Study of Procymidone and Propargite Residue Levels Resulting from Application to Greenhouse Tomatoes

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Levels of procymidone and propargite residues were studied in an experiment in greenhouse tomatoes. The pesticides were applied according to recommended application procedures in Greece. Tomatoes received six sprayings with procymidone, at 10-day intervals, at rate of application 62.5 g of ai/100 L and a single spraying with propargite, at rate of 60 g of ai/100 L. In separate experimental plots double doses were applied, according to the same scheme. Residues were determined with a simple gas chromatographic method; the recovery of procymidone from tomatoes was 85–104% and of propargite 94–107%; the limits of determination were 0.005 mg/kg for procymidone and 0.01 mg/kg for propargite. Procymidone residues were very persistent, and a detectable decline was observed only 35 days after the last application. Repeated applications of procymidone showed a significant residue accumulation effect in tomatoes. Propargite residues were found to decline slowly with time. The results show that the recommended preharvest interval in Greece, which is 3 days for both pesticides should be reconsidered in the case of procymidone with repeated applications.

Keywords: *Procymidone, propargite, residues, dissipation, accumulation, greenhouse tomatoes*

INTRODUCTION

Procymidone is the common name of a preventive, curative, and persistent dicarboximidic fungicide with moderate systemic activity. It is used against *Botrytis*, *Cochliobolus*, *Helminthosporium*, and *Sclerotinia* spp. on field crops, fruits, and vegetables, particularly in greenhouses (British Crop Protection Council, 1987). Propargite is the common name of a nonsystemic acaricide with predominantly contact action and long residual activity. It is effective for the control of many species of phytophagous mites on a variety of crops including cotton, fruit trees, vegetables, maize, cucumbers, and others (Royal Society of Chemistry, 1989).

In Greece both pesticides are known to be used on greenhouse tomatoes. Procymidone is usually applied repeatedly, at 7–14-day intervals, while propargite has a 40-day application interval and is therefore usually applied only once. The recommended preharvest interval (PHI), in Greece, i.e., the number of days from the final application to harvest, for this crop is 3 days for both pesticides. However, the known persistence of both pesticides suggested that this value, which is not supported by experimental data, should be evaluated on a more realistic basis. The objective of this study was therefore to obtain data on the levels of deposit and the dissipation rates of residues of the two pesticides, to re-evaluate the PHIs already established in Greece, and to study the influence of repeated applications on accumulating procymidone residues.

MATERIALS AND METHODS

Field Experiments. The different modes of action of the two pesticides used allowed the application of both on the same plants. The experiment was conducted in a greenhouse located in Marathon, 42 km from Athens, from September to December 1992. Tomato plants of the Caruso variety were planted in August 1992. The experimental area comprised 6 plots, receiving routine horticultural practices, and irrigation of plants was done by the drip method. Each single plot consisted of 12 plants, placed in two rows spaced 0.8 m from one another. The distance between two consecutive plants in the row was 0.4 m. Four of the experimental plots received the recommended application doses (RD) and the other two double the recommended doses (DD). Application was performed with a hand gun airblast sprayer to run off. The daily minimum air temperatures recorded in the greenhouse during the trial were 12–14 °C in September, 10–16 °C in October, 2–11 °C in November, and 3–8 °C in December. The corresponding maximum temperatures were 33–36 °C in September, 29–36 °C in October, 26–31 °C in November, and 24–29 °C in December.

An aqueous solution of a 50% (w/w) procymidone formulation (Sumisclex 50WG, Sumitomo) was applied at rates of 62.5 (RD) and 125 g of ai/100 L of water (DD). Applications of the procymidone formulation were performed on September 28 and repeated, at 10-day intervals, on October 8, 19, and 29 and November 9 and 19.

An aqueous solution of a 30% (w/w) propargite formulation (Omite 30 W.P., Uniroyal) was applied at rates of 60 (RD) and 120 g of ai/100 L of water (DD). A single application of the propargite formulation was performed for each dose on November 17.

Sampling and Storage. Sampling was performed by collecting randomly 12 fruits from each plot, according to FAO/WHO (1986) recommendations. Samples were also collected periodically from untreated plants, to be used as control. The collected fruits were put in polyethylene bags and transferred to the laboratory. The fruits were chopped and blended, and the homogenized material was refrigerated in glass jars until analysis.

Samples were taken 1 h following the last application of the procymidone formulation, to allow enough time for the solution to dry. Samples were also taken 1, 2, 3, 4, 7, 14, 21, 28, and 35 days after the last application, to study the dissipation of the fungicide. For evaluating the accumulation effect of procymidone due to repeated sprayings, samples were also taken before each application.

