DEVELOPMENT OF BIOFILTERS TO TREAT THE PESTICIDES WASTES FROM SPRAYING APPLICATIONS

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SUMMARY

Several studies carried out in Europe showed the importance of direct losses to the contamination of surface water by pesticides. These pesticides losses can occur at the farm site when the sprayer equipment is filled with the pesticide formulation (spills, overflowing, leaking) and during the clean-up (rinsing) of the sprayer after the treatment. In Belgium studies are carried out on biofilters to treat in an efficient way effluents containing pesticides.

The biofilter substrate is elaborated from a homogenised mixture of local soil, chopped straw and peat or composted material, able to absorb or degrade the active substances. Biofilters consist in systems of 2 or 3 units depending on the spray equipment of the farmer and on the configuration of the farmyard. Each unit is made from a 1 m^3 plastic container and the different units are stacked in a vertical pile and connected between them using plastic valves and pipes. Eight pilot systems were installed in March 2002 in seven farms and in one agricultural school, all selected in the loamy region of Belgium specialised in arable crops such as cereals, sugar beets and vegetables. The efficacy (yield) of the systems was determined by measuring the balance of the inputs and outputs of the pesticides. Results were expressed in percent of pesticide retained on the biofilters. The results obtained after two years with 5 tracer pesticides (atrazine, carbofuran, diuron, lenacil and simazine) brought on the biofilter installations are very satisfactory since the percentage of retention is generally higher than 95 % of the amount applied.

In the beginning of 2004, ten new pilot biofilters were installed in several farms or agricultural technical centres (producing cereals, sugar beets, potatoes, vegetables, fruits or ornamental plants), and in a municipal maintenance service. Some biofilters were installed in duplicate in order to compare the efficacy of different substrates. The efficacy of the biofilters was studied for the 5 classical tracer pesticides but also for other chemical classes of herbicides (sulfonylurea, aryloxyalcanoic acids, chloroacetanilides), insecticides (pyrethroids, carbamates) and fungicides (dicarboximides, phenylamides, triazoles and strobilurines). To monitor these pesticides in elutes and substrates, two analytical methods were developed, optimised and validated : the first one by Gas Chromatography with Mass Spectrometry Detection (GC-MS), and the second one by High Performance Liquid Chromatography with UV Diode Array Detection (HPLC-DAD). The micro-organisms activity in the substrate was also measured in some situations.

INTRODUCTION

Several studies carried out in Europe showed the importance of direct losses to the contamination of surface water by pesticides. Pesticide losses are known to occur at the farm site in relatively high amounts when the sprayer equipment is filled with the pesticide formulation (spills, overflowing, leaking equipment ...) and, most of all, during the clean-up (rinsing) of the sprayer after treatment. Evaluations were made on a small river catchment in Belgium where it appeared that the point losses occurring in the farmyard when the sprayer was filled and cleaned can be considered as the main entry source (ca 70 %) of agricultural pesticides to surface waters (Pussemier *et al.*, 2004). The highest priority has to be given to find some prevention measures in order to avoid such losses. In the framework of Good Agricultural Practices farmers are advised to perform all cleaning activities in the field of application by using a cleaning tank and spray the diluted spray and washing rests on the treated field (Spanoghe *et al.*, 2004). Unfortunately all leftovers cannot be eliminated in this way and it is thus important to have the possibility to eliminate them on-farm. Several systems are proposed to help farmers but also other pesticides users like gardeners or road and municipal maintenance services to cope with the problems of pesticide wastes and to prevent the water pollution in an efficient way. Among them, biobed systems were developed in Sweden and are already installed in a large number of farms. The biobed is a kind of hole excavated in the soil of the farmyard and filled with a substrate made from a mixture of soil, peat and straw in order to adsorb and degrade the pesticides. Phytobacs, developed in France by the agrochemical company Bayer CropScience, can be considered as a variation of the biobed. Phytobacs are indeed similar to biobeds but they are watertight and eliminate water only through evaporation (Pussemier *et al.*, 2004). In Belgium, another variation of the biobed, called biofilter, was studied at VAR (Veterinary and Agrochemical Research Centre). Biofilters are now studied at the CRA-W (Walloon Agricultural Research Centre) in order to optimise them and to investigate the feasibility of the development of the systems at large scale.

