



P-ISSN: 2349-8528

E-ISSN: 2321-4902

IJCS 2020; 8(1): 2433-2437

© 2020 IJCS

Received: 04-11-2019

Accepted: 06-12-2019

**CS Patil**

AINP on Pesticide Residues,  
Department of Agril.  
Entomology, Mahatma Phule  
Krishi Vidyapeeth, Rahuri,  
Dist.: -Ahmednagar,  
Maharashtra, India

**BV Deore**

AINP on Pesticide Residues,  
Department of Agril.  
Entomology, Mahatma Phule  
Krishi Vidyapeeth, Rahuri,  
Dist.: -Ahmednagar,  
Maharashtra, India

**YS Saindane**

AINP on Pesticide Residues,  
Department of Agril.  
Entomology, Mahatma Phule  
Krishi Vidyapeeth, Rahuri,  
Dist.: -Ahmednagar,  
Maharashtra, India

**Corresponding Author:****CS Patil**

AINP on Pesticide Residues,  
Department of Agril.  
Entomology, Mahatma Phule  
Krishi Vidyapeeth, Rahuri,  
Dist.: -Ahmednagar,  
Maharashtra, India

## Residues and dissipation of mancozeb 75% WP in/on onion

CS Patil, BV Deore and YS Saindane

DOI: <https://doi.org/10.22271/chemi.2020.v8.i1ak.8630>

**Abstract**

Supervised field trial was conducted to determine the dissipation of mancozeb (based on CS<sub>2</sub>) in/on onion and in cropped soil resulting from spray application of mancozeb 75 WP at recommended dose (1500 g a.i./ha) and double the recommended dose (3000 g a.i./ha). The initial residues of mancozeb (based on CS<sub>2</sub>) in immature onion including leaves were found to be 3.44 mg/kg and 5.89 mg/kg at recommended dose and double the recommended dose, respectively. Mancozeb residues (based on CS<sub>2</sub>) dissipated below limit of quantification (LOQ) on 10<sup>th</sup> and 15<sup>th</sup> day with half-life values of 1.91 and 2.33 days at recommended dose and double the recommended dose, respectively. The residues of mancozeb (based on CS<sub>2</sub>) in mature onions and soil collected at harvest were found to be below limit of quantification (LOQ).

**Keywords:** Mancozeb, residue, dissipation and onion

**1. Introduction**

Onion (*Allium cepa*) is an important vegetable crop in India grown for its strong flavor and pungent odour which is mellowed and sweetened by cooking. In India, onion is grown round the year. Globally, India ranks first in total area of 1284.99 thousand hectares and ranks second in production after China with total production of 23262.33 thousand million tonnes with a productivity of 18.10 million tonnes per hectare (Anonymous, 2018) [1]. Maharashtra, Karnataka, Madhya Pradesh, Rajasthan, Bihar, Andhra Pradesh, West Bengal, Odisha, Haryana, Tamil Nadu, Uttar Pradesh, Chhattisgarh and Gujrat are the major onion growing states in the country (Anonymous, 2018) [1].

Several factors have been attributed for the low productivity of onion in India. Among these diseases are the most important factors. Onion is affected by numerous diseases throughout growing period under field condition. Alternaria blight is one of the most devastating disease (Marmath *et al.*, 2013). Purple blotch of onion caused by *Alternaria porri* (Ellis) Cif., is a major disease affecting the foliage severely resulting in crop loss ranging from 30 to 100 percent. Mancozeb is a dithiocarbamate non-systemic fungicide with multi-site, protective action on contact and controls many fungal diseases in a wide range of field crops, fruits, nuts, vegetables, and ornamentals. Mancozeb was effective in reducing the leaf blight caused by *A. alternata* causing Chrysanthemum leaf blight (Arun Kumar *et al.*, 2011) [2] and both were recommended for purple blotch (Gevens 2011) [6]. Chatage and Bhale (2011) showed the effectiveness of mancozeb and chlorothalonil against *A. pluriseptata* incitant of IVY ground fruit. Mancozeb was reported as highly effective fungicide in the management of purple blotch of onion (Chethana and Kachapur 2010, Shahnaz, 2013) [3, 11]. Considering the significance of dithiocarbamates in plant protection of vegetable crops, the studies on their persistence in vegetable crop like onion and soil environment would be of immense value. Onion is the major crop which has drawn much attention of the farmers for domestic as well as for the export purpose and has significant contribution to Indian economy. Dithiocarbamate are the commonly used pesticides against various diseases of vegetable crops (Baruha *et al.*, 1980). Since onion is consumed as raw in both immature and mature growth stages, the study on dissipation pattern of commonly used fungicide like mancozeb will help to decide the safe waiting period.

