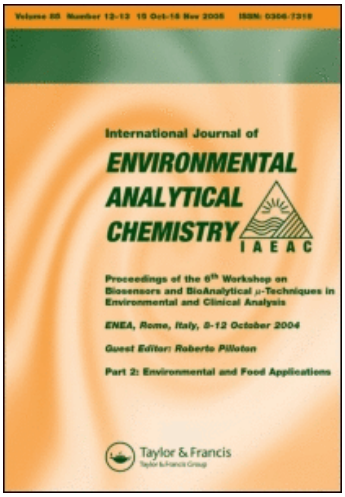

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Dimitrios T. Likas[a]; Nikolaos G. Tsiropoulos[a]
[a] Analytical Chemistry and Pesticide Laboratory, Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Volos, Greece

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Behaviour of fenitrothion residues in leaves and soil of vineyard after treatment with microencapsulate and emulsified formulations

DIMITRIOS T. LIKAS and NIKOLAOS G. TSIROPOULOS*

Analytical Chemistry and Pesticide Laboratory,
Department of Agriculture Crop Production and Rural Environment,
University of Thessaly, Fytokou str., 38446 Nea IoniaVolos, Greece

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The rate of decline of fenitrothion residues was investigated in leaves and soil of vineyard over 2 months after treatment with two different kinds of commercial formulations: emulsifiable concentrate (EC) and microencapsulate (ME). Fenitrothion residues were determined with GC-NPD after acetone extraction of soil and leaves. The measured initial deposits in soil and leaves varied between 2.6 and 3.8 mg kg^{-1} and between 89 and 101 mg kg^{-1}, respectively. Fenitrothion residues in soil dropped at 0.1–0.2 mg kg^{-1} after 60 days following application with EC formulation showing a more rapid decline than the ME. Fenitrothion residues in leaves from ME formulation treatment showed a longer persistence and lower decline rate than those from EC formulation. During the experimental period, fenitrothion remaining in leaves from ME application was 10 times more than from the EC one. Mathematically defined decline curves were established by determining optimal relationships between fenitrothion residues and time. The RF1st-order and RF1.5th-order equation achieved the best adjustment to the experimental data of fenitrothion dissipation on leaves for the ME and EC formulation, respectively, giving fenitrothion half-lives of about 2–3 days for ME and <1 day for EC formulation. In vineyard soil, the best adjustment to the experimental data for ME and EC formulation was achieved by the 1st-order and 1.5th-order equations, respectively, giving fenitrothion half-lives in soil of about 17–21 days for ME and 5 days for EC formulation.

Keywords: Fenitrothion; Microencapsulate formulation; Residues decline curves

1. Introduction

Pest control often requires periodic application of pesticide to the crop using conventional formulation, e.g. powders, granules or concentrated emulsions. These result in significant levels of environmental pollution due to application of extensive quantities of pesticide. The industry is active in developing better products with new, safer, more potent compounds, but also novel products using established chemistries, with improved safety to the user [1], safety in the environment, and efficient use of product applied in the field. Controlled-release systems are becoming increasingly

*Corresponding author. Fax: +302-421093144. Email: ntsirop@uth.gr

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popular because they are considered as generally safe, inert, non-allergic, and non-toxic when touched or accidentally ingested. The principal advantage of controlled release formulation is that they allow much less pesticide to be used for the same period of activity. Moreover, when the normal half-life of a potential pesticide is short, the controlled release formulation is especially advantageous in comparison with conventional formulations. The conventional emulsifiable formulation releases immediately all of its active ingredient while the microencapsulate formulation has a mechanism to release the ingredient over a period which depends on the environmental conditions, in particular relative humidity. Thus, microencapsulate formulations make active ingredient available for a longer period, resulting in a higher persistence [2].

Fenitrothion (*O*,*O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate) is a toxic organophosphorus ester recognized as a non-systemic insecticide active by contact and ingestion against a wide range insects [3]. The use of fenitrothion is currently increasing due to the ongoing reassessment of the European registration of pesticides that is strongly limiting the use of other organophosphorus compounds. Fenitrothion, as a microencapsulated formulation, is largely used in the integrated pest management (IPM) protocols to control insects on cereals, vegetables, fruits, and other crops. Fenitrothion dissipation after application of the emulsifiable concentrate formulation has been studied in leaves, soil, and forest environments [4–7], but few studies have been reported about the behaviour in field treatments of fenitrothion or other organophosphorus pesticides in microencapsulate formulations [8, 9]. The present study investigated the fate of fenitrothion residues in soil and leaves from vineyard treated with emulsifiable concentrate (EC) or microencapsulate (ME) formulation of fenitrothion and their persistence in the field. In addition, an evaluation of extraction procedures to measure fenitrothion residues in soil and leaf samples was performed.

