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Dicofol Residues on Field Sprayed Apricots and in Apricot Juice

K. S. Liapis, G. E. Miliadis, P. Aplada-Sarlis

Pesticide Residues Laboratory, Benaki Phytopathological Institute, 7 Ekalis Street, 145 61 Kifissia, Athens, Greece

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Dicofol is the common name of 2,2,2-trichloro-1,1-bis-(4-chlorophenyl)ethanol, a non-systemic organochlorine acaricide with contact action and little insecticidal activity (British Crop Protection Council 1987). It is recommended for control of bryobia mites, red spider mites, sweet cherry spider mites (*Tetranychus viennensis*), two-spotted spider mites, *Eriophyes* spp. plum rust mites (*Aculus fockeni*), and other spider mites. It is used on cultivations of citrus and other fruits, tomatoes, cucurbis and other vegetables, cotton, tobacco and other field crops, and ornamentals (Royal Society of Chemistry 1989).

The degradation behaviour of dicofol has been studied in tomatoes (Cabras et al. 1985), citrus (Van Dyck 1975), pear fruits (Rawash et al. 1975), tea leaves (Rajukkannu et al. 1981). Information concerning the persistence of the compound in apricots and its residues in the resulting apricot juice is lacking. The recommended in Greece preharvest interval (PHI), i.e. the number of days from the final application to harvest, for dicofol in apricots is 14 days. The objective of this study was to obtain data on the degradation behaviour of dicofol in apricots, a significant crop in Greece in which dicofol is known to be used widely. These data are also required by the European Union procedure to set maximum residue limit (MLR) for dicofol in this crop. Since apricot juice is a major export product of Greece, the removal of dicofol residues after processing the apricots into apricot juice was also examined.

MATERIALS AND METHODS

The field experiment was carried out in June and July 1993 in an apricot orchard at Era, near Nauplion (Southern Greece). The experimental area comprised 7 plots of eight trees each, receiving routine horticultural practices. An aqueous emulsion of a 15.4% w/v dicofol formulation was applied at rates 30.8 g a.i./100L water, which is the lowest recommended dose (LRD), and 38.5 g a.i./100L water, which is the highest recommended dose (HRD). Three of the experimental plots received the LRD, three received the HRD and one was not treated, to be used as a control. The emulsion was applied with a hand gun airblast sprayer and the trees were sprayed to run off. Application of dicofol formulation was performed on June 14. Sampling was performed by collecting randomly 48 apricot fruits from various

Correspondence to: G. E. Miliadis

places of the eight trees of each plot, according to FAO/WHO recommendations (1986). Samples were taken 1 hour following application, in order to allow enough time for the emulsion to dry, for determining the initial deposit of the pesticide on apricots. Samples were also taken 2,4,7,10,14,18,22,28 and 32 days following application, in order 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 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 in two equal parts. The first part was forwarded to the laboratory, chopped, blended and the homogenized material was refrigerated in glass jars until analysis. The second part was processed, in a juicing industry, to produce apricot juice, by using a technique which was simulated to the production line of the industry. According to that technique, the apricot fruits were washed by dipping in water and the stones were removed. The fruits were chopped in a blender, the resulting pulp was heated at 90°C for 90 sec. and filtered through a linen to produce apricot juice. The juice was pasteurized at 95°C for 3 min. and, after cooling, refrigerated in glass jars until analysis.

All samples (apricots and juice) were analyzed by a general method suitable for electron-captive compounds (Ministry of Welfare, Netherlands 1988), properly modified. According to the method, 50g of the sample are mixed with 100 mL toluene and 50 mL propanol-2. The mixture is blended for 3 min. and the extract filtered in a separatory funnel, where it is washed with 2x250 mL solution of 2% Na_2SO_4. The washed extract is filtered through anhydrous Na_2SO_4 in a volumetric flask, ready for gas chromatographic analysis. A Varian aerograph model 3700 gas chromatograph was used, equipped with an electron capture detector and a 0.95m x 2mm i.d. glass column containing 3% OV-101, Carbowax 20M treated. The injection port temperature was 220°C, the detector 300°C and the column temperature 160°C. Nitrogen carrier gas flow rate was 30 mL/min. 1-μL of the sample extract was injected and quantification of dicofol was performed by measuring the peak height.