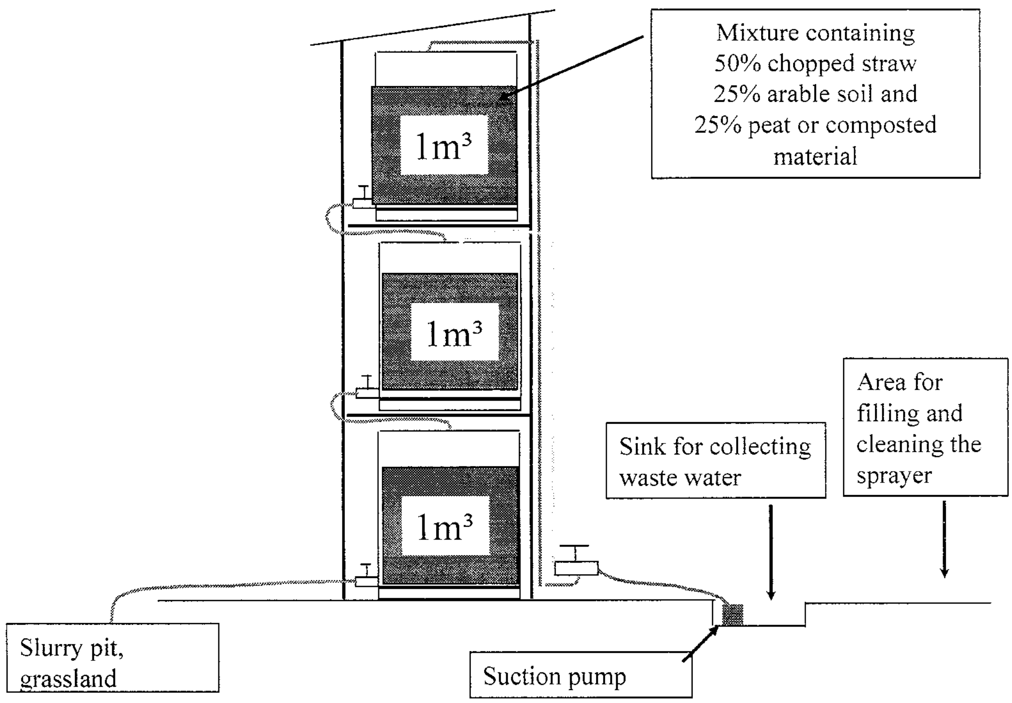

Figure 1 : schematic representation of the biofilter.

Biofilters consist in systems of 2 or 3 units depending on the spray equipment of the user and on the configuration of the farmyard. Each unit is made from a 1 m³ plastic container and the different units are stacked in a vertical pile and connected between them using plastic valves and pipes. Figure 1 shows a schematic representation of the biofilter. The biofilter offers the advantage of combining the positive aspects of both biobed and phytobac because it offers a lot of flexibility in the design of the system (large or small containers, single unit or filter lines made from 2 or 3 units, possibility to recover waste effluents in a sink and to pump them on the top of the biofilter, use of different kinds of substrates ...). The biofilter substrate is elaborated from a homogenised mixture of local soil, chopped straw and peat or composted material, able to absorb or degrade the active substances. After the end of the spaying season, the biofilters are refreshed (recycled) by mixing the one year aged substrate with new straw. The containers are refilled with this new mixture and allowed to settle during about 2 months before the new spraying season and therefore the new application of pesticides wastes.

MATERIALS AND METHODS

Eight pilot systems (6 biofilters and 2 phytobacs) were installed in March 2002 in seven farms and in one agricultural school, all selected in the loamy region of Belgium specialised in arable crops such as cereals, sugar beets and vegetables. The efficacy (yield) of the systems was determined by measuring the balance of the inputs and outputs of the pesticides. Results were expressed in percent of pesticide retained on the biofilters. The results obtained after two years with 5 tracer pesticides (atrazine, carbofuran, diuron, lenacil and simazine) brought on the biofilter installations are very satisfactory since the percentage of retention is generally higher than 95 % of the amount applied. Two other biofilters were installed in 2003. In the beginning of 2004, ten new pilot biofilters were installed in several farms or agricultural technical centres (producing cereals, sugar beets, potatoes, vegetables, fruits or ornamental plants), and in a municipal maintenance service. Some biofilters were installed in duplicate in order to compare the efficacy of different substrates. The figure 2 shows the localisation of the pilot biofilters.