The most common way for mathematical characterization of the decline is the transformation of data to obtain a linear relationship between residues and time, by plotting the logarithms of residues vs. time. Nevertheless, in most cases, during the first period after application, residues decline at a faster rate and thereby deviate from the first-order equation. Therefore, it is necessary to investigate other scale transformations that give simple linear relationships, thus allowing decline curves to be described mathematically. In this way, the methodology proposed by Timme *et al.* [10, 11] was followed to determine the mathematical model that best fits the experimental data and to calculate half-lives of fenitrothion on leaves and soil.

2. Experimental

2.1 *Chemicals and solutions*

Fenitrothion analytical-grade standard (99.5% purity) was purchased from Chem Service. Commercial formulations Fenitrothion IPM 40 CS (microencapsulate formulation a.i. 40% w/v) and Sumithion 50 EC (emulsifiable concentrate formulation, a.i. 50% w/v) were purchased from ALFA Agricultural Supplies S.A. (Greece) and Efthymiadis K. & N. S.A (Greece), respectively.

Fenitrothion stock standard solution (1000 mg L^{-1}) was prepared in acetone from fenitrothion analytical standard. Fenitrothion stock solutions (500 mg L^{-1}) were also

prepared in water from ME and EC formulations. Two types of fenitrothion working solutions were prepared for spiking matrices at the recovery experiments, one from the stock standard solution by appropriate dilution in acetone and one from fenitrothion stock solutions in water. Fenitrothion standard solutions (0.10–10 mg L^{-1}) for calibration and quantitation were prepared (a) in 2,2,4 trimethylpentane/toluene, (b) in ethyl acetate, and (c) in both soil and leaf extracts (matrix-matched standard solutions).

2.2 *Field trials and sampling*

The experimental trials were carried out in a vineyard (Roditis variety), located at Nea Aghialos, Magnesia, in central Greece. Three trials were conducted in the above vineyard: one on 28 August 2002 with application of ME formulation and two on 28 August 2003; one with application of ME formulation and the other with EC formulation. Each experimental trial was divided into four randomized plots (23×8.10 m, 60 plants each); three of them were used as replicate, and one was left untreated to be used as control. Fenitrothion was applied as a water solution of Fenitrothion IPM 40 CS or of Sumithion 50 EC at the recommended rates of 1.9 mL L^{-1} of water (corresponding to 0.76 kg a.i./ha) or 1.5 mL L^{-1} of water (corresponding to 0.75 kg a.i./ha), respectively, using a pressurized hand-gun applicator until runoff. During the trials (28 August–28 October), the average daily air temperature was 18.8 and 19.8°C, the average relative humidity was 81.3 and 65.9%, and the rainfall was 36.0 and 8.4 mm for the years 2002 and 2003, respectively.

Leaf samples (50 whole leaves) were collected randomly from each plot at 0 (4 h after application), 7, 15, 30, 45, and 60 days after application. The samples were taken to the laboratory, blended, subdivided into 25-g aliquots as analytical replicates, and stored in individual bags at −18°C until extraction. Soil samples were taken at the same day as leaf samples. At each sampling, five soil cores (8 cm diameter × 5 cm deep) were removed randomly from each plot and combined to one sample. Soil samples from each plot were put into article bags, taken to the laboratory, air-dried in the shade, screened through a 2-mm mesh sieve, and then stored frozen (−18°C) until extraction.

2.3 *Extraction of leaves*

Leaves were extracted according to a routine multiresidue pesticide extraction schema used for several agricultural commodities [12], with some modifications. Ten grams of homogenated leaf sample was blended with 20 mL of acetone for 30 s in an Ultra Turrax homogenizer. Twenty millilitres of dichloromethane and 20 mL of petroleum ether were added, and the mixture was homogenized for another 30 s. The homogenate was centrifuged for 5 min at 4000 rpm, and 10 mL of the organic layer was evaporated to dryness on a rotary evaporator. The residue was redissolved in 2 or 20 mL 2,2,4 trimethylpentane/toluene (9 + 1 v/v) for samples of low or high fenitrothion concentration, respectively. On the basis of this extraction procedure, the concentration factor of the leaves sample in the final solution corresponds to 0.83 g mL^{-1} when the final volume is 2 mL.

