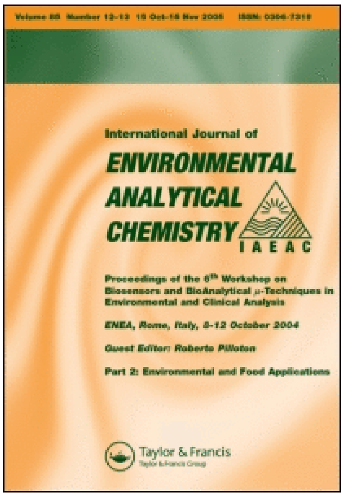

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Impact Monitoring of Residues in Tomato

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Residues of methyl parathion, malathion and fenitrothion were determined in tomato fruits using gas–liquid chromatography. The decline of residues was followed for 14 days. Residues were well below the tolerance limits after 3 days from spraying and show less persistance in the environment. Based on the studies a waiting period is suggested.

KEY WORDS: Residues, pesticides, tomato, GLC, impact monitoring.

INTRODUCTION

There is constant need for environmental monitoring of pesticide residues in the developing countries like India where large amounts of pesticides are being used.[1-3] Recommendations of the Seminar and Workshop in Pesticide Management held in Alexandria, Egypt, give importance to impact monitoring programmes under tropical climates. This paper presents the data about one of such attempts in Madurai, Tamil Nadu, representing semi-tropical climate.

Organophosphorus pesticides are generally preferred to organochlorine pesticides for their effective "Knock-down" effect as well as for their lower persistency in the environment.[4] Three most commonly used organophosphorus compounds (methyl parathion, malathion and fenitrothion) were selected in this study for impact monitoring in tomato fruits.

MATERIALS AND METHODS

Crop and application of insecticides

The experiments were conducted under field conditions on tomato plants. No pesticidal treatment had been attempted in the field previous to our study.

Metacid 50 EC, Malathion 50 EC, Folithion 50 EC, the commercial formulations of methyl parathion, malathion and fenitrothion, were used in field experiments. The insecticidal emulsions were sprayed at commonly recommended doses (Table I). Each treatment with a plot size of 4 × 10 m was replicated three times in a randomized block design. A bakpak hand-operating sprayer was used.

TABLE I

Pesticide	No. of applications	Applied dosage of formulations	Applied dosage of active ingredient	Applied volume of spray	Applied concentration of spray
Methyl parathion	Once before analysis	225 ml/ac	112.5 g/ac	400 l/ac	0.028 %
Fenitrothion	Once before analysis	350 ml/ac	175.0 g/ac	400 l/ac	0.043 %
Malathion	Once before analysis	500 ml/ac	250.0 g/ac	400 l/ac	0.062 %

Sampling

Composite, representative, fruit samples of 200 g were taken for the analysis. Fruits collected at specified intervals were tagged in polythene bags and brought into the laboratory (Table II).

Extraction and clean-up

The extraction and clean-up method described by Mollhaff[5] was followed. Tomato fruits (200 gm) were washed with tap-water and then macerated in a fruit mixer with 300 ml of acetone. The filtered extract was then shaken three times with chloroform. The chloroform extract was stored in a cold room at 4°C in tightly capped reagent bottles. Fortified samples were prepared simultaneously which were analysed along with sample analysis. It was, however, observed that no loss occurred during storage.

Florisil (deactivated) 8 gm was packed in a column. The residue derived by the evaporation of stripping solutions and which was then taken in benzene was loaded and eluted with benzene. The eluted residue samples are then concentrated and taken for GLC determination.

GLC equipped with electron capture detector (^3H) and a glass column packed with 3 % OV 1 on Anakrom-2 was used, nitrogen being the carrier gas (flow rate = 40 ml/min). The temperature schedule of the various ports were as follows: Injector port, 216°C; column port, 160°C; detector port, 160°C. ECD is being mainly used for organochloride pesticides, however,

TABLE II

Residues of pesticides in tomato

Pesticide	Interval between treatment and sampling in days	Residue in ppm average of three replications	Percentage of reduction of residue
Methyl parathion	00	1.12	—
	01	0.32	71.4
	02	0.21	81.3
	03	0.04	96.4
	07	0.04	96.4
	10	0.08	92.9
	14	0.03	99.1
Malathion	00	1.58	—
	01	1.00	36.3
	02	0.75	52.2
	03	0.59	62.4
	07	0.45	71.3
	10	0.56	64.3
	14	0.45	71.3
Fenitrothion	00	1.32	—
	01	0.07	94.7
	02	0.05	96.2
	03	0.05	96.2
	07	0.05	96.2
	10	0.06	95.5
	14	0.06	95.5

