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Original Research Article

Persistence and dissipation of mancozeb residues in/on tomato in Bidar District of Karnataka State, India

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An experiment was conducted during 2012-2013 to study the persistence and dissipation of mancozeb residue during fruit growth stage of tomato hybrid indoamericon-Hyb-F1. Treatment spray application of mancozeb75% WP (Crystal M-45) was given two times at 7 days intervals, at the recommended and double the recommended dosage of 1.0 g/ L and 2.0 g/L. Spray application was carried out in Kharif (July to Oct, 2012) and Rabi (Nov 2012 to Mar, 2013) seasons. Initial residue deposits of mancozeb (as CS_2) in two different seasons were found in the range of 3.41 to 6.07 mg/kg. Residue dissipated after 3 days of application in Kharif (1.86 mg/kg) and Rabi (1.79 mg/kg) seasons for the recommended dose. At the harvest time (10 days after the last spray) the residue level reached below detectable limit of recommended dose in Kharif (0.1 mg/kg) and Rabi (0.12 mg/kg), at double the recommended dose the residues were 0.24 and 0.32 mg/kg. The half-life of mancozeb residue was found to be 2.12 to 2.29 days. Based on the maximum residue limit value of 3.0 mg/kg (as CS_2) as Codex Alimentarius the pre harvest interval for recommended and double recommended dose of mancozeb treatment was 2 and 3 days, respectively.

Key words: CS_2, mancozeb, tomato, persistence, pesticide residue analysis.

INTRODUCTION

India is the third largest consumer of pesticides in the world and highest among the South Asian countries. During the last four decades, consumption of pesticides in India has increased several folds from 154 tons in 1953 - 54 to 80,000 tons in 1994 - 95 and 88,751 tons in 1998 - 99 (Agnihotri, 2000). The release of vast variety of pesticides for pest control is polluting the ecosystem leading to their toxic residues. Regardless of method of application, large amount of pesticides reach the soil in one way or the other. The soil is the final sink of pesticide and their residues. This is not only harmful to soil ecosystem including flora, fauna and environment, but also is translocated within plant system (Choudhury, 1994). The pesticide residues or their toxic metabolites present could affect man's health. The above situation warrants detailed investigations on the behaviour of pesticides for their residues in plants, soil and water from the point of safety to human being as well as protection of environment from the pesticide pollution (Parmar and Dureja, 1990).

It is evident that in India the work on pesticides mainly shared by insecticides (Parmar and Dureja, 1990; Agnihotri, 1999). However, the work on fungicides could not get serious attention in environmental aspects. Dithiocarbamates fungicides form major group in plant protection for the control of several diseases. The dithiocarbamates are mainly used in agriculture and form part of the large group of synthetic organic pesticides that have been developed and produced on a large scale in the last 50 - 60 years. The development of dithiocarbamate derivatives with pesticidal properties occurred during and after the Second World War.

However, a few compounds, such as thiram and ziram, were introduced in the 1930s. The worldwide consumption of dithiocarbamates is between 25000 and 35000 metric tons per year. Dithiocarbamates are used as fungicide, being effective against a broad spectrum of fungi and plant

diseases caused by fungi. Over 200 diseases caused by fungi, bacteria, viruses, nematodes and by other physiogenic causes have been reported (Altherton and Rudich, 1986). These diseases can be effectively mangled with the use of mancozeb belonging to ethylene bisdithiocarbamate (EBDC) group of fungicides (Rajgopal and Vidhyasekaran, 1983; Zayedet al., 1983; Singh and Sharma, 1986; Bharadwaj, 1991). Use of these fungicides against diseases of vegetables is most common and regular practice of growers.

