Decontamination of wasted plastic pesticide containers

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Keywords: Wasted plastic pesticide containers, residual analysis, triple rinsing, hazardous waste

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1. Introduction

Pesticides are used to fight insects, fungi and weeds. They can be toxic to humans and must be properly and safety managed [1]. Spain, France, Italy and Germany are the main consumers of pesticides in European Union. Approximately 610,000 tons of pesticides were sold in 2017 in 28 countries of EU [2]. The period 1992-2010, pesticide manufactures in USA has collected and recycled 50,000 Mg of wasted plastic pesticide containers (WPPC). Open burning of WPPC in USA is banned due to the release of of toxic polychlorinated dibenzodioxin and dibenzofurans (PCDD/PCDF) [3]. Management of WPPC in Greece includes landfilling, burning and discarding in water bodies [4]. Mismanagement of WPPC affects soil, water and human health. WPPC contain toxic residues and are classified as hazardous waste [5]. Special practices for decontaminating WPPC include triple rinsing with tap water, rinsing with tap water under pressure and integrated rinsing and rinsing with an organic solvent [6]. Pilot management programs of WPPC have been developed and recycling has been an efficient choice [7]. A National Project has been run by Benaki Phytopathological Institute in Greece more than fifteen years ago to develop an efficient management system of WPPC [5]. Another project, the AgroChePack, was developed for the efficient management of WPPC in Europe. This project includes three main principles: decontamination at the source, control and sorting at the source of WPPC [8]. According to European Crop Protection Agency, triple rinsing of WPPC is an efficient waste management practice and keeps the contents of the active substance of the residual liquid in WPPC below the threshold limits [9]. This work aims to investigate the effectiveness of triple rinsing of WPPC and their classification according το hazard level. It is a first attempt to analyze absorbed active substance in the shredded WPPC as a percentage of total active substance contained in WPPC. Based on the above, the objectives of our study were:

a) to determine the residual active substance contained in WPPC
b) to control the effectiveness of triple rinsing of WPPC
c) to classify WPPC as hazardous or no hazardous waste

2. Materials and methods

During the summer of 2020 and 2021, fifty six (56) wasted (empty) plastic pesticide containers (WPPC) were randomly collected with the aid of farmers near the city of Drama (North Greece). The sampling of WPPC took place right after the preparing of the spraying solution. Thirty one of the sampled WPPC were triple rinsed and all the selected containers were transported to Benaki Phytopathological Research Institute (BPI) in Athens (Greece) for residual pesticide analysis. Some of the containers were shredded and then two analytical techniques were used for residual analysis, the High-Performance Liquid Chromatography (HPLC) with Diode array detector (DAD), and the Gas chromatography (GC) with flame ionization detector (FID). HPLC analysis was performed for pyraclostrobin, clopyralid, florasulam, pinoxaden, cloquintocet-mexyl, folpet, oxathiapiprolin, difenoconazole, cyflufenamid and mandipropamid. GC analysis was performed for quizalofop-P-ethyl, 2.4 D-2-ethylhexyl ester, fluopyram and trifloxystrobin. Total mass of active substance in WPPC includes both liquid active substance in triple rinsed WPPC and absorbed active substance in shredded WPPC according to equation 1.

$$M_T = M_L + M_A \qquad (1)$$

Where M_T is the total mass of active substance in WPPC, M_L is the mass of liquid active substance in triple rinsed WPPC and M_A is the mass of absorbed active substance in shredded WPPC.

3. Results and discussion

The residual active substance, the mass of the selected containers and the remaining ingredients as a percentage of the weight of as received WPCC were analyzed in all the sampled WPPC. The residual active substances contained in the WPPC that were not triple rinsed are presented in Table 1.

Table 1. Residual active substances of the sampled WPPC that were not triple rinsed.

Active Substance	Mass of WPPC (as Received) (g)	Content of Active Substance[1] (g/L)	Mass of Active Substance Contained in the WPPC (mg)	Remaining Ingredients as a Percentage of the Weight of as Received WPCC (% w/w)	Legislation limits (%w/w)[3]
Pyraclostrobin	112±0.749	198±0.531	4840±300	4.30±0.300	1
Pinoxaden	101±1.70	66.6±0.489	1750±287	1.73±0.27	1
Cloquinticet-mexyl	101±1.70	15.6±0.0152	411±70.6	0.41±0.0700	10
Clopyralid	46.5±1.22	228±103	2050±1790	4.15±3.74	n/a [2]
Florasulam	46.5±1.22	18.7±6.85	164±134	0.350±0.280	25
Quizalofop-P-ethyl	206±0.208	23.4±27.3	78.2±94.2	0.0400±0.0500	25
2.4 D EHE	102±0.545	889±34.4	8870±2020	8.69±1.99	10
Folpet	103±1.25	153±224	612±979	0.580±0.930	1
Oxathiapiprolin	103±1,25	2.98±4.63	11.8±18.5	0.0100±0.0200	25
Mandipropamid	118±0.450	227±11.0	1580±532	1.34±0.450	25
Fluopyram	70.9±2.63	9.27±2.86	44.7±24.0	0.0600±0.0300	25
Trifloxystrobin	70.9±2.63	9.96±2.78	48.4±25.3	0.0700±0.0400	10
Difenoconazole	61.9±0.400	54.8±0.137	387±93.0	0.630±0.150	1
Cyflufenamid	61.9±0.400	27.5±0.435	194±44.1	0.310±0.0700	25

[1]Analyses were performed at the Benakion Phytopathological Institute (BPI), Means ± Standard Deviations are based on n = 3; all values are expressed with a precision of 3 significant digits, [2] not classified, [3] according to the regulation of the European Committee No 1357/2014

According to table 1 residual active substances of Pyraclostrobin, Pinoxaden, 2.4 D EHE and Folpet exceeded hazard threshold limits, and these WPPC are classified as hazardous. The residual active substances contained in the shredded WPPC are presented in table 2.

