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Mancozeb Residues on Field Sprayed Apricots

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Ethylenebisdithiocarbamates (EBDC's) are a group of non-systemic fungicides widely used for the control of important fungal diseases on certain fruit, vegetable and ornamental crops.

EBDC's are subject to decomposition at elevated temperatures and high humidity and yield ethylene thiourea (ETU) as the principal metabolite in plants (Lentza-Rizos 1990).

Mancozeb, a polymeric complex of ethylenebis(dithiocarbamate) manganese and zinc salts, is one of the most widely used EBDC fungicides in Greece.

The present study was conducted to evaluate mancozeb residues in apricots, a significant crop in Greece and one for which no EBDC residue data are available to date. Residue data are required by the EEC procedure to set maximum residue limit (MRL) for this crop. The effect on the mancozeb residues of fruit washing was also examined.

MATERIALS AND METHODS

The field experiment was carried out from May to July 1990 in an apricot orchard at Velo near Corinth (Southern Greece). The experimental area comprised 13 plots of two trees each, receiving routine horticultural practices.

An aqueous suspension of an 80% mancozeb wettable powder formulation (Dithane M-45, Rohm and Haas) was applied at rates 200 g a.i./100 L water (recommended dose) and 400 g a.i./100 L water. The suspension was applied with a hand gun airblast sprayer and the trees were sprayed to run off.

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Each experimental plot received a single treatment. Applications started 5 weeks before the expected harvest day and were continued on a weekly basis, a different plot being treated each time. Thus, six different samples were collected for each dose on the day of harvest, corresponding to trees sprayed 0, 7, 13, 21, 28 and 35 days before sampling. One sample was collected from untreated trees, to be used as a control.

From the two plots (one for each dose) that were sprayed on the day of harvest, additional samples were collected 3, 7, 15, 22 and 28 days after application. There was no rainfall at anytime during the experimental period.

Each sample taken from the experimental plot consisted of 24 apricot fruits collected randomly from several places of the two trees, according to FAO recommendations (FAO/WHO, 1984). Samples were put in polyethylene bags, forwarded the same day to the laboratory, stored at 5°C in a refrigerator and analysed in triplicate within two days.

Apricots were cut in wedged-shaped portions that included outer surfaces from each unit. Opposite quarters were always taken, the sample was weighted and analysis proceeded without undue delay.

The analytical method used was the carbon disulfide evolution procedure of Keppel (1971) as described by Thier *et al.*, (1987), which involves heating the sample with a solution of stannous chloride and hydrochloric acid. The envolved carbon disulphide was distilled, purified and absorbed by an ethanolic solution of cupric acetate and diethanolamine. The developed yellow copper dithiocarbamate was evaluated by spectrophotometry at 435 nm. The recovery of the method was evaluated by analyzing untreated samples spiked with sodium diethyl dithiocarbamate at concentrations of 1, 5, 10 and 20 mg CS_2/kg. The spiked samples were analysed in triplicate.

The reduction of mancozeb residues achieved by washing was also studied for some of the samples. All results are expressed as mg of CS_2 per kg of the fruit. The conversion factor to mancozeb residues is 1.776.

RESULTS AND DISCUSSION

The method of analysis used was simple and fast, as is essential for routine analyses. Recoveries of spiked samples ranged from 85 to 95% with a coefficient of variation less than 15%. These values are within the accepted limits for residue analysis methods (FAO/WHO, 1983). The limit of detection of the method was found to

be 0.1 mg CS_2/kg.

The reproducibility of the results for the samples with incurred residues was not satisfactory. This is attributed to sample variability, since each laboratory sample was not homogenized but cut into pieces, from which the three analytical subsamples were taken. This was done in order to avoid homogenization during which EBDC's are known to decompose. Since all the residue was located on the outer surface of the apricots, sample variability increased when smaller samples were used as was the case with samples containing high residues of mancozeb which required only 50 g of fruit for analysis. To minimize this effect, all residue containing samples were analysed in triplicate. The results of the analyses expressed as the concentration of CS_2 are presented in Table 1.

Table 1. Concentration of CS_2 (mg/kg) in apricots sprayed at various intervals before harvest (Three analyses for each sample).