RESULTS AND DISCUSSION

The method of analysis was very simple and fast, as it is essential for routine analysis. The response of the detector for dicofol was linear in the range 0.01-0.3 ng, the regression line been $y=0.133 + 58.7 x$ ($N=13$), the standard deviations of the slope and the intercept 1.203 and 0.168 respectively and the correlation coefficient 0.998. Quantitation of dicofol 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 dicofol at various concentration levels. Figure 1a shows a gas chromatogram of a fortified apricot sample. The results of the recovery study are presented in Table 1. As seen from this table, average recoveries were from 94 to 106% except 77% for the lowest fortification level and relative standard deviations from 5.1 to 11%, 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., E.P.A. 1984), which at 99% confidence level and for 2 degrees of freedom is 6.96, was found to be 0.004 mg/kg.

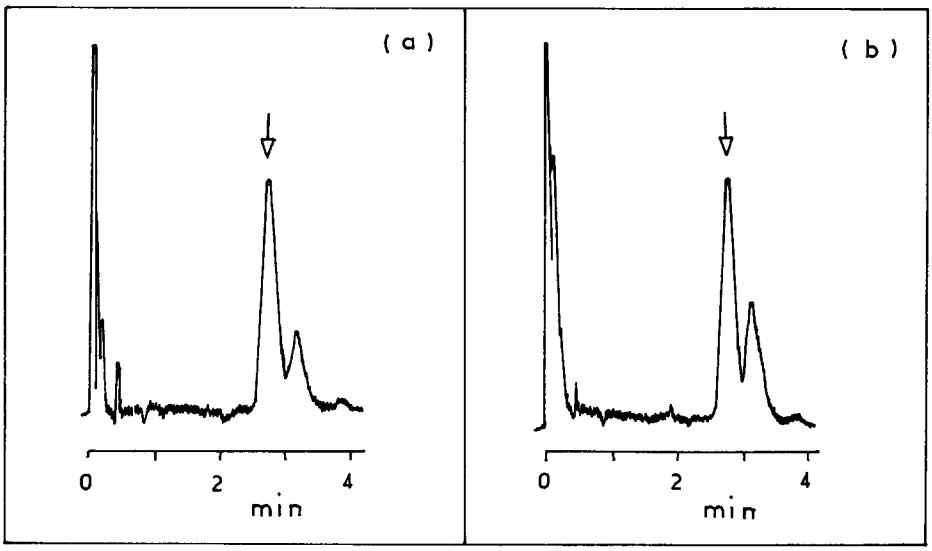

Figure 1. 1µL gas chromatograms of a) Fortified apricot sample with 0.2 mg/kg dicofol b) 0.1 ng dicofol reference standard.

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

Concentration (mg/kg)	Recovery %	R.S.D.%
0.01**	77	7.3
0.05	101	7.4
0.1	100	11.0
0.2	102	6.9
0.5	106	5.2
1	96	7.0
2	94	5.1

*Three samples for each fortification level
**Concentration was required for the samples fortified at 0.01 mg/kg

All control samples of apricots and apricot juice were found not to contain dicofol residues. Dicofol residues found in apricots and the resulting from them apricot juice, at various time intervals following application, are shown in figure 2. As shown from this figure, initial deposits of dicofol on apricots were 0.43 mg/kg for the LRD-experiment and 0.46 mg/kg for the HRD-experiment. A relatively rapid loss of residues was observed in apricots within two days following application. Volatilization seems to be a significant factor in this loss, which is approximately 35% in the case of the LRD-experiment and 25% in the case of the HRD-experiment. Thereafter residues declined relatively slowly related to time and this seems to be due primary to physical removal by weathering, heat decomposition and UV-radiation of the sunlight. The percentage dissipation of dicofol residues in apricots 32 days after application was 93% for the LRD-experiment and 90% for the HRD-experiment. The residue half-lives (Gunther 1969) evaluated from the dissipation lines are 7 days for the LRD-experiment and 9 days for the HRD-