## 2. Materials and Methods

### 2.1 Field Experiment

The experiment was laid out in a Randomized Block Design (RBD) with three treatments i.e. Untreated control (T<sub>0</sub>), Recommended dose @ 1500 g a.i. /ha (T<sub>1</sub>) and Double the recommended dose @ 3000 g a.i. /ha (T<sub>2</sub>). The treatments were replicated thrice with individual plot size of 20 m<sup>2</sup> (5m x 4 m). Three foliar applications of mancozeb 75 WP were given by Knapsack sprayer fitted with hollow cone nozzle at 10 days interval starting first application at 25 days after transplanting. The sample (1 kg) of immature onion (including leaves) was separately collected from each replication and treatment at 0, 3, 5, 7, 10, 15, and 20 days after last application. The sample (1 kg) of mature onion and soil was collected at harvest. The collected samples were brought immediately to the laboratory in polythene bags for further residue estimation.

### 2.2 Apparatus

An electronic weighing balance (Mettler Toledo) capable of weighing 0.1 mg supplied by M/s. Mettler Toledo, Switzerland, Remi make centrifuge, Remi Elektrotechnike Ltd, Vasai, Waterbath, Vortex. Robot coupe homogenizer (Blixer 6.6), Centrifuge with maximum speed 5,000 rpm (Remi-R-24), LV evaporator (Caliper Life Sciences, USA) were used during the study.

### 2.3 Glassware & equipment cleaning procedure

All glass items were of 'A' grade. Glassware was initially cleaned with aqueous soap solution and was rinsed thoroughly with tap water. Acetone rinsed glassware was oven-dried prior to use.

### 2.4 Reagents & Chemicals

Certified reference standards of carbon disulfide and mancozeb with purity of 99 percent and 86.74 percent, respectively were provided by M/s. Dow AgroSciences India Pvt. Limited.

Ethyl acetate (HPLC grade), Stannous chloride, Hydrochloric acid, Acetone (AR grade) and Isooctane was procured from M/s. Rankem Fine Chemicals, Ltd., New Delhi.

### 2.5 Residue Analysis

#### 2.5.1 Standard Preparation

Residues of mancozeb in onion leaves, mature onion and cropped soil were estimated by following carbon disulphide evolution method on GCMS after the validation of the method in the laboratory.

#### 2.5.2 Stock Solution of Carbon disulphide (CS<sub>2</sub>)

A stock solution of carbon disulphide in isooctane with approximate concentration of 1073 mg CS<sub>2</sub>/L was prepared as follows:

Took 10 ml volumetric flask and tarred the weight. Filled the flask upto designated mark with isooctane and noted down the weight of isooctane. Again, tarred along with isooctane contained in the flask and added 20 µL of pure carbon disulphide and closed the flask and note down the weight in mg. The actual concentration of the stock solution was calculated by using following formula.

#### Actual weight of the standard

$$= (\text{Weight of standard} * \text{Purity of Standard})/100 \\ = (22 * 99)/100 = 21.78$$

#### Weight of the solvent in ml

$$= (\text{weight of the solvent in gram/specific gravity of isooctane in g/ml}) \\ = (14/0.69) = 20.29$$

#### Actual concentration of CS<sub>2</sub> mother standard (stock) solution (C1)

$$= \text{Actual weight of the standard/ ml of the solvent} \\ = 21.78/ 20.29 = 1073 \text{ mg CS}_2/\text{L}$$

An intermediate standard and working standards of CS<sub>2</sub> were prepared by serial dilution. Because of the volatility of carbon disulphide and isooctane, laboratory glassware needs to be quickly and tightly closed.

#### 2.5.3 Stock Solution of Mancozeb

A stock solution of mancozeb in ethyl acetate with approximate concentration of 625.27 mg/L was prepared by weighing approximately 10 (± 0.05) mg of mancozeb in closed standard bottle and dissolved in 10 ml ethyl acetate. The weight of solvent in g was recorded and actual concentration of mancozeb stock solution was calculated by using formula given below.

#### Actual weight of the Standard

$$= (\text{Weight of standard} * \text{Purity of standard})/100 \\ = (16.2/86.74)/100 = 14.05$$

#### Weight of the ethyl acetate solvent in ml

$$= (\text{weight of solvent in g/ density of ethyl acetate in g/ml}) \\ = (20/0.89) = 22.47$$

#### Actual concentration of mancozeb stock solution

$$= \text{Actual weight of the Std/ml of the solvent} \\ = 14.05/22.47 = 625.27 \text{ mg/L}$$

#### 2.5.4 Preparation of reaction mixture SnCl<sub>2</sub>/HCl

Thirty g stannous chloride was dissolved in 1 L of concentrated hydrochloric acid and then one-L deionised water was added to it. The solution was prepared prior to use.