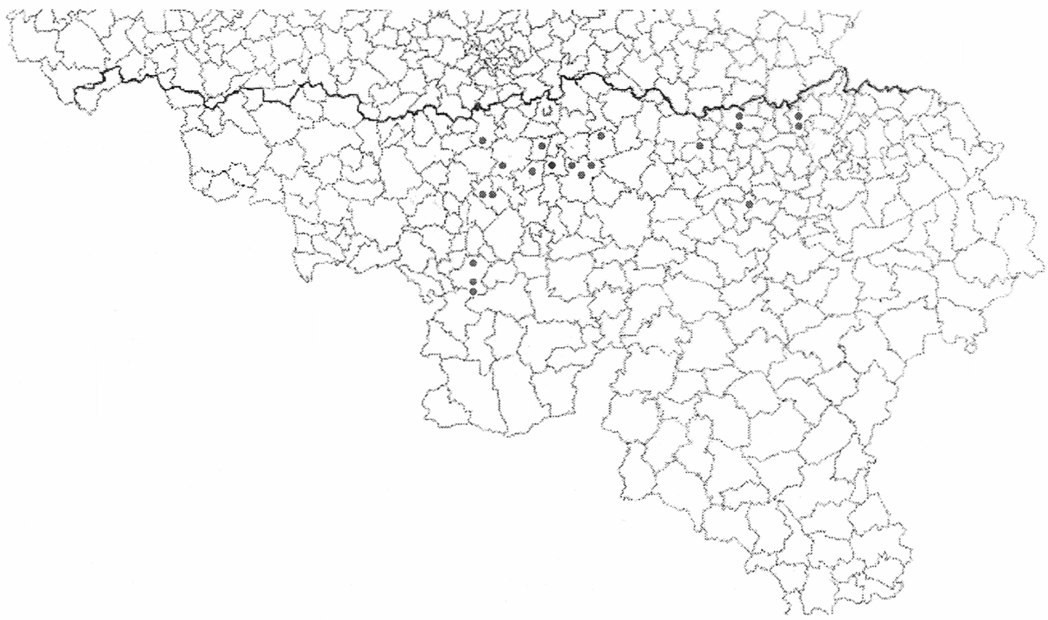

Figure 2 : localisation of the pilot biofilters.

From the 2004 spraying season, the efficacy of the twenty biofilters was studied for the 5 classical tracer pesticides but also for other chemical classes of herbicides (sulfonylurea, aryloxyalcanoic acids, chloroacetanilides), insecticides (pyrethroids, carbamates) and fungicides (dicarboximides, phenylamides, triazoles and strobilurines). The table 1 shows the physico-chemical properties of the tracer pesticides.

Table 1 : physico-chemical properties of the tracer pesticides (Koc = adsorption coefficient to organic carbon of soil, GUS = Groundwater Ubiquity Score = log (DT50soil) x (4-log (Koc)).

Molecules	Type	DT50 soil (days)	DT50 water (days)	Koc	GUS	Water solubility (mg/L)
iprodione	fungicide	41	/	172	2.84	13
metalaxyl	fungicide	42	/	598	1.98	8
azoxystrobine	fungicide	21	/	500	1.72	6
metconazole	fungicide	120	33	139	3.85	15
cypermethrin	insecticide	61	/	3675	0.77	0.004
carbofuran	ins/nem	30	/	19	4.02	320
atrazine	herbicide	29	84	97	2.94	33
simazine	herbicide	53	45	102	3.43	6
lenacil	herbicide	179	/	17	6.22	6
diuron	herbicide	124	334	399	2.92	36
flupyrsulfuron-methyl	herbicide	8	/	20	2.50	63
nicosulfuronr	herbicide	33	15	30	3.84	70
metolachlor	herbicide	18	/	177	2.19	488
ethofumesate	herbicide	97	/	145	3.65	50
MCPP	herbicide	42	/	1388	1.39	734