2.4 *Soil extraction*

Soil samples (10 g) were extracted with 20 mL of solvent by shaking on a wrist-action shaker (for 2 h), and after centrifugation (at 4000 rpm for 15 min) 10 mL of the supernatant was evaporated to dryness, under vacuum, using a rotary evaporator at 40°C. The residue was redissolved and evaporated twice with 2×5 mL ethyl acetate before finally redissolving with 2 mL of ethyl acetate. Acetone, methanol, and ethyl acetate were tested as extraction solvent. On the basis of this extraction procedure, the concentration factor of the sample in the final solution corresponds to 2.5 g of soil mL^{-1}.

2.5 *Residue analysis*

Fenitrothion residues were determined in a Hewlett-Packard mode 6890 gas chromatography, fitted with a nitrogen–phosphorous detector (NPD) and with a BPX-5 ($30\,m \times 0.32\,mm$ i.d.) column. The gas chromatograph oven-temperature programme started from 60°C for 1.5 min, increased to 220°C with a rate of $14°C\,min^{-1}$, then increased to 280°C (with $20°C\,min^{-1}$) and held for 5 min. The carrier gas (helium) flow rate was $1.6\,mL\,min^{-1}$. The injector temperature was at 230°C, and the pulsed splitless injection was carried out with the purge valve on for 1 min. The detector temperature was at 310°C, and hydrogen ($3\,mL\,min^{-1}$) and air ($60\,mL\,min^{-1}$) were used as fuel gases with helium ($5\,mL\,min^{-1}$) as make-up. Under these conditions the fenitrothion peak was well separated in all samples, and no matrix co-eluates or other compounds interfered with its determination. An HP-35 ($30\,m \times 0.25\,mm$ i.d.) gas chromatography column was used as a confirmatory column.

3. Results and discussion

3.1 *Determination of fenitrothion residues*

Quantification of fenitrothion was performed by an external standard procedure. To determine if there is a different response between matrix-matched standards (soil, leaves) and standards in solvent, a comparison of the slopes of calibration curves from matrix-matched standards to those in solvent was made using Student's t test according to Zar [13, 14]. Even though no significant ($P = 0.05$) difference between matrix-matched standards and the standards in solvent was observed at any of the matrices studied, determination of fenitrothion residues was performed by the use of matrix-matched standards as recommended by the *Quality Control Procedures for Pesticide Residues Analysis* [15].

In the studied range of calibration standards ($0.1–10\,mg\,L^{-1}$, $n = 9$), a good linearity for the GC-NPD was achieved with a correlation coefficient $R^2 > 0.998$ for all kind of standard solutions. The method's limit of detection (LOD), evaluated as three times the signal-to-noise ratio, was calculated at $0.03\,mg\,L^{-1}$. The method's limit of quantification (LOQ), as a signal to noise from fenitrothion-free samples equal to 10, was calculated at $<0.04\,mg\,kg^{-1}$ for soil and to $0.12\,mg\,kg^{-1}$ for leaves samples.

Table 1. Mean recovery (average of five replicates for each level) and relative standard deviation (RSD) of fenitrothion extracted from soil and leaves spiked with fenitrothion standard solution (STD) and diluted solution of EC and ME formulations using different solvents.

		Recovery (%) ± RSD					
		Fortification level					
		0.10 mg kg^{-1}			2.0 mg kg^{-1}		
Matrix soil	Extraction solvent	STD	EC	ME	STD	EC	ME
	Methanol	89 ± 10	94 ± 10	54 ± 6	95 ± 4	97 ± 6	62 ± 8
	Ethyl acetate	87 ± 6	94 ± 8	60 ± 7	95 ± 3	89 ± 4	69 ± 7
	Acetone	93 ± 7	102 ± 6	82 ± 5	101 ± 6	94 ± 5	89 ± 5
		0.50 mg kg^{-1}			5.0 mg kg^{-1}		
Leaves		STD	EC	ME	STD	EC	ME
	Acetone[a]	91 ± 8	95 ± 7	79 ± 10	98 ± 7	87 ± 9	81 ± 12

[a]Acetone, dichloromethane, and petroleum ether.

