Disappearance of Tetradifon from Field-Sprayed Apricots and the Apricot Juice Produced from Them

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The disappearance of tetradifon residues was studied in an experiment on field-sprayed apricots. The pesticide was applied according to the recommended application procedures in Greece. Apricots received a single application with tetradifon at rates of 11.56 and 14.45 g of ai/100 L. Residues were determined with a simple gas chromatographic method; the recovery of tetradifon from apricots was found to be 99–105% and the limit of determination 0.004 mg/kg. Tetradifon residues were found to dissipate relatively rapidly, with a half-life of 7 days, and in all cases the residues were lower than the maximum residue limits of most European countries. The transfer of tetradifon residues from the fruits into the apricot juice produced from them, after processing, was approximately 20% of the total residues of the fruit.

Keywords: *Tetradifon; residues; dissipation; apricots; apricot juice*

INTRODUCTION

Tetrafidon is the common name of 4-chlorophenyl 2,4,5-trichlorophenyl sulfone, a nonsystemic, long-acting acaricide that penetrates through the plant tissue (British Crop Protection Council, 1987). It exhibits contact action on eggs and larvae of *Brevipalpus, Tetranychus, Bryobia, Panonychus*, and other species of tetranychid mites, including the resistant strains. It also acts indirectly by sterilization of females, leading to the development of nonviable eggs. It is used on fruit trees including citrus and nuts, vines, vegetables, cotton, field crops, and ornamentals (Royal Society of Chemistry, 1989).

Tetradifon has approved uses in 10 of the 12 countries of the European Union (EU). A common application in Greece is on apricot trees. Apricot is a significant crop tree in Greece, cultivated mainly in the Peloponnese peninsula, and a major part of the total apricot production is processed by the local juicing industries. Residues of tetradifon, due to its field application, may appear in the apricot fruits, as well as in the apricot juice produced after processing. Apricot juice exported to Germany, in 1992, was found to contain tetradifon residues. Tetradifon is not used in Germany, and since no acceptable daily intake has been established yet by FAO/WHO for this pesticide, the maximum residue limit (MRL) set now in Germany for tetradifon is the analytical detection limit, that is 0.01 mg/kg. Much higher MRLs have been set for tetradifon in fruits by other countries, e.g. 1.5 mg/kg in Italy, 2 mg/kg in Sweden, and 3 mg/kg in Switzerland. No MRL has been set by the EU for this acaricide.

The degradation behavior of tetradifon has been studied extensively by Gunther (1969) in citrus fruits of California. Information concerning the persistence of the compound in apricots and its residues in the resulting apricot juice is lacking. In Greece and other European countries the recommended preharvest interval (PHI), i.e. the number of days from the final application to harvest, for tetradifon in apricots is 14 days. The objective of this study was therefore to obtain data on the degradation behavior of tetradifon in apricots. These data are also required by the EU procedure to set the MRL for tetradifon in this crop. Since apricot juice is a major export product of Greece, the removal of tetradifon residues in the processing of apricots into apricot juice was also examined.

MATERIALS AND METHODS

Field Experiment. The field experiment was carried out in 1993, in an apricot orchard at Era, near Nauplion (southern Greece). The experimental area comprised seven plots, of eight trees each, receiving routine horticultural practices. The age of the trees was approximately 20 years. An aqueous emulsion of a 5.78% w/v tetradifon formulation (Mition C EC, Sipcam, Italy) was applied at rates of 11.56 g of active ingredient (ai)/100 L of water, which is the lowest recommended application dose (LRD), and 14.45 g of ai/100 of water, which is the highest recommended application dose (HRD). Three of the experimental plots received the LRD, three received the HRD, and one was not treated with tetradifon, to be used as a control. The emulsion was applied with a motorized mistblower, and the trees were sprayed to runoff. Application of tetradifon formulation was performed on June 14, when the fruits were at the growing stage. There was no rainfall at anytime during the experimental period. The average minimum daily temperatures, during the experiment, were from 11 to 16 °C, and the average maximum ones from 28 to 41 °C.

Sampling, Processing, and Storage. Sampling was performed by randomly collecting 48 apricot fruits from various places of the eight trees of each plot, according to FAO/WHO (1986) recommendations. Samples were taken 1 h following application, to allow enough time for the emulsion to dry, for determining the initial deposit (0 days) of the pesticide on apricots. Samples were also taken 2, 4, 7, 10, 14, 18, 22, 28, and 32 days following application, to study the dissipation of the acaricide. The commercial harvest took place on July 8 and 9, that is 23 and 24 days, respectively, following the application; samples collected by that time consisted of fruits at the development stage, while later samples consisted of fully mature fruits.

Each sample taken was divided into two equal portions. The first one was forwarded to the laboratory, chopped after the stone was removed, and blended, and the homogenized material was refrigerated in glass jars until analysis. The second portion was processed in a nearby juicing plant to produce apricot juice, by using a technique that simulated the production line of the industry. According to that technique, the apricot fruits were washed by dipping into water, the stones were removed, and the remaining fruits were chopped in a blender. The resulting pulp was heated at 90 °C for 1.5 min and filtered (pore size ~1 mm) to produce apricot juice. The juice was pasteurized at 95 °C for 3 min and, after cooling, refrigerated at −18 °C in glass jars until analysis, which was conducted within 2 months.