The quantity of tracer active substances loaded in the beginning of 2004 on each pilot system was 20 g for biofilters and 40 g for phytobacs, excepted for sulfonylurea where 1 g was loaded for nicosulfuron and 0.5 g for flupyrsulfuron-methyl. Samples of elutes were collected during the 2004 season and analysed for determination of pesticides residues. Pesticides content was determined into elutes and therefore the efficacy (yield) of the systems was determined by measuring the balance of the inputs and outputs of the pesticides. The pesticides loaded from the biofilters users were also taken into account for the calculation of the efficacy by evaluating the pesticide wastes remaining in the tank. Samples of substrates were also collected in the lower container of each biofilter and in phytobacs for pesticides residues and microbiological analysis in order to evaluate the degradation rate of pesticides into the substrate. On basis of the quantity of active substances remaining into the biofilter, analysed into elutes and loaded onto the biofilter, the amount of active substance degraded could be calculated. To evaluate the microbiological activity of the substrate, dry matter content, pH, total N, N-NH4 and N-NO3 content, biological oxygen demand (BOD) and respiration were determined.

To monitor the tracer pesticides in the elutes and the substrates, two analytical methods were developed, optimised and validated : the first one by Gas Chromatography with Mass Spectrometry Detection (GC-MS), and the second one by High Performance Liquid Chromatography with UV Diode Array Detection (HPLC-DAD). GC-MS was used to determine simazine, atrazine, metalaxyl, ethofumesate, metolachlor, lenacil, iprodione, metconazole, cypermethrin and azoxystrobine after extraction with acetone / water (70/30, v/v) (for substrates) and cleanup by Solid Supported Liquid / Liquid Extraction (SSLLE) on a diatomaceous earth cartridge. HPLC-DAD was used to determine chloridazon, nicosulfuron, carbofuran, isoproturon, diuron, MCPP and flupyrsulfuron-methyl after extraction with acetonitrile / water (80/20, v/v) containing 1 % H_3PO_4 (for substrates). Before the analysis of elutes and substrates the analytical methods were successfully validated by determining specificity, linearity of the detector response, accuracy (recoveries using untreated samples), reproducibility, limit of detection (LOD) and limit of quantification (LOQ). When no pesticide residues appeared (not detected) in the samples of elutes and substrates, the LOD level was used for calculation of retention or degradation instead of the 0 value. This choice overestimates the losses of pesticides into elutes and therefore underestimates the efficacy of the biofilters. It also overestimates the quantity of pesticides into the substrate and therefore underestimates the degradation rate.

RESULTS AND DISCUSSION

Efficacy of biofilters (retention of pesticides)

The figure 3 represents for each biofilter (and phytobac) the total losses of herbicides in elutes expressed as % of the total quantity loaded onto the biofilter from the beginning of use until 2004. The most important losses are obtained with MCPP (nearly 33 % in one biofilter). Some pesticides losses are observed with some molecules (for example simazine, ethofumesate, chloridazon, isoproturon) in some biofilters but these losses can be explained by the lack of accuracy concerning the pesticides loaded by the farmers and which can therefore underestimate the efficacy. In overall, except for MCPP, the retention of herbicides by the biofilters is good.