Mancozeb is one of the prominent dithiocarbamates being used to the tune of 6800 tons technical grade (Anonymous, 2001). Propineb (Zinc – propylene – bis - dithiocarbamate) is newly introduced dithiocarbamate, as fungicide in India. In preliminary trials, it has shown promising results against diseases of several agricultural and horticultural crops (Rawal, 1986). From the consumers' safety point of view, dithiocarbamate fungicides are assessed for residues on the basis of carbon disulfide. Moreover, the Maximum Residue Limits (MRL) are expressed as the CS_2 in ppm (FAO / WHO, 2000). Considering the significance of dithiocarbamates in plant protection of vegetable crops, the studies on their persistence in vegetable crop and soil environment would be of immense value. Tomato is the major crops which have drawn much attention of the farmers for domestic as well as for the export purpose and have significant contribution to Indian economy. These crops suffer heavily from several pests and diseases causing considerable reduction in yield and quality of fruits (Jayakumar et al., 1995). Dithiocarbamates are the commonly used pesticides against various diseases of vegetable crops (Baruha et al., 1980). Since these vegetables are consumed as salad and curry and taking into account the aforesaid environmental aspects, the following objectives are envisaged to carry out the research work so that some answers can be given to the present day situation.

Tomato (*Solanum lycopersicum* L. Mill. nom. cons.) is the popular worldwide grown vegetable. It is also called as economically important crop. Tomato occupies second largest position among other vegetables produce in India with an average production of 10 million tonnes. Early blight of tomato and fruit borer (*Helicoverpa armigera*) are the major constraint sand causes serious damage to tomato during ripening time of fruits. Mancozeb is a dithiocarbomate foliar applied fungicide with long residual activity. It is used as a productive treatment on several crops for the control of several fungal diseases including Anthroconose. It has been found to give excellent control for infecting pomegranate along with an antibiotic (Sing and Bassu, 2006) and also good controlling agent of Anthraconose caused by *Colletotrichum gloeosporioides*. No information is available on the persistence of residues of mancozeb on/in tomato and the residue level at harvest time in Bidar district of north Karnataka. An experiment was therefore carried out to study the persistence and dissipation of mancozeb during the growth stage of tomato. Fadel et al. (1993) reported field test method worked on the efficacy of various fungicides against tomato early blight disease caused by *Alternaria solani* and reported that chemical control of tomato early blight disease by mancozeb and propineb in Egypt field trial was best.

Kamble et al. (2000), found that among the six fungicides tested against tomato leaf spot pathogen *Alternaria alternata*, mancozeb was highly effective in inhibiting the mycelial growth at 1000 ppm. Mancozeb was also effective in reducing the disease intensity in pot culture at 0.2 per cent concentration. Dubey et al. (1999) monitored 51 samples of apple and tomato from different production centres in Himachal Pradesh, India in 1997. The residues of dithiocarbamate pesticides were detected in 92.16 per cent of apple samples and 80.39 per cent of tomato samples, in the range of 0.11 - 0.38 and 0.013 – 0.251 mg/kg respectively. None of the samples exceeded the maximum residue limit of 3 mg / kg.

The present work describes dithiocarbamate fungicides, Mancozeb (Crystal M-45) pesticide residual analysis of Kharif and Rabi of Bidar. Method used for analysis of pesticides was very simple efficient and rugged.

MATERIAL AND METHODS

Chemicals

Stannous (II) chloride, lead acetate, Sodium hydroxide, cupric acetate monohydrate, ethanol, diethanolamine were procured from S.D.Fine chemicals and Mancozeb from Crystal crop protection private limited. All other reagents used were of analytical grade.

Methods

Analysis of dithiocarbamate residues

Dithiocarbamate residues on crops are decomposed by refluxing crop with boiling 30 ml hydrochloric acid. The evolved CS_2 was carried by gas stream through trap to remove H_2S and other volatile interferences. It then reacts, in second trap, with colour reagent to form yellow complex, the cupric salt of N, N - bis (2 hydroxyethyl) dithiocarbamic acid, which is measured calorimetrically at 435 nm. Dithiocarbamate is calculated from CS_2 calibration curve.

Mancozeb residual analysis from tomato was measured according to the method of (Keppel, 1971). 10 ml lead acetate solution was added to the first of the three absorption tubes attached to the distillation apparatus. The second one was filled with 10 ml sodium hydroxide solution. To the third absorption tube (best fitted with Widmer helix), added 15 ml colour reagent (cupric acetate monohydrate solution-0.012g + 25 g diethanol amine make up the volume to 250 ml with ethanol). To check for complete absorption of evolved carbon disulphide, a fourth absorption tube containing colour reagent was attached. Its contents remained colorless during the procedure.

