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Toxicological and environmental aspects of carrot fly (*Psila rosae* Fabr.) control

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Abstract: The objectives of this work were to describe the residual behaviour of chlorpyrifos (insecticide) and chlorothalonil (fungicide), applied for the protection of carrot and parsley plantations. The field tests were carried out at farms located near Rzeszów (South-Eastern Poland) on processing carrot and parsley destined for baby food production. The results obtained indicated that disappearance rate of chlorothalonil on carrot leaves was significantly faster and its half-life time was about 7 times shorter than that of chlorpyrifos. In weather conditions of 2006, chlorpyrifos residues in rape carrot and parsley roots were reduced to levels lower than MRL and even the rigorous value of 0.01 mg/kg.

Keywords: residues, chloropyrifos, chlorothalonil, carrot and parsley

INTRODUCTION

Consumers' exposure to pesticides used for the treatment of crops is of growing health concern, especially in case of infants and young children that represent the most vulnerable group of human population (high food consumption per body weight unit and yet undeveloped detoxication mechanism). Therefore uniform residue limit as low as 0.01 mg/kg was established by Commission Directive 1999/39/EC for any pesticide in baby food [1]. In order to estimate and than to minimize the risk of placing on the market such products containing

harmful residues, studies on the decline of kinetics of pesticide residues in fruit and vegetables seem necessary.

The paper reports the results of tests which aim to describe the residual behaviour of chlorpyrifos (insecticide) and chlorothalonil (fungicide), applied for the protection of carrot and parsley plantations.

MATERIALS and METHODS

The field tests were carried out in 2006 at farms located near Rzeszów (South-Eastern Poland) on processing carrot and parsley destined for baby food production. The treatments against second generation of carrot fly (*P. rosae* Fabr.) were performed within the third decade of July using Nurelle D 550 SC (active ingredients: chlorpyrifos and cypermethrin). Because of high pressure of powdery mildew (*Erysiphe heraclei* DC.) Bravo Plus 500 SC was applied and then included in the study.

Rainfall data were obtained from Meteorological Station of the Institute of Meteorology and Water Management (IMGW) in Jasionka Airport near Rzeszów.

The first samples (four carrot plants and four soil samples) were taken immediately after treatments. Pesticide residues were extracted with acetone, transferred to dichlorometane and determined by using the 6890 Agilent apparatus equipped with capillary columns, chemstation and nitrogen phosphorous (NPD) and electron capture (ECD) detectors [2-5]. Pesticide residue levels were evaluated in relation to their Maximum Residue Levels/Limits (MRLs) [6-10].

RESULTS and DISCUSSION

Chlorpyrifos is a toxic crystalline organophosphate insecticide that inhibits acetylcholinesterase. The substance acts primarily by contact activity and as a stomach-poison. In Poland chlorpyrifos is mainly used under the tradenames Nurelle D 550 SC and Dursban 480 EC. Chlorothalonil is a nitrile compound used as a preventative foliar fungicide [11]. The fungicide is widely used in plant protection under the tradenames Bravo 500 SC and Gwarant 500 SC. The compound can be found in formulations with many other pesticides. Chlorpyrifos and chlorothalonil residues detected at different sampling times are shown in Tables 1-3.

Leaves. As expected, chlorpyrifos and chlorothalonil residues on carrot leaves

(5 and 3 days after last application) were in proportion to their application rates. Thus, a higher average initial deposit was recorded for chlorothalonil (48.2 mg/kg) (Tables 2A and 2B).

