

LIMITATION OF POINT SOURCE PESTICIDE POLLUTION: RESULTS OF BIOREMEDIATION SYSTEM

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SUMMARY

Groundwater and surface water is at risk of contamination from the use of some agricultural pesticides. In many circumstances pesticide contamination of water resources is more likely to result from point sources than from diffuse sources following approved application to crops in the field. Such point sources include areas on farms where pesticides are handled, filled into sprayers or where sprayers are washed down. To overcome this way of contamination different kind of bio-remediation systems are nowadays in development.

In Flanders, Belgium two pilot plants of bioremediation systems for the in situ retention and/or degradation of pesticides were installed. Both systems were based on the Phytobac concept, a watertight excavation filled with straw, peat, compost and soil. The channel was made in the bottom from plastic foil. All kinds of spray rests were captured by the phytobacs. This study focuses on what level pesticides leach, bio-degrade or are retained by the filling of the phytobac. The soil-properties of the filling were investigated. Pesticide tracers were added for monitoring to both phytobacs. Soil and water samples were taken during one year. Pesticides are retained at least for one month by the filling of the phytobac. Almost no pesticide leached out. In winter hardly any pesticide degradation was observed in the filling of the phytobac. In summer no detectable pesticides were still left in the phytobacs.

Key words: bio-remediation system, spray rests and washings, pesticide retention and degradation.

INTRODUCTION

Water resources can be adversely impacted by pesticides that originate from diffuse or point sources in the agricultural environment.

Diffuse sources relate to the movement of pesticides from the field of application to water resources through mechanisms such as spray drift, runoff, leaching and drain flow.

Activities involved in the mixing and loading of pesticides, spray equipment filling, washing spray equipment and pesticide waste disposal operations, all of which tend to take place year after year in the farmyard, cause pesticide contamination or point source pesticide pollution (Basford *et al.*, 2004). High concentrations of pesticide residues have been found at such sites (Torstensson and Castillo, 1997).

In the framework of Good Agricultural Practices farmers are advised to work out all cleaning activities in the field of application and spray the diluted spray and washing rests on the treated field. The conditions to meet this way of working maybe not fulfilled. The possibility for example to provide cleaning water and a cleaning station at the border of each field is not always evident and cleaning is mostly done at the farmyard. Crop sprayer loading and wash down areas are seen therefore to represent significant potential point sources of pesticide pollution. The

characteristics of the farmyard surface and associated drainage will control the rate at which any spilt pesticide, washings of waste reaches the water resource (Basford *et al.*, 2004).

Recently techniques to solve the problems concerning effluents of sprays are under development: 1. the effluents may be burned, 2. the effluents may evaporated or dehydrated, 3. the pesticides may be physicochemically coagulated or flocculated and filtrated or 4. the pesticide molecules may be degraded by chemical or biological agents. The possibility to evaporate water out of the pesticide effluents is heavily depending on the climate (wind, temperature and humidity) and the implementation of the collection tank. Some volatile pesticides may also evaporate which results in an undesired pesticide pollution of the atmosphere. An implementation of active carbon in the system may retain these pollutants. Dehydration is based on filtration technology. Water is flowing through a polymer filter medium, pesticides and other hydrophobic pollutants are retained. Coagulation or flocculation (chemical or electrical) concentrates pesticides. The supernatant is filtered on active carbon, by reverse osmose or filtration framework e.g. Carbo-Flo/Sentinel process (Maaskant, 1993). However treatments using activated carbon to remove unwanted pesticide residues are expensive (Rose *et al.*, 2003). Chemical degradation techniques are based on oxidation reaction techniques (electrochemical or photo catalytic) using free hydroxyl radicals. Bio-remediation can be based on biological water cleaning principles where micro-organisms are selected to biodegrade pesticides and are mixed in a water environment collecting the effluent to be treated. Reed field filtration already commonly used for water cleaning purposes is also proposed as a solution to degrade pesticides. Finally, the biobed (Sweden) (Torstensson and Castillo, 1997), the phytobac[®] (Bayer Cropscience France) or the biofilter (VAR, Belgium) (Pussemier *et al.*, 2004) may be used to retain and to bio-degrade pesticides. Most of these constructions are excavations or different sizes of containers, filled with biologically active material (mixtures of top soil, straw, compost and/or peat, etc.) (Alliot *et al.*, 2003). The straw serves as C-substrate for lignin-degrading micro-organisms, which are also thought to produce enzymes catalysing the degradation of a broad spectrum of pesticide chemicals. The compost serves as a Nitrogen source for the micro-organisms. The top soil supplies binding capacity and micro-organisms. It should be rich in humus but have a low content of clay. This encourages micro-organisms and provides binding capacity whilst limiting possibilities for the pesticides to remain in micro pores (Torstensson and Castillo, 1997). The peat fraction ensures high water-holding capacity and a high level of organic matter for adsorption sites (Henriksen *et al.*, 2003).