Table 1. Dissipation of mancozeb residues on tomato fruits in *Kharif* season

Days after spray	**Mean residue as CS_2 in PPM**				
	Untreated control	**Mancozib 75 WP @ 1 g/l**		**Mancozib 75 WP @ 2 g/l**	
	PPM	**PPM**	**% Loss**	**PPM**	**% Loss**
0	BDL	3.85	-	5.95	-
1	BDL	3.12	18.96	5.24	11.93
3	BDL	1.86	57.69	3.36	43.54
5	BDL	0.93	75.84	1.72	71.09
7	BDL	0.47	87.79	0.76	87.23
10	BDL	BDL		0.24	95.93
Regression equation		Y=3.61910.1316x		Y=3.86810.1420x	
RL50 (days)		2.29		2.12	
TBDL (Days)		12.3		13.16	

*BDL= Below detectable limit of 0.1 ppm as CS_2; MRL= Maximum residue limit of 3ppm as CS_2

Extraction method

Transferred 100 g of sample to the flask, cutting into small pieces and quartering to mix opposite quarters for representative sample, added mixture of 200 ml of distilled water, 30 ml hydrochloric acid and 5 ml stannous chloride solution from the dropping funnel. Quickly heated the contents of the flask to boiling for a total period of 60 minutes. At the end of this period, switched of the water jet pump and disconnected the third absorption tube. The contents of this tube were transferred to 25 ml volumetric flask, using ethanol as wash liquid. Diluted to mark with ethanol and mixed well. Measuring the absorbance at 435 nm by Shimadzu UV-1700 spectrophotometer determined the relevant amount of CS_2 from the standard curve obtained by using a cell of same light path.

Calibration curve

In order to realize a quantitative analysis, amounts of standard CS_2 solution varying from 0.1 to 5.0 ml was added to a series of 25 ml volumetric flasks. To each flask, added 15 ml coloring reagent and mixed. Mixture was allowed to stand for 15 min and read absorbance at 435 nm (Shimadzu UV-1700) against mixture of 15 ml coloring reagent and 10 ml of ethanol as reference blank. Absorbance values were plotted against mg CS_2. Method specified by Keppel, (1971) was used for the determination of residues.

RESULTS AND DISCUSSION

Mancozeb residual analysis of Kharif crop

The residues on tomato fruits of Kharif season trial (June 2012 planting) are given in Table 1. Initial residues of 3.85 ppm dissipated to MRL of 3 ppm in 1.1 days after the last spray of mancozeb 75 WP at the rate of 1.0 g/L. In case of higher dose of 2.0 g/L, the initial residues of 5.95 ppm took 2.8 days to reach the said MRL. The residue half-life at the evaluated doses was 2.29 and 2.35 days, respectively. Considering the dissipation pattern (Figure 1), it is noticed that mancozeb degraded fast to safe limits. In this method residue of mencozeb are estimated as the quantity of carbon disulfide (CS_2). The maximum residue limits of dithiocarbomates are also fixed based on CS_2 level by FAO/WHO (2000) and the maximum residue limit 3.0 mg/kg for tomato. Using this method CS_2 can be detected up to the level of 0.1 ppm. Tomato mature fruits samples 2 kg each were randomly collected on 0 (1hr), 1, 3, 5, 7 and 10 days after the last day application of the fungicide.

Mancozeb residual analysis of Rabi crop

The residue data on samples of Rabi season experiment (October 2012 planting) are given in Table 2. At the recommended rate 1.0 g/L of mancozeb 75 WP, the initial residues were 3.41 ppm, which required 0.99 days to reach the MRL of 3 ppm. Residues reached below detectable limit of 0.1 ppm in 11.02 days with the half-life of 2.04 days (Figure 2). In case of double rate of 2.0 g/L, the initial residues of 6.07 ppm reached MRL of 3 ppm in 2.88 days. The residue half-life and time required to reach detectable limit was the 2.29 and 14.14 days. Similar results were observed in Jayakumar et al. (1995) in evaluation of mancozeb residues in tomato recommended a waiting period of 2 day after the third spray before tomato consumption, when spraying mancozeb at 0.25 and 0.5 per cent. Reddy et al. (1995) also studied the pattern, range and recovery of EBDC residues in tomato fruits for two seasons at 2 concentrations (0.25 and 0.5 per cent) with Dithane Z-78 (Zineb) and Dithane M-45 (Mancozeb) fungicides. A gradual reduction of fungicide residues was observed in 10 days after spraying. The amount of residues recovered when the crop was sprayed with 0.5 per cent fungicides was higher than that of lower concentration. Residues of Dithane M- 45 were higher than that of Dithane Z-78.