Recovery studies were conducted, following section 2, after spiking fenitrothion-free leaf and soil samples with fenitrothion working solution prepared from (a) a fenitrothion stock standard solution, (b) a diluted solution of EC formulation, and (c) a diluted solution of ME formulation. In particular, 10 g of control samples was fortified with the appropriate volume of fenitrothion working solutions, mixed well and allowed to stand for 30 min at room temperature prior to extraction. Five replicates were analysed at each fortification level.

All soil samples spiked with the standard solution or the solution of EC formulation gave satisfactory recoveries ranging from 87 to 102% and relative standard deviation (RSD) values <10% for all three extraction solvents tested as presented in table 1. In contrast, only acetone, between the three solvents tested, gave satisfactory results (recovery >75%) for fenitrothion extraction from soils spiked with the solution of ME formulation, while extraction with methanol or ethyl acetate gave mean recoveries ranging from 54 to 69%. Following these results, acetone was used as extraction solvent for the analysis of all soil samples for fenitrothion residues.

Recovery values obtained from the recovery experiments with vine leaves (table 1) at two fortification levels of 0.50 and 5.0 mg kg^{-1} ranged from 79 to 98% with RSD values < 12% for all types of fortification solutions showing a good precision and repeatability of the followed analytical methodology. This acetone extraction procedure has also been proven in our laboratory to be the most adequate to extract fenitrothion residues from fruits and vegetables sprayed with microencapsulated formulations compared with other solvents used accordingly [16].

3.2 *Fenitrothion residues in soil*

Fenitrothion residues in vineyard soil and their dissipation during 2 months after application are shown in table 2. Initial residues in soil ranged from 2.6 to 3.8 mg kg^{-1}, while after 60 days after application (DAA), fenitrothion residues dropped to

Table 2. Mean fenitrothion residue levels, relative standard deviation[a] (in parentheses) and percentage of initial concentration remaining in vineyard soil at various time intervals after vineyard treatment with EC and ME fenitrothion formulations for 2002 and 2003.

	2003 (EC formulation)		2003 (ME formulation)		2002 (ME formulation)	
DAA[b]	Level ($mg\,kg^{-1}$)	Remaining (%)	Level ($mg\,kg^{-1}$)	Remaining (%)	Level ($mg\,kg^{-1}$)	Remaining (%)
0	3.8 (16)	100	2.8 (22)	100	2.6 (42)	100
7	1.6 (14)	42	2.4 (21)	85	1.7 (19)	66
15	0.66 (41)	17	2.2 (31)	78	1.6 (16)	62
30	0.55 (18)	14	1.3 (14)	46	1.4 (49)	54
45	0.11 (18)	3	0.55 (44)	20	0.90 (28)	35
60	0.12 (26)	3	0.23 (29)	8	0.24 (26)	9

[a]$n = 3$ different samples.
[b]DAA: days after application.

0.1–0.2 $mg\,kg^{-1}$ levels (3–9% of the initial residues remaining). Although residues of EC and ME fenitrothion formulations at 60 DAA were similar, during the experimental period fenitrothion from EC formulation dissipated faster than ME formulation. As volatilization and microbial degradation are considered the main aspects that explain dissipation of fenitrothion in soil [7], the observed different dissipation rates are attributed to the slow release of active ingredient in ME formulation.

3.3 *Fenitrothion residues in leaves*

Fenitrothion residues in leaves as well as their decrease with time after application are shown in table 3. The mean values of the initial deposit of fenitrothion residues ranged from 89 to 101 $mg\,kg^{-1}$. These initial concentrations measured in leaves are much higher than those measured in grapes from sprayed vines in our laboratory (4–5 $mg\,kg^{-1}$), and this is attributed to the observed difference of the exposed surface to mass ratio between leaves and fruits. The same behaviour was also observed for pesticide concentrations measured in fruits and leaves from orange trees [8] and from tomato plants [17].

Fenitrothion from EC formulation application dissipated very quickly so that only 3% of the initial fenitrothion concentration was measured in leaves collected a week after application (table 3). After 15 DAA, fenitrothion concentrations were below 1 $mg\,kg^{-1}$, i.e. lower than 1% of the initial deposits. Similar results for the initial deposits and dissipation of fenitrothion on leaves and soil were also observed in cucumber culture after spraying with fenitrothion EC formulation [18].