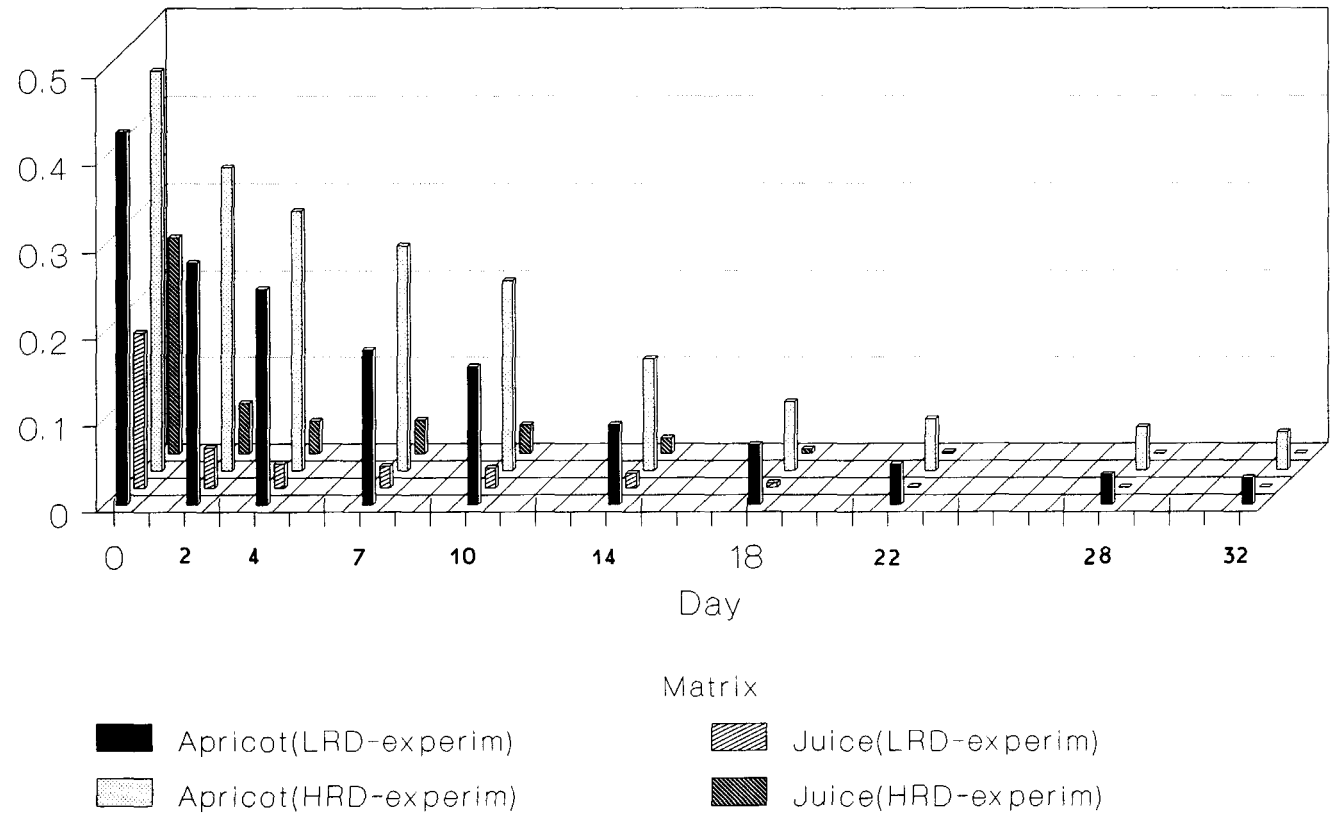

Figure 2: Dicofol residues (mg/kg)

experiment and it seems that they are independent of the initial application dose. In all cases dicofol residues in apricots were lower than the MRLs set by many European countries, which are between 0.5 and 3 mg/kg, and the 5 mg/kg MRL set by the Codex Alimentarius Commission of FAO/WHO. No MRLs have been established yet for this acaricide by the European Union.

From the same figure it is also seen that dicofol residues are partially transferred from the apricots into the produced from them apricot juice. Therefore, while approximately 45% of residues was transferred into the juice from the 0-day apricots, only 15% of residues was transferred in the juice for the apricots collected between 2 and 18 days after application, and less than 3% was transferred in the juice for the apricots collected between 22 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 dicofol on apricots was not complete yet. However, by the time, adhesion and permeation of dicofol in the fruits was more complete and, as the results demonstrate, dicofol residues were concentrated mostly in the solid commodity of the fruit, rather than in the juice product.

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