Biomassbed: a biological system to reduce pesticide point contamination at farm level

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Abstract

A potential method for cleaning water from point-source pollution by organic compounds is using biological reactors. In this study, four reactors were tested for their ability to retain and degrade pesticides. The pesticides tested were the insecticide chlorpyrifos, the fungicide metalaxyl and the herbicide imazamox. The reactors were filled with differing mixtures of vine-branch, citrus peel, urban waste and public green compost. The reactor volume was 188 l. Forced circulation of the contaminated solution was programmed to decontaminate the solution. Both retention and degradation of the compounds by the reactors was studied.

Chlorpyrifos was the best retained, due to its physico-chemical characteristics, while only one substrate effectively retained metalaxyl and imazamox (citrus peel + urban waste compost). Degradation of the pesticides in the reactors was faster than published values for degradation in soil. The half-life of all pesticides in the reactors was less than 14 days, compared to literature values of 60–70 days in soil. The combined retention and fast degradation make the biofilter a feasible technique to reduce spill-related and point environmental contamination by pesticides. The technique is most effective against persistent pesticides, while for mobile pesticides, the efficiency can be improved with several passages of the contaminated solution through biofilters.
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1. Introduction

In order to protect the environment and human health, it is important to develop methodologies to prevent pesticide contamination from point sources. Although environmental protection is well guaranteed by the European registration process (91/414/EEC) following the approved use of pesticides, no legislation tool has been developed to prevent point source contamination.

The EU directive for drinking water allows a maximum residue of 0.1 $\mu g \, l^{-1}$ for an active ingredient and of 0.5 $\mu g \, l^{-1}$ for the total pesticide load (98/83/EEC). This standard requires investment in both water treatment and prevention of contamination. Recent research has demonstrated that only a small part of applied pesticides reach surface and ground waters because of diffuse contamination via percolation, runoff, drainage and drift (Capri et al., 1999). In some research at the catchment scale, losses of 1–2% of applied pesticides have been found from diffuse contamination, while the main contamination derives from bad agronomic practices, e.g. regarding preservation and spilling zones (Isensee and Sadeghi, 1996; Torstensson and Castillo,

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1997; Bach, 1999; Mason et al., 1999; Shepherd and Heather, 1999). The application of treatment systems at the farm level could allow an improved management of the aquatic ecosystem and a reduction of water treatment costs.

One potential decontamination technique is the biobed. The biobed is a simple system: a hole in the ground is filled with organic matter (peat) mixed with soil, and covered with a grass layer which maintains a right level of temperature for microbial activity (Torstensson and Castillo, 1997; Fogg and Carter, 1998; Pussemier et al., 1998). A grid over the surface allows the passage of tractors to wash the equipment used for pesticide treatments. The main function of the biobed is to reduce environmental pesticide concentrations due to the strong adsorption of the pesticide on the organic components and rapid degradation by the active microbiological component. The final aim is to reduce environmental pollution from sources of contamination such as discharge of sprayers after pesticide field treatment.

In the present paper a modified biobed system (biomassbed) utilizing waste agricultural by-products, for example vine-branch and citrus pulp, were mixed with urban waste and green compost, providing a filter through which, pesticide contaminated water was circulated. Four different biofilters were constructed with different physical and chemical characteristics. A pesticide mixture containing the insecticide chorpyriphos (C), the fungicide metalaxyl (M) and the herbicide imazamox

(I) was re-circulated through the biofilter. The studies helped determined a suitable substrate for water decontamination and rapid pesticide degradation by the active microbiological component.

2. Materials and methods

2.1. Biofilters and reactors

Four biofilters were prepared with farm-available materials: vine-branch and citrus pulp, each mixed (1:1, v/v) with compost from urban waste (UWC) and compost from public garden (GC), the last one coming from mowing and lopping of plants. The physico-chemical characteristics of the four starting organic materials are reported in Table 1.

