	k deg (days^{-1})	r^2	DT_{50} (days)	±1 SE	DT_{90} (days)	±1 SE	k deg (days^{-1})	r^2
11	9.4[b]	0.5	31.3[b]	1.5	0.0735	0.98	8.6[b]	0.2	28.5[b]	0.8	0.0809	0.99
23	10.8[b]	0.6	35.9[b]	2.0	0.0641	0.96	11.1[b]	0.1	36.9[b]	0.2	0.0624	0.99
46	19.2[c]	0.4	29.1[c]	2.3	k_1, 0.0888; k_2, 0.1132	1.00	13.1[b]	0.2	43.4[b]	0.8	0.0530	0.99
91	22.1[c]	3.4	31.8[c]	6.3	k_1, 0.0533; k_2, 0.1192	1.00	16.2[b]	0.1	53.9[b]	3.2	0.0427	0.99
228	30.4[c]	2.7	37.7[c]	2.3	k_1, 0.0048; k_2, 0.1637	1.00	29.2[b]	1.4	97.1[b]	4.6	0.0237	0.97
456	34.7[c]	5.9	51.7[c]	5.5	k_1, 0.0771; k_2, 0.0664	1.00	44.2[b]	1.8	146.9[b]	5.9	0.0157	0.91

[a] $k1$ and $k2$ determine the decline of the first and second part of the degradation curve, respectively. [b] The integrated form of the first-order rate equation (eq 2) was used to calculate the DT_{50} and DT_{90} values, respectively. [c] The two parameter empirical model (eq 3) was used to calculate the DT_{50} and DT_{90} values, respectively.

Table 3. DT_{50} and DT_{90} Degradation Rates, Degradation Rate Constants (k), and Determination Coefficients (r^2) for Chlorothalonil in Topsoil and Biomix[a]

	topsoil						biomix					
concn (mg kg^{-1})	DT_{50} (days)	±1 SE	DT_{90} (days)	±1 SE	k deg (days^{-1})	r^2	DT_{50} (days)	±1 SE	DT_{90} (days)	±1 SE	k deg (days^{-1})	r^2
7	6.1[b]	0.1	20.2[b]	0.5	0.1141	0.99	0.6[b]	0.3	2.1[b]	1.0	1.1159	1.00
14	11.5[b]	0.5	38.1[b]	1.7	0.0605	0.99	0.9[b]	0.1	3.0[b]	0.3	0.7649	1.00
29	23.0[c]	1.1	105.9[c]	7.7	k_1, 0.8949; k_2, 0.0230	0.99	2.3[b]	0.3	7.6[b]	1.1	0.3048	1.00
57	47.9[c]	1.3	178.3[c]	6.3	k_1, 0.0909; k_2, 0.0123	0.93	3.8[b]	0.5	12.5[b]	1.6	0.1845	1.00
143	46.4[c]	3.7	184.7[c]	17	k_1, 0.1259; k_2, 0.0116	1.00	20.4[b]	1.2	67.9[b]	4.0	0.0339	0.99
287	79.6[b]	1.8	264.3[b]	6.1	0.0087	0.94	10.0**	9.0	126.5[c]	9.5	k_1, 0.0138; k_2, 0.5331	0.97

[a] $k1$ and $k2$ determine the decline of the first and second component of the degradation curve, respectively. [b] The integrated form of the first-order rate equation (eq 2) was used to calculate the DT_{50} and DT_{90} values, respectively. [c] The biexponential model (eq 3) was used to calculate the DT_{50} and DT_{90} values, respectively.

Table 4. DT_{50} and DT_{90} Degradation Rates, Degradation Rate Constants (k), and Determination Coefficients (r^2) for Isoproturon and Chlorothalonil in Topsoil and Biomix Applied Individually and as a Mixture

	topsoil				biomix			
	DT_{50} (days)	DT_{90} (days)	k deg (days^{-1})	r^2	DT_{50} (days)	DT_{90} (days)	k deg (days^{-1})	r^2
isoproturon	18.5	22.8	(a) 0.0044; (b) 0.2744	1.00	13.1	43.4	0.0530	0.99
isoproturon + chlorothalonil	71.5	140.9	(a) 0.4868; (b) 0.0124	0.96	16.0	53.2	0.0433	0.96
chlorthalonil	37.5	124.4	0.0185	0.98	2.0	6.7	0.3429	1.00
chlorothalonil + isoproturon	30.0	99.6	0.0231	0.97	2.2	7.2	0.3178	1.00

between degradation rates in topsoil and biomix with DT_{90} values ranging from 29.1 to 51.7 days and 28.5 to 147 days, respectively.