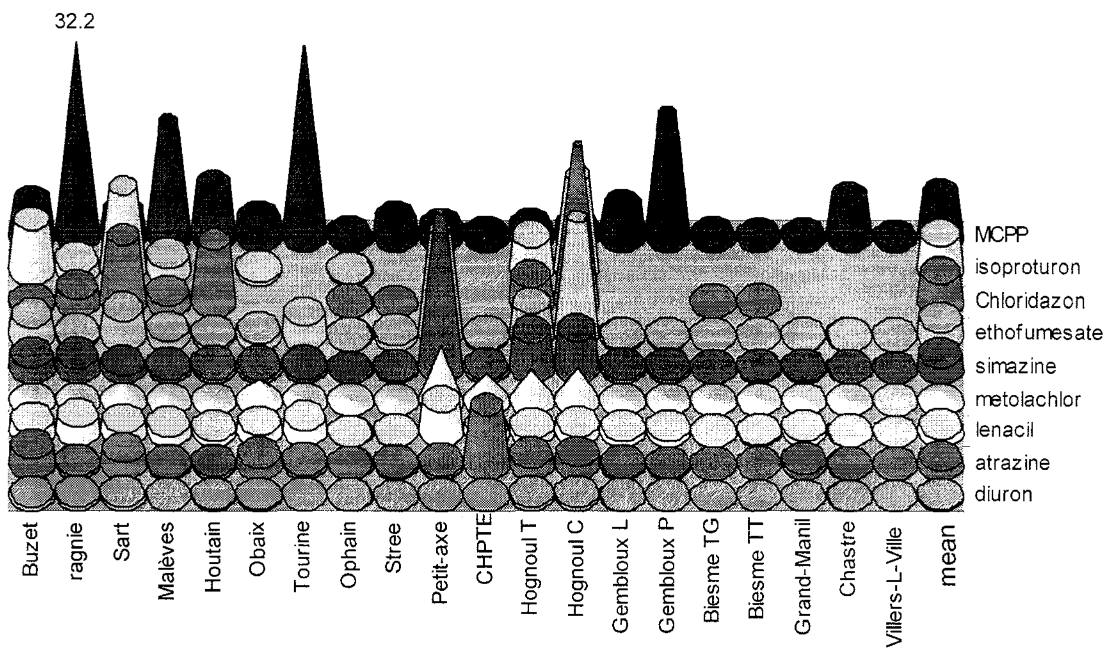

Figure 3 : total losses for herbicides in elutes from biofilters expressed as % of the total quantity loaded onto the biofilter.

For sulfonylurea herbicides (nicosulfuron and flupyrsulfuron-methyl) all the elutes showed residue values below the LOQ. But due to the fact that the quantity loaded by the cocktail tracer is small (1 g and 0.5 g respectively) and that the analytical method (HPLC-DAD) is not enough sensitive, it was very difficult to conclude on the efficacy of biofilters for sulfonylurea herbicides. Nevertheless it could be possible to conclude for nicosulfuron an efficacy more than 95 % for all the systems (except for 3 biofilters and 1 phytobac).

The figure 4 represents for each biofilter (and phytobac) the total losses of fungicides and insecticides in elutes expressed as % of the total quantity loaded onto the biofilters from the beginning of use until 2004. For insecticides, carbofuran losses are more important than cypermethrin losses in 3 biofiltres. For fungicides, the most important losses are obtained with metalaxyl. In overall, the retention of insecticides and fungicides by the biofilters is very good.

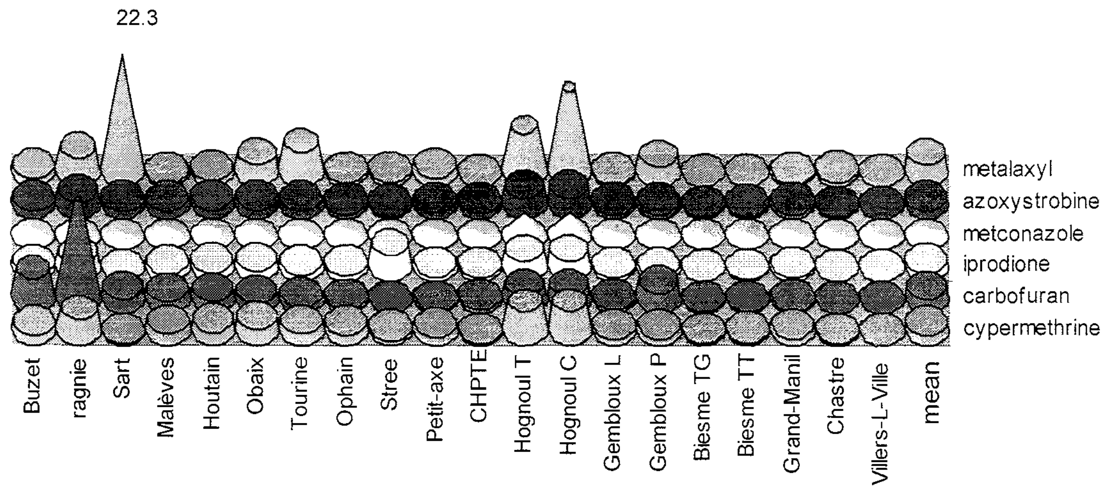

Figure 4 : total losses for insecticides and fungicides in elutes from biofilters expressed as % of the total quantity loaded onto the biofilter.

