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DISSIPATION BEHAVIOR OF PESTICIDES APPLIED IN MULTIPLE TREATMENTS IN APPLES

COMPORTAMENTUL UNOR PESTICIDE APLICATE ÎN TRATAMENTE MULTIPLE ÎN MERE

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Abstract. *The main objective of this work addresses kinetic studies on the dissipation of 12 pesticides applied in single recommended dose and double dose treatments in apples, considering 6 kinetic models which determine the statistical parameters describing pesticide behavior, including their half-lives. The half-lives of pesticides in apples at BBCH (Biologische Bundesanstalt, Bundessortenamt and CHemical industry) scale 76-79 resulted from the linear regression equations considering single dose treatments were between 0.01 days (for λ-cyhalothrin) and 74.90 days (for myclobutanil). Data on the rate of dissipation and half-lives of pesticides in various plant compartments are particularly significant for pesticide monitoring and human health impacts and risk assessment.*

Key words: active substances, half-life, modeling, plant protection products, monitoring

Rezumat. *Obiectivul principal al acestei lucrări are în vedere studii cinetice ce vizează disiparea a 12 pesticide aplicate în tratamente pentru mere, cu doze recomandate şi doze duble, considerând 6 modele cinetice care determină parametrii statistici ce descriu comportamentul pesticidelor, inclusiv timpul de înjumătăţire. Timpul de înjumătăţire al pesticidelor în mere pentru scara fenologică BBCH (Biologische Bundesanstalt, Bundessortenamt and CHemical industry) 76-79, rezultat din ecuaţiile de regresie liniară, este cuprins între 0,01 zile (pentru λ-cihalotrin) şi 74,90 zile (pentru miclobutanil). Datele privind viteza de degradare sau timpul de înjumătăţire a pesticidelor în diferite compartimente ale plantelor sunt deosebit de importante pentru monitorizarea pesticidelor şi pentru evaluarea impacturilor şi riscurilor asupra sănătăţii umane.*

Cuvinte cheie: substanţe active, timp de înjumătăţire, modelare, produse pentru protecţia plantelor, monitorizare

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INTRODUCTION

The apple tree is a crop plant affected by a large number of diseases and pests. Fruit trees species health and productivity are strongly influenced by a number of pathogens (e.g. viruses, fungi, bacteria, mycoplasma) and pests (e.g. insects, birds, rodents). Throughout the vegetative cycle, it is therefore necessary to ensure a permanent protection of the plants. According to the information provided by farmers, apple trees are mainly affected by 4-6 pathogens (e.g. apple scab - *Venturia inaequalis*, apple powdery mildew - *Podosphaera leucotricha*, fire blight - *Erwinia amylovora*, brown rot - *Monilinia fructigena*, Apple mosaic virus (ApMV), etc.) and 12-15 pests (e.g.codling moth - *Cydia (Lasperesya) pomonella*, mites (red spider - *Panonychus ulmi*), aphids (San-José scale - *Quadraspidiotus perniciosus*, green apple aphid - *Aphis pomi*), apple blossom weevil (*Anthonomus pomorum*) etc.). If no action is taken against these pests, the production of susceptible varieties is compromised to around 80-100% (Tomşa and Tomşa, 2003). Fruit trees can also be affected by other factors, such as climatic, soil and agro-industrial factors. Considering these aspects, the number of treatments with pesticides can reach, in an apple orchard, even 14 per season. The Jonathan apples with smooth bark, a sweet-sour taste and yellowish, juicy and sweet pulp, have a very intense flavor, a high content of vitamin C, along with other vitamins and mineral salts, all being substantial for the human body. A high consumption of fruit and vegetables, generally five or more servings per day, can prevent vitamins deficiency and can reduce the incidence of major diseases such as cancer, cardiovascular disease and obesity (Dietary Guidelines, 2005; Lewis *et al.*, 2005; Pogăcean *et al.*, 2014).

