

MANAGEMENT OF EMPTY PESTICIDE CONTAINERS

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INTRODUCTION

As many consumption products, pesticides generate a high volume of empty packaging. In the past, little attention was given to the collection of this «waste» in the short or long term (users burned or buried empty containers), today, different sectors care about that in order to avoid any pollution of the environment.

In spite of its definite economic impact, the main objective of the rinsing of containers is not to use the last drop of product. The aim is to obtain a «clean» packaging, harmless for the environment and human health.

The disposal of packaging which contained pesticides is an important and difficult problem. Two aspects are to be taken into account: on one hand, the volume of packaging is considerable on a farm scale, on the other hand, this packaging is legally considered as dangerous waste. These two factors will guide the choice of the disposal process.

In Belgium, empty pesticides packaging is collected in a special way. This activity has been initiated by Phytofar Recover (Belgian Association of Pesticides Manufacturers). At defined periods, users bring their empty containers to the collecting points (pesticides' traders). The packaging is then collected by truck containers and is driven to waste destruction centres in order to be treated.

Since 1996 the recovery rate has been continually increasing to exceed 85% in 2001. This action and results are the world's first. More than 500 tons of containers are collected yearly. Last year the budget reached 1 million of Euros. It means about 2 Euros per kg of packaging. The cost includes the collection, transport, shipping and finally the treatment.

Up to now, the disposal of all the containers collected by Phytophar-Recover is carried out by specific incineration at high temperature ($> 1200^{\circ}\text{C}$) with the treatment of the smoke. This process is the only one giving sufficient guarantee when the waste's toxicity is not known. Such treatment seems to present the re-

quired security with regard to rejections in the atmosphere, but its cost is very high (1 euro/kg). It is about four times higher than the simple thermal valorization: lime kiln or cement kiln.

MAXIMUM QUANTITY OF RESIDUE

Whatever the unit used (% , ppm, mg/kg, ...), the limit will be a quantity of product remaining in the packaging (= residue) and which should not be exceeded. More precisely, the residue will be the quantity of active ingredient (a.i.) and not the formulation [6]. This precision is logical as the a.i. is the principal harmful or dangerous product of the formulation.

The limit commonly accepted up to 1998 is that the non-volatile residue does not exceed 0,01% of the initial content of the packaging. The origin of this criterion is included in the specifications of FAO for pesticides and was widely used in the Netherlands.

A rinsed container whose pesticide residue does not exceed the limit will be considered as non dangerous domestic waste [3]. Even though this pragmatic limit was widely used by scientists in order to carry out comparative studies (rinsing methods, containers, products, ...), it is still empirical and has no direct significance in terms of risk for the environment and human health [4]. It is the reason why it was removed during the formal meeting of the FAO specifications group, in October 1998.

Currently, a new European concept is being discussed. The problems of the rinsing of containers will not only concern pesticides but will be included in the global management of waste.

Therefore, a European Directive concerning the classification of dangerous waste was adopted in 1997 in a Belgian Decree. Dangerous wastes are classified according to their origin, their composition. More particularly, waste, in this case a container, will be considered as dangerous if it contains "biocides and agro-chemical products (pesticides, etc.)" in some quantities stated in %.

The limits of residue container range from 1000 to 250 000 ppm depending on the dangerousness of the product in the container (very toxic, corrosive, irritating or harmful).

Table 1 shows the limits according to the dangerousness of the product contained in the container.

Waste is considered as dangerous if it contains a substance having a concentration higher than the acceptable limit.

Table 1. Limits in residue according to the classification of pesticides

Characteristics of the product	Classification of pesticides	Maximum quantity of product in mg/kg (ppm)
Very toxic product	A	1000
Toxic product	A	30 000
Corrosive substance	A	from 10 000 to 50 000
Harmful product	B	250 000
Irritating product	B	from 100 000 to 200 000

This new classification has the advantage of being legislated and will normally be accepted in all European Member States. Concerning the waste disposal, this classification leads to an increase of the acceptable residues. Indeed, the limit is stated in ppm of the total mass of waste (in our case, of the empty and rinsed container). For the same capacity container, the heavier it will be, the easier it will be considered as non-dangerous. However, a study of Döhnert (1997) showed that the quantities of container's residue were far below (22 to 180 times lower) the limits imposed for most pesticides and disposable with an adequate rinsing.

AIMS OF THE STUDY

Manual rinsing is still the most current method to clean packaging. Many studies showed that this technique made it possible to rinse containers efficiently. So, triple manual rinsing became the traditional reference in all studies of rinsing efficiency. Nevertheless, the quality of cleaning strongly depends on the way users proceeded.