The degradation patterns for chlorothalonil in topsoil and biomix are shown in **Figure 2**. With the exception of biomix treated at 287 mg a.i. kg^{-1}, degradation could be interpreted using first-order reaction kinetics (eq 2). The pattern of degradation in biomix treated at the highest concentration showed a biphasic pattern where residues decreased slowly after an initial rapid decline and persisted at low levels until the end of the experimental period. Data were therefore fitted to a biexponential decay curve (eq 6). DT_{50} values ranged from 6.1 to 76.9 days in topsoil and 0.6 to 20.4 days in biomix (**Table 3**). Chlorothalonil degradation was significantly ($P < 0.001$) faster in biomix than in topsoil. However, in both matrixes, degradation rates decreased with an increase in chlorothalonil concentration ($P < 0.001$). There was a marked increase in the both DT_{50} and DT_{90} values in topsoil up to 57 mg kg^{-1} concentration. At concentrations above 57 mg kg^{-1}, degradation rates showed comparatively lower increases in magnitude.

3.2. Effect of Pesticide Mixtures on Degradation Rate. Degradation rates in biomix for either isoproturon or chlorothalonil applied individually or as a mixture were similar (**Table 4**). Degradation data were interpreted by first-order kinetics (eq 2, **Figure 3a**). For isoproturon, DT_{50} values of 13.1 and 16.0 days were calculated for individual and mixture treatments, respectively. For chlorothalonil, half-lives of 2.0 days were calculated for chlorothalonil alone and 2.2 days when mixed with isoproturon.

Patterns of isoproturon and chlorothalonil degradation in topsoil are shown in **Figure 3b**. The data for chlorothalonil degradation in the presence or absence of isoproturon were fitted to the first-order rate equation (eq 2) with similar DT_{50} values of 30.0 days for chlorothalonil alone and 37.5 days in the presence of isoproturon. First-order kinetics could not be fitted to the data for isoproturon degradation whether applied alone or in combination with chlorothalonil. As observed previously, at concentrations above 46 mg kg^{-1}, isoproturon degradation rates increased with time, with the curves showing a short lag phase before the onset of rapid degradation, particularly for the individual treatment. Data were therefore fitted to eq 3. A DT_{50} of 18.5 days was calculated for isoproturon applied alone to topsoil. In the presence of chlorothalonil, there was a significant ($P < 0.01$) increase in DT_{50} to 71.5 days.