MATERIALS AND METHODS

Construction of phytobacs

In France the Agrochemical company "Rhône-Poulinc Agro France" took the initiative to experiment with the "Phytobac" system. The phytobac finds his root in the biobed concept. The difference between a biobed is that it is watertight; it is a kind of cistern made from concrete or plastic foil. It eliminates water only through evaporation. As a result, Phytobacs present more flexibility in the use of the substrate and in the overall design of the system. For instance, it is possible to recuperate rinsing water from the floor of a nearby located filling (and cleaning) area of the sprayer. Phytobacs are generally large installations because, due to the slowness of water evaporation from the water-tight system, large volumes of substrates are needed in order to avoid complete saturation or even flooding of the substrate (Pussemier *et al.*, 2004).

Phytobac construction with buffer tank and drain

Both Phytobacs were protected against rainfall with a transparent ceiling. In our system next to the phytobac a buffer tank of 500 litres was installed. It served as collection tank of the waste effluents from crop sprayer loading and wash down areas. A sewer system leads the effluents to the buffer tank. With a pump in the tank the collected water is sprayed above the phytobac. A drain at the bottom of the phytobac was connected to the same buffer tank. In this way water could be recycled on the phytobac and the filling of the phytobac serves as a filtering agent. The other advantage of the system with the buffer tank is that it serves as an extra reservoir in case of complete saturation of the phytobac. It also allows much greater flexibility with regard to the rate and timing at which the liquid can be discharged to the bioremediation system. A scheme of the phytobac is given in Figure 1

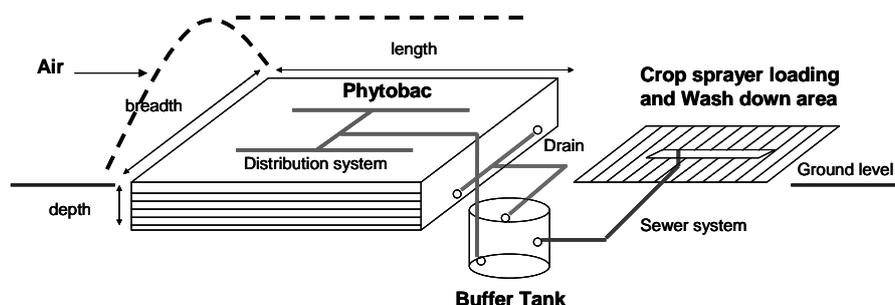


Figure 1. Scheme of the Phytobac

Filling of both phytobacs

For both phytobacs the same filling was chosen to be able to compare results. 25% soil (5.3% clay, 85.4% sand and 9.3% loam), 25% green compost, 37.5% straw and 12.5% leek rests. This was left to mature and compost naturally two months prior to waste disposal from pesticides actually used under the normal practical conditions by the workers at the research centres.

Phytobac at the provincial centre for applied research on vegetables (PCG)

The dimensions of the phytobac at the vegetable growth research centre were 13 m length x 1.8 m width x 1 m depth. The length of the phytobac made it possible to empty the spray boom above the phytobac.

Phytobac at the provincial centre for applied research on ornamental plants (PCS)

The dimensions of the phytobac at the ornamental research centre were 6 m length x 3 m width x 1 m depth. The phytobac is designed to empty the sprayers used in greenhouses above the filling.

Properties of the filling of the phytobac

pH_{KCl} of samples of the filling

Ten g soil of the phytobac was mixed with 25 mL 1M KCl. The pH of the suspension was determined after 10 min with a pH-meter of Orion.

Volume density of the filling (NBN EN 13040:2000)

Ground sample was added to a tarrated measuring cylinder. After filling of the cylinder (Ø: 100 mm, height: 127mm), a plunger of 650 g was put on the top and held there for 3 min. The volume was known and the ground was measured with a balance.

Organic matter

The total carbon content (TC) and the inorganic carbon content (IC) were determined with a "Total Organic Carbon Analyser" (SSM-5000A). The organic carbon (OC) was derived from the equation: OC = TC - IC. To relate the percentage organic carbon to the content organic matter a factor of multiplying with 2 was applied. This comes from the fact that most soils in Belgium contain about 50 % carbon.

