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DEGRADATION OF MANCOZEB RESIDUES IN PEPPER AND THE EFFECT OF PROCESSING ON THE REMOVAL OF RESIDUES

The production of black pepper is facing a major threat due to the heavy incidence of various fungal diseases. Persistence of fungicides is one of the important factors for scheduling disease control. Fungicides from dithiocarbamate group are commonly used against diseases. Mancozeb, is one of the sulphur containing fungicides from ethylene bis-dithiocarbamate group which is used frequently. Though the ethylene bis-dithiocarbamates are easily degradable in tropical conditions, it is important to study the persistence and the effect of processing on the residues in pepper berries. Therefore, the present investigation was undertaken to study the dissipation of mancozeb and to suggest waiting period after the last treatment and harvest.

The experiment was conducted in a well maintained pepper garden with the variety Panniyoor 1 at Kalliyoor, Vellayani, Trivandrum during October-December 1993. The proprietary product of mancozeb used in this study was Dithane M45 of M/s Indofil Chemicals Company, Bombay, containing 75 per cent active ingredient. The fungicide was sprayed on the vines at a concentration of 0.2 and 0.2 per cent (1.25 kg ai ha^{-1}) twice at the tender spike formation stage and berry maturation stage. The vines were sprayed thoroughly to the run off level using a rocker sprayer. The spike samples were collected at 1, 3, 7, 14, 21 and 28 days after the second application for estimation of residues. A quantity of 1.0 kg fresh berries was collected from each plot and two analytical sample of 50 g each were drawn from this by quartering. One set was subjected directly to analysis of fresh berries and the second set to drying.

The residues were estimated by the CS_2 evolution method as per Keppel (1971). Fifty gram sample was digested with boiling 10 *N* sulphuric acid over a heating mantle for 45 min in a decomposition absorption apparatus under a gentle stream of air bubbles. Hydrogen sulphide liberated was allowed to react with zinc acetate solution in Trap 1 and the carbon disulphide evolved was allowed to react with a colouring reagent in Trap 11 (cupric acetate + diethanolamine) to form a yellow coloured copper chelate of carbon disulphide which could be detected in *a* spectrophotometer at 435 nm. The concentration of CS_2 read was calculated from a standard curve and the concentration of mancozeb equivalent was worked out by multiplying with a constant 1.81. The residue data were subjected to mathematical calculations to find out the residual half life (RL 50) values as an index of fungicide dissipation and waiting period (T tol.) values based on maximum residue limit of 3 mg kg^{-1} prescribed by FAO / WHO. For the purpose of comparison between the fresh and dry berries the residues on moisture free basis were calculated from the values for fresh berries. The corresponding percentage reduction of residues as a result of drying was worked out considering all on dry weight (moisture free) basis. This was essential since the number of berries in a unit weight of dry sample will be more than the number in corresponding fresh sample thereby increasing the total surface area of sample and the fungicide deposit on them.

The residues of mancozeb in fresh and dry berries of pepper at different sampling intervals are given in Table 1. A perusal of the data indicated that the initial deposit of mancozeb in fresh berries one day after application was 9.80 mg kg^{-1} for the dose of 0.2 per cent. The initial deposit dissipated to 6.37, 4.82, 1.49, 0.14 and 0.02 mg kg^{-1} resulting in 35.00, 50.08, 84.79, 98.52 and 99.79 per cent loss after 3, 7, 14, 21 and 28 days after treatment respectively. In the higher dose of 0.4%, the mancozeb residues obtained 1 day after treatment was 13.46 mg kg^{-1} which dissipated to 10.75, 8.90, 3.87, 1.49 and 0.29 mg kg^{-1} by 3, 7, 14, 21 and 28 days after treatment respectively. Considering the rate of dissipation in the lower and higher doses, it is seen that it is comparatively faster in the low

Table 1. Mancozeb residues in pepper berries (mg kg ^{1})

Days after application	Mancozeb (0.2%)			Removal on drying %	Mancozeb (0.4%)			Removal on drying, %
	Fresh (fresh wt. basis)	Fresh (dry wt. basis)	Dry		Fresh (fresh wt. basis)	Fresh (dry wt. basis)	Dry	
1	9.80 + 1.48	41.83 + 7.1	23.54 + 5.2	43.72	13.46 + 2.3	57.4 + 2.3	38.86 + 6.2	33.17
3	6.37 + 1.10	25.58 + 4.1	13.84 + 1.9	45.89	10.75 + 1.15	48.61 + 2.4	24.96 + 6.1	48.65
7	4.82 + 0.59	19.86 + 2.9	9.19 + 0.4	53.73	8.90 + 1.35	36.64 + 4.2	11.67 + 2.3	68.81
14	1.49 + 54	6.09 + 2.2	3.22 + 1.1	47.13	3.87 + 0.64	15.94 + 0.4	6.67 + 1.9	58.22
21	0.14 + 0.11	0.58 + 05	0.42 + 0.4	27.59	1.49 - 0.61	5.84 + 2.4	2.72 + 0.8	53.42
28	0.02 + 0.03	0.07 + 0.1	0.02 + 0.1	71.43	0.29 + 0.20	1.1 + 0.8	0.58 + 0.5	47.27
Reg. equation	Y - 3.23 - 0.0981 t	Y - 3.865 - 0.1009 t	Y - 3.478 - 0.082 t		Y - 3.28 - 0.59 t	Y - 3.929 - 0.0612 t	Y = 3.28 - 0.059 t	-
T(tol.) days	14.62	20.74	19.43		19.43	23.65	21.56	-
RL50, days	3.04	3.98	3.65		5.11	4.91	4.26	-

dose than the higher and the corresponding RL 50 values were 3.04 and 5.11 days. The waiting period of mancozeb in fresh berries when treated at 0.2 per cent was 14.62 days and at the higher dose was 19.43 days. Information on the rate of dissipation of mancozeb in pepper or any other spice crop is not available. A more or less similar dissipation was observed in apple fruits (Nath and Sharma, 1993). However, the rate of dissipation in pepper was much slower when compared to that of tomato and brinjal. In tomato 99 per cent of the initial deposit dissipated within 15 days of spraying and in brinjal 85 per cent dissipated within seven days (Jayakumar *et al.*, 1995; Kumar and Agarwal, 1990). Comparatively higher level of initial deposit and slower rate of dissipation in pepper berries may be due to the lesser dilution effect and slower growth rate of the berries.

The effect of drying on the removal of residues of mancozeb indicated that substantial reduction was noticed and the percentage removal was to the tune of 27.59 to 71.43 (Table 1). However, on the basis of the present studies a waiting period of 14 to 19 days should be observed to ensure that the pepper berries meet the requirements of freedom from mancozeb residues.

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