The manual rinsing procedure is defined in the following way by the European Crop Protection Association (1993): "Before being rinsed, the packaging must be perfectly empty. You have therefore to drain it for 30 additional seconds after its first emptying, to fill in the container with clear water between 20 and 25% of its capacity, to put the cap back and shake the container vigorously in all directions in order to spread the rinsing liquid on the inside walls, to empty the rinsing liquid in the spraying tank. The recommended draining time is 30 s. The operation must be repeated twice until the container is obviously free from residue". Even though this rinsing procedure seems clear, some laboratories used afterwards a modified manual rinsing procedures in their studies [3].

If "plastic" type containers represent an important part of packaging, paper bags are also frequently used. Unfortunately, these packaging container cannot be rinsed with water because of paper's decomposition.

A specific study was therefore carried out in order:

- to analyse the influence of different practical parameters on the efficiency of manual rinsing of containers having contained pesticides;
- to quantify the percentage of pesticide remaining in a paper bag after emptying.

The results will make it possible to advise the user on the way of rinsing pesticides' containers and to assess the quantities remaining in packaging like "paper bag", after emptying.

MATERIALS AND METHOD

We will use, both for the study of rinsing containers and for the emptying of bags, the limits 1000 and 10 000 mg/kg. It should be noticed that the most used pesticides in agriculture are classified "B" or "not included in the list".

PLASTIC CONTAINERS

For plastic containers (EC), 5 parameters were analysed: the “container capacity”, the “water volume”, the “number of rinsing”, the “shaking intensity” and the “user”.

Containers of three different capacities were rinsed (1, 5, 10 liters) with three different volumes of rinsing water (10, 20, and 30% of the nominal volume of the container). The efficiency of two different rinsings (double or triple rinsing) was analysed as well as the efficiency of two shaking intensities (light or hard shaking). Indeed, the way farmers shake the container is a very hazardous variable. In order to control this parameter, the upside down shakings carried out are:

- 3 upside down movements to 180° to rinse the container and the cap;
- 5 upside down movements to 180° to rinse the container and the cap.

All the tests were carried out by 3 different users. These tests having to correspond as much as possible to the practise, the “user” effect is also analysed.

Only one pesticide (Pyramin SC 520 de BASF) was used to cover the inside of the containers before rinsing. Trials conducted by Mostade et al [4] showed that this pesticide is very hard to rinse. Its characteristics are: concentrated suspension (SC), 520 G of chloridazon per liter (42.7% w/w), bulk density (method CIPAC MT 3.3.2.) of 1,1813 g/ml.

On the whole, 108 samples were analysed: 3 volumes \times 3 fillings \times 2 rinsing procedures \times 2 rinsing intensities \times 3 users.

Concerning the procedure of the trials, the pesticide is poured in the container up to 20% of its capacity. After having put the cap back, an energetic shaking makes it possible for the product to cover all the inside walls. The container is emptied and remains upside down for 15 seconds in order to evacuate the surplus of product. According to the experimental process, clear water is poured in the container which is then covered and shaken. Once all the rinsing operations with water are carried out, a double rinsing with technical acetone (200 ml + 100 ml) is carried out in order to recover any potential pesticide's residue still remaining in the tank. The acetone is collected in an identified bottle.

In the laboratory, the content is poured in a phial as well as a small additional quantity of acetone which was used to rinse the testing bottle. Most of the acetone is evaporated with the rotovapor (vacuum machine evaporating solvent at a temperature of approximately 30°C). At the end of the evaporation, the remaining acetone is recovered and placed in a tared capsule made of porcelain. After dry evaporation, the drying and weighing of the capsule follows. The residue contained in this one corresponds to the residue of active matter still present in the plastic container after rinsing with water and is stated in ppm.

PAPER BAGS

For paper bags, two parameters were studied: the formulation and the bag's volume. Two formulation parameters were retained: a Water Powder (WP)

called Jupiter at 80° of maneb and a Water Granulate (WG) called Hermosan 80 WG at 80° of thirame. Paper bags had a 10 to 20 kg capacity.

For each parameter, 5 bags were used. The “user” factor was not taken into account and only one bag’s volume was retained for study B, in order to limit the quantities of pesticides.

On the whole, 60 samples were analysed: 2 volumes \times 2 products \times 3 weightings \times 5 bags.

The experimentation is based on gravimetric analyses. The bag is emptied in a container in order to weigh its content. The bag is regarded as empty after 5 “shakings”. The empty bag is weighed one more time (with its closing system). The bag is then put upside down and completely washed (air under pressure and dry cloth) in order to withdraw as much remaining product as possible. The bag thus cleaned is also weighed. The residue of active matter of the bag after emptying is calculated and stated in ppm

RESULTS AND ANALYSIS

PLASTIC CONTAINERS

The analysis first concerns the analysis of the influence of different parameters on the rinsing efficiency. Then, the rinsing procedures making it possible to reach the expected limits about residue will be determined.

An analysis of the variance with four classification criteria was also carried out for the variable: “residue in mg/kg”. The efficiency of the different procedures will be analysed for each container.