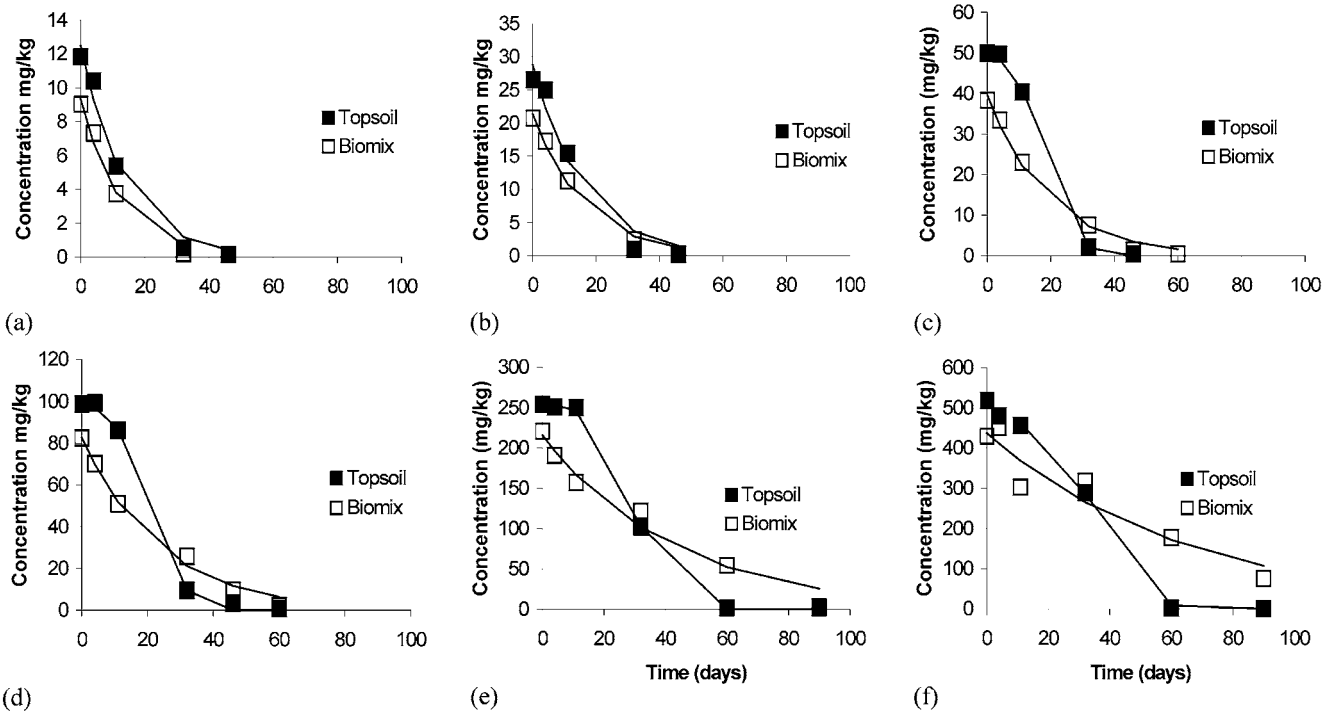

Figure 1. Degradation of isoproturon in topsoil and biomix at treatment rates of (**a**) 11, (**b**) 23, (**c**) 46, (**d**) 91, (**e**) 228, and (**f**) 456 mg kg^{-1}.