Total Pore Volume (EN 13041:1999)

For the determination of the total pore volume, the moisture content, the organic content, the ashes content and the particle density was needed. The moisture content was measured following equation 1.

$$\% \text{H}_2\text{O} = \left(1 - \left(\frac{x \text{ g dry soil}}{y \text{ g wet soil}}\right)\right) * 100 \quad [1]$$

For the determination of the organic (C_{om}) and ash content (C_{ash}) soil was dried at 105° to obtain the weight dry soil. Afterwards it was milled to put in the oven at 550° to be fully burned. Equation 2 and 3 show the way of calculation of the ash and organic content.

$$\% \text{ ash content } (C_{\text{ash}}) = \left(\frac{\text{a g rest ash after burning}}{\text{x g dry soil}} \right) * 100 \quad [2]$$

$$\% \text{ organic content } (C_{\text{om}}) = \left(\frac{\text{x g dry soil} - \text{a g rest ash after burning}}{\text{x g dry soil}} \right) * 100 \quad [3]$$

The particle density was determined by the formula 4.

$$D_p = \frac{1}{\left[\frac{C_{\text{om}}}{(100 * 1550)} \right] + \left[\frac{C_{\text{ash}}}{(100 * 2650)} \right]} \quad [4]$$

with D_p = particle density (kg/m^3), 1550 = density organic matter (kg/m^3) and 2650 = density ash (kg/m^3)

The total pore volume is finally obtained from equation 5. The density of the bulk on dry base (D_{BD}) was derived from the moisture content and the volume density.

$$\text{TPV} = \left(1 - \frac{D_{\text{BD}}}{D_p} \right) * 100 \quad [5]$$

with P_s = Total pore volume (vol %) and D_{BD} = dry base density (kg/m^3)

Minimum retention time pesticides before leaching

A water soluble salt KBr was chosen as a tracer to find out what the minimum retention time of pesticides might be. It is supposed that KBr, a very mobile and inert salt, will leach out before any other chemical that have been added on the phytobac leaches. Fifty $\text{g Br}^-/\text{m}^3$ was added to the phytobac of PCS. This was $18 \text{ m}^3 \times 50 \text{ g Br}^-/\text{m}^3 \times 1.4893 \text{ KBr}/\text{Br}^- = 1350 \text{ g KBr}$.

The analysis of Br^- ions was done with an ion selective fixed membrane electrode. The used electrode from Orion was specific sensitive for Br^- ions. The concentration in the samples was determined from a standard equation from different concentrations (0.25-100 mg/L) after calibration of the electrode.

Pesticides

Tracer Pesticides

Atrazine, simazine, lenacil, diuron and carbofuran were chosen for their physico-chemical properties and the associated risks of water pollution, see Table 1. They were also chosen because they were not mentioned in the spray scheme of the coming season of the research centres. In the first week of august (vegetable growth centre, PCG) and the first week of October (ornamental growth centre, PCS) 2002 artificial pesticide applications of $10 \text{ g}/\text{m}^3$ phytobac were made to each phytobac. This meant an amount of 240 g active ingredient on the phytobac of PCG and an amount of 180 g active ingredient on the phytobac of PCS.

The used pesticides are summarised in the Table 1. Also an estimation of their persistence and mobility is given. The mobility was derived from the GUS or Groundwater Ubiquity Score. This score can be obtained from equation 6.

$$\text{GUS} = \log \text{DT}_{50} \times (4 - \log K_{oc})$$

[6]

Table 1. Persistence and mobility of the applied tracer pesticides

Pesticide	Persistence	DT ₅₀ soil (d) (median)	Mobility <1,8 and >2,8	GUS	K _{om} (dm ³ /kg) (median)	K _{oc}	Water solub. (mg/L)
Atrazine	Low	29	Median	2,61	96	163	33
Simazine	Median	64	Mobile	3,80	46	79	5
Lenacil	High	179	Mobile	5,55	20	34,5	6
Diuron	Median	94	Low	1,93	608	1047	35
Carbofuran	Low	28	Median	2,13	19,5	336	320
Bifentrin	Median	95	Immobile	-2,68	131000	225844	7100
Metalaxyl	Median	53	Mobile	4,66	12	20	0.0001

Season monitoring

Among the different pesticides applied by the workers of the research centres metalaxyl and bifentrin were considered as relevant regarding the risks of persistence or water pollution and were analysed. They were also both used at both research centres. For the rest pesticide effluent the amount of pesticide follows from the sprayed concentration active ingredient and the rest volume. For the cleaning effluent, it was supposed that about 5% of the applied formulated product was ending up in the cleaning water. Taken into account the concentration of the active ingredient in the formulation gave the amount of active ingredient added to the phytobac.