The test is significant for the parameters: water volume, number of rinsing, shaking intensity and the container capacity.

Moreover, the interaction between the two first ones is also significant. At last, the statistics show that the influence of the parameters “water volume” and “number of rinsing” is more important than the others. The “user” parameter has less influence on the rinsing results than during the emptying of the container. This means that different users following the same rinsing procedure will reach a similar result.

We notice that the increase of the rinsing volume (from 10% to 30% of the the container capacity) makes it possible to reduce by 6 the quantity of residues after rinsing. Triple rinsing is on average three times more efficient than double rinsing. On the other hand, the increase of the number of shakings can only reduce the quantity of residues about twice.

The interaction (“water volume” and “number of rinsing”) is significant. The average values of residues for the combination of these two parameters clearly show that the combination of these two parameters has more influence on the rinsing efficiency than when they are taken separately. The rinsing is 30 times more efficient with the best combination than with the worst one. More-

over, the number of rinsing has a prevalent effect in the relation. Indeed, triple rinsing is more efficient than double rinsing with a bigger volume of water. Table 2 summarises the influence of determining parameters during the rinsing procedure in terms of the reduction of the quantity of residues for the 3 containers analysed.

Table 2. Reduction of the quantity of residues for the 3 containers analysed, according to rinsing parameters

Rinsing parameters	Reduction of the quantity of residue			
	Container 1 L	Container 5 L	Container 10 L	Average
Increase of the water volume of 10% to 30% of the container capacity	6 times	10 times	14 times	10 times
Increase of the number of rinsing from 2 to 3	3 times	5 times	7 times	5 times
Increase of the number of shakings from 3 to 5	2 times	2 times	4 times	3 times
From double rinsing with a water volume of 10% to triple rinsing with a water volume of 30% of the container capacity	30 times	56 times	174 times	120 times

Table 2 still shows the importance of the combination of the parameters “water volume and number of rinsing”. For the 10 l container, a good combination of these two parameters improves of more than 170 times the rinsing efficiency compared with a bad combination. The joint effect increases individual effects.

Until now the important parameters of the rinsing procedure were determined as well as a significant interaction. It is also necessary to determine the adequate rinsing procedure which will make it possible to reduce the quantity of residue below the expected level.

The tolerances retained for the analysis will be those imposed by the Walloon legislation. The 2 acceptance levels are 1000 and 10 000 mg of pesticide per 1 kg of an empty container.

Residues (ppm) were subjected to a conformity test at both acceptance levels. The tests related to the different rinsing procedures and were repeated for each of the three containers. For each rinsing procedure, the values of residues are supposed to follow a normal distribution whose average is calculated from the results (an average of the results given by 3 users for the same rinsing procedure) and the standard deviation is calculated on the basis of a relation between the average and the standard deviation established for each rinsing procedure. The test will show the probability of being over or under the expected limits.

Triple rinsing with a water volume of at least 20% of the container capacity will make it possible to reduce systematically pesticide residues under 10 000 mg/kg. On the other hand, in order to reduce the residue level to 1000 mg/kg, it will be necessary to carry out a triple rinsing with at least 30% of water. This advice concerns the 3 containers analysed. It should however be noticed that rinsing is easier due to the increasing volume of the container. So much that a triple rinsing with 20% of water will allow the 10 l container to reach 1000 mg/kg.

PAPER BAGS

Table 3 shows the average values of residue calculated for the different testing conditions and shows that results are very distinct according to the type of formulation. WG residues will on average be 5 to 6 times lower than WP residue.

Table 3. Average values of residue still present after the emptying of the bags

		Residue	
		(%)	(ppm)
Small conditioning	Water Powders (WP) – 80% manèbe	1.489	14892
	Water Granulate (WG) – 80% thirame	0.281	2809
Large conditioning	Water Powders (WP) – 80% manèbe	2.615	26149
	Water Granulate (WG) – 80% thirame	0.395	3952

As to the containers, it is interesting to compare residues with acceptable limit values. Once again, we will take the tolerances established by the regional legislation, that is, 1000 and 10 000 mg of pesticide per 1 kg of an empty bag. It appears clearly that the quantity of residues will never be lower than 1000 mg/kg whatever the kind of product or packaging. On the other hand, the use of WG makes it possible to limit the quantity of residue systematically below 10 000 mg/kg. This conclusion cannot concern WP.

CONCLUSIONS

The disposal of empty pesticides packaging is just part of the global problem of waste disposal. This idea makes it possible to answer directly the first question of the rinsing or the emptying of pesticides packaging: When is a packaging clean?

The EC established a Directive which classifies dangerous waste. This Directive was transposed and enforced in the countries legislation. This legislation classifies as dangerous waste an empty packaging which contained a dangerous product. However, the packaging comes out of this classification if the residue of dangerous product does not exceed a certain limit. This limit varies according to the dangerousness of the product (see Table 1).