Analytical Procedure. All samples were analyzed by a general method suitable for electron-captive compounds (Ministry of Welfare, Health and Cultural Affairs, 1988), properly modified. According to the method, 50 g of the sample was

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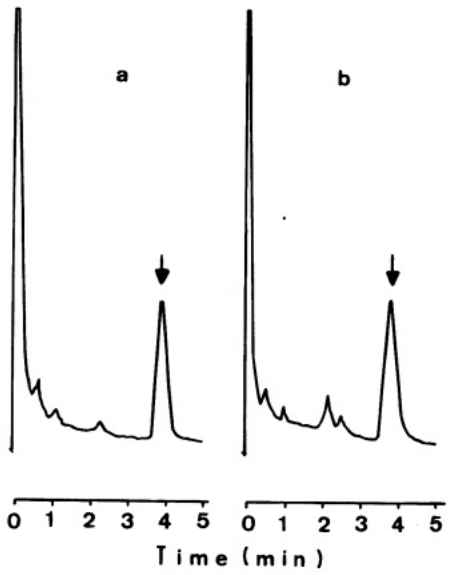

Figure 1. One microliter gas chromatograms of (a) 0.05 ng of tetradifon reference standard and (b) fortified control apricot sample with 0.5 mg/kg tetradifon. Tetradifon is indicated with the arrow.

Table 1. Mean Recovery[a] and Relative Standard Deviation (RSD) for Tetradifon at Various Fortification Levels

concn (mg/kg)	recov (%)	RSD (%)	concn (mg/kg)	recov (%)	RSD (%)
0.01	102	5.7	0.5	103	5.5
0.05	101	6.0	1	100	4.4
0.1	99	4.8	2	101	12.8
0.2	105	3.2			

[a] Three samples for each fortification level.

mixed with 100 mL of toluene and 50 mL of 2-propanol. The mixture was blended for 3 min and the extract filtered through Whatman No. 1 filter paper into a separatory funnel, where it was washed with 2 × 250 mL of 2% Na_2SO_4 solution. The washed extract was filtered through anhydrous Na_2SO_4 in a volumetric flask, of suitable volume, so that the final concentration of tetradifon was brought into the linear range of the detector.

Gas Chromatographic Determination. A Varian 3700 gas chromatograph was used, equipped with a Ni-63 electron capture detector and with a 0.95 m × 2 mm i.d. glass column containing 3% OV-101, on Chrom WAW 100/120 mesh support, Carbowax 20M (Chrompack) treated. The injection port temperature was 220 °C, the detector temperature 300 °C, and the column temperature 200 °C. Nitrogen carrier gas flow rate was 30 mL/min. One microliter of the sample extract was injected, and quantification of tetradifon was performed by measuring the peak height.

RESULTS AND DISCUSSION

Determination and Recovery. The method of analysis was simple and fast, as is essential for routine analysis. The response of the detector for tetradifon was linear in the studied range 0.005−0.1 ng, the equation of the regression line being $y = -0.863 + 195x$ (N = 12), the standard deviations of the slope and the intercept 3.87 and 0.177, respectively, and the correlation coefficient 0.998. Quantitation of tetradifon in samples was made by comparing the detector response for the sample to that measured daily for the calibration standard within the linear range.

The efficiency of the method was evaluated by spiking control samples with tetradifon at various concentration levels, covering the whole range of tetradifon concentrations in the samples. Figure 1b shows a gas chromatogram of a fortified apricot sample. The results of the recovery study are presented in Table 1. As seen from

