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Persistence of Monocrotophos Residues in Greenhouse Tomatoes

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Monocrotophos is the common name of dimethyl (E)-1-methyl-2-(methylcarbamoyl) vinyl phosphate, a fast acting organophosphorus insecticide with both systemic and contact action, used against a wide range of pests including mites, sucking insects, leaf-eating beetles, bollworms and other lepidopterous larvae (British Crop Protection Council 1987). It is used on cultivations of cotton, maize, sugarcane, sugarbeet, vegetables, potatoes and certain fruits.

The degradation behaviour of monocrotophos has been studied in cotton, beans, maize, cabbage and apple (Beynon et al. 1973), grape fruits (Sarode and Krishnamurthy 1990) and other products. Information concerning the persistence of the compound in greenhouse tomatoes is lacking. The recommended monocrotophos preharvest interval in Greece is between 21 and 28 days. However, there is evidence of high residue levels of the compound persisting in grapes after field application (Aplada-Sarlis et al. 1993). The objective of this study therefore, was to obtain data on the degradation behaviour of monocrotophos in greenhouse tomatoes and to study the influence of accumulation resulting from repeated applications.

MATERIALS AND METHODS

The experiment was conducted from September to December 1992 in a greenhouse located in Marathon, 42 km from Athens. Tomato plants of the Caruso variety were planted in August 1992. The experimental area comprised 6 plots, receiving routine horticultural practices. Each single plot consisted of 12 plants, placed in two rows, spaced 0.8m from each other. The distance between two consecutive plants on the row was 0.4m. An aqueous solution of a 40% w/v monocrotophos formulation (Nuvacron^R 40SCW, Ciba-Geigy AG) was applied at rates 40g

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a.i./100 L water (recommended dose) and 80g a.i./100 L water. The solution was applied with a hand gun airblast sprayer to run off. Four of the experimental plots were receiving the recommended dose and the other two double the recommended dose. Application of monocrotophos formulation was performed on October 6 and repeated with 15 days intervals on October 21 and November 4.

Samples collected consisted of twelve fruits, taken at random from each plot, according to FAO/WHO recommendations (1986). Samples were taken one hour following last application, in order to allow enough time for the solution to dry. Samples were also taken 1,2,3,5, 8,12,15,22,29 and 36 days after last application, in order to study the degradation kinetics of the insecticide. For evaluating the accumulation effect, due to repeated sprayings, samples were taken before each application. Samples were also collected periodically from untreated plants, to be used as a control.

As soon as the fruits were picked up, they were put in polyethylene bags and transferred to the laboratory. The fruits were chopped and blended. The blending was thoroughly mixed, 2 sub-samples (50 g of each) were weighted into 100-mL beakers, capped with aluminium foil and kept deep frozen until analyzed.

The analytical method used is a general method suitable for organophosphorus compounds (Ministry of Welfare, Netherlands 1988). According to the method, 50 g of homogenized sample are mixed with 50 g Na_2SO_4 (preheated for 3 hr at 500°C) and 100-mL ethyl acetate. The mixture is blended for 3 min. and the extract filtered. The filtrate is transferred in a sealed flask for gas chromatographic analysis.

A Varian aerograph model 3700 gas chromatograph was used, equipped with a nitrogen-phosphorus detector and a 0.95m x 2mm i.d. glass column containing 3% OV-101, Carbowax 20M treated. The injection port temperature was 210°C, the detector 300°C and the column temperature 170°C. Nitrogen carrier-gas flow rate was 30 mL/min. 1-µL of the sample extract was injected and quantification of monocrotophos was performed by measuring the peak height.

