

Full Length Research Paper

Dissipation rate of different commercial formulations of malathion applied to tomatoes

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Dissipation of malathion following one application of different commercial formulations of Malathion 57% EC, Malathiom-kemanova 57% EC, Malatox 57% EC and Actathion 57% EC were estimated by employing optimized QuEChERS technique and gas chromatography with flame photometric detector (GC-FPD). The average recoveries of malathion on tomato for fortification levels of 0.01 and 1.0 mg kg⁻¹ were observed to be 91.7 and 96.9%, respectively. The LOQ for tomato was found to be 0.1 µg kg⁻¹. Malathion residue was dissipated below its maximum residue limit (MRL) of 0.5 after 14 days. Half-life and preharvest interval (PHI) were calculated to be 2.88 (13), 3.59 (14), 3.58 (11), 3.21 (11) days for Actathion, Malatox, Malathiom-kemanova and Malathion, respectively. These data could provide guidance for the proper and safe use of malathion on tomato.

Key words: Dissipation, malathion, formulation, tomatoes, QuEChERS.

INTRODUCTION

Tomatoes (*Lycopersicon esculentum*) are one of the most important vegetable crops in Egypt. Annual tomatoes production in Egypt was estimated to be seven million tones and area under cultivation was about 221 thousand hectares which represent about 34% of the average area of vegetables in Egypt. The cultivation of tomatoes demands frequent application of a large number of pesticides and more than 100 pesticides have been recommended for use in Egypt to control a variety of pests and diseases (APC, 2010). Due to intensive use of pesticides in vegetable farming, residues may be accumulated at levels higher than those permitted by the international maximum residue levels (MRLs). Assessment of dissipation rate of a pesticide after application is a key process for determining the residual behavior of pesticides in agricultural crops. Additionally, residue

dissipation curves can be used to estimate the time required for decreasing the residues below MRLs (Ambrus and Lantos, 2002; Castillo-Sanchez et al., 2000; Fenoll et al., 2009).

Malathion is a widely used insecticide around the world due to its relatively low toxicity to mammals and high selectivity toward insects as well as its moderate persistence in the environment when compared with other Organophosphorus Pesticide (OPs) (Wauchope et al., 1992). Impurities, such as iso-malathion and various trimethylphosphorothioate esters present in the technical grade malathion or formed during storage can potentiate malathion-induced toxicity up to 10-fold (Aldridge et al., 1979; Pellegrini and Santi, 1972) and have been considered responsible for other effects, including DNA lesions (Blasiak et al., 1999; Flessel et al., 1993). Hence, only limited data are available on the fate of this insecticide. The present study examines the behaviour of four commercial formulations of malathion on tomatoes, and determines residual behaviour, pre-harvest intervals and half-lives in/on cucumber.

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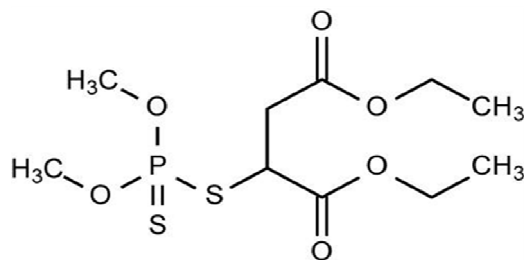


Figure 1. Chemical structure of malathion.

MATERIALS AND METHODS

Certified reference standard of malathion of more than 99% purity was obtained from Central Agricultural Pesticides Laboratory (CAPL), Giza, Egypt. Acetonitrile (MeCN) and methanol (MeOH) of HPLC grade were purchased from Merck. Bulk primary secondary amine (PSA) sorbent (Bondesil-PSA, 40 μm) was bought from Supelco. Ammonium acetate (cryst. Extra pure), acetic acid and sodium chloride were purchased from Merck. Magnesium sulphate anhydrous fine powder, trisodium citrate dihydrate (Extra pure) and disodium hydrogencitrate sesquihydrate (Extra pure) were purchased from Merck Limited.

The field experiment was carried out on a field located in Al-Monufia Governorate, Egypt. A complete randomized block design (CRBD) was applied with three replicates. Malathion was applied with a backpack motorized sprayers with an adjustable nozzle size of 1 mm using the commercial formulations of Malathion 57% EC, Malathion-kemanova 57% EC, Malatox 57% EC and Actathion 57% EC. The pesticide application was carried out using the recommended dose by the manufacturers 100 cm^3 20 L^{-1} water. Samples were collected 1 h after application (initial) and then after 1, 3, 7, 10 and 14 days, a control sample was also taken at each sampling time. Immediately after collecting the samples, each individual sample were put into plastic bags and transported to the laboratory.