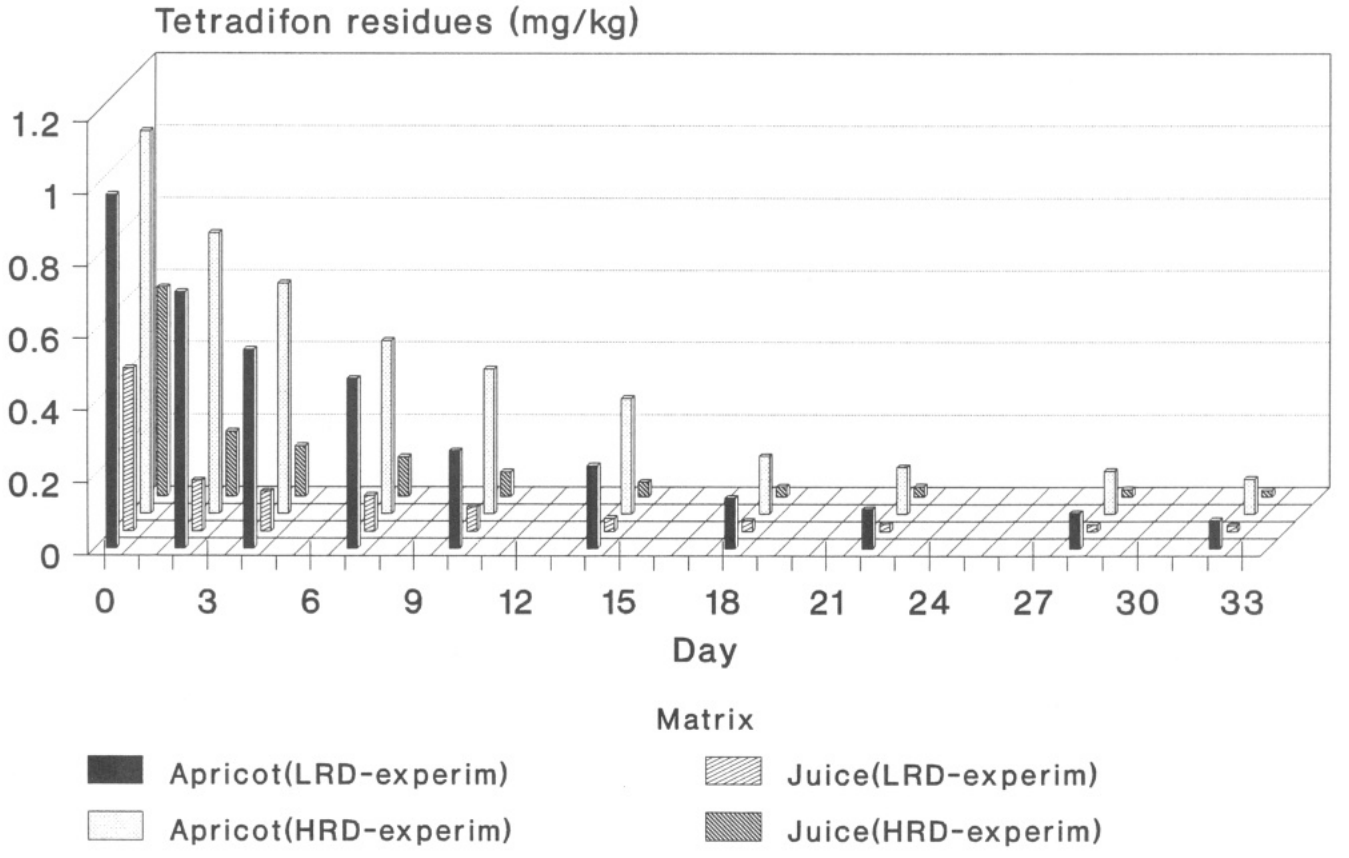

Figure 2. Tetradifon residues (mg/kg) in apricots and the juice resulting from them, at various time intervals following application. LRD, low recommended dose (11.56 g of ai/100 L); HRD, high recommended dose (14.45 g of ai/100 L).

this table, average recoveries were from 99 to 105% and relative standard deviations from 3.2 to 12.8%, values 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 0.004 mg/kg.

Disappearance of Residues. All control apricot samples that were collected at various sampling dates and consequently all apricot juice samples produced by processing the control apricots, according to the described technique, were found to contain no detectable tetradifon residues. Tetradifon residues in apricots and the apricot juice resulting from them at various time intervals following application are shown in Figure 2. The residues of tetradifon in this figure are those found in the edible portion of the fruits, after the stones were removed. This facilitates the comparison of the residues found in the fruits and in the juice produced by them (the weight of the stones was found to correspond to approximately 10% of the total fruit weight). As seen in Figure 2, initial deposits of tetradifon on apricots were 0.98 mg/kg for the LRD experiment and 1.06 mg/kg for the HRD experiment. Thereafter, tetradifon residues declined steadily with time, and 32 days after application 8 and 9%, respectively, of the initial deposits are only found in the whole fruit samples for the LRD and HRD experiments. The residue losses may be attributed to volatilization during the first days following application, or to removal by weathering, heat decomposition, and UV radiation by the sunlight, or to growth dilution between application and sampling (growth factor = 1.7). However, as seen from the same figure, residues in apricots declined much more slowly after the 18 days following application, and this is possibly because apricots were mature by that time and there was no further growth dilution effect on the residues. Tetradifon half-life in apricots, as evaluated from the dissipation lines, was found to be 7 days for both application doses, indicating that it is independent of the initial deposit. In all cases, including the 0-day samples, tetradifon residues in apricots were lower than the previously mentioned MRLs set by most European countries.

From Figure 2 it is also seen that tetradifon residues are only partially transferred from the apricots into the juice produced from them. Therefore, while approximately 50% of the residue was transferred into the juice from the 0-day apricots, only 20% of the residue was transferred to the juice for the apricots collected between 2 and 32 days after application. The high residue transfer in the juice for the 0-day apricots may be attributed to the fact that adhesion of tetradifon on apricots was not yet complete. However, by the time adhesion and permeation of tetradifon in the fruits were more complete, and as the results demonstrate, tetradifon residues were concentrated mostly in the solid commodity of the fruit rather than in the juice product.

In conclusion, the above data indicate that the use of tetradifon in apricots does not result in levels of residue above the MRLs set by several European countries. Furthermore, only 20% of the residue is transferred into the juice after processing of the fruits.

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