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Dissipation kinetics of dimethoate and malathion residues on tomato-cropped soil

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ABSTRACT

A supervised field trial was carried out in the Department of Entomology, Dr YS Parmar University of Horticulture and Forestry, Nauni, Solan, Himachal Pradesh during the year 2016. The dissipation pattern of dimethoate and malathion residues was estimated on tomato-cropped soil using dispersive QuEChERS technique and detected with a gas chromatograph (SHIMADZU-2010) coupled with a flame photometric detector (FPD). Dimethoate and malathion were sprayed on tomato fruit crop at 200 and 400 g ai/ha and 750 and 1,500 g ai/ha respectively. The analysis showed that the average initial deposit of 0.169 mg/kg in tomato-cropped soil was found to be below the level of determination after 3rd day of treatment of dimethoate 200 g ai/ha. On the contrary dimethoate application of 400 g ai/ha yielded initial deposits of 0.337 mg/kg in cropped soil which further degraded to 0.121 mg/kg on day 3 of application. The residue was reduced by 64.16 per cent and was not further detected in successive interval on 7th day. For malathion the initial residues in soil were 0.280 and 0.505 mg/kg when sprayed with 750 and 1,500 g ai/ha. The initial deposit residues were reduced to 66.43 per cent on day 7. Dimethoate residues persisted up to 3 days whereas those of malathion remained for 3-7 days in soil.

Keywords: Dimethoate; malathion; residue; tomato; soil

INTRODUCTION

The use of pesticides has become an integral and economically essential part of modern agriculture. Due to the increasing demand for food, modern agriculture has been widely adopted worldwide. Modern agriculture has successfully increased the crop yields and food supply however this has caused disadvantageous impacts to the environment such as soil erosion, contamination of surface and ground waters from pesticides and nitrate-based fertilizers, loss of diversity and increased pest resistance (Lu 2014). Tomato (*Solanum lycopersicum* L) is one of the most popular and widely grown vegetable crops in the world. It is a self-pollinated crop and belongs to family Solanaceae. It is native to central and south America (Vavilov 1951).

Dimethoate and malathion are recommended by the CIBRC for the control of white fly and other sap sucking insect-pests. Dimethoate is a widely used organophosphate insecticide and acaricide. Like other organophosphates, dimethoate is an acetylcholine esterase (AChE) inhibitor and results in tremors, convulsion, respiratory arrest and death. It acts both by contact and through ingestion (Singh 2013). Malathion is a non-systemic and wide spectrum organophosphate insecticide. Malathion is suited for the control of sucking and chewing insects on fruits and vegetables and is also used to control mosquitoes, flies, household insects, animal parasites (ectoparasites) and head and body lice (http://npic.orst.edu/factsheets/malagen.html). Frequent application of pesticides more than the recommended dose affects the soil microflora and fauna resulting in poor soil fertility and ultimately affects crop yield (Sharma et al 2010). Pesticides are often applied several times during one crop season and a part always reaches the soil. Hence to generate persistence data of dimethoate and malathion in tomato-cropped soil the study was carried out by laying supervised field trials. The behaviour of the pesticides in soil depends upon the chemical and physical properties of the pesticide itself, environmental factors such as temperature, precipitation, wind, sunlight, soil properties such as moisture, organic matter, pH, redox status, available nutrients, interactions between solid, liquid and gaseous phases of the soil and between abiotic and biotic components. The physico-chemical nature of the soil is important for persistence, metabolism and binding of pesticides in the soil (Vig et al 2001). The contamination of soil by pesticide chemicals can occur through direct application to control some inhabiting insect pests of a variety of economic plants while indirect avenues can occur through aerial applications, spray drifts, wash-off from the atmosphere, treated plants through precipitation, erosion and run-off from agricultural and forest lands. It is obvious therefore why a great deal of attention must be paid to study the many complex interactions that occur between pesticides and the soil. The fate of pesticides and their behaviour in soil is influenced by several factors including adsorption, movement and decomposition. The breakdown of pesticides in soil is brought about by a variety of biological and non-biological mechanisms; frequently total decay is due to a combination of events (Getenga et al 2000).

MATERIAL and METHODS

Chemicals and reagents

Dr Ehrenstrofer certified reference materials (CRMs) of pesticide standard under study for dimethoate and malathion were procured from their authorized agent M/s J Kundan and Company, Mumbai, Maharashtra, India. All reagents, solvents and absorbents used were of analytical grade and procured locally.