Table 1
Characteristics of organic materials used in biofilters

	cp	vb	GC	UWC
Density ($kg\,m^{-3}$)	403.5	159.0	354.0	273.0
Humidity (%) at -33 kPa	15.6	34.5	49.0	28.6
oc ($g\,kg^{-1}$)	177.6	264.2	302.0	308.0
N total ($g\,kg^{-1}$)	13.4	4.83	1.79	2.1
C/N ratio	13.3	54.6	16.8	14.7

cp = citrus peel, vb = vine branch, oc = organic carbon, GC = garden compost, UWC = urban waste compost.
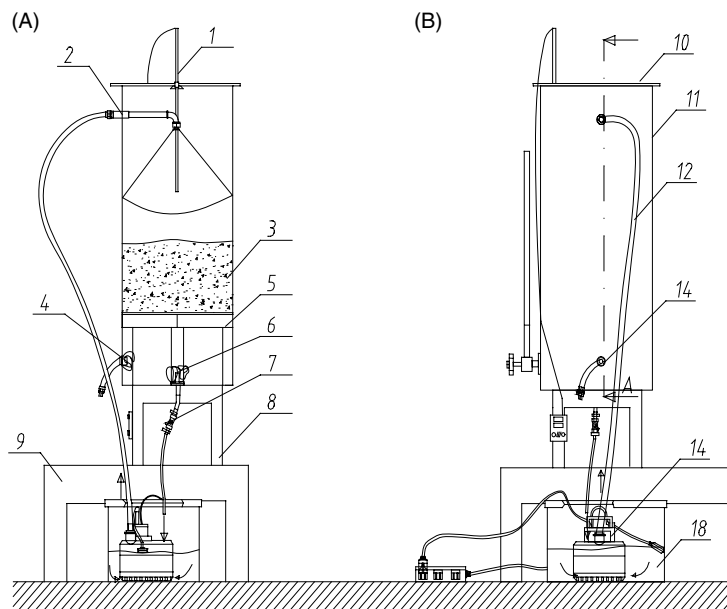

Fig. 1. Schematic representation of the measurement (A) and reference (B) reactors. [Legend: (1) thermometer, (2) wetting nozzle, (3) biofilter, (4) solid retention mesh, (5) iron support and perforated plate, (6) filtering mesh, (7) outlet tap for water, (8,9) reactor support, (10) plastic cover, (11) reactor body, (12) tube for entry water, (14) tube for water sampling, (18) water deposit.]

The four different mixtures (8 kg) were placed in confined tin reactors of 188 l volume after a conditioning period of 15 days, useful to give a mixing of different materials. An additional reactor with no biofilter was used as a reference. The reference and measurement reactors are shown in Fig. 1. Daily, 47 l of water (based on volumes of waster likely to be generated on a farm) was washed through the reactor (taking 13 min). The water was previously contaminated with the three pesticides: C at 0.75 g l^{-1} a.i. (active ingredient), M at 0.96 g l^{-1} a.i. and I at 0.075 g l^{-1} a.i. The three pesticides were used in actual vine and citrus crop system in Italy and the doses are related to normal agricultural applications.

The main experiment continued for six weeks. Weekly, three 100-ml of water samples were collected from each reactor and analyzed for the three pesticides. Every two weeks 200-g samples of solid organic materials were collected from biofilters and analyzed for the three pesticides. A further experiment was performed only with C in order to investigate pesticide behavior during the first week.

2.2. Pesticide extraction and analysis

2.2.1. Biofilter materials

Three 50 g subsamples coming from a 200 g sample of each biofilter material were extracted twice with 100 ml of a mixture CH$_3$OH/H$_2$O (80/20), shaken for 1 h, and centrifuged at 5000g for 15 min. The extracts were filtered on a extra rapid filter paper, and 100 ml of H$_2$O was added. The pesticides were partitioned into CHCl$_3$ (100 ml×2), and the sample was evaporated to dryness, rinsed with 1 ml of CH$_3$OH and analyzed by high performance liquid chromatography (HPLC). For I, the pH

of the aqueous phase of CHCl$_3$ partition was adjusted to 2 with HCl.

Recovery values for the three pesticides in the four biofilter materials ranged between 85% and 93%.

2.2.2. Water

The same procedure was followed, starting at the partitioning into CHCl$_3$ for each of the three 100-ml samples coming from each reactor.

Recovery values for the three pesticides in water samples coming from the four biofilter materials ranged between 88% and 97%.