Table 2. Residual active substances of the shredded WPPC

Active Substance	Mass of triple rinsed WPPC (g)	Content of liquid active substance[1] in the rinsed WPPC (mg/kg)	Content of absorbed active substance[1] in the shredded WPPC (mg/kg)	(Mass of total active substance contained in the rinsed and shredded WPPC mg)	Remaining ingredients as a percentage of the weight of WPCC (% w/w)	Legislation limits (%w/w)[3]
Pinoxaden	98.8	1.80	0.400	0.217	0.000219	1
Cloquinticet-mexyl	98.8	1.60	3.80	0.533	0.000539	10
Clopyralid	40.6	107	131	9.66	0.0237	n/a [2]
Florasulam	40.6	1.20	41.0	1.71	0.00421	25
Fluopyram	69.8	721	36.5	52.8	0.0756	25
Trifloxystrobin	69.8	751	23.2	54.0	0.0773	10
Difenoconazole	60.4	33.0	14.5	2.86	0.00473	1
Cyflufenamid	60.4	16.0	7.80	1.43	0.00236	25
Azoxystrobin	66.8	1080	39.9	74.8	0.111	3.5

[1]Analyses were performed at the Benakion Phytopathological Institute (BPI), all values are expressed with a precision of 3 significant digits, [2] not classified, [3] according to the regulation of the European Committee No 1357/2014

According to tables 1 and 2, triple rinsing removes up to 99.99% of residual active substances in WPPC. All concentrations of the residual active substances were below hazard threshold limits as presented in table 2. 10% of the total active substance (M_T of equation 1) is absorbed into the walls of WPPC after triple rinsing. Content of active substances of Fluopyram, Trifloxistrobin and Azoxystrobin in shredded WPPC were below those of rinsed WPPC as concluded in figure 1.

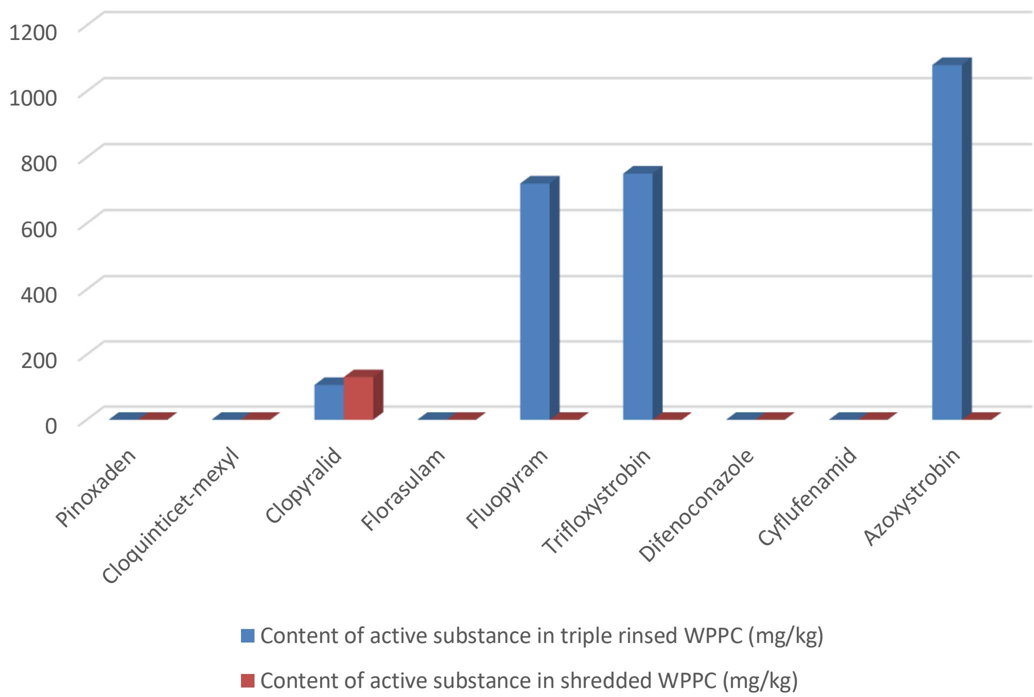

Figure 2. Content of active substances in triple rinsed and shredded WPPC

4. Conclusions

The conclusions of this research work are:

- Triple rinsing removes up to 99.99% of the liquid residual active substances in WPPC and is the most appropriate practice to safely manage WPPC.
- After triple rinsing, however, the residual amount of active substance that remains absorbed on the container walls is 10% of the total mass of the residue that remained inside the bottle. This adsorbed amount must be taken into account for proper WPPC management although it is less mobile than the liquid form.
- Triple rinsed WPPC contain liquid residual active substances below hazard threshold limits and can be classified as nonhazardous waste. Thus, they are classified under the 15 01 02 code of the European Waste Catalogue (EWC).

Acknowledgements

The authors wish to acknowledge Fotis Cheimonakis and Dimitrios Mpreskas (farmers) for their assistance during the sampling of WPPC

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