Location and field experiment

The experiment was laid out in randomized block design at the experimental farm of the Department of Entomology, Dr YS Parmar University of Horticulture and Forestry, Nauni, Solan, Himachal Pradesh during the year 2016. Agro-climatically the location falls under the mid-hill zone of Himachal Pradesh. The tomato seeds (*Solanum lycopersicum* L) of variety Solan Lalima were sown in the nursery bed. Mature seedlings after 50 days were transplanted in a plot size of 3.0 × 2.0 m at a planting distance of 60 × 45 cm as per standard package of practices of the university (Anon 2016). The tomato crop was sprayed twice ie the first at fruit initiation stage followed by the second spray at 10 days interval. The fruits and foliage were thoroughly covered with spray fluid to run-off stage. Dimethoate and malathion were sprayed on tomato crop at the recommended rate (RR) and double recommended rate (DRR) using Knapsack sprayer fitted with hollow cone nozzle. Dimethoate was sprayed at the rate of 200 g ai/ha (RR) and 400 g ai/ha (DRR). Malathion was applied at the rate of 750 g ai/ha (RR) and 1,500 g ai/ha (DRR). Untreated plots were sprayed with water only. Each treatment was replicated thrice.

Sampling

Soil samples (1 kg each) from the sprayed field were collected at 0, 3 and 7 days for analysis. At each sampling occasion, soil samples were collected randomly from both the treatment plots and the control plots from different depths ranging from 0-20 cm. The samples were placed into plastic containers and allowed to shade dry at room temperature in the laboratory. The air-dried samples were de-segregated manually using a pestle and a marble mortar, passed through a number 20 mm brass soil sieve and mixed thoroughly to achieve homogeneity.

Extraction and cleanup

Extraction: Soil was analysed by QuEChERS technique with some modifications (Asensio-Ramos et al 2010). A representative 10 g sieved dry soil sample was taken in a 50 ml polypropylene centrifuge tube; 20 ml acetonitrile was added to it and was shaken for up to 1 minute using a Rotospin mixer. Then 4 g of magnesium sulphate and 1 g of sodium chloride were added and centrifuged at 3,300 rpm for 3 minutes.

Cleanup: After centrifugation, a 10 ml of supernatant was taken in another centrifuge tube of 15 ml containing 1.5 g of magnesium sulphate and 0.250 g of primary secondary amine. Thereafter it was shaken for 3 minutes. After shaking the tube was sonicated for 3 minutes and then centrifuged for 10 minutes at 4,400 rpm. Four ml aliquot of the supernatant was taken in a glass turbo tube and evaporated to dryness at 45°C in presence of nitrogen current. The residues were redissolved in 2 ml of n-hexane for analysis by GC-FPD.

Residue estimation

The cleaned extract was analyzed on Shimadzu GC 2010 equipped with capillary glass column, Rxi®-5ms (30 mt, 0.25 mm ID, 0.25 ìm film thickness) coupled with flame photometric detector (FPD). The oven operating parameters in a multi-ramp system were applied. The initial temperature was kept at 170°C for 5 min, raised to 250°C @ 20°C/min having hold time of 10 min followed by increase to 280°C @ 4°C with a hold time of 7 min. Under these operation parameters, retention time of dimethoate and malathion was 7.735 and 9.562 min respectively.

Method validation

The analytical method employed to estimate dimethoate and malathion residues was validated by spiking the control soil samples at four different concentrations viz 0.05, 0.25, 0.50 and 1.00 mg/kg fortification levels each spiking level replicated thrice. The limit of determination (LoD) for dimethoate and malathion was 0.05 mg/kg. The LoD is generally determined by considering a signal-to-noise ratio of 3 with reference to the background noise obtained from blank samples whereas the LoQ was determined by considering a signal-to-noise ratio of 10 by matrix matched standards.

RESULTS and DISCUSSION

Linearity

The linearity studies of dimethoate and malathion at different levels were expressed as correlation coefficients (R^2). The R^2 value of dimethoate was 0.999 (Fig 1a) and for malathion the value was 0.998 showing linear response in mass analyzer at 0.05, 0.1, 0.25 and 1.00 mg/kg (Fig 1b). The values obtained were in accordance with the acceptable limit of >0.99 as established by Hubner (2004).

Efficiency of the method

As evident from the data the recovery of dimethoate from tomato-cropped soil at various fortification levels viz 0.05, 0.25, 0.50 and 1.00 mg/kg was found to be 99.60, 105.12, 100.68 and 102.36 per cent respectively (Table 1). The average per cent recovery from tomato-cropped soil varied from 99.60-105.12 from minimum to maximum fortification level. These results are in the agreement with the average recovery obtained by Getenga et al (2000) where the recovery rate was 90.50 per cent of dimethoate from the spiked garden pea-cropped soil samples at a concentration of 15.53 µg/g. The work done by Manduu (2015) provides conformity to these results who achieved similar trend of recovery of dimethoate ranging 108.02 per cent from French bean soils when spiked with dimethoate at 1.00 mg/kg concentration.