Table 1. Chlorpyrifos residues (mean values \pm RSD, mg/kg) in soil and in carrot roots, test 1

Sampling date	Weight of carrot	Soil	Roots
25 July	$54 \text{ g} \pm 7 \text{ g}$	0.0013 ± 0.0005	0.0050 ± 0.0060
16 August	not analysed	0.0014 ± 0.0007	0.0032 ± 0.0027
1 September	$115 \text{ g} \pm 25 \text{ g}$	0.0022 ± 0.0006	0.0060 ± 0.0027

Last application of Nurelle D 550 EC (a.i.: chlorpyrifos+cypermethrin, application rate-0.5 l/ha): **20 July**

Table 2A. Chlorpyrifos residues (mean values \pm RSD, mg/kg) in soil and in carrot, test 2

Sampling date	Weight of carrot	Soil	Roots	Leaves
28 July	$47 \text{ g} \pm 9 \text{ g}$	0.006 ± 0.003	0.004 ± 0.003	not analysed
1 August	$51 \text{ g} \pm 11 \text{ g}$	0.009 ± 0.001	0.008 ± 0.004	2.93 ± 1.20
16 August	$89 \text{ g} \pm 22 \text{ g}$	0.017 ± 0.010	0.008 ± 0.006	1.92 ± 0.31
25 August	$113 \text{ g} \pm 22 \text{ g}$	0.011 ± 0.004	0.004 ± 0.002	1.46 ± 0.54

 $\textbf{Last applications} \ of \ Nurelle \ D\ 550 \ EC\ (a.i.: chlorpyrifos+cypermethrin, application\ rate-0.5\ l/ha): \ \textbf{20} \ \textbf{and} \ \textbf{27} \ \textbf{July}$

Table 2B. Chlorothalonil residues (mean values \pm RSD, mg/kg) in soil and in carrot, test 2

Sampling date	Weight of carrot	Soil	Roots	Leaves
28 July	$47 \text{ g} \pm 9 \text{ g}$	not analysed	not analysed	not analysed
1 August	$51 g \pm 11 g$	0.106 ± 0.036	0.000 ± 0.000	48.2 ± 25.5
16 August	$89 \text{ g} \pm 22 \text{ g}$	3.629 ± 4.754	0.015 ± 0.023	4.1 ± 1.6
25 August	$113 \text{ g} \pm 22 \text{ g}$	0.070 ± 0.056	0.000 ± 0.000	0.4 ± 0.6

Last applications of Bravo 500 SC (a.i.: chlorothalonil, application rate 2.5 l/ha): 29 July and 9 August

parsies, test s				
Sampling date	Weight of carrot	Soil	Roots	Leaves
1 August	not analysed	0.003 ± 0.001	not analysed	not analysed
16 August	not analysed	0.016 ± 0.008	not analysed	not analysed
1 September	$29 \text{ g} \pm 5 \text{ g}$	0.007 ± 0.002	0.048 ± 0.020	0.638 ± 0.172
12 September	$49 \text{ g} \pm 12 \text{ g}$	0.007 ± 0.003	0.005 ± 0.004	1.981 ± 0.713

Table 3. Chlorpyrifos residues (mean values \pm RSD, mg/kg) in soil and parsley, test 3

Last application of Nurelle D 550 EC (a.i.: chlorpyrifos+cypermethrin, application rate-0.5 l/ha): **20 July**

First order kinetics were found for chlorpyrifos and chlorothalonil when residual concentrations were plotted against time for each data set obtained for carrot leaves (Table 4). The decay rate of chlorothalonil was significantly faster than for chlorpyrifos and its half-life time was about 7 times shorter. Disappearance trends of the two compounds are presented in Figures 1 and 2.

Table 4. Kinetic parameters for chlorpyrifos and chlorothalonil decline, carrot leaves

Active ingredient	Equation	R ²	K _{dec} (days ⁻¹)	t _{1/2}	t _{1/10}
Chlorpyrifos	$y = 3.50 \times e^{-0.029x}$	0.999	0.029	10.4	34.5
Chlorothalonil	$y = 68.38 \times e^{-0.2008x}$	0.981	0.206	1.5	5.0

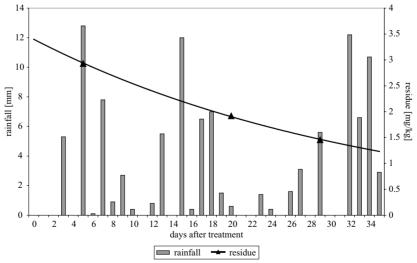


Figure 1. Disappearance trend of chlorpyrifos residues on carrot leaves.