HPLC analysis for C and M was performed with a C18 inertsil column, 25 cm×4.6 mm, a UV detector at 230 nm, a mobile phase CH$_3$CN/H$_2$O (70/30) and a flow of 0.7 ml min^{-1}. Under these conditions, the retention times were 5.2 min for M and 12.0 min for C. The limit of detection was 10 ng for both pesticides and the limit of quantification of the extracts was 2 µg l^{-1} and 2 µg kg^{-1} for both pesticides in the aqueous phase and in the organic materials, respectively.

HPLC analysis for I was performed like that for C and M but with a mobile phase H$_2$O/CH$_3$CN/HCOOH (70/29/1). The retention time was 8.2 min, the limit of detection was 8 ng and the limit of quantification 1 µg l^{-1} and 1 µg kg^{-1} in the aqueous phase and in the organic materials, respectively.

3. Results and discussion

The depuration efficiency of the different biofilters was tested by the difference between the concentration of the pesticides in the water of the reference reactor and

Table 2
Depuration efficiency of different biofilters (%) tested by difference between the concentration in water of the reference reactor and of the measurement reactor at the same time of sampling (standard error in parenthesis)

Week	cp + GC			cp + UWC		
	C	M	I	C	M	I
1	100	70 (5.8)	73 (10.7)	89 (7.1)	55 (5.5)	42 (9.8)
2	100	96 (4.3)	73 (5.9)	98 (4.3)	100	13 (2.5)
3	100	97 (3.2)	97 (3.2)	100	89 (5.4)	11 (2.7)
4	100	97 (3.1)	40 (7.4)	100	98 (2.7)	27 (2.3)
5	100	100	44 (7.2)	100	78 (5.9)	6 (2.1)
6	100	100	80 (5.3)	100	97 (1.4)	42 (7.1)
	vb + GC			vb + UWC		
1	100	10 (1.7)	1 (0.7)	94 (3.7)	0	4 (0.7)
2	100	0	18 (2.9)	100	0	24 (7.9)
3	100	14 (2.5)	6 (4.1)	72 (5.4)	0	16 (5.4)
4	100	0	27 (5.7)	100	100	6 (1.1)
5	100	25 (4.1)	7 (1.1)	100	94 (2.2)	5 (0.7)
6	100	37 (4.9)	27 (6.6)	100	100	24 (4.9)

C = chlorpyrifos, M = metalaxyl, I = imazamox, cp = citrus peel, vb = vine branch, UWC = urban waste compost, GC = garden compost.

in the measurement reactor at the same time of sampling. This is because pesticides in the reference reactor undergo some degradation due to photolysis, volatilisation and temperature variation due to heat transmission. Results of the measurements for six weeks are reported in Table 2. The depuration efficiency depends greatly on the pesticide, and, to a lesser degree, on the biofilter type. Due to its physico-chemical characteristics (Table 3), C is the most strongly retained pesticide, followed by M and I. The high adsorption characteristics of C allow a rapid retention on the biofilter, which never releases the pesticide in the further washing cycles, low values of K_{ow} for M and I do not allow a good retention on biofilters for these two pesticides.

Vine branch has an organic carbon content 50% higher than citrus peel, while the two types of compost have a similar organic carbon content (Table 1). If organic carbon is the main factor in pesticide adsorption (Rao and Davidson, 1980; Jury et al., 1987), vine branch should be much more effective in pesticide depuration. This was not confirmed by the data in Table 2 especially for M and I which remain at high levels in water from vine branch, until the fourth week of observation. The percentage decrease of M and I with respect to the reference reactor is small in both vine branch + UWC and vine branch + GC, while in the citrus reactors, a good depuration efficiency was observed. This could be explained by the different size of two organic materials: vine branch is a coarse material, with a specific active surface lower than citrus pulp (see density values in Table 1). In this case, this characteristic seems to be more relevant to sorption capacity than the organic carbon content. This finding suggests that the organic material must be carefully prepared (more chopped and, if possible, more composted), with attention to its physical characteristics.