#### 2.5.5 Linearity and Recovery studies:

During the study linearity was studied with standard of CS<sub>2</sub> in matrix at five linear concentrations i.e. 0.05, 0.10, 0.25, 0.40 and 0.50 mg/kg to find out the range of the instrument. Recovery studies were carried out in order to establish the reliability of the method of analysis by fortifying samples collected from untreated control plot. The samples of immature onion (including leaves), mature onion and cropped soil were spiked by mancozeb standard at three different concentrations i.e. 0.05 mg/kg (LOQ Level), 0.25 mg/kg (5 times LOQ level) and 0.50 mg/kg (10 times LOQ level). The quantity of mancozeb to be spiked to achieve desired fortification level was calculated by following formula.

$$\text{Concentration to be achieved} * \text{Weight of Sample} \\ \text{Spike Quantity} = \text{-----} \\ 0.557 (\text{conversion factor}) * \text{Concentration of Stock solution}$$

Extraction and cleanup of spiked samples were done by the methodology as described below.

### 2.5.6 Extraction and Cleanup of immature onion (including leaves), mature onion and soil

Mancozeb residues in immature onion (including leaves), mature onion and cropped soil were analysed by the method based on carbon disulphide (CS<sub>2</sub>) elution on GCMS.

Homogenized sample 25 g was weighed in a 250 mL glass bottle where 75 mL of the reaction mixture (SnCl<sub>2</sub>/HCl) was added with pipette, followed by 25 mL iso-octane. The bottle was closed immediately (gas-tight) and placed in a water bath at 80 °C for 1 h with intermittent shaking and inverting the bottle after every 20 min. The bottle was taken out of the bath after one hour, cooled at < 20 °C by ice water and then transferred 1 mL aliquot of the upper iso-octane layer into a micro centrifuge tube. The content was then centrifuged at 5000 rpm for 5 min at 10. The supernatant was transferred into GC vials, and the residues of mancozeb were estimated on GC-MS by determining the CS<sub>2</sub> concentration.

### 2.5.7 GC-MS Analysis

Gas Chromatograph Mass Spectrometer, Model GCMS QP 2010 Plus (Shimadzu, Japan) equipped with split/split less auto-injector model AOC-20i and GCMS solution data software was used for the analysis. The separation was achieved on capillary column (VF 5 MS, 30 m, 0.25 mm i.d., and 0.25 µm film thicknesses) by Agilent Technology, Mumbai. The GC separation was conducted at following conditions: N<sub>2</sub> gas flow, 1.1 mL/min; Make up, 30 mL/min; injector temperature, 110 °C; Interface Temperature, 285 °C; Ion source Temperature, 200 °C; injection volume, 1 µL; initial

oven temperature, 37 °C, held for 1 min, then a 4 °C/min ramp to 50 °C, held for 2 min followed by a 40 °C/min ramp to 210 °C.

The quantitative estimation of mancozeb (based on CS<sub>2</sub>) in unknown sample was done by using following formula.

$$\text{Con. of mancozeb (based on CS}_2\text{) (mg/kg)} = \frac{\text{Sample Area-Intercept}}{\text{Slope}} \times \text{DF}$$

$$\text{CS}_2 \text{ mancozeb equivalent} = 541.045/4 * 76.139 = 1.77 * \text{CS}_2 \text{ mg/kg}$$