Table 2. Estimation of amount pesticides brought on the phytobac during spray season

Product	date	total g a.i. cumulative	date	total g a.i. cumulative
	PCS	PCS	PCG	PCG
<i>Bifentrin</i>	7 July '3	1.1		
	1 Oct '3	2.3	1 Oct '3	1.67
	19 Jan '3	2.62		
<i>Metalaxyl</i>	7 July '3	21.58	1 Oct	16.86
			19 Jan	17.56

Sampling and detection

Soil

The phytobacs were sampled on 10 different places and 3 different heights within the phytobac (20, 40 and 60 cm depth). The 10 samples (each ca. 50 g) were homogeneously mixed and then analysed 8 times because the obtained data were in the neighbourhood of the detection limit.

For the pesticides *atrazine*, *simazine*, *lenacil*, *diuron* and *carbofuran*, 50 g of the mixture sample was extracted with 200 mL ethanol, 1 h shaken and left over the night and filtrated on a Buchner filter. The ethanol was evaporated and the pesticides were resolved in a 50 mL water/acetonitrile (65/35) mixture. A filtration step on a PVDF filter 0.2 µm (Alltech) was done before analysis.

For *bifentrin* and *metalaxyl*, 50 g soil was shaken during 1h in 200 mL hexane/acetone (50/50) mixture and filtrated on a Buchner filter. It was cleaned with another 5 mL hexane/acetone. Bifentrin and metalaxyl were separated in a dividing funnel with 2 times 200 mL H₂O. Bifentrin was in the hexane/acetone phase and dried up with Na₂SO₄ and ready to be analysed. For metalaxyl in the immiscible water phase half of the water layer was extracted with 2 times 50 mL CH₂Cl₂. The CH₂Cl₂ phase was dried up with Na₂SO₄ and cleaned with CH₂Cl₂. Two evaporation steps and re-dissolution steps in respectively 25 mL, 5 mL and 5 mL acetone before analysis were done.

Water

Water samples were taken from the water tank, from the drain water and two days after the water was recycled in the buffer tank.

For the pesticides *atrazine*, *simazine*, *lenacil*, *diuron* and *carbofuran*, 15 mL of each sample was filtered on a Grade 2 V Whatman filter. 10 mL of the filtrate was diluted with a 10 mL solution of water/acetonitrile (50/50, HPLC-grade). A second filtration step was needed to remove dirt. A PVDF filter 0.2 µm (Alltech) was used.

For *bifentrin* and *metalaxyl* 200 mL sample was extracted with a liquid-liquid extraction method from the water into 2 times 50 mL hexane (bifentrin) or 2 times 50 mL CH₂Cl₂ (metalaxyl). After drying on Na₂SO₄ in the case of bifentrin the samples were ready for analysis. To analyse the bifentrin, CH₂Cl₂ was evaporated and bifentrin was re-dissolved in acetone.

Chromatographic analysis by HPLC and GC

Atrazine, *simazine*, *lenacil*, *diuron* and *carbofuran*. The five tracer pesticides are analysed together by isocratic HPLC with UV-detector. The limit of detection is mentioned for the different pesticides with the results and a standard curve varied from 0.01 to 10 mg/L, solved in the mobile phase of acetonitrile-water (35/65 ratio). 200 µL was each time injected on the column. A flow of 1 mL/min was taken. A C18 - column (Platinum EPS, 5µ type: Female) was used and the wave length was set on 210 nm.

Bifentrin. Bifentrin was analysed by GLC with an Electron Capture Detector. The carrier gas was N₂ at a flow rate of 2 mL/min. The capillary column was a HP-5 Agilent column. The length of the column was 30 m and the inner diameter was 0.32 mm. The temperature program of the oven started with 120° for 1 min and was continued with an increase in temperature of 9°/min until a final temperature of 300° was obtained. The detector temperature was set at 300°. The limit of detection was 0.01 mg/L and a standard curve varied from 0.01 to 5 mg/L and was solved in hexane. 1 µL was each time injected on the column. All samples were stored at 4°C in a refrigerator before analysis.