Stock solution of malathion (Figure 1) was prepared by dissolving 50 mg of malathion reference standard in 50 mL MeOH to obtain solution concentration 1 mg mL^{-1} . A working standard solution of 10 $\mu\text{g mL}^{-1}$ was prepared by appropriately diluting the stock solution with MeOH. Stock solution was stored at $-20 \pm 2^\circ\text{C}$, and working standard solutions were stored in the dark at $\leq 4^\circ\text{C}$ when not in use.

Samples were extracted according to the procedure described and modified by Lehotay et al. (2010) and validated by Abd-Alrahman et al. (2011). Briefly, 10 g of the homogenized sample was weighed in a 50 ml centrifuge tube and 10 ml of 1.0% acidified acetonitrile with acetic acid was added, closed and vigorously shaken for 1 min using a vortex mixer at maximum speed. Then, 4 g of anhydrous MgSO_4 , 1 g of NaCl, 1 g sodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate were added, and then extracted by shaking vigorously using vortex for 2 min following centrifugation for 10 min at 5,000 rpm. An aliquot of 3 ml was transferred from the supernatant to a new clean 5-ml centrifuge tube and cleaned by dispersive solid-phase extraction with 75 mg of PSA and 500 mg of magnesium sulfate. Afterwards, centrifugation was carried out as mentioned earlier. Then 2 ml from the supernatant was filtered through a 0.2 μm PTFE filter (Millipore, USA) and then analyzed by Agilent 7890 GC-FPD.

Malathion residue analysis was performed with gas chromatographic GC-7890 series (Agilent Technologies, USA) equipped with a flame photometric detector. The separation was performed on a capillary column HP-5 (30 m \times 0.25 mm \times 0.25 μm) and nitrogen gas was used as mobile phase at a flow rate of 2 ml/min with temperature program that was started at 180°C and

held for 1 min was increased to 220 rate in $25^\circ\text{C min}^{-1}$ and then, held for 2 min and increased to 245°C rate in 5°C min^{-1} .

Data were statistically evaluated by one-way analysis of variance (ANOVA). Determination the differences among means were carried out by using the least significant differences (LSD) test. All statistical analyses were done using the Statistical Package for social sciences (SPSS 16.0) program.

RESULTS AND DISCUSSION

Method selectivity was evaluated using untreated tomato samples. The absence of any signal at the retention time of malathion indicated that no matrix compounds are present, which could give false positive signal. The calibration curve of malathion showed a good linearity and strong correlation between concentrations and peak area in the studied range (0 to 10 $\mu\text{g mL}^{-1}$) ($r^2 \geq 0.992$). A recovery of malathion from tomatoes was 94.3% ranged from 91.7 to 96.9%. Precision was studied by performing repeatability studies expressed as RSD. Satisfactory precision was obtained for malathion. Repeatability was lower than 6% for all three levels assayed. Similarly, with the examination of the matrix effect, a general tendency was observed towards higher values of RSDs at low spiking concentrations. Instrumental LOD based on S/N of 3:1 and LOQ based on S/N of 10:1 was (0.05 and 0.1 $\mu\text{g kg}^{-1}$).

Malathion mean residue levels during the sampling period for each application derived from three sub samples are shown in Table 1 and Figure 2. Residue levels of malathion was found to be below the MRL established by the Codex Committee (0.5 mg kg^{-1}) after the application of recommended dose was 250 cm^3 100 L^{-1} water for potatoes throughout the experimental period (FAO/WHO, 2006).

The highest residue levels were found in samples taken in the first sampling time 1 h after pesticide application. The highest mean initial concentration of malathion residue was found in samples treated with Actathion 7.81 mg kg^{-1} followed by Malatox 3.98 mg kg^{-1} , Malathion-kemanova 3.05 mg kg^{-1} and Malathion 2.03 mg kg^{-1} residue levels of malathion had been decreasing in the following period, reaching levels of 0.37, 0.48, 0.28 and 0.195 mg kg^{-1} for Actathion, Malatox, Malathion-kemanova and Malathion, respectively.