Samples were taken 1 h following the application of the propargite formulation. To study the dissipation of the acaricide, samples were also taken 1, 2, 3, 6, 13, 20, 27, and 34 days following its application.

Analytical Procedure. The general method of Ambrus et al. (1981) was followed for the extraction. According to the method, 150 mL of acetone was added to 50 g of homogenized sample and the mixture blended at high speed. The extract was filtered through a Büchner funnel; rinsed with 50 mL of acetone, and transferred into a 1-L separatory funnel; 450 mL of a 4% Na_2SO_4 solution was added in the funnel, and the two pesticides

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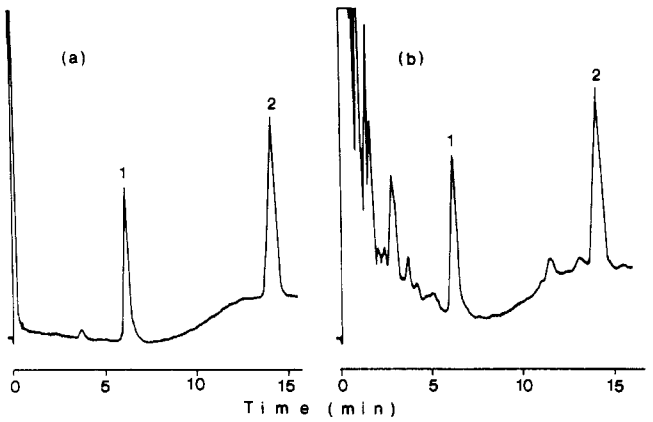

Figure 1. One-microliter gas chromatograms of (a) 0.5 ng of procymidone (peak 1) and 5 ng of propargite (peak 2) (reference standards) and (b) fortified control tomato sample with 0.1 mg/kg procymidone and 1 mg/kg propargite.

were extracted with 100-, 50-, and 50-mL portions of CH_2Cl_2. The extract was filtered through Na_2SO_4, the filtrate was evaporated to dryness by use of rotary evaporator, and 4 mL of toluene was added. For the cleanup of the samples, a suspension of 1 g of activated charcoal and 4 g of silanized Celite was placed in a 18 mm i.d. column, toluene was allowed to flow through the column, and the sample extract was then added. The two pesticides were eluted with 150 mL of CH_2Cl_2. The eluate was concentrated to ca. 2 mL and, after 2 × 10 mL of acetone was added, evaporated to dryness. Ten milliliters of acetone was added and the extract transferred to a sealed vial for gas chromatographic analysis.

Gas Chromatographic Determination. A Varian 3700 gas chromatograph was used, equipped with a ^{63}Ni electron capture detector and a 0.95 m × 2 mm i.d. glass column containing 3% OV-101, Carbowax 20M treated. The injection port temperature was 210 °C and that of the detector 300 °C; the column temperature was programmed from 160 (7 min) to 180 °C (5 min) at a rate of 3 °C/min. Nitrogen carrier gas flow rate was 30 mL/min. One microliter of a proper dilution of the sample extract was injected directly in the gas chromatograph, and quantitation of the pesticides was performed by measuring the peak height.

RESULTS AND DISCUSSION

Determination and Recoveries. The response of the detector was linear for procymidone in the range 0.05–0.5 ng and for propargite in the range 0.5–6 ng. The equations of the regression lines were, respectively, $y = -0.937 + 22.5x$ and $y = -0.884 + 2.69x$ and the correlation coefficients 0.989 and 0.995. Quantitation of both pesticides in samples was made by comparing the detector response for the sample to that measured for the calibration standard within the linear range.

The recovery of the pesticides from tomatoes was determined by spiking control samples with the pesticides at various concentration levels. Figure 1a shows a gas chromatogram of a fortified tomato sample. Table 1 presents the results of the recovery study. All values in this table are within the accepted range for residue determinations (Greve, 1984). 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. EPA, 1984), which at 99% confidence level and for 2 degrees of freedom is 6.96, was found to be 0.005 mg/kg for procymidone and 0.01 mg/kg for propargite.

Levels of Residues. Table 2 shows the residues of procymidone found in tomatoes after the last application and the residues of propargite after the sole application. As shown from this table initial deposits of procymidone on tomatoes were 9.25 and 17.0 mg/kg for the recommended and the double-application doses, respectively. Thereafter, procymidone residues remained relatively stable for 28 days for both application doses and declined considerably (approximately 45%) between 28 and 35 days following application. On the contrary, propargite residues declined slowly with time from 0.95 (RD) and 2.13 mg/kg (DD) initial deposits to 0.42 (RD) and 1.05 mg/kg (DD) 34 days after application. The percentages of dissipation of propargite residues, 34 days after application, were 56% (RD) and 51% (DD).