## 3. Results and Discussion

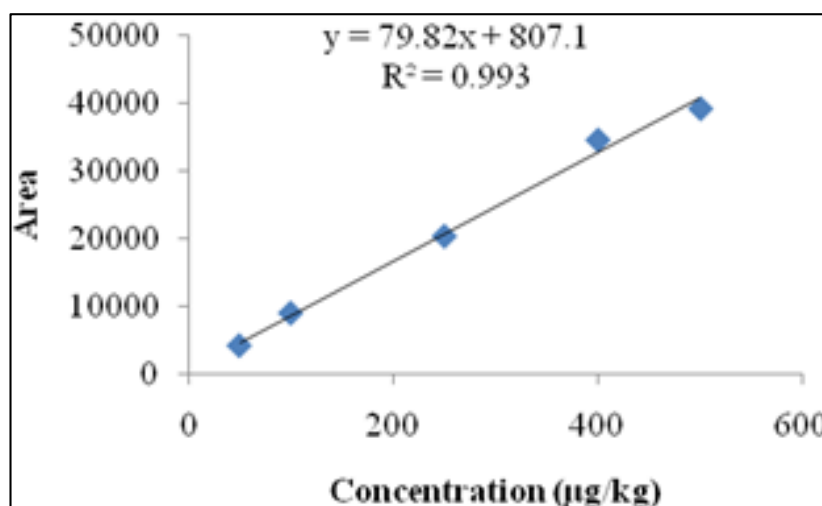
### 3.1 Linearity and Recovery studies

Calibration Curve was established with concentrations of the standard and corresponding peak area (Fig. 1). The regression coefficient (R<sup>2</sup>) obtained from the curve was greater than 0.99 over the range tested. The result of the linearity study proved the methods ability to obtain test results, which are directly proportional to the concentration of analyte in the sample. The results of the recovery studies are presented in Table 1 and depicted in Fig. 1. The result revealed that recovery of mancozeb in immature onion, mature onion and cropped soil was within acceptable range of 70 to 120 percent as per SANTE/11813/2017. Results of recovery clearly indicated the fitness of the analytical method for extracting the analyte of the interest from given sample matrix.

**Table 1:** Recovery of mancozeb in onion

Substrate	Percent Recovery (Mean* ± SD)		
	Fortification Level		
	0.05 mg/kg	0.25 mg/kg	0.50 mg/kg
Immature onions with leaves	88.29 (±1.66)	84.47 (±2.06)	87.63 (±0.44)
Mature onions without leaves	97.16 (±2.01)	92.49 (±1.79)	93.80 (±0.35)
Soil	81.11 (±0.83)	80.42 (±0.42)	82.32 (±0.71)

Astrisk represents the mean of three replications



**Fig 1:** Standard curve of concentrations of the CS<sub>2</sub> standard and corresponding peak area

### 3.2 Residues / dissipation of mancozeb

Mean initial residues of mancozeb (based on CS<sub>2</sub>) in immature onion (including leaves) were found to be 3.44 mg/kg at recommended dose and 5.89 mg/kg at double the recommended dose, respectively (Table 2 and Fig. 2 & 3). Residues dissipated below limit of quantification (0.05 mg/kg) on 10<sup>th</sup> and 15<sup>th</sup> day with a half-life of 1.91 and 2.33

days at recommended dose and double the recommended dose, respectively. The residues of mancozeb (based on CS<sub>2</sub>) in mature onions and soil collected at harvest were found below limit of quantification. At recommended dose the mancozeb dissipated to 39%, 43.3% and 80.50% at 3, 5 and 7 days, respectively. Whereas for the double dose dissipation was 21.39, 52.91, 50.45 & 68.52 at 3, 5, 7 & 10 days,

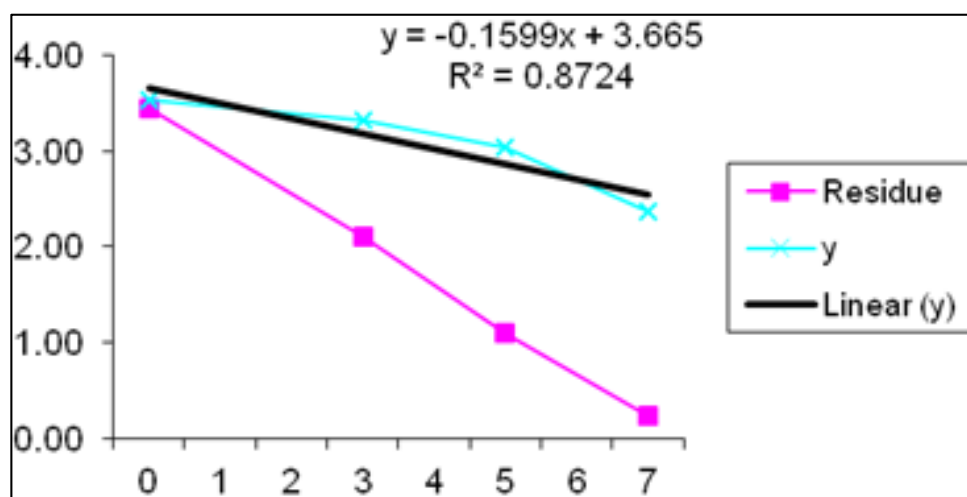
respectively. Present findings agree with Sarkar *et al* (2005) [10] who reported that mancozeb residues were below detectable limits on the 5th day for the recommended dose and 7th day for double the recommended dose in the case of onion whole plant. The half-life values varied from 0.97 to 1.22 days. Jagdish *et al.* (2015) reported the initial residue deposits of mancozeb (as CS2) in tomato crop in two different seasons 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 CS2) as Codex Alimentarius, the pre-harvest interval for recommended and double recommended dose of mancozeb treatment was 2 and 3 days, respectively. Similarly, according to El Habib Ait Addi, (2017) [5], degradation rate