Due to potential risks to human health, pesticide residues in food are carefully regulated and monitored by the authorized agencies and institutions (Hill and Reynolds, 2002; Hlihor *et al.*, 2016; Stoleru *et al.*, 2015). In the last decade, increasing demand for food has stimulated the research concerning the risks associated with fruit and vegetables consumption. Therefore, the food security is a major public concern in the world. As the main route of exposure is ingestion, dietary exposure to pesticides is considered to be five orders of magnitude greater than other exposure routes, such as drinking water ingestion or air inhalation (Cozma *et al.*, 2017; Fantke *et al.*, 2014; Juraske *et al.*, 2009). Increased doses of pesticides may have undesirable effects, including the accumulation of large amounts of residues in products (Van Klaveren and Boon, 2009). Understanding pesticides degradation mechanisms in plants in relation with other factors and the determination of pesticide residues in samples based on the phenological growth stages and at harvest are very important, not only for the proper assessment of food risks, but also for the optimization of pesticide application techniques, so as to create an efficient management (Fantke and Juraske, 2013; Stoleru *et al.*, 2016).

This paper focuses on the dissipation rates of the most common pesticides applied in Jonathan apples, considering their phenological growth stages, as well as estimating their half-lives when single recommended dose or double dose (overdoses) treatments at different stages of fruit development are applied**.**

MATERIAL AND METHOD

Chemicals and analysis

Solvents used for extraction (e.g. acetone, petroleum ether and dichloromethane) were of analytical grade and were purchased from Chem Service (West Chester, SUA) and Sigma Aldrich Laborchemikalien GmbH (Seelze, Germany). The list of pesticide products applied for apple treatments along with their commercial name, doses, and Maximum Residue Levels (MRLs) are described in the work of Pogacean *et al.* (2014). The residual concentrations of pesticides in apples were analyzed by a gas chromatograph (Agilent 7890 type with 2 ovens) coupled with a mass spectrometer with flight time, CG*GC-TOFMS Pegasus 4.21 (LECO, SUA). Details regarding the experimental protocol of gas chromatography analysisis described by Pogacean *et al*. (2014).

Experimental field trials

Field experiments were performed in an apple orchard, within the Phytosanitary Office Mures, Tg. Mures, Romania. Five treatments with 6 fungicides (captan, folpet, chlorothalonil, myclobutanil, tebuconazole, triadimenol), 5 insecticides (bifenthrin, deltamethrin, α-cypermethrin, λ-cyhalothrin, chlorpyrifos-methyl) and 1 acaricide (propargite) were applied during the growth of Jonathan apples according to BBCH scale (Biologische Bundesanstalt, Bundessortenamt and CHemical industry). Temperature, precipitations and humidity were monitored using a weather station available in the Technical Department, located within the Phytosanitary Office Mures. The entire treatment procedure is discussed in detail by Pogacean *et al.* (2014).

Kinetic modeling of pesticide dissipation

Kinetic modeling of pesticide residues behavior in apples was performed considering single recommended dose and double dose treatments with pesticides for BBCH scale 76-79 (2/3 of normal size) and measuring their concentration in time (t) from 2 days (d) to 2 months after harvesting as indicated in the work of Pogacean *et al.* (2014). In order to evaluate the dissipation behaviour of pesticides in time and to determine the statistical parameters that describe the processes leading to dissipation, we used 6 kinetic models: 1st-order, 1.5th-order, 2nd-order, RF-1st-order, RF-1.5th-order, RF-2nd-order. Time and pesticide residues values were converted by the kinetic models described in tab. 1. The linear regression equation is described in the form of $y = a + b x$, where a is the intersection point of the straight line with the x-axis at $t = 0$ and b represents the slope of the straight line. An important parameter consistent with the persistence of pesticide residues is the decline time (T/X), which denotes the time after which the residue concentration decreased to $1/X$ of the initial concentration. According to this definition, $t_{1/2}$ represents the time required to reduce by half the initial concentration of the pesticide residue. A particular case is the 1st-order model, where the relative declining rate remains constant throughout the process, being independent of the initial concentration (in analogy to the 1st-order reaction). Therefore, $t_{1/2}$ corresponds to the half-life of pesticides. In the case of the other models described, the declining rate, T/X, decreases progressively over time, and the half-life is not proper to be used in this context (Timme and Frehse, 1980; Timme *et al.*, 1986).