The figure 5 represents for each pesticide analysed the total losses in elutes (mean of all biofilters and phytobacs) expressed as % of the total quantity loaded onto the system from the beginning of use until 2004. We can conclude that 75 % of biofilters have an efficacy (retention) above 90 % for all the molecules analysed and above 97 % for all the molecules exept chloridazon, isoproturon and MCPP.

The figure 6 represents for each biofilter and phytobac the average amount of active substance loaded onto the biofilter, the average amount and percentage of active substance lost in elutes. We can conclude that the efficiency for the mean of all the pesticides analysed is above 92 % for all the biofilters and above 96 % for 17 biofilters on 20. The efficacy is good even with a high quantity of pesticides loaded onto the biofilter. Losses of pesticides into elutes are more dependent of the quantity of water treated by the system than of the total quantity of active substance loaded onto the biofilter. These two last observations should be confirmed with further investigations.

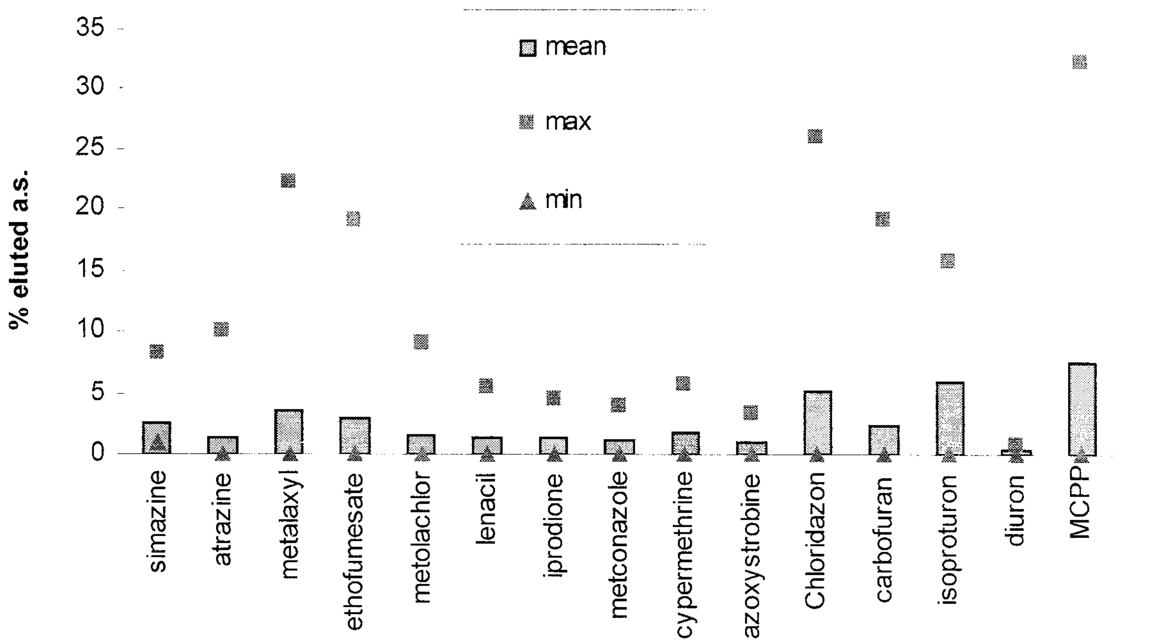

Figure 5 : total losses in elutes for each pesticide analysed (mean of all biofilters and phytobacs) expressed as % of the total quantity loaded onto the system.