Metalaxyl. Metalaxyl was analysed by GLC with an TSD Detector. The carrier gas was N₂ at a flow rate of 40 mL/min. The packed column was filled with 3% OV17 on Chrom W-HP (80-100 mesh). The length of the column was 1 m and the inner diameter was 2 mm. The temperature of the injector, oven and detector was respectively 210, 210 and 250°C. The limit of detection was 0.5 mg/L and a standard curve varied from 0.5 to 5 mg/L and was solved in hexane. 2 µL was each time injected on the column. All samples were stored at 4°C in a refrigerator before analysis.

RESULTS AND DISCUSSION

Properties of the filling of the phytobac

pH_{KCl} of samples of the phytobac material

At low pH only fungi will survive, at high pH micro-organisms as bacteria's, actinomycetes as well as fungi will be activated. In this way the degradation time at high pH will be faster. When the pH increases from 4 to 9, a factor 1.5 to 2 is observed. In our phytobacs a pH between 7.51 and 7.75 was measured. This meant that the conditions for a good microbial growth in the mixture of the phytobac were fulfilled.

Organic matter of the phytobac material

Table 3. Determination of TC, IC and OC in the filling of the phytobacs

Date	Depth	% TC	% IC	% OC = %TC-%IC	% organic matter = % OC × 2
02/09/02	0-20 cm	10.67	5.49×10^{-3}	10.67	21.34
02/09/02	20-40 cm	9.42	100×10^{-3}	9.32	18.64
02/09/02	40-60 cm	11.93	43.4×10^{-3}	11.88	23.76
08/04/03	0-20 cm	9.31	0.4×10^{-3}	9.30	18.60
08/04/03	20-40 cm	11.86	29.4×10^{-3}	11.83	23.66
08/04/03	40-60 cm	10.38	63.4×10^{-3}	10.38	20.76

The determination of the organic matter should give an indication if the phytobac is still further mineralised after the initial composting of two months. Further mineralization indicates microbial activity and possible improved degradation of pesticides. Results in Table 3 show that it was difficult to conclude, because after 8 months in the upper and lower layer of the phytobac the percentage organic matter was decreased (meaning it was further mineralised) but in the middle layer of the phytobac the percentage organic matter was increased.

Volume density of the phytobac material

A mean volume density of 0.675 kg/L was measured. This low value is possible due to the high percentage organic matter added to both phytobacs. Although it has also to be mentioned that the way of determination was done on disturbed ground which may change some characteristics compared to direct measurement from the soil.

Buffer capacity phytobac and moisture content of the phytobac material

Table 4. Determination of the total pore volume

Mixed sample from the three levels of the phytobac on 02/09/2002		
% H ₂ O (wet base)	%H ₂ O	32.9 %
% ash content (dry base)	C _{ash}	80.5 %
% organic content (dry base)	C _{om}	19.5 %
Particle density (dry base)	D _p	2328 kg/m ³
Volume density (wet base)	VD _{vs}	675 kg/m ³
Volume density (dry base)	D _{BD}	452 kg/m ³
T.P.V. (dry base)	P _s	80.6 %

The total pore volume was around 80 %, see Table 4. This meant a maximum buffer capacity of $18 \text{ m}^3 \times 0.8 \times 1000 \text{ L/m}^3 = 14400 \text{ L}$ for the phytobac at PCG and $13.5 \text{ m}^3 \times 0.8 \times 1000 \text{ L/m}^3 = 10800 \text{ L}$ for the phytobac at PCS. If a spray and washing rest liquid of 300 L has to be processed after each time of spray service and evaporation is not taken into account, one can roughly say that PCG may process 48 spray services and PCS 36. In Belgium it rains yearly around 700 to 900 mm. 300 to 400 mm of this rain is evaporated by sunshine and plant growth. Because there are no plants on the phytobac this amount decreases until a poor 120 to 160 mm. But regarding to the surface of both phytobacs this is still enough to process the maximum amount of water sprayed on both phytobacs. Also the transparent roof against rainfall increases the evaporation rate.

Although no water delivery curve was made, one could see on the base of total pore volume and the amount of organic matter that the substrate of the phytobac could not hold the water. The upper layers dried up and got a more hydrophobic character. This resulted in a fast drain of the water when the water was recycled. For this reason a lock on the drain has to be provided to inhibit fast flow of the spray liquids from the top of the phytobac during delivery, to the buffer tank.