Table 1

Calculation formulas for regression equations in the linearized systemand for the decline time

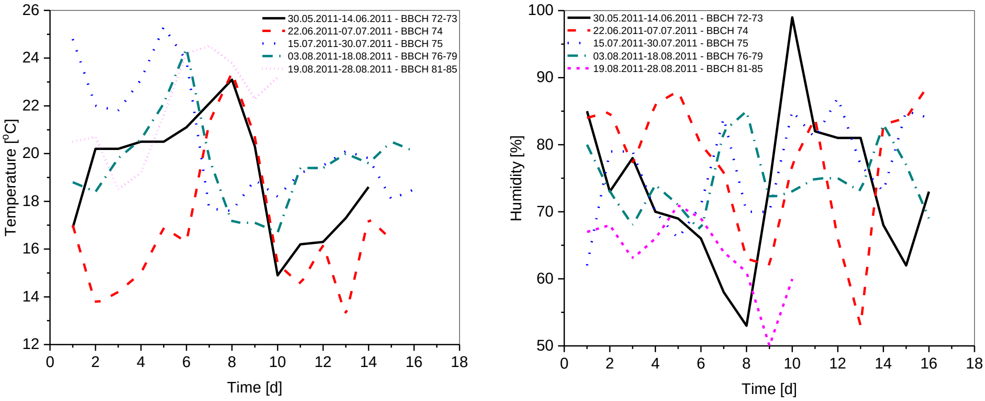
Model	Linear regression	T/X
1st-order kinetics	$\log C = a + bt$	$\frac{\log X}{-b}$
1.5th-order kinetics	$\frac{1}{\sqrt{C}} = a + bt$	$\frac{a}{b}\left(\sqrt{X} - 1\right)$
2nd-order kinetics	$\frac{1}{C} = a + bt$	$\frac{a}{b}(X - 1)$
RF-1st-order kinetics	$\log C = a + b\sqrt{t}$	$\left(\frac{\log X}{-b}\right)^2$
RF-1.5th-order kinetics	$\frac{1}{\sqrt{C}} = a + b\sqrt{t}$	$\left(\frac{a}{b}\left(\sqrt{X} - 1\right)\right)^2$
RF-2nd-order kinetics	$\frac{1}{C} = a + b\sqrt{t}$	$\left(\frac{a}{b}(X - 1)\right)^2$

RF, Root Function; T/X, decline time

RESULTS AND DISCUSSIONS

Climatic conditions

The behavior of pesticides analyzed in various phenological phases of apples growth is strongly influenced by climatic conditions (e.g. temperature, humidity and precipitations) as seen in figs. 1-2. Physical properties of pesticides play an important role in the dynamics of pesticide concentrations, andare included in tab. 2.



(a)

(b)

Fig. 1 Temperature (a) and humidity (b) variation during phenological growth phases of apples