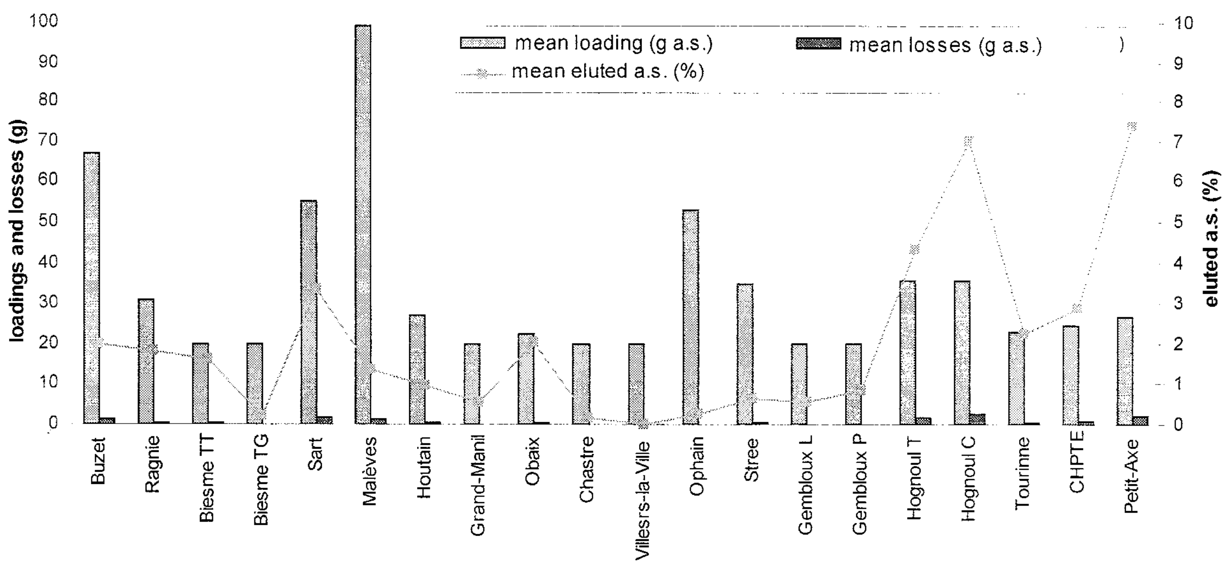

Figure 6 : average amount of active substance loaded onto the biofilter, average amount and percentage of active substance lost in elutes for each biofilter.

Degradation of pesticides into the biofilters

Substrates samples were taken on September - October 2004 in the lower container of each biofilter or in the phytobac and were analysed for the determination of pesticides residues in order to evaluate the degradation rate. The results presented in figure 7 represent the percentage of degradation for each pesticide analysed (mean of all biofilters and phytobacs) and are only a picture of the degradation rate at a given period. The further analysis which are planned on substrates samples taken after the recycling of substrates and after the end of the 2005 spraying season will permit to better evaluate the degradation kinetic of pesticides into the biofilters. These degradation results will be compared with the microbiological activity of the substrate.