RESULTS AND DISCUSSION

The method of analysis was very simple and fast, allowing as many as 10 samples to be analysed per day. In order to have good repeatability of the pesticide peaks, aliquots (1-2µL) of standard solutions were injected for one hour before injecting the samples. The syringe was solvent-rinsed and 2-µL of ethyl acetate solvent were injected between each calibration standard and sample extract, to reduce apparent residues due to carry-over. The response

of the detector for monocrotophos was linear in the range 0.1-2.0ng, the regression line been y=12.6x-1.39 (N=9), the standard deviations of the slope and the intercept 0.5166 and 0.6152 respectively and the correlation coefficient 0.994. Quantitation of monocrotophos in samples was made by comparing the detector response for the sample to that measured for the calibration standard, within the linear range.

The efficiency of the method was evaluated by spiking control samples with monocrotophos at various concentration levels. Figure 1b shows a gas chromatogram of a fortified tomato sample. The results of the recovery study are presented in Table 1. As seen from this table, average recoveries were from 97 to 113% and relative standard deviations from 1.7 to 7.6%, values within the accepted range (Greve, 1984). The higher value of recovery that was found at the lowest validated level may be attributed to the increased noise effect at that level. The method's limit of determination, evaluated as the product of the standard deviation at the lowest validation level with the Student t-value (U.S., E.P.A. 1984), which at 99% confidence level and for 2 degrees of freedom is 6.96, was found to be 0.02 mg/kg.

Table 1. Mean recoveries* (%) and relative standard deviations (R.S.D.) for monocrotophos in tomatoes, at various fortification levels.

Concentration (mg/kg)	Recovery %	R.S.D.(%)
0.05	113	5.6
0.1	102	7.6
0.2	101	2.1
0.5	102	4.6
1	102	1.7
2	97	4.7
5	104	5.6

* Three samples for each fortification level

As shown in Table 2, maximum concentrations (initial deposits) of monocrotophos on greenhouse tomatoes, were 2.71 and 3.36 mg/kg for the recommended and the double application dose respectively. A rapid loss of residues was observed within one day following application. Volatilization appears to be the major factor in this loss (Vettorazzi 1976), which is approximately 60% in the case of the recommended dose experiment and 40% in the case of the double dose experiment. Between days 1 and 5 following application a very slight increase was observed in residues for both application doses. This increase may be attributed to adhesion of monocrotophos on tomatoes, followed by permeation of the pesticide in the fruits. Between days 5 and 36 following application, residues

Table 2. Monocrotophos residues (mg/kg) ± standard deviation in tomatoes at intervals (days) after application. The reported values are the means of duplicate analyses from four replicates (application dose 40g a.i./100 L) or two replicates (application dose 80g a.i./100 L)

Day	Application dose	
	40g a.i./100L	80g a.i./100L
0	2.71 ± 0.332	3.36 ± 0.092
1	1.07 ± 0.042	1.90 ± 0.106
2	1.39 ± 0.067	1.81 ± 0.665
3	1.20 ± 0.218	1.86 ± 0.354
5	1.51 ± 0.396	1.95 ± 0.028
8	1.02 ± 0.280	1.35 ± 0.723
12	1.15 ± 0.270	1.56 ± 0.459
15	0.85 ± 0.123	1.35 ± 0.078
22	0.84 ± 0.078	1.18 ± 0.269
29	0.67 ± 0.048	1.06 ± 0.071
36	0.56 ± 0.141	0.91 ± 0.048

declined linearly, related to time. The equations of the regression lines were $y = 1.40 - 0.025x$ and $y = 1.82 - 0.027x$ for the results of the recommended and the double application dose respectively. The correlation coefficients were $r = -0.893$ and $r = -0.888$ respectively, statistically significant at $P = 0.01$, indicating a high correlation. This linear decrease in residues suggests that monocrotophos dissipation at that stage may be attributed to degradation by mainly chemical mechanisms. No monocrotophos residues were found in all the control samples analysed (Figure 1a).

The percentage dissipation of monocrotophos residues 36 days after last application was 80% and 73% when sprayed at the recommended and the double dose respectively, but monocrotophos levels still remained relatively high, i.e. 0.56 and 0.91 mg/kg for each application dose. However, these values are both lower than the maximum residue limit (MRL) set by the Codex Alimentarius Commission (FAO/WHO) for monocrotophos in tomatoes, which is 1 mg/kg. Nevertheless, this is not the case, when comparing these values to the national MRLs of many European countries which are between 0.05 and 0.1 mg/kg.