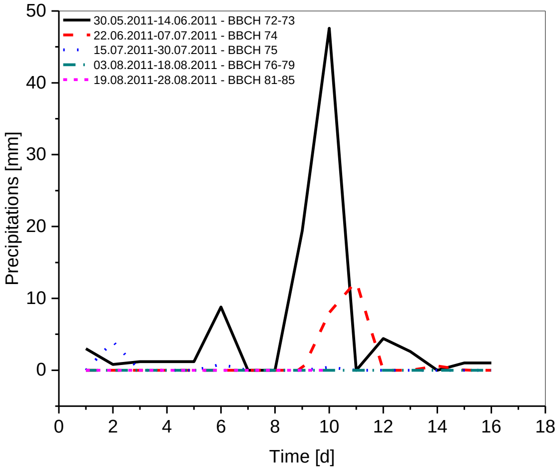


Fig. 2 Precipitations variation during phenological growth phases of apples

Table 2

Basic properties of pesticides applied in the treatment of appletrees

Pesticide	**Formula**	**Molecular mass [g/mol]**	**Solubility in water [mg/L]**	**Vaporization pressure [mPa]**	**Henry constant**	**log P /octanol-water**
Captan	$C_9H_8C_{l3}\ NO_2S$	300.6	3.3	<1.3	$3*e^{-4}$ Pa*m^3/mol at 20°C	2.8 at 25°C pH 7
Folpet	$C_9H_4Cl_3NO_2\ S$	296.6	0.8	2.1 *10^{-2} mPa at 25°C	7.8*10^{-3} Pa*m^3/moli	3.11
Triadimenol	$C_{14}H_{18}C_lN_3O_2$	295.8	95	A: 6*10^{-4} mPa at 20°C B: 4*10^{-4} mPa at 20°C	A: 3*10^{-6} Pa*m^3/mol at 20°C B: 4*10^{-6} Pa*m^3/mol 20°C	A: 3.08 at 25°C B: 3.28 at 25°C
Myclobutanil	$C_{15}H_{17}ClN_4$	288.8	142	0.213 mPa at 25°C	4.33*10^{-4} Pa*m^3/mol	2.94 at 25°C pH 7-8
Chlorothalonil	$C_8C_{l4}N_2$	265.9	0.81	0.076	2.5*10^{-2} Pa*m^3/mol at 25°C	2.92 at 25°C
Tebuconazole	$C_{16}H_{22}ClN_3O$	307.8	36	1.7*10^{-3} mPa at 20°C (OECD 104)	1*10^{-5} Pa*m^3/mol at 20°C	3.7 at 20°C
Chlorpyrifos-methyl	$C_7H_7C_{l3}NO_3PS$	322.5	3	3.35 mPa at 25°C	0.372 Pa*m^3/mol	4.24
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	422.9	<1 µg/L	0.024 mPa at 25°C	1.02*10^2 Pa*m^3/mol	>6
α-cypermethrin	$C_{22}H_{19}C_{l2}NO_3$	416.3	0.67 µg/L pH 4 3.97 µg/L pH 7	2.3 *10^{-2} mPa at 20°C	6.9*10^{-2} Pa*m^3/mol	6.94 pH 7

			4.54 µg/L pH 9 all at 20°C			
λ-cyhalothrin	$C_{23}H_{19}ClF_3NO_3$	449.9	$5*10^{-3}$	0.2 µPa at 20°C	0.02 Pa*m^3/mol la 20°C	7 la 20^0 C
Deltamethrin	$C_{22}H_{19}Br_2\ NO_3$	505.2	0.0002 mg/L at pH 7.5	$1.24*10^{-5}$ mPa	$3.13\ *10^{-2}$ Pa*m^3/mol at 25°C	4.6 at 25°C pH 7.6
Propargite	$C_{19}H_{26}\ O_4S$	350.5	0.215	0.04 la 25°C	$6.4*10^{-2}$ Pa*m^3/mol	5.70

Dissipation behavior of pesticides in apples

After application of treatments, it is considered that pesticides suffer degradation in environmental compartments (e.g. soil above ground, soil layer, root-soil layer) and vegetation compartments (e.g. land and fruit deposits, leaves, fruits, stem and root thickness) (Fantke *et al.*, 2011). Photochemical oxidation, photolysis, hydrolysis and metabolism driven processes could contribute to the overall pesticides degradation. The rate of degradation of pesticides increases with temperature, soil organic matter content and pH; a higher temperature may favor both microbial decomposition and chemical decomposition. According to literature, the kinetics of pesticide degradation is a first-order reaction (Vanclooster *et al.*, 2000). In this paper, the influences of the aforementioned factors on the rate of degradation of pesticides in apples were not considered separately being incorporated into the kinetic parameters calculated according to the specificity of the kinetic model considered. In the case of most pesticides, the dissipation behavior didn't follow the 1st-order kinetics as is often highlighted in the literature. The correlation coefficients which indicate the best fit, from the six kinetic models applied, are included in tab. 3 for single recommended dose treatments and in tab. 4 for double dose treatments. The half-lives are included in tab. 5 and tab. 6.