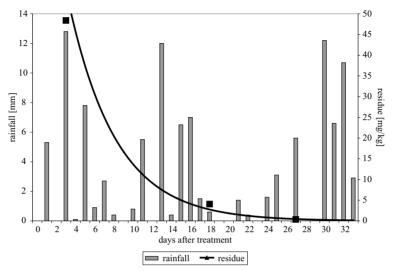


Figure 2. Disappearance trend of chlorothalonil residues on carrot leaves.

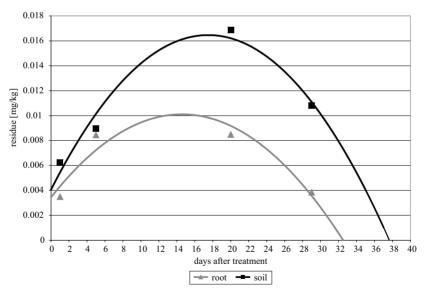


Figure 3. Disappearance trends of chlorpyrifos residues in soil and carrot roots.

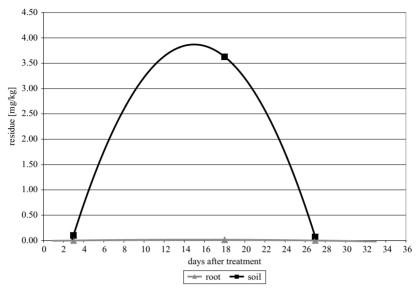


Figure 4. Disappearance trends of chlorothalonil residues in soil and carrot roots.

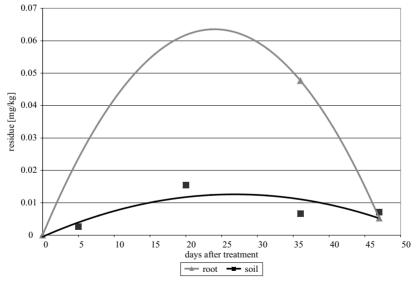


Figure 5. Disappearance trends of chlorpyrifos residues in soil and parsley roots (likely).

Roots. About two months after sowing time (and after first treatment), Nurelle D 550 EC was applied against second generation of carrot fly (*P. rosae* Fabr.). Chlorpyrifos residues in roots were found to be at trace levels 0.005 and 0.004 mg/kg (carrot) and 0.048 mg/kg (parsley). Final levels of chlorpyrifos residues resulted from complex process consisting of washing leaves, absorption by roots, dilution by root growth and successive degradation (Tables 1-3). Due to weather conditions in the 2006, average residues in rape carrot (0.006 and 0.004 mg/kg) and parsley roots (0.005 mg/kg) were reduced to levels lower than MRL (carrot - 0.1 mg/kg, parsley - 0.05 mg/kg) and even the rigorous value of 0.01 mg/kg.

Soil. Chlorpyrifos residues in soil samples taken from under carrot roots were similar to those found in carrot and parsley roots. The highest value detected was 0.017 mg/kg. Chlorothalonil being a contact fungicide moved from the leaves to the soil and then degraded rapidly (initial concentration of 3.629 mg/kg almost completely disappeared within nine days) and hence could not be detected in the roots at any stage of periodic sampling. The disappearance trends of chlorpyrifos and chlorothalonil in soil (Test 2) were presented in Figures 3 and 4.

CONCLUSIONS

- The decay rate of chlorothalonil was significantly faster than decay rate of chlorpyrifos and its half-life time was about 7 times shorter,
- Chlorpyrifos in rape carrot and parsley roots was reduced to levels lower than MRL (carrot - 0.1 mg/kg, parsley - 0.05 mg/kg) and even the rigorous value of 0.01 mg/kg,
- Chlorothalonil disappeared and hence could not be detected in roots at any stage of periodic sampling,
- If used by baby food producer, fresh parsley leaves should be carefully tested.

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