Sharma (1995) determined residues after two sprays of mancozeb (1.5 kg/ha) applied at an interval of 8 days. Mancozeb residues were below detectable levels on 9th day for tomato. The suggested waiting period for crop was

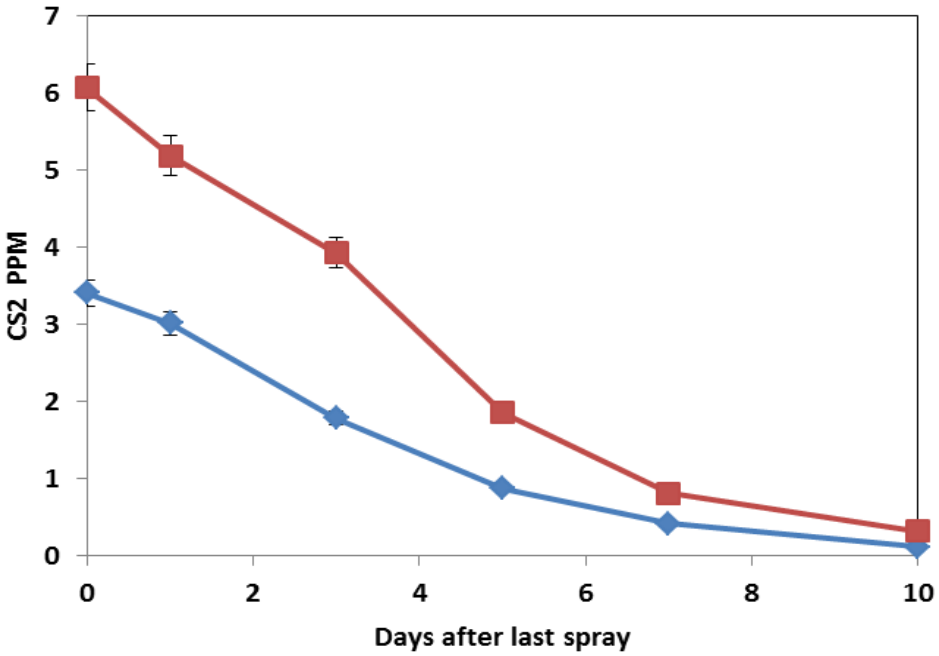

Figure 1. Shows dissipation of mancozeb on tomato fruits in Kharif season (♦) mancozeb 1 g/l and (♦) mancozeb 2 g//l

Table 2. Dissipation of mancozeb residues on tomato fruits in *Rabi* season

Days after spray	Mean residue as CS2 in PPM				
	Untreated control	Mancozib 75 WP @ 1 g/l		Mancozib 75 WP @ 2 g/l	
	PPM	PPM	% Loss	6.07	% Loss
0	BDL	3.41	-	5.18	-
1	BDL	3.02	11.44	3.43	14.66
3	BDL	1.79	47.51	1.86	43.49
5	BDL	0.88	74.19	0.81	69.36
7	BDL	0.42	87.68	0.32	86.66
10	BDL	0.12	96.48	6.07	
Regression equation		Y=3.6232-0.1473x		Y=3.85440.1312x	
RL50 (days)		2.29		2.12	
TBDL (Days)		12.3		13.16	

*BDL= Below detectable limit of 0.1 ppm as CS2, MRL= Maximum residue limit of 3ppm as CS2

calculated as 1.5 days for tomato the maximum residue level of 3 ppm CS_2. Residues reached below detectable limit of 0.1 ppm in 12.3 and 14.4 days after spraying at lower and higher dose, respectively. At the spray rate of 1.0 g/L mancozeb 75 WP, the waiting period was 0.99 and 1.1 days in *Rabi* and Kharif season, respectively. By allowing maximum safety factor to consumers, a gap of 2 days can be considered safe between spraying and harvest of edible quality tomato fruits. In studies carried out by Sharma (1995) and Jaykumar et al. (1995), the waiting periods were 1.5 and 2 days, respectively, which matched with the results obtained in the present study.