Fig. 2 shows the change in concentration of the three pesticides in the water of the reference and measurement reactors. The quote of pesticide decay due to temperature effect and photodecomposition and volatilization is very slight or completely absent, looking at curves of reference reactors. Decay curves in measurement reac-
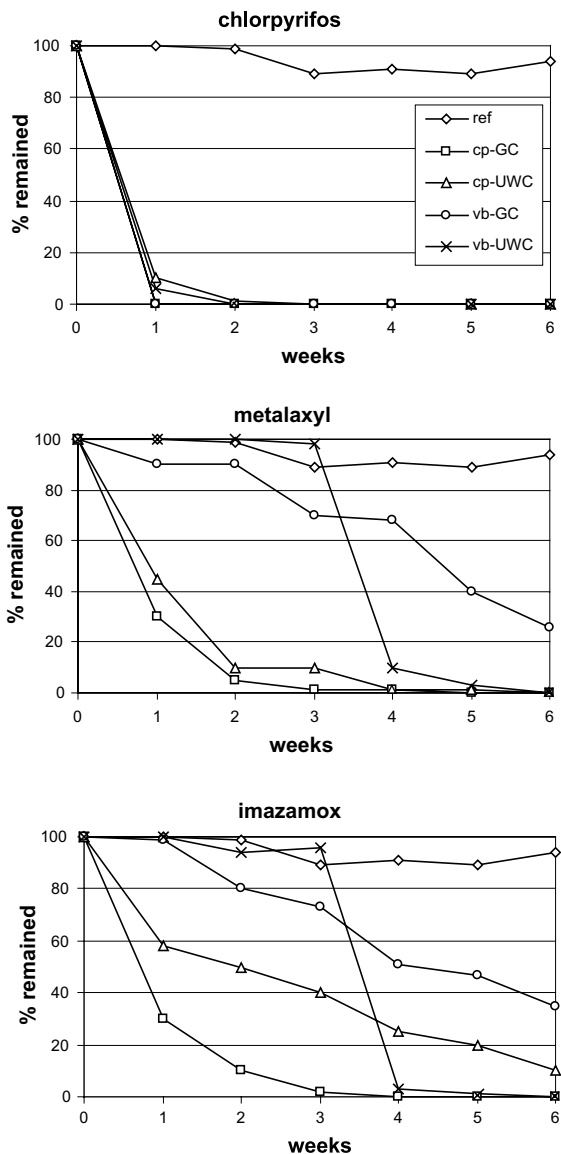

Fig. 2. Concentration of the three pesticides in water of the reference and measurement reactors (ref = reference reactor, cp = citrus peel, vb = vine branch, GC = garden compost, UWC = urban waste compost).

tors show a very rapid disappearance of C from water of all reactors, mainly due to the immediate and very strong adsorption on biofilters, and a moderate disappearance of M and I from citrus peel biofilter, while in vine branch the disappearance of M and I is slight and the gap with curves of reference reactor is short, indicating a low depuration efficiency of this biofilter for these two pesticides. The effect of the two composts is clear for M and I in vine branch biofilters: GC showed depuration efficiency lower than UWC especially from third to sixth week. At week 6 24% of M and 38% of I

Table 3
Physico-chemical characteristics of the three pesticides used in the experiment

	Chlorpyriphos[a]	Metalaxyl[a]	Imazamox
Molecular weight	351	279	322
Water solubility ($g\,l^{-1}$)	1.4	7100	4.4
$\log K_{ow}$	4.99	1.65	0.73
Soil $t_{1/2}$ (days)	60	70	60[b]

[a] Nicholls (1994).
[b] Cobucci et al. (1998).

remained in water from vb + GC while the water was clean in vb + UWC for both pesticides. On cp biofilter the effect of the two composts was less evident especially for M but this could be due to the prevalent effect of cp, which showed a good depuration efficiency vs M and I.