Degradation of pesticides in aerobic environment is normally faster compared to anaerobic circumstances. Mixing the phytobac with cutted wood improves the structure of the material and also aeration. But if too much pores are filled with water, the degradation ability will be limited due to a limited diffusion of oxygen. Also at high moisture content the problem of leaching of pesticides will increase. Table 5 represents the measurements on moisture content in September '2 and April '3, each time before recycling of water of the buffer tank on the phytobac. An optimal moisture content of 45 to 55% is needed for an optimal development of microbial live. As can be noticed in the table the moisture content was a little to low.

Henriksen *et al.* (2003) reduced the percolation of water to an extent where the pesticides were not washed out by covering their open biobed in the winter season and the development of a well-established turf. Also the places where the systems were installed were taken under consideration. If biobeds were placed close to a building with a big roof without a gutter or if they were placed at the lowest point of the farmyard, where too much rainwater could be introduced into the bed, it is advised to replace the systems.

Because our system is already covered and the grass would be only wetted by spray rests, it is thought to improve the water control by mixing peat or leafy ground throughout the existing material.

Table 5. Determination of moisture content of the phytobac

Sample filling phytobac	Moisture content (%)
Mixed sample 02/09/2002	32.9
Sample 0-20 cm 08/04/2003	27.6
Sample 20-40 cm 08/04/2003	36.5
Sample 40-60 cm 08/04/2003	36.3

Minimum retention time pesticides in phytobac before leaching

KBr was applied on the 6th of October on the phytobac. Figure 2 represents the measurements of Br⁻ in the water coming out the drain, the water present in the buffer tank and the water after two days in the buffer tank when it was recycled on the phytobac. A peak in Br⁻ concentration can be seen around the 6th of November. This peak is followed with a fast decrease downwards and is continued around the 20th of November. The gap in the curve is caused and is explained due to the high rainfall. The buffer tank was initially connected with the crop spray loading and was down area. At that week in November a heavily rainfall was responsible for saturation of the sewer system and the rainwater ended up in the buffer tank instead of the stream nearby. Anyway from the graph, it was concluded that a minimum retention time of 1 month for pesticides was obtained with the chosen filling of the phytobacs. Pesticides are different from KBr and normally they will stay longer in the filling. Secondly rainfall has to be under control. Rain may enter the phytobac either from a bad coverage or from the sewer system. After cleaning on the spray loading and was down area, in a climate with a lot of rainfall, the connection between that platform and the buffer tank should be locked, if not the system risks to be oversaturated.

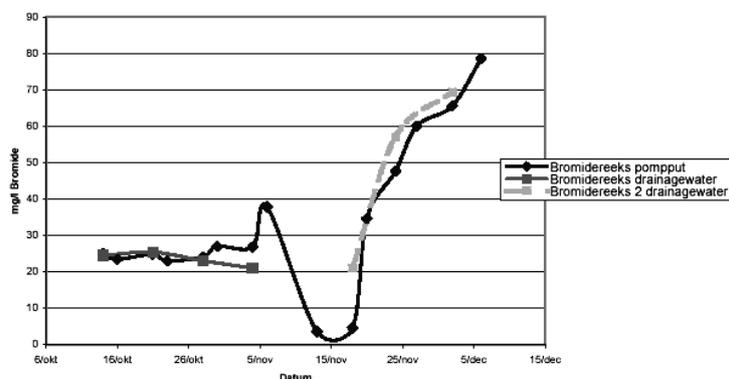


Figure 2. Concentration of Br- in the water samples of the phytobac PCS (square line = samples drain, dotted line = samples drain after two day, full line = samples buffertank)

Tracer pesticides

Soil

Table 6. Total amount atrazine in the phytobac PCS in 20 cm substrate (g)

Depth (cm)	Date 02.09.02	Date 04.11.02	Date 02.12.02	Date 08.04.03	Date 07.07.03	Date 13.10.03	Date 19.01.04
0-20	n.a.	[157-159]	[120-122]	[147-149]	n.a.	n.a.	n.a.
20-40	n.a.	[20-22]	[9-11]	[95-98]	n.a.	n.a.	n.a.
40-60	n.a.	[39-42]	[6-9]	[95-98]	n.a.	n.a.	n.a.
Total	n.a.	[216-223]	[135-142]	[337-345]	n.a.	n.a.	n.a.