Average weather conditions:

Maximum temperature = 31.96°C
Minimum temperature = 21.71°C
Relative humidity = 86.47%
Rainfall = 16.20 mm (5th day of spray)
02.60 mm (6th day of spray).

it was noticed that the three particular OP compounds under study could be detected quantitatively up to a concentration of 10 nanograms.

As much of the interfering compounds of plant origin and others were removed in the clean-up, only the residue due to parental compounds was studied. Moreover, no pesticidal peak as metabolites appeared in our study. This is in agreement with Mollhoff's observations.[6]

Samples of each replicate were injected and the mean residue value of the three replicates were then considered to represent the residue level.

RESULTS AND DISCUSSION

The decline of residues were followed for a period of 14 days. Meteorological data recorded during that period are also given.

The initial deposit of methyl parathion in the fruit was 1.12 ppm. This decreases by 71% (i.e. to 0.32 ppm) in the second day and by 81% (i.e. to 0.21 ppm) in the third day. By about the 14th day the level comes to 0.03 ppm.

Fenitrothion shows an initial deposit of 1.32 ppm This comes to 0.07 ppm even on the 2nd day until a 95% reduction is noticed on the 14th day. An initial deposit of 1.58 ppm noticed in malathion decreases to 1 ppm on the next day (i.e. 36% reduction). Further reduction in the residue levels, on the subsequent days is also found to be slow. A residue value of 0.45 ppm or 28% is noticed even on the 14th day.

Initially an attempt was made to compare the GLC, TLC and colorimetry for the detection of these compounds. As the later methods were found to be less sensitive and variable, GLC was used for residue detection. The retention times of these compounds in GLC are shown in Fig. 1. DDT is shown for comparison. Quantitative recovery and noninterference by plant extract is shown in Fig. 1d.

Methyl parathion with its step-wise, fast degradation attains the safer limit—as per the EPA tolerance limit on tomato (i.e. 1 ppm) on three days.[7]

Fenitrothion appears to be the fastest degrading chemical. To reach the tolerance limit of Japan viz. 0.2 ppm or that of Switzerland[8] viz. 0.75 ppm, fenitrothion takes just one day. An initial deposit of 1.32 ppm reduces by 94.69% in one day to reach a value of 0.07 ppm.

Malathion's rate of degradations is comparatively much slower. The percentage of reduction is so slow that to attain a safer limit of 0.5 ppm, as enforced in Japan[9] it takes more than 3 days.

Generally these results suggest the following:

1. Organophosphorus insecticides are not generally persistent. It agrees with the low values of organophosphorus residues in the food reported in an extensive survey by Abbott *et al.*[10] and Corneliussen.[11]

2. Contrary to the popular opinion that washing may remove all the chemicals sprayed, at least on the "0" day significant amount of residues persist even after washing (Rajakkannu *et al.*[12] and Stobwasser[13]). Due to the high solubility in lipid medium, these organophosphorus pesticides penetrate into the cuticle via the waxy outer layers of fruit.[14] Fenitrothion and methyl parathion behave in