Days after application	Dose of mancozeb	
	200 g a.i./100 L	400 g a.i./100 L
0	11.5 ± 0.6	16.7 ± 2.7
7	9.14 ± 3.5	13.5 ± 5.0
13	7.35 ± 1.6	12.1 ± 0.7
21	6.03 ± 0.2	13.2 ± 2.3
28	1.65 ± 0.6	6.48 ± 1.0
35	1.32*	5.6*

* No replications for these samples

Control samples were found to have a CS_2 concentration of 0.1 mg/kg. This was atributed to an earlier treatment with a dithiocarbamate fungicide during the bloom stage. The results in Table 1 represent the mean value of three analyses for each sample. The values of the coefficients of variation range between 3 and 20%, but in some samples approach 38%. This is attributed to the sampling variability since the coefficient of variation for the fortified samples was less than 15%.

As shown by the data in Table 1, there was a slow decrease in the CS_2 concentration during the first 3 weeks after the application of mancozeb, while the decrease was much faster during the fourth week. Thus, the initial CS_2 concentrations of 11.5 mg/kg and 16.7

mg/kg immediately after application with the recommended and double dose, respectively, decreased by about 50% and 20% respectively 21 days after application, while 28 days after application the reductions were about 85% and 60%, respectively. This greater decrease in residues closer to harvest may be attributed to dilution due to fruit growth, as well as to climatic conditions (Engst and Schnaak, 1974).

The data in Table 1 show that CS_2 concentration is linearly related to time. The equations of the regression lines are $Y=11.4 - 0.3x$ and $Y=16.5 - 0.31x$ for the results of the recommended and the double application doses, respectively. The correlation coefficients are respectively, $r= -0.982$ and $r= -0.929$ (statistically significant at $P=0.01$) indicating a high correlation.

To evaluate the dissipation of mancozeb residues, samples of fully matured fruits were taken from the same trees at certain intervals after the last application. The results are presented in Table 2.

Table 2. Dissipation of mancozeb in mature apricots with time (Three analyses for each sample).

Days after application	Concentration of CS_2 (mg/kg)	
	Dose 200 g*/100 L	Dose 400 g*/100 L
0	11.5 ± 0.6	16.7 ± 2.7
3	10.0 ± 3.4	15.6 ± 1.6
7	10.5 ± 2.4	17.6 ± 7.0
15	6.4 ± 0.9	14.5 ± 2.3
22	10.5 ± 0.1	14.3 ± 3.9
28	**	8.0 ± 0.6

* Active ingredient of mancozeb
** No sample available

As seen from the data of Table 2, dissipation of mancozeb during the first 22 days after application was very slow, about 10% for both application doses. Between the 22nd and 28th day following application, dissipation of mancozeb was about 40% for the sample with double the recommended dose. No sample was available 28 days after application from the trees treated with the recommended dose.

Tables 1 and 2 indicate that mancozeb dissipates faster in the case of green fruits (20-50%) than in the case of mature ones (10%) during the first 21 days after

application. The dissipation rate was much higher (40%) and similar in both cases between 21-28 days following application.

Results reported by other workers indicate that the dissipation rate of mancozeb depends not only on the kind of fruit but also on the kind and size of its surface area. Newsome (1976 and 1979) found a fast dissipation in tomatoes, while Ross *et al.* (1978) found slower dissipation in apples. Fida (1979) found a fast dissipation in tomatoes and cucumbers and a slow dissipation in lettuce. The slow dissipation of mancozeb in apricots that was found in the present study, may be due to the relatively high surface area and the apricot surface characteristics.

Eight apricot samples from the field experiment were analysed, in triplicate, after dipping consecutively in two beakers of water and agitating for 1 minute in each beaker. Mancozeb residues were removed by 35 to 70% compared to the unwashed samples. These results are in agreement with the study of Fillips *et al.* (1977), who found that 33-87% of the EBDC's are removed following a simple washing procedure of the raw agricultural produce.

In conclusion, the above data indicate that the use of mancozeb on apricots results in a significant level of residues during the first three weeks after application.

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