n.a.: not able to detect

Results of the analysis of one of the tracer pesticides (atrazine) in the phytobac are presented in Table 6. The analysis of the month September '02 showed that no tracer pesticides existed in the filling of the phytobac. In the month November, December and April atrazine was detected. Most atrazine was found in the upper layer of the phytobac. In July and October '03 no more atrazine was detected. Microbial activity seems to have taken place at the higher temperatures of the spring and summer months. Without degradation of the pesticides theoretically 180 g should have been detected. The figures of November and April show a higher total amount of atrazine in the phytobac. This illustrates the variability and the difficulty to relate the result of three mixed samples of 50 g to a phytobac of 18 m³ material. A lot of more separated and no mixed sample analysis should refine the results and represent a better view of what is exactly in the phytobac. Now gave a rough idea. This problem is also illustrated with Table 7, representing the analysis of the tracer pesticides after one year in PCG. After 1 year in October '03 no lenacil was still detected but in January '04 it was. That lenacil was not degraded after one season was also found by Pussemir *et al.* (2004) and Genot *et al.* (2002). They mention that the biodegradation was not complete after one year and there are still quite important losses during the second year after application of this tracer.

Table 7. Total amount pesticides in the phytobac of PCG after one year

Date	Depth (cm)	atrazine substr (g)	carbofuran substr (g)	simazine substr (g)	diuron substr (g)	lenacil substr (g)
13.10.03	0-20	n.a.	n.a.	2.4	n.a.	n.a.
13.10.03	20-40	n.a.	n.a.	n.a.	n.a.	n.a.
13.10.03	40-60	n.a.	n.a.	n.a.	n.a.	n.a.
Total		n.a.	n.a.	2.4	n.a.	n.a.
19.01.04	0-20	n.a.	n.a.	n.a.	n.a.	76.1
19.01.04	20-40	n.a.	n.a.	n.a.	n.a.	32.4
19.01.04	40-60	n.a.	n.a.	n.a.	n.a.	51.9
Total		n.a.	n.a.	n.a.	n.a.	160.4

n.a.: not able to detect

Water

Carbofuran and atrazine were analysed weekly from October until February in the phytobac of PCS. Only after one week atrazine was found in the water of the drain at a concentration of 0.47-0.89 mg/L. Some peaks around the detection limit (det. lim. = carbofuran, 0.036 µg/mL; atrazine 0,013 µg/mL) were also observed in the water samples of the second week of October. After that period neither carbofuran nor atrazine was detected anymore. The retention time and the filling seem to be sufficient enough to avoid leaching and to adsorb the pesticides. It is essential that the pesticide residues that are retained within the biomix are degraded and not simply retained within the organic matrix of the system. Analysis were done after one year, to check if there were no pesticides bound to the phytobac material that might be later remobilized due to mineralization of the organic matter. For both phytobacs the five tracer pesticides were not detected above the detection limit. This is in accordance to the work of Basford *et al.* (2004) In their study three bio-remediation systems were able to reduce pesticide concentrations in excess of 100000 µg/l to below 0.5 µg/l, and often to below 0.1 µg/l throughout the monitoring period of the drain. Pussemir *et al.* (2004) and Genot *et al.* (2002) who experimented with their so-called bio-filters, filtered spray rests on containers of 1 m³ and report retention and/or degradation rates of 95% and more for one unit. When our phytobac concept is seen as an extreme bio-filter it is obvious we should notice the same or even better purification. This was also the case.

Season monitoring

Soil

Torstensson (2000) mentions from previous studies that the highest amounts of pesticides are found during the spraying season and that most of the pesticides degrade during the period until the start of the next spraying period. In our study bifenthrin and metalaxyl are added during the season to both phytobacs at the same size order. As can be noticed in Table 8 for both phytobacs the pesticides are also detected in the same size order after the spray season in the material of the phytobac. Bifenthrin was almost not degraded which could be explained by the properties of this pesticide (see Table 1). Metalaxyl was added at an amount of about 20 g and degraded for both phytobacs with ca. a factor 4. Less degradation might also be explained due to winter time.

Table 8. Total amount bifentrin en metalaxyl found in both phytobacs

Date	Depth (cm)	bifentrin in 20 cm	metalaxyl in 20 cm	bifentrin in 20 cm	metalaxyl in 20 cm
		substr. (g)	substr. (g)	substr. (g)	substr. (g)
		PCS	PCS	PCG	PCG
07.07.03	0-20	0.230	1.44		
07.07.03	20-40	0.105	1.49		
07.07.03	40-60	0.086	0.98		
Total		0.421	3.98		
01.10.03	0-20	1.934	2.301	1.338	0.914
01.10.03	20-40	4.945	2.962	1.697	1.828
01.10.03	40-60	1.640	3.574	1.044	1.338
Total		8.519	8.837	4.079	4.080
19.01.04	0-20	2.399	1.567	7.834	0.522
19.01.04	20-40	1.395	1.616	1.730	1.273
19.01.04	40-60	1.787	0.294	2.220	0.685
Total		5.581	3.477	11.784	2.480