Fenitrothion residues from ME formulation application showed a slower decay than those from the EC one. At 7 DAA, 26 and 36% of initial deposits remained in leaves during 2002 and 2003 trials, respectively (table 3). Fenitrothion decay was slowest at the period from 15 to 60 DAA and, during this period of about 1.5 month, fenitrothion residues in leaves for 2003 ranged from 2.0 to 6.8 $mg\,kg^{-1}$, i.e 10 times higher than those of EC formulation.

Comparing the two ME formulation applications fenitrothion residues measured in leaf samples at 2002 were higher than those measured at 2003 for the period from

Table 3. Mean fenitrothion residue levels, relative standard deviation[a] (in parentheses) and percentage of initial concentration remaining in vine leaves at various time intervals after vineyard treatment with EC and ME fenitrothion formulations for 2002 and 2003.

	2003 (EC formulation)		2003 (ME formulation)		2002 (ME formulation)	
DAA[b]	Level ($mg\,kg^{-1}$)	Remaining (%)	Level ($mg\,kg^{-1}$)	Remaining (%)	Level ($mg\,kg^{-1}$)	Remaining (%)
0	89 (17)	100	101 (10)	100	96 (17)	100
7	2.5 (23)	3	36 (30)	36	25 (30)	26
15	0.70 (14)	< 1	6.8 (13)	7	15 (25)	16
30	0.21 (19)	< 1	3.3 (26)	3	12 (12)	13
45	0.19 (28)	< 1	2.8 (17)	3	4.5 (19)	5
60	0.30 (15)	< 1	2.0 (22)	2	nd[c]	

[a] $n = 3$ different samples.
[b] DAA: days after application.
[c] nd: not determined.

Table 4. Decline curves, corresponding regression lines, and decline time functions for different models.

Model	Decline curve	Corresponding regression line	Decline time T/X $(X = 2)$
1st-order	$C = 10^{a+bt}$	$\log C = a + bt$	$(\log X/-b)$
1.5th-order	$C = 1/(a+bt)^2$	$1/\sqrt{C} = a + bt$	$a/b(\sqrt{X}-1)$
2nd-order	$C = 1/(a+bt)$	$1/C = a + \mathrm{bt}$	$a/b(X-1)$
RF1st-order	$C = 10^{a+b\sqrt{t}}$	$\log C = a + b\sqrt{t}$	$(\log X/-b)^2$
RF1.5th-order	$C = 1/(a+b\sqrt{t})^2$	$1/\sqrt{C} = a + b\sqrt{t}$	$(a/b)^2(\sqrt{X}-1)^2$
RF2nd-order	$C = 1/(a+b\sqrt{t})$	$1/C = a + b\sqrt{t}$	$(a/b)^2(X-1)^2$

15 DAA and after. The higher fenitrothion concentrations observed in the 2002 trial could be due to the different climatic conditions at the time of experimental periods (higher relative humidity and lower temperature observed for 2002).

3.4 *Fenitrothion decline curves*

To evaluate the decline of fenitrothion residues in the studied matrices, residue data should be subjected to statistical analysis to determine the statistical parameters that describe these processes, as proposed by Timme *et al.* [10]. A linear regression can be obtained after an appropriate transformation of the residue and/or time values using the six formal models described in table 4. To select the best fit model, the modified coefficient of determination r^2 and the test quantity D were calculated for each model and matrix. As is well known, $r^2 \leq 1$, and the larger this coefficient, the better the decline curve fits the data. If r^2 becomes negative or zero for any model, then the fit is automatically rejected. If $r^2 > 0$, then the correlation is tested with the aid of the test quantity D to determine whether r^2 differs significantly from zero [19]. The correlation is confirmed when $D > 0$. Equations of the decline curves, for the 1st-order and optimal model for which we have the best fit of data for each matrix, as well as the respective modified coefficients of determination r^2 with their corresponding test quantity D are

Table 5. Decline curves, modified coefficient of determination (r^2), test quantity for correlation (D), half-lives ($T/2$ in days) and its confidence interval (CI in days) for fenitrothion residues on soil, derived from both the optimal[a] and the 1st-order models.