The results showed different half-life ($t_{1/2}$) and PHI for malathion of (2.88, 13), (3.59, 14), (3.58, 11) and (3.21, 11) days for Actathion, Malatox, Malathion-kemanova and Malathion, respectively. Other report from the study of Singh et al. (2006) showed different rate of dissipation and initial deposit was 29.31 mg gk^{-1} which declined quickly in 10 days to 94.0% dissipation and reached 99.7% dissipation in 15 days. In another study by Beouwer, it was reported that the dissipation of pesticide deposit was a complex process depending on various environmental factors like temperature, relative humidity and UV irradiation), metabolism and translocation (pesticide penetration and plant growth), application

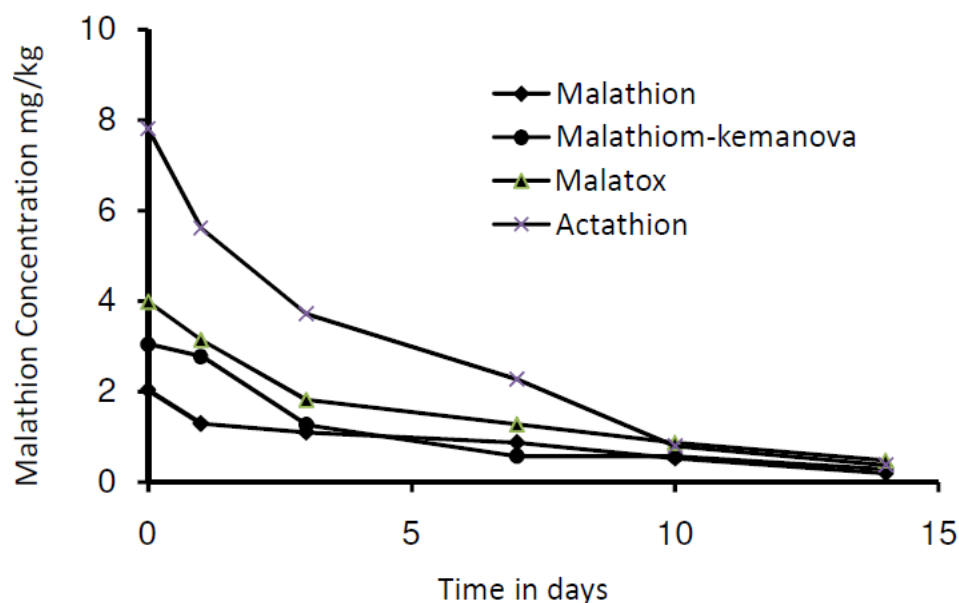


Figure 2. Dissipation rate of different four commercial formulations of malathion applied to tomatoes.

Table 1. Malathion mean concentration, half-live ($t_{1/2}$) and pre-harvest interval (PHI) on tomatoes.

Time	Malathion		Malathion-kem anova		Malatox		Actathion	
	Conc. (mg/kg)	Loss (%)	Conc. (mg/kg)	Loss (%)	Conc. (mg/kg)	Loss (%)	Conc. (mg/kg)	Loss (%)
0	2.03	-	3.06	-	3.98	-	7.81	-
1	1.29	36.45	2.78	8.85	3.14	21.11	5.61	28.17
3	1.1	45.81	1.26	58.69	1.82	54.27	3.71	52.50
7	0.87	57.14	0.57	81.31	1.27	68.09	2.27	70.93
10	0.53	73.89	0.56	81.64	0.87	78.14	0.79	89.88
14	0.196	90.39	0.28	90.82	0.48	87.94	0.37	95.26
$t_{1/2}$	3.21		3.58		3.59		2.88	
MRL (mg/kg)			0.5					
PHI	11		11		14		13	

technique and pesticide formulation (Brouwer et al., 1997; Katagi, 2004; McCrady and Maggard, 1993).

Dissipation rates of four commercial formulations of malathion (Actathion, Malatox, Malathiom-kemanova and Malathion) after a single application at recommended dose on tomatoes were evaluated. An optimized quick, easy, cheap, effective, rugged, and safe (QuEChERS) method was used for sample preparation. Through this method, we achieved a good analytical performance in terms of sensitivity (LOD $0.05 \mu\text{g kg}^{-1}$ and LOQs, $0.1 \mu\text{g kg}^{-1}$) and recovery rates (91.7 to 96.9%). Malathion residues analysis was determined using gas chromatograph equipped with FPD detector (GC-FPD). Thus, this method of sample preparation and residues determination can be used for detection of malathion residue even with low levels. Malathion has shown different

dissipation rates: half-life(s) and PHI for the studied four different formulations which were applied to tomatoes. Our results indicated that the dissipation rate might be affected by the difference of commercial formulations.

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