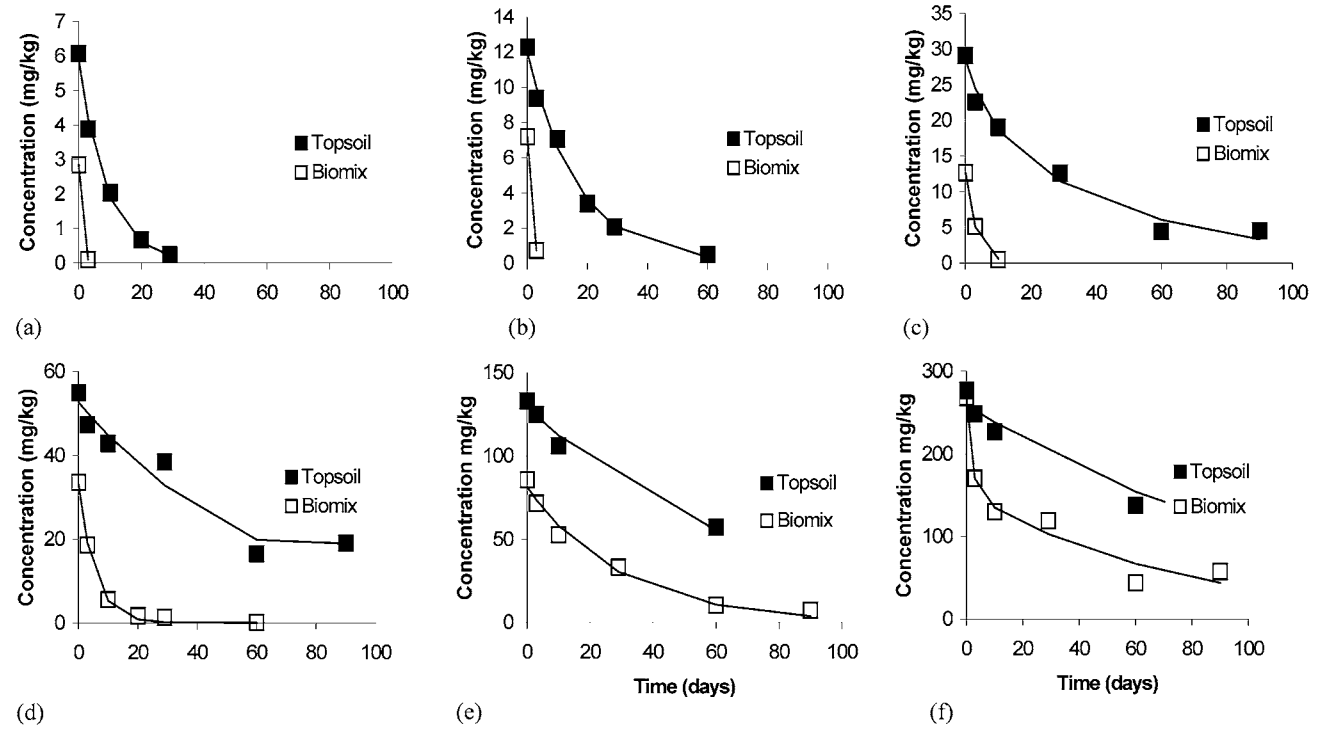

Figure 2. Degradation of chlorothalonil in topsoil and biomix at treatment rates of (**a**) 7, (**b**) 14, (**c**) 29, (**d**) 57, (**e**) 143, and (**f**) 287 mg kg^{-1}.

4. DISCUSSION

Significant contamination of the spray fill site can occur due to its repeated use and can represent a significant pesticide load even when following best agricultural practices (*1*, *18*, *19*). To minimize the impact of these normal practices on water quality within agricultural catchments, biobeds are being developed. The experiments presented herein were made to investigate the ability of biobeds to treat such pesticide waste.

In both topsoil and biomix, the rate of isoproturon degradation decreased with increasing concentration. Similar results for isoproturon degradation in topsoil at elevated concentrations have been reported (*2*). DT_{50} values for isoproturon in biomix and topsoil were similar and were <45 days for both matrixes, which can be classified as moderately persistence (*20*). However, for biobed treatment systems, the DT_{90} measurement may be of more significance in order to determine whether compounds are likely to accumulate. DT_{90} values of >1 year indicate that accumulation may be a problem when routine applications are made (*21*). For isoproturon, DT_{90} values in biomix were <147 days and for topsoil <52 days. One possible explanation for the higher overall rate of isoproturon degradation in topsoil relative to biomix is the fact that the topsoil used for the

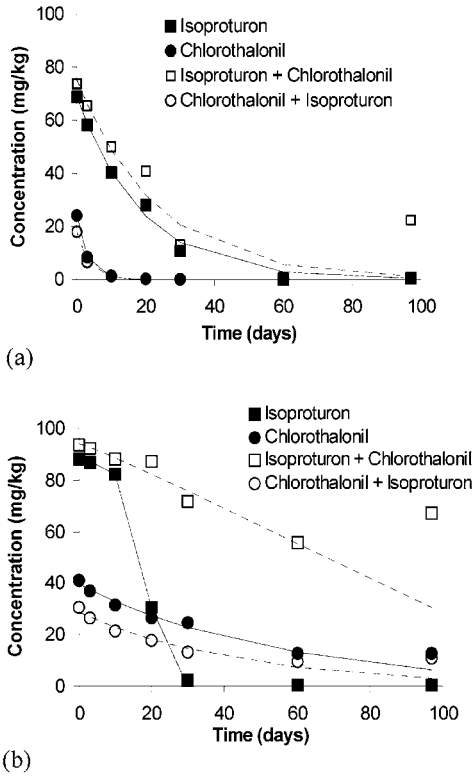

Figure 3. Isoproturon and chlorothalonil degradation in (**a**) biomix and (**b**) topsoil when applied individually and as a mixture.

experiment had been treated on previous occasions with isoproturon as part of normal agricultural practices. These previous treatments may have resulted in the proliferation of microbial communities specifically adapted to utilize the compound as an energy source, resulting in enhanced biodegradation, as reported by Cox et al. (*22*).