Table 3 presents the effect of repeated applications, at 15-day intervals, on monocrotophos residues in tomatoes. As seen from the data, the first application had no effect on monocrotophos residues. This happened because the tomato fruits, by that time, were at the growing stage and there was therefore a high dilution effect. However following the second application, when the fruits

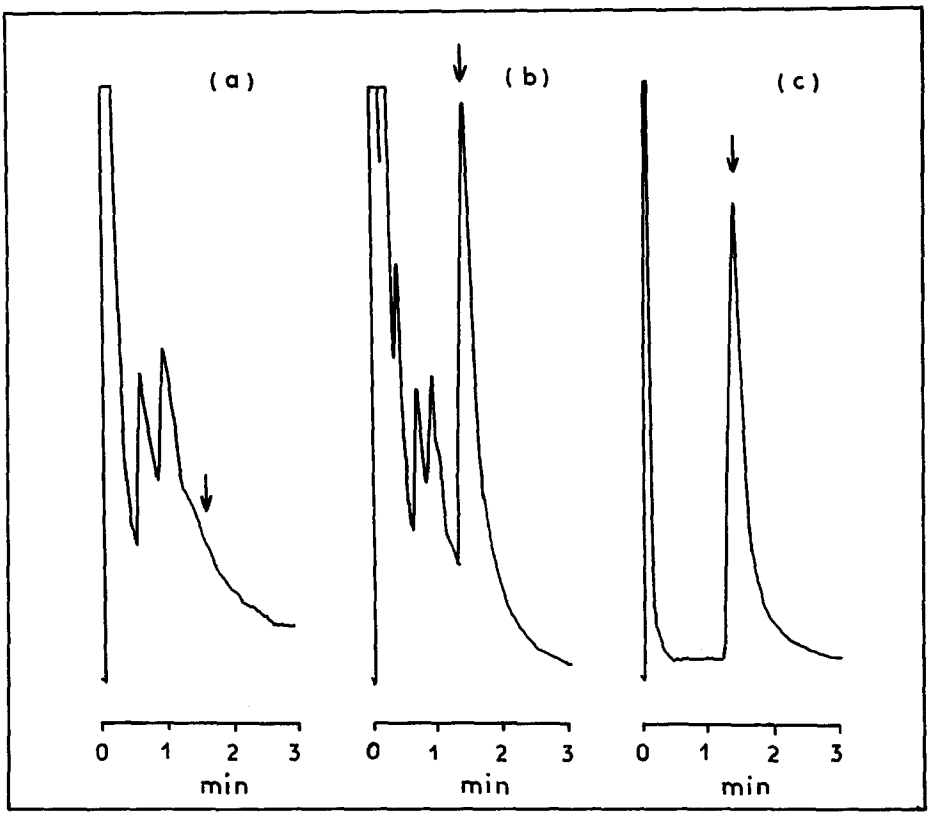

Figure 1. 1-μL gas chromatograms of a) Control tomato sample b) Fortified control tomato sample with 0.2 mg/kg monocrotophos c) 1 ng monocrotophos reference standard

were at the harvesting period and mature, a significant accumulation effect is observed for both application doses.

The above results seem to show that monocrotophos has a high persistence on greenhouse tomatoes and should be used with care, avoiding repeated sprayings, especially on mature fruits, and in any case sufficiently long time should elapse before harvesting.

Table 3. Monocrotophos residues* (mg/kg), 15 days after the last of repeated, at 15-day intervals, applications.

No of applications	Application dose	
	40g a.i./100L	80g a.i./100L
1	1.31	1.78
2	0.25	0.47
3	0.85	1.35

*The reported values are the means of duplicate analyses.

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