Procymidone residues in tomatoes sprayed at the recommended dose were approximately as low as the maximum residue limit (MRL) of 5 mg/kg, suggested by the Codex Alimentarius Commission of FAO/WHO (1992) only 35 days after the last application at the recommended dose. However, these residues exceeded 2 mg/kg, which is the MRL set by the EEC (1993). On the contrary, propargite residues in tomatoes, when sprayed at the recommended dose, were always lower than the MRL of 2 mg/kg, suggested by FAO/WHO (1992), but tomatoes contained residue values lower than the MRL of 0.5 mg/kg, set by some European countries (Royal Society of Chemistry, 1989), only 34 days after application. For this acaricide no EEC MRL has been established.

Repeated Sprayings. Table 3 presents the effect of repeated applications, at 10-day intervals, on procymidone residues in tomatoes. The results of this table show that the practice of successive applications of procymidone leads to significant increase of the residue levels, even in the case of tomato fruits at the growing stage, when a dilution effect due to growing exists. It is also seen that 10 days after a single application, the fungicide shows residue levels in tomatoes of 0.67 (RD) and 1.60 mg/kg (DD), values lower than the MRLs of FAO/WHO and of many European countries. These findings are in accordance with the results of another study using an HPLC method (Cabras et al., 1985).

Table 1. Mean Recovery[a] ± Relative Standard Deviation for Procymidone and Propargite in Tomatoes at Various Fortification Levels

procymidone		propargite	
addition (mg/kg)	recovery (%)	addition (mg/kg)	recovery (%)
0.01	104 ± 6.9	0.1	95 ± 1.8
0.02	85 ± 4.2	0.25	97 ± 3.0
0.05	90 ± 5.6	0.5	94 ± 3.0
0.1	90 ± 10.0	1	107 ± 5.3
1	91 ± 3.8	2.5	104 ± 4.3
5	85 ± 1.2	5	96 ± 1.9
20	86 ± 7.8		

[a] Three samples for each fortification level.

Table 2. Residues[a] (Milligrams per Kilogram) in Tomatoes at Intervals after the Last of Six Applications (Procymidone) or the Sole Application (Propargite)

procymidone			propargite		
day	RD[b]	DD[c]	day	RD	DD
0	9.25 ± 1.91	17.0 ± 2.40	0	0.95 ± 0.39	2.13 ± 0.07
1	10.4 ± 1.25	14.7 ± 0.21	1	0.85 ± 0.16	1.87 ± 0.32
2	9.77 ± 1.42	15.1 ± 2.97	2	0.80 ± 0.21	2.05 ± 0.69
3	9.51 ± 1.58	15.6 ± 2.54	3	0.81 ± 0.14	1.83 ± 0.49
4	9.50 ± 1.42	15.0 ± 2.12	6	0.79 ± 0.26	2.10 ± 0.86
7	10.4 ± 2.65	15.3 ± 2.05	13	0.78 ± 0.33	2.02 ± 0.39
14	10.4 ± 1.04	13.2 ± 0.35	20	0.71 ± 0.10	2.05 ± 0.20
21	9.30 ± 0.77	14.0 ± 4.24	27	0.66 ± 0.15	1.82 ± 0.57
28	10.2 ± 1.28	14.2 ± 0.64	34	0.42 ± 0.04	1.05 ± 0.39
35	5.39 ± 0.49	8.45 ± 2.90			

[a] Means of duplicate analyses from four replicates (RD) or two replicates (DD). [b] Recommended dose. [c] Double dose.

Table 3. Procymidone Residues[a] (Milligrams per Kilogram) in Tomatoes 10 Days after the Last of Repeated, at 10-Day Intervals, Applications

no. of applications	crop stage	application dose RD	application dose DD
1	growing	0.67	1.60
2	growing	1.08	2.09
3	growing	4.66	4.80
4	mature	5.90	8.35
5	mature	9.31	12.5
6	mature	10.4[b]	14.4[b]

[a] The reported values are the means of duplicate analyses. [b] Values estimated from the data of Table 2 by interpolation.

Conclusions. The high residue values found in tomatoes after successive applications with procymidone may be attributed to accumulative effect and the stability of the fungicide for 28 days to the absence of (a) any dilution effect, since the tomatoes were already mature and (b) environmental factors such as wind, rain, and ultraviolet solar irradiation, since the experiment was carried out in a greenhouse. These findings for procymidone suggest that either the maximum number of applications should be limited or the recommended preharvest interval in Greece should be adjusted. On the contrary, the relatively low residue values of propargite in tomatoes suggest that the established preharvest interval in Greece of 3 days of the acaricide in tomatoes is satisfactory, as far as the FAO/WHO MRL is considered.

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