The data presented in Table 1 also reveal the recovery of malathion from tomato-cropped soil at various fortification levels viz 0.05, 0.25, 0.50 and 1.00 mg/kg which was found to be 96.00, 92.72, 96.48 and 103.18 per cent respectively. The average recovery from tomato-cropped soil varied from 92.72-103.18 per cent at all fortification levels. The findings are in agreement with the average recoveries obtained by Getenga et al (2000) who reported the recovery rate of 95.00 per cent of malathion from the spiked garden pea-cropped soil samples at a concentration of 15.53 µg/g.

Persistence and dissipation in soil

Residue dissipation pattern of dimethoate is presented in Table 2 and the analysis showed that the average initial deposit of 0.169 mg/kg in tomato-cropped soil was found to be below the level of determination after 3rd day of treatment/application of dimethoate @ 200 g ai/ha. On the contrary dimethoate application @ 400 g ai/ha on tomato fruit crop yielded initial deposits of 0.337 mg/kg in cropped soil which further degraded to 0.121 mg/kg on day 3 of application and the residue was reduced by 64.16 per cent and was not further detected in successive interval on 7th day. Brar et al (2017) reported average initial deposits of acephate (OP) on brinjal-cropped soil as 0.270 and 0.473 mg/kg at recommended (560 g ai/ha) and double the recommended dose (1,120 g ai/ha) respectively and these residues were reported below the determination limit after 3rd and 5th day. These findings support the results presented on tomato of present finding for dissipation of dimethoate.

The persistence data due to the application of malathion @ 750 g ai/ha on the tomato crop are presented in Table 3. The initial residues of 0.280 mg/kg in the tomato-cropped soil were found below the level of determination after 3rd day of application. But when it was applied @ 1,500 g ai/ha on crop recorded initial deposits of 0.505 mg/kg in tomato-cropped soil which degraded to 0.080 mg/kg at 7 day