For this study, we retained the most constraining limits, namely, 1000 and 10 000 mg of residue per kg of packaging. These limits correspond to very toxic and corrosive products. It should be noted that this type of product represents only one small part of the pesticides used in agriculture. Generally, agricultural pesticides are classified as toxic and their residue limit is fixed at 30 000 mg/kg (ppm). Finally, for this study, we considered a packaging as “clean” when pesticide residues were under the limits (1000 or 10 000 ppm).

The second question of the rinsing or emptying of pesticides packaging is: How to obtain a clean packaging?

For paper bags, there is no rinsing procedure. Any clear water rinsing break up the paper bags very quickly. The only solution to limit the residue is to empty

the bag carefully while limiting the exposure of the user. The study simply quantified the residue after the emptying of the bag.

For plastic containers, it is possible to strongly limit the quantities of residue by rinsing with clear water. There are two techniques: the manual rinsing and the automatic rinse system on the sprayer. The first one still remains the most widely used.

The rinsing of pesticide containers has already been the subject of many studies. However, a certain empiricism remains for the manual rinsing: Does one need a double or a triple rinsing? Is it necessary to put much water? Should the container be shaken very hardly? ... The impact of these parameters on the rinsing efficacy was studied. A reliable and practicable manual rinsing procedure was defined.

EFFICIENCY OF THE MANUAL RINSING OF PLASTIC CONTAINERS

The rinsing procedure is limited by three constraints:

1. The pesticides formulation influences the rinsing efficiency. Physico-chemical characteristics such as viscosity, outflow limit, emptying efficiency may all influence the rinsing efficiency. For this study, we selected a suspension concentration (Pyramin SC 520, BASF) which is very difficult to [4].

2. The container capacity influences the draining. After emptying, only few residues remain in the larger container. The surface/volume ratio is smaller. For this study, three capacities of container were studied (1 l, 5 l, 10 l).

3. The legal residue limit influences the rinsing efficiency. The lower are the limits, the less reachable they are. For this study we retained the more restricted legal limits (1000 and 10 000 mg/kg or ppm). The limits are expressed in mg of active ingredient (a.i.) per kg of packaging (ppm).

The study aimed to determine the relative importance of the most important parameters (water volume, shaking intensity, number of rinsing) of the manual rinsing procedure on the rinsing efficacy. The target was also to define a manual rinsing procedure allowing to decrease the remaining residues under the legal limit (1000 or 10 000 mg/kg). The main questions to be answered are:

What quantity of water is it necessary to introduce into the container?

How should containers be shaken?

How much time is it necessary to repeat the rinsing operation?

About the relative importances of these three parameters in the procedure of rinsing, the study concludes:

- the shaking intensity does not significantly improve the rinsing efficiency;
- the water volume improves the rinsing efficiency, but great volumes of clean water are not necessary;
- the most efficient and practicable rinsing procedure is based on a triple rinsing with a water volume ranging between 20 and 30%.

Indeed, it appeared that the combination of the “number of rinsing” and the “water volume” amplifies the individual effects of these two parameters. For example, a triple rinsing with 30% of water is on average 120 times more efficient than a the double rinsing with 20% of water.

Triple rinsing with 30% of water and five shakes systematically makes it possible for most constraining conditions to reach the smallest limit in residue (1000 ppm). In general, triple rinsing with a volume of water ranging between 20 and 30% makes it possible to reach the residue limit of 10 000 ppm.

EFFICIENCY OF THE EMPTYING OF PAPER BAGS

The study aimed to determine the quantity of residue after emptying paper bags.

The residue remaining in the paper bags after emptying depends on the formulation of the pesticides. The water powder (WP) leaves 6 times more residue than water granulate (WG).

About the legal limits, paper bags with WP always contain more residue than 10 000 ppm. On the other hand, paper bags with WG systematically satisfy this limit. The limit of 1000 ppm is never reached for any of the studied formulations.

WP formulations are relatively cheap, even though presenting a high risk for the user and more residues in the packaging after emptying.

WG formulations present a better safety for the user and leave definitely less residue in the packaging.

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SUMMARY

After use, empty pesticide containers retain some active ingredient. Usually, users burn or bury them.

The study aims at determining the quantities of residue contained in empty containers and the parameters reducing the rinsing efficiency: the formulation, the container's size, packaging's type (plastic container or paper bag), the rinsing technique. Almost 150 tests and analyses of residue have been carried out.

A manual rinsing procedure has been set up in order to meet the standards for residue. Rinsing three times with an average volume of water (20 to 30%) allows to reach the lowest residue level. As bags containing powder container cannot be rinsed, it is necessary to empty them completely. It is however difficult to reach the 1000 ppm residue limit.