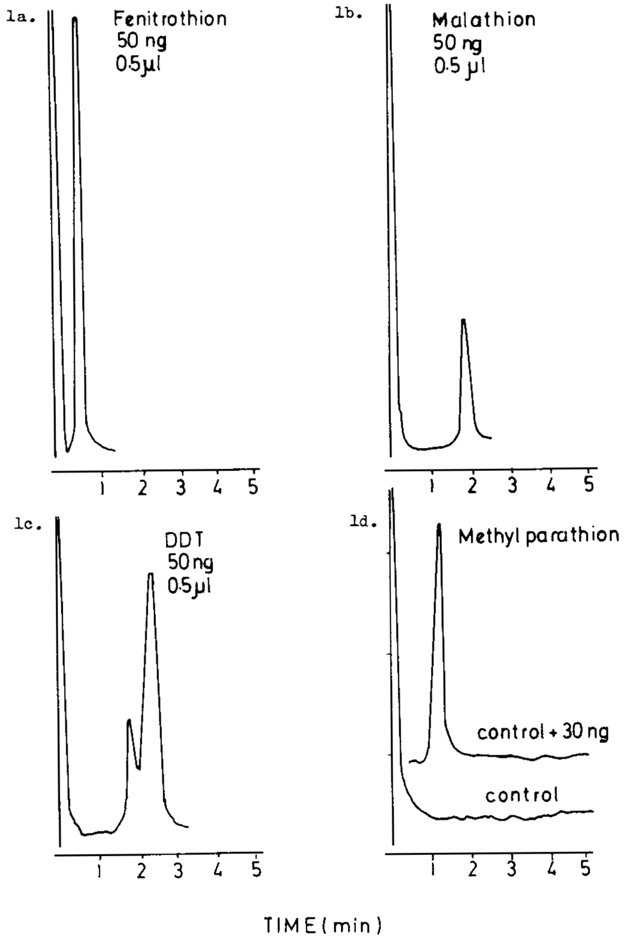

FIGURE 1 Active ingredient separation on GLC.

1a) Fenitrothion: 50 ng, 0.5 µl injection.
1b) Malathion: 50 ng, 0.5 µl injection.
1c) DDT: 50 ng, 0.5 µl injection.
1d) Control sample: 1 µl injection.
Control + 30 ng methyl parathion: 1.0 µl injection.

a similar way in rice, where the residues ranging from 1–7 ppm are detected in the dehusked grains suggesting probably the penetrating capacity.[15]

3. The results when plotted in a semi-log graph give a "biphasic" curve (Fig. 2). It is suggested that the first phase with its characteristic

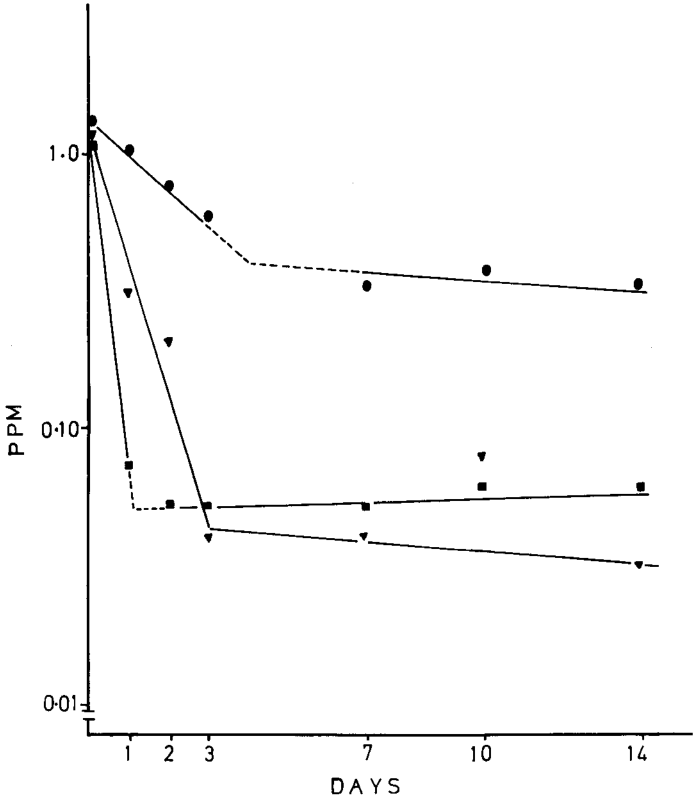

FIGURE 2 Degradation curve for tomato sprayed with methyl parathion, malathion and fenitrothion. ▼—methyl parathion; ●—malathion; ■—fenitrothion.

sharp decline in residue level, may be influenced much by the abiotic factors like the hot tropical solar radiation, temperature, wind, rain, humidity etc. and the much slower second phase is somehow protected from these effects. There is a possibility that the second phase represents the observed residues inside the fruit which is protected by the peel of the fruit from environmental factors and its reduction appears to be mainly by enzymatic action of the plant or other biotic factors.

4. There appears to be a steady but slow increase in the content of fenitrothion in the fruits. One possible explanation for this could be translocation inside the plant or from soil.

Based on the results obtained, a preharvest waiting period of 3 days is suggested ideal.

Acknowledgements

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