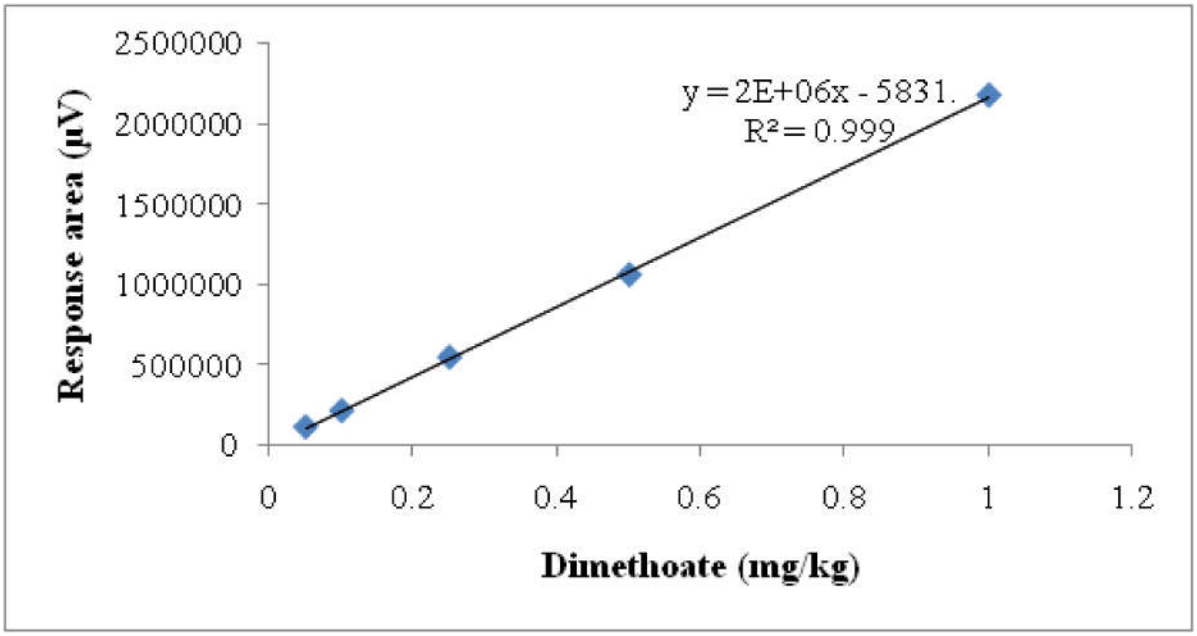

Fig 1a. Linearity of dimethoate

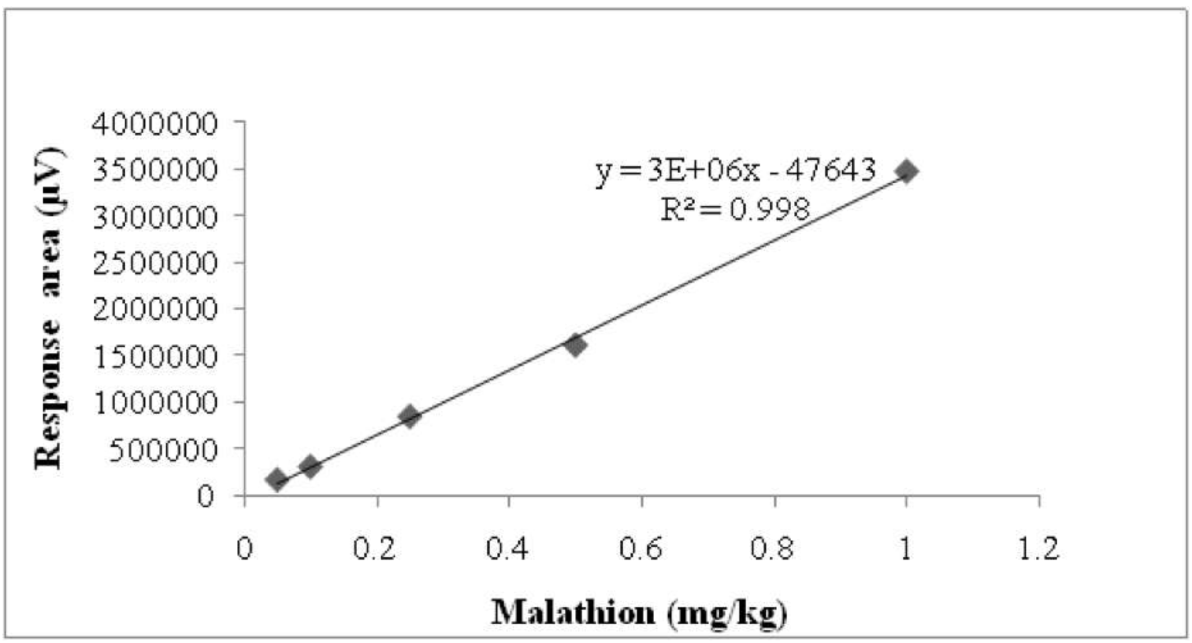

Fig 1b. Linearity of malathion

of application and were found below the limit of determination in successive interval sampling. The initial deposit residues reduced to 66.43 per cent on day 7. Brar et al (2017) reported that when profenophos (OP) was applied on the crop @ 500 g ai/ha, 0.950 mg/kg residues were detected in 0 day sampled soil which reduced to 0.336 and 0.173 mg/kg at 3 and 5 days interval respectively and when applied at double dose (1,000 g ai/ha) showed average initial deposits of 1.423 mg/kg on brinjal-cropped soil which were further reduced to 0.623, 0.463 and 0.213 mg/kg after 3, 5 and 10 day of application respectively.

CONCLUSION

The initial residues of dimethoate were 0.169 mg/kg and 0.337 mg/kg when sprayed @ 200 and 400 g ai/ha respectively. For malathion the initial residues

Table 1. Recovery of dimethoate and malathion from fortified tomato-cropped soil

Fortification level (mg/kg)	Amount recovered ± SD (mg/kg)	Recovery (%)
Dimethoate		
0.05	0.050 ± 0.002	99.60
0.25	0.263 ± 0.016	105.12
0.50	0.503± 0.047	100.68
1.00	1.024± 0.122	102.36
Malathion		
0.05	0.048 ± 0.005	96.00
0.25	0.232 ± 0.030	92.72
0.50	0.482 ± 0.064	96.48
1.00	1.032± 0.105	103.18

Table 2. Dissipation of dimethoate residues from tomato-cropped soil

Interval (days)	Dimethoate (200 g ai/ha)		Dimethoate (400 g ai/ha)	
	Residue (mg/kg) (Mean ± SD)	Dissipation (%)	Residue (mg/kg) (Mean ± SD)	Dissipation (%)
0	0.169 ± 0.007	-	0.337 ± 0.005	-
3	0.055 ± 0.004	67.52	0.121 ± 0.008	64.16
7	BDL	100	BDL	100

Table 3. Dissipation of malathion residues from tomato-cropped soil

Interval (days)	Malathion (750 g ai/ha)		Malathion (1,500 g ai/ha)	
	Residue (mg/kg) (Mean ± SD)	Dissipation (%)	Residue (mg/kg) (Mean ± SD)	Dissipation (%)
0	0.280 ± 0.004	-	0.505 ± 0.011	-
3	0.116 ± 0.004	58.74	0.238 ± 0.007	52.81
7	BDL	100	0.080 ± 0.001	66.43
10	-	-	BDL	100

in soil were 0.280 and 0.505 mg/kg when sprayed @ 750 and 1500 g ai/ha respectively. Dimethoate residue persisted up to 3 days whereas in malathion the residues persisted for 3-7 days in soil.

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