Considering the single recommended dose treatments, deltamethrin is the only pesticide which follows the 1st-order kinetic model having a correlation coefficient of 0.96 (tab. 3). From the regression equation, the half-life of deltamethrin in apples for BBCH 76-79 stage is of 0.21 d. Pesticides α-cypermethrin, chlorpyrifos-methyl and bifenthrin follow the 1.5th-order kinetic model with correlation coefficients between 0.97 and 0.99. The corresponding $t_{1/2}$ of these pesticides are 5.25 d, 2.57 d and 10.54 d, respectively (tab. 5). The dissipation of chlorotalonil, folpet, captan and triadimenol applied in recommended doses is best described by the 2nd-order kinetic model (R^2>0.97), while the corresponding $t_{1/2}$ values are 0.21 d, 20.76 d, 5.41 d and 0.76 d, respectively. The dissipation of miclobutanyl follows the RF-1st-order kinetic model (R^2>0.81) and its half-life in apples is of 74.9 d. For tebuconazole, the concentration variation is best described by RF-1.5th-order kinetic model (R^2>0.98), while its resulted $t_{1/2}$ in apples is of 5.61 d. Propargite and λ-cyhalothrin behaviour in apples is best fitted by RF-2nd-order kinetic model (R^2>0.98). The corresponding half-lives are 0.01 d for propargite and 1.36 d for λ-cyhalothrin.

Table 3

The correlation coefficients determined from kinetic modeling applied for dissipation of pesticides applied in single recommended dose treatments in apples

Pesticide	R^2					
	1st-order	**1.5th-order**	**2nd-order**	**RF-1st-order**	**RF-1.5th-order**	**RF-2nd-order**
Chlorothalonil	0.79	0.92	**0.97**	0.93	0.95	0.90
Propargite	0.75	0.82	0.88	0.89	0.92	**0.93**
Folpet	0.82	0.95	**0.98**	0.95	0.96	0.90
Tebuconazole	0.83	0.91	0.96	0.96	**0.98**	0.98
Captan	0.83	0.98	**0.99**	0.97	0.97	0.88
Triadimenol	0.81	0.98	**0.98**	0.95	0.95	0.84
Deltamethrin	**0.96**	0.75	0.57	0.87	0.58	0.39
α-cypermethrin	0.83	**1.00**	0.97	0.97	0.96	0.83
λ-cyhalothrin	0.40	0.59	0.74	0.66	0.82	**0.91**
Chlorpyrifos-methyl	0.79	**0.97**	0.97	0.90	0.92	0.82
Bifenthrin	0.83	**1.00**	0.97	0.97	0.96	0.83
Myclobutanil	0.68	0.74	0.80	**0.81**	0.81	0.81

Table 4

The correlation coefficients determined from kinetic modeling applied for dissipation of pesticides applied in double dose treatments in apples

Pesticide	R^2					
	1st-order	**1.5th-order**	**2nd-order**	**RF-1st-order**	**RF-1.5th-order**	**RF-2nd-order**
Chlorothalonil	0.84	0.98	**0.99**	0.98	0.98	0.89
Propargite	0.65	0.73	0.79	0.85	0.89	**0.91**
Folpet	0.82	0.93	**0.98**	0.94	0.95	0.91
Tebuconazole	0.87	0.94	0.98	0.98	**0.99**	0.98
Captan	0.82	0.96	**0.99**	0.96	0.98	0.92
Triadimenol	0.80	0.95	**0.98**	0.93	0.95	0.88
Deltamethrin	0.86	**0.99**	0.95	0.95	0.90	0.77
α-cypermethrin	0.63	0.78	0.88	0.84	0.92	**0.94**
λ-cyhalothrin	0.66	0.79	0.88	0.85	0.90	**0.91**
Chlorpyrifos-methyl	0.65	0.81	**0.91**	0.84	0.90	0.90
Bifenthrin	0.88	**0.99**	0.98	0.98	0.96	0.86
Myclobutanil	0.87	0.94	**0.96**	0.85	0.85	0.82

In the case of double dose treatments with pesticides applied in apples, the kinetic models applied accurately describe the dissipation behaviour of pesticide residues. Thus, the 1.5th-order kinetic model describes the dissipation of deltamethrin and bifenthrin with correlation coefficients, R^2>0.98. The 2nd-order kinetic model describes the dissipation of chlorothalonil (R^2>0.99), folpet (R^2>0.97), captan (R^2>0.99), triadimenol (R^2>0.98), chlorpyrifos-methyl (R^2>0.90) and myclobutanil (R^2>0.95), while the RF-1.5th-order model accurately fits the dissipation of tebuconazole in apples (R^2>0.99). The dissipation of propargite, α-cypermethrin and λ-cyhalothrin pesticides is very well described by the RF-2nd-order kinetic model with correlation coefficients higher than 0.91 in both cases (tab. 4). The corresponding half-lives of pesticides applied in double dose treatments in apples range from 1.51 d to 17.91 d (tab. 6).