However, in studies on dissipation of mancozeb by Singh et al. (2000), the initial residues of mancozeb on tomato fruits were less than the MRL of 3 ppm stating it as most safe for consumers. Patil et al. (2003) studied the dissipation of mancozeb on tomato fruits and suggested a waiting period of one day after spraying at 0.25% mancozeb 75WP on the basis of formulated product.

Keeping in view the dissipation rate of residues in two season trials and allowing sufficient safety factors, a pre-harvest interval of about 2 days can be considered suitable after spraying of mancozeb 75 WP at the rate of 1 g/L on tomato crop. Tomato hybrid Indo-American hybrid-F1 was grown at dhannura (H) Bhalki taluka, Bidar district of Mr.Sangamesh S/o Shankareppa Sajjanshetty field spray application of Mancozeb 75% WP (Crytal M-45) was given at the recommended and double the recommended dose of 1 g /L and 2g /L two times at 7 days intervals during fruit growth stage. The experiment was carried out during July-

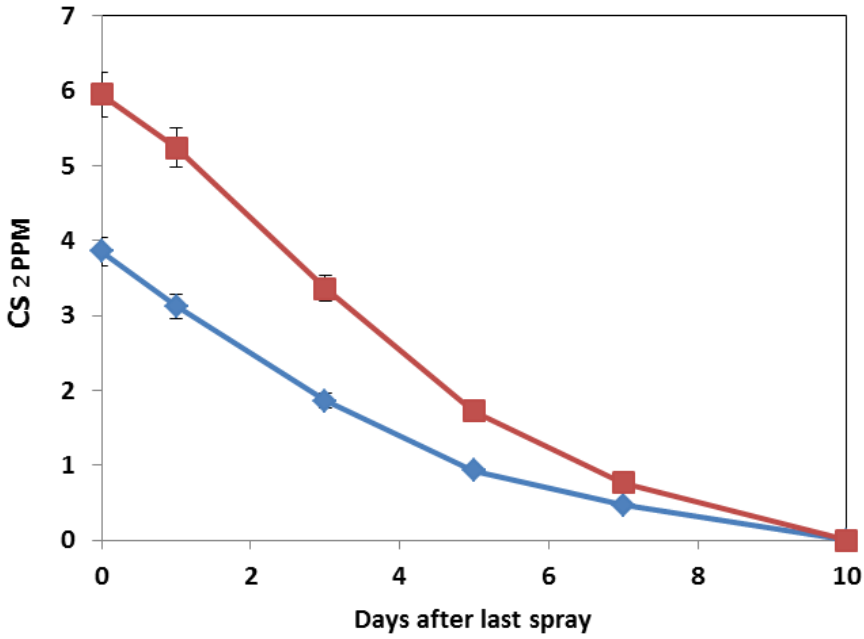

Figure 2: Figure shows Dissipation of mancozeb on tomato fruits in Rabi season (♦) mancozeb 1 g/l and (♦) mancozeb 2 g/l.

Oct-2012 & Nov-2012 to March-2013 (winter season). Pesticide was sprayed with hand sprayer at two doses therefore at the recommended (1 g/L/) and double recommended (2 g/L) dose along with untreated control in randomized row designed with three replication for every treatment. For every treatment 8-10 matured plants (30 days) were selected. Studies were carried out for dissipation by drawing periodic samples after the last spray.

CONCLUSION

Spraying of mancozeb 75 WP at the rate of 1 g/L /spray can be recommended on tomato with the waiting period of 2 days respectively for a residue free harvest. Mancozeb 75 WP can be considered safe to soil and water environment provided they are used at the recommended doses in plant protection work. Pesticide residual analysis of Kharif and Rabi of Bidar and methods used for analysis of pesticides was very simple and effective.

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