Water

Due to the dry summer of 2003 no water samples could be taken in the month October '03. In the water samples of January '04 pesticides were detected neither in the buffer tank nor in the drain for the phytobac of PCS. On the contrary although the phytobac of PCG was larger, metalaxyl was detected at a concentration of 3.5-3.9 mg/L. This shows that a difference in retention capacity has been established after two years between both phytobacs.

CONCLUSION

Two phytobacs were monitored during the first two years after implementation. The pH of a composted mixture of straw, ground, green compost and leek rests was around 7.5, indicating good environment for microbial life. Careful management of the water entering these systems was critical. If too much rainfall enters the system, it risks to be oversaturated. A maximum buffer capacity for the phytobac at PCG of 18 m³ was predicted to be 14400 L and for the phytobac at PCS of 13.5 m³ was predicted to be 10800 L.

A minimum retention time of pesticides within the phytobac material is supposed to be at least 1 month. This statement was derived from a monitoring study following the leachability of KBr.

Atrazine, simazine, lenacil, diuron and carbofuran were chosen as tracer pesticides. After two weeks no tracer were still detected in the drain water. During winter months pesticides were still in the material of the phytobac, except for lenacil, during spring and summer they disappeared indicating that microbial (and chemical) degradation might have taken place. Attention has to be taken when samples of the phytobac are taken for analysis and related to the whole phytobac. During the spray season with sprays containing metalaxyl and bifentrin, both pesticides were detected at the same concentration in the material of the phytobac. Looking at the degradation capacity, only the amount of metalaxyl was 4 times decreased after 6 months. Metalaxyl was also found after 6 months in the drain of one phytobac showing that both phytobacs differ in retention capacity.

The result from this study has shown that specifically designed and managed on-farm bioremediation systems can effectively limit point source pesticide pollution.

The biologically active matrix within the phytobac system provides numerous opportunities for the pesticides to be adsorbed onto organic matter, where enhanced microbial populations could then degrade the pesticides.

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LITERATURE

- ALLIOT C., DEMARS J.L., ROCHARD J. & ROUSSEAU H. (2003). La gestion des reliquats de pulvérisation. *Vigne et vin publications internationales - Bordeaux*, 33:74-79.
- BASFORD W.D., ROSE S.C. & CARTER A.D. (2002). On-farm bioremediation (biobed) systems to limit point source pesticide pollution from sprayer mixing and wash down areas. *Aspects of applied biology* 71, International Advances in Pesticide Application, pp. 27-34.
- GENOT P., VAN HUYNH N., DEBONGNIE PH. & PUSSEMIER L. (2002). Effects of addition of straw, chitin and manure to new or recycled biofilters on their pesticides retention and degradation properties. *Med. Fac. Landbouww. Univ. Gent*, 67:117-128.
- HENRIKSEN V.V., HELWEG A., SPLIID N.H., FELDING G. & STENVANG L. (2003). Capacity of model biobeds to retain and degrade mecoprop and isoproturon. *Pest management science*, 59:1076-1082.
- MAASKANT M. (1993). The Carbo-Flo/Sentinel process, for the treatment of water contaminated by pesticides, results of a 3 year evaluation in the Netherlands. The win and staring centre for integrated land, soil and water research (SC-DLO), Wageningen, The Netherlands, ANPP-BCPC - second international symposium on pesticides application techniques Strasbourg - 22-24 September 1993. 18p..
- PUSSEMIER L., DE VLEESCHOUWER C. & DEBONGNIE P. (2004). Self-made biofilters for on-farm clean-up of pesticides wastes. *Outlooks on Pest Management*, 2:60-63.
- ROSE S.C., BASFORD W.D. & CARTER A.D. (2003). Practical on-farm bioremediation systems to limit point source pesticide pollution. BCPC international congress - Crop science and technology pp. 597-602
- TORSTENSSON L. & CASTILLO M. (1997). Use of biobeds in Sweden to minimize environmental spillages from agricultural spraying equipment. *Pesticide Outlook*, pp. 24-27.
- TORSTENSSON L. (2000). Experiences of biobeds in practical use in Sweden. *Pesticide outlook*, 5:206-211.