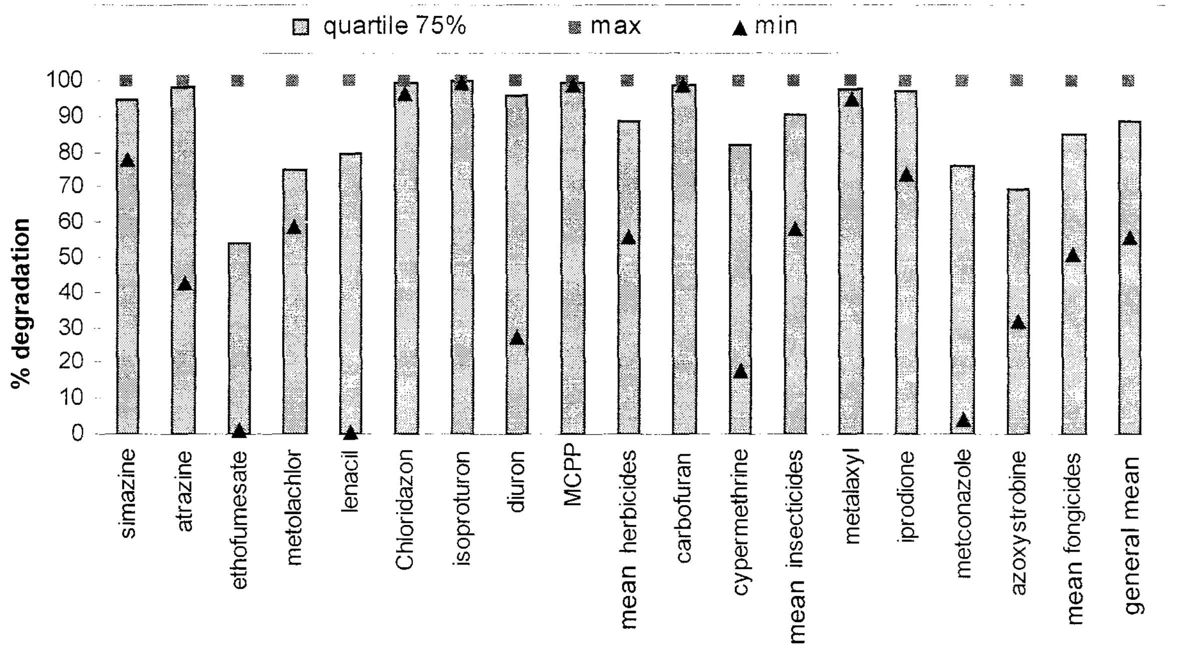

Figure 7 : percentage of degradation for each pesticide analysed.

We can conclude that for all the pesticides analysed in 75 % of biofilters the degradation percentage is more than 60 %. If we consider the mean of pesticides in 75 % of biofilters, the degradation percentage is more than 90 %. The degradation rate decreases if the remanence increases. It is the case for ethofumesate, metolachlor and lenacil. Pesticides with a high elution profile (presenting more important losses in elutes) have also a high degradation rate (for example MCPP, carbofuran and metalaxyl).

Phytotoxicity of biofilter wastes (elutes and substrates)

Some phytotoxicity test were performed on elutes by spraying elutes on grassland every 2 weeks between April and June 2004 at different concentrations (20, 50, 100 and 200 L/ha). No significant toxicity was observed by comparison with the untreated plot. Elutes from biofilters are easy to spray and could be used for total weedings (by mixing with total herbicides). Some phytotoxicity test were also performed on substrates by sowing sugar beet and winter wheat seeds on soil containing 1 m^3/ha of biofilter substrate. No significant phytotoxicity was observed by comparison with the untreated plot. Biofilter substrates after final use could therefore be spread on the field eventually after compostage. These possible uses of biofilter wastes (elutes and substrates) will require the agreement from the authorities.

CONCLUSIONS

Biofilters reduce highly the quantity of pesticides from rinsing and cleaning waters of sprayers. Considering the efficacy (retention) by pesticide, results obtained after 3 years of investigation for systems installed in 2002 and after 1 year of investigation for systems installed in 2004 showed that 75 % of biofilters have an efficacy more than 90 % for all the pesticides analysed. This efficacy is more than 97 % if we exclude chloridazon, isoproturon and MCPP. Considering the efficacy (retention) by biofilter (for the mean of all molecules analysed) results obtained after 3 years of investigation for systems installed in 2002 and after 1 year of investigation for systems installed in 2004 showed an efficacy more than 92 % for all biofilters and more than 96 % for 17 biofilters on 20. The volume of water influence the elution of pesticides from the biofilters more than the total quantity of active substance loaded onto the system. Further experiments have to be performed to confirm this observation. The good efficacy obtained after 2 years of use with herbicides was confirmed after 3 years of use with herbicides but also with insecticides and fungicides.

Concerning the degradation of pesticides into the substrate, the experiments carried out by analysing pesticides residues in the substrate sampled in September and October 2004 showed that 75 % of biofilters have a degradation rate of more than 95 % for 9 pesticides on 15. Degradation rate is lower for more remanent herbicides like ethofumesate, metolachlor and lenacil. Pesticides with a high elution profile (presenting more important losses in elutes) have also a high degradation rate (for example MCPP, carbofuran and metalaxyl). Further investigations have to be performed in order to evaluate the degradation kinetic of pesticides into the biofilters and to compare the degradation results with the microbiological activity of the substrate. These experiments would permit to optimise the efficacy of the biofilters.

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