Chlorothalonil at concentrations of 7−287 mg kg^{-1} degraded more quickly in biomix than in topsoil at all concentrations, with the amount degraded per unit of time decreasing with increasing concentration. In biomix, the decrease in degradation rate with increasing concentration was linear over the range of concentrations investigated. However, in topsoil, the rate of degradation decreased rapidly up to 57 mg kg^{-1} concentration. Above 57 mg kg^{-1}, the decrease in degradation rate was less pronounced. The differences in chlorothalonil degradation rate may be a consequence of two effects, which respond differently in biomix and soil. First, chlorothalonil is degraded both biologically and by chemical transformation (*23*). Second, there is strong evidence that a metabolite of chlorothalonil (4-hydroxy-2,5,6-trichloroisophthalonitrile, TPN-OH) inhibits the degradation of the parent compound (*24*). Other studies have shown that microbial activity is depressed in chlorothalonil-treated soils (*10*, *24*). Thus, the association of decreasing degradation rates with increasing chlorothalonil concentrations suggested that biodegradation may have been suppressed. The observed degradation of chlorothalonil may have been due to the predominance of the comparatively slower chemical hydrolysis. Chemical transformation may be slower than the rate of biodegradation. However, if hydrolysis rate is independent of concentration, this could explain why the relationship between concentration and degradation was not linear above 57 mg kg^{-1} concentration. In biomix, it is possible that there is both increased microbiological activity and increased sorption of TPN-OH. While there was a gradual decrease in the rate of chlorothalonil degradation with increased concentration, the effects were less significant than in topsoil over the range of concentrations investigated.

Most studies of the environmental fate of pesticides are done with single applications of one compound. However, in practice, repeated applications of tank mixes containing herbicides, fungicides, and insecticides are made (*10*−*12*, *14*). Biobeds are likely to receive complex mixtures of more than one active substance applied repeatedly at concentrations far higher than field treatment rates. Studies investigating isoproturon and chlorothalonil degradation when applied as a mixture demonstrated that the rate of degradation of either compound in biomix was similar when applied individually or in the presence of the other pesticide. However, while the rate of chlorothalonil degradation in topsoil was similar when applied individually or with isoproturon, isoproturon degradation was inhibited in the presence of chlorothalonil. This inhibition may be due to a number of factors. The presence of the metabolite (TPN-OH) as reported by Montonaga et al. (*24*), who found that applications of chlorothalonil inhibited the degradation of chlorothalonil. Similar inhibition has been reported for other pesticides Singh et al. (*10*). Alternatively, one of the side effects from applying chlorothalonil may have been to suppress the activity of nontarget soil microorganisms (*25*, *26*), thus inhibiting the rate at which isoproturon was degraded.

5. CONCLUSIONS

Biobeds are intended to retain and subsequently degrade the pesticide waste originating from spray fill sites. They aim to create an environment whereby maximum sorption is achieved while maintaining bioavailability. Because of repeated use of the same filling sites, biobeds are likely to be exposed to high concentrations of more than one pesticide. This study investigated the effects of concentration and mixtures on pesticide degradation rate. At concentrations ranging from half to 20 times the maximum recommended application rate for isoproturon and chlorothalonil, the rate of degradation decreased with increasing concentration. Degradation was generally faster in biomix than in topsoil at all concentrations with the exception of isoproturon at concentrations above 91 mg kg^{-1}. The higher rates of isoproturon degradation in topsoil are thought to be due to previous treatments of isoproturon that resulted in the proliferation of microbial communities adapted to use of isoproturon as an energy source (*22*). Studies with a mixture of isoproturon and chlorothalonil showed inhibitory effects of chlorothalonil on isoproturon degradation in topsoil. These antagonistic effects were not apparent in the biomix soil. The results suggested that biobeds are capable of treating high concentrations of more than one pesticide. However, mixture studies were performed using only a single application of two active substances. We have also examined the effects of applying a mixture of six pesticides applied repeatedly to biobeds. The results from these more intensive studies will be presented elsewhere.

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