Year	Formulation[a]	Model	Decline curves	r^2	D	$T/2$	CI[b]
2002	ME	1st-order[c]	$C = 10^{0.433-0.014t}$	0.850	0.111	20.9	12.0
2003	EC	1st-order	$C = 10^{0.398-0.025t}$	0.813	0.090	12.0	5.3
		1,5th-order[c]	$C = 1/(0.490 + 0.044\,t)^2$	0.979	0.178	4.7	5.0
2003	ME	1st-order[c]	$C = 10^{0.539-0.018t}$	0.873	0.123	16.5	4.7

[a]Emulsifiable EC and microencapsulate ME formulation.
[b]At a confidence level of 95%.
[c]Optimal model.

Table 6. Decline curves, modified coefficient of determination (r^2), test quantity for correlation (D), half-lives ($T/2$ in days) and its confidence interval (CI in days) for fenitrothion residues on vine leaves, derived from both the optimal and the 1st-order models.

Year	Formulation[a]	Model	Decline curves	r^2	D	$T/2$	CI[b]
2002	ME	1st-order	$C = 10^{1.741-0.025t}$	0.661	−0.065	12.0	8.9
		RF1st-order[c]	$C = 10^{1.947-0.184\sqrt{t}}$	0.984	0.237	2.7	1.8
2003	EC	1st-order	$C = 10^{0.925-0.034t}$	−0.002			
		RF1,5th-order[c]	$C = 1/(0.127 + 0.282\sqrt{t})^2$	0.883	0.128	<1	<1
2003	ME	1st-order	$C = 10^{1.634-0.026t}$	0.540	−0.076	11.4	8.0
		RF1st-order[c]	$C = 10^{1.973-0.234\sqrt{t}}$	0.967	0.228	1.7	1.2

[a]Emulsifiable EC and microencapsulate ME formulation.
[b]At a confidence level of 95%.
[c]Optimal models.

shown in tables 5 and 6. The coefficient of determination r^2 was higher for the optimal model than the 1st-order one (when this model is not optimal), and for all optimal models, r^2 varied from 0.850 to 0.984. On the other hand, r^2 for the 1st-order model, when this was not the optimal, varied from 0.540 to 0.813 except for leaves treated with the EC formulation, where $r^2 < 0$. The correlation was confirmed from the fact that $D > 0$ in all cases except for the 1st-order models on leaves where $D < 0$.

Functions which best fit the experimental data on vineyard soil were the 1st-order and 1.5th-order for the treatment with ME and EC formulations, respectively (table 5). On the other hand, for vineyard leaves, the RF1st-order and RF1.5th-order for the treatment with ME and EC formulations, respectively, best fit the experimental data (table 6).

A number of studies have been carried out fitting decline curves in a first-order model for many pesticides. However, that interpretation is not always applicable, because the residues frequently diminish quicker at first and much more slowly at a later stage in comparison with the 1st-order model [20, 21]. In the present work, the half-live ($T/2$) has been estimated (tables 5 and 6) from the optimal model as well as from the 1st-order model (when this model is not optimal) according to Timme *et al* [10, 11]. It can be seen that for the optimal models, the estimated values of fenitrothion half-lives for the ME formulation ranged between 1.7 and 2.7 and between 16.5 and 20.9 days for leaves and soil, respectively. In the case of the EC formulation, the corresponding fenitrothion half-lives were lower: <0.1 and 4.7 days for leaves and soil, respectively. These values

are in agreement with the half-lives (0.7–0.8 days) observed by others in tomato leaves after EC formulation application [17]. It is interesting to note that according to our results, when the 1st-order and optimal model were not the same, $T/2$ values obtained from the optimal model were lower than those obtained from the 1st-order model. This means that, shortly after application, the residues decline at a faster rate than suggested by an assumed pseudo-first-order kinetic reaction.

4. Conclusions

The results obtained in this study showed that residues of fenitrothion measured in leaves and soil of vineyard treated with two types of fenitrothion formulations presented a different persistence related to the type of formulation sprayed. Microencapsulate formulations provided prolonged persistence of fenitrothion residues in leaves and lower degradation rate than the emulsifiable formulation. Although the microencapsulate formulation improved handling safety, the fact that fenitrothion residues remained in leaves for prolonged period should be taken into account for eventual additional risk to agricultural workers. Also, the different behaviours of the two types of formulations in the soil may be useful to evaluate their impact on non-target organisms.

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