It is important to know what happened in the biofilter, once the pesticides were retained in order to evaluate not only their retention capacity, but also their degradation ability. Degradation curves in biofilters are reported in Fig. 3. The start of the curves (100%) represents the amount of pesticides in biofilters after the first washing cycle which is different depending on sub-
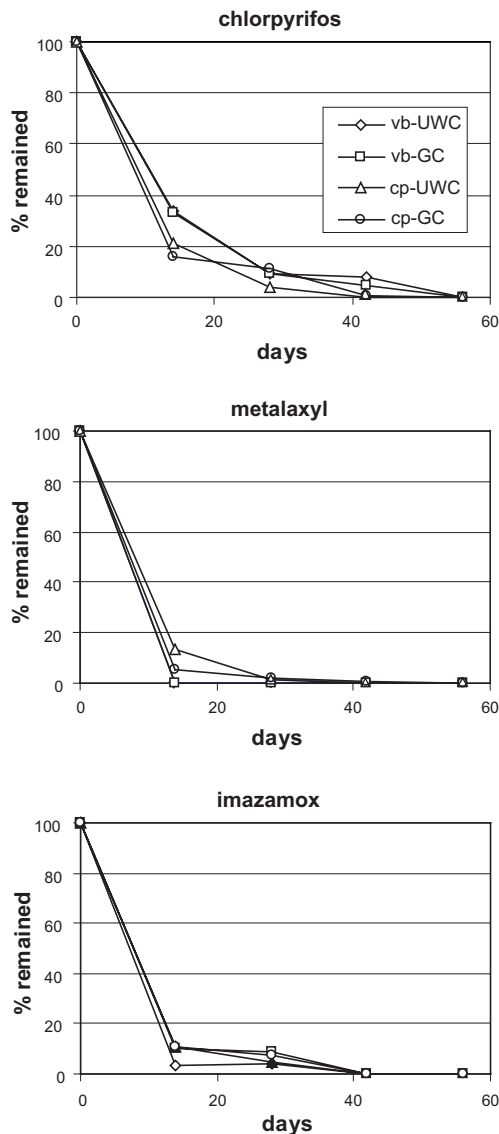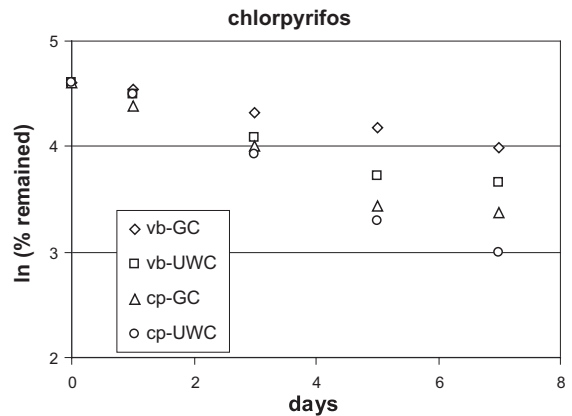

Fig. 4. Degradation of chlorpyriphos in the four substrates during the first week of incubation (cp = citrus peel, vb = vine branch, GC = garden compost, UWC = urban waste compost).

strate and pesticide. In spite of long half-life of the three pesticides in standard soils (Table 3), the half-life values in biofilters varied from 5.7 to 10.8 days for C, while M and I disappeared after 14 days. These results indicate that degradation in the biofilter appears to be fast enough to allow a decontamination of the substrates occurring a few weeks after the beginning of the experiment, with the possibility of re-utilizing the materials more than once or for agricultural uses, such as amendments, and to avoid the presence of pesticides in the environment. The most rapid degradation was in the reactors with cp combined with other compost types; vb reactors degraded pesticides slower than cp reactors, but faster than standard soils.

An additional experiment with C in the four biofilters allowed assessment of the degradation behavior in the first seven days. The results are shown in Fig. 4. The half-life values, calculated by applying first order kinetics to the degradation data ($p < 0.001$), varied from 3.7 days in the cp + UWC to 7.7 days in the vb + GC, indicating a rapid disappearance from the substrates.

Fig. 3. Degradation curves of the three pesticides in the four substrates (cp = citrus peel, vb = vine branch, GC = garden compost, UWC = urban waste compost).

4. Conclusions

The reactor technique presented here has proved to be very efficient for the cleaning of water contaminated with pesticides.

The degradation rate of the pesticides in the reactors was fast. The reactors retained C very strongly, and retained M and I less strongly. When applied at the field scale, polluted water would pass several times through the filter, allowing even poorly retained pesticides time to degrade. Therefore the biomassbed proposed could help in reducing the pesticide point contamination at farm level.

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