Table 5

Linear regression equations and half-lives of pesticides determined from the best fitting model considering single recommended doses treatmentsof pesticides in apples

Pesticide	Linear regression system	$t_{1/2}$ [d]	$k_{deg} = \ln2/t_{1/2}$ [$d^{/1}$]
Chlorothalonil	$y = 0.0048 + 0.0228 x$	0.21	3.30
Propargite	$y = 0.0623 + 0.0533 x$	1.36	0.50
Folpet*	$y = 0.8156 - 0.0145 x$	20.76	0.03
Tebuconazole	$y = 0.4770 + 0.0834 x$	5.61	0.12
Captan*	$y = -0.0556 + 0.0426 x$	5.41	0.12
Triadimenol*	$y = -0.3953 - 0.0197 x$	0.76	0.91
Deltamethrin	$y = -0.0446 + 0.1181 x$	6.74	0.10
α-cypermethrin	$y = 1.2489 + 0.0984 x$	5.25	0.13
λ-cyhalothrin	$y = 0.2206+ 1.8725 x$	0.01	69.32
Chlorpyrifos-methyl	$y = 0.6541 + 0.1054 x$	2.57	0.26
Bifenthrin	$y = -0.4709 - 0.0185 x$	10.54	0.06
Myclobutanil	$y = 0.2838 - 0.1634 x$	74.90	0.01

**calculated from the 1st-order kinetic model*

Table 6

Linear regression equations and half-lives of pesticides determined from the best fitting model considering single recommended doses treatmentsof pesticides in apples

Pesticide	Linear regression system	$t_{1/2}$ [d]	$k_{deg} = \ln2/t_{1/2}$ [$d^{/1}$]
Chlorothalonil*	$y = 1.1931 - 0.0140 x$	21.50	0.03
Propargite	$y = 0.0860 + 0.0293 x$	8.61	0.08
Folpet	$y = 0.0617 + 0.0109 x$	5.66	0.12
Tebuconazole	$y = 0.4269 + 0.0535 x$	10.92	0.06
Captan	$y = 0.0556 + 0.0170 x$	3.27	0.21
Triadimenol*	$y = -0.1547 - -0.0168 x$	17.91	0.03
Deltamethrin	$y = 0.5459 + 0.1044 x$	2.16	0.32
α-cypermethrin	$y = -2.1523 + 1.7470 x$	1.51	0.45
λ-cyhalothrin	$y = -2.6001+ 1.7828 x$	2.12	0.32
Chlorpyrifos-methyl	$y = 0.2618 + 0.2289 x$	1.14	0.60
Bifenthrin	$y = 0.9076 + 0.0310 x$	12.12	0.05
Myclobutanil*	$y = 0.1153 – 0.0134 x$	2.61	0.26

**calculated from the 1st-order kinetic model*

CONCLUSIONS

Modeling pesticide residues in apples was performed considering six well-known kinetic models. For most pesticides, the dissipation didn't follow the 1st-order kinetic model, as is otherwise often emphasized in literature. Taking into account this result, we considered applying other kinetic models and we found that these models fit well the experimental data, with adequate values of correlation coefficients, R^2.

The half-lives, $t_{1/2}$ resulted from the linear regression equations considering single recommended dose treatments are between 0.01 days (for λ-cyhalothrin) and 74.90 days (for myclobutanil). Regarding double dose treatments, the half-life values of pesticides ranged between 1.51 days and 17.91 days. Understanding the degradation of pesticides in relation to other factors and evaluation of pesticide residues is very important not only for a correct estimation of food risks, but also to optimize pesticide application techniques in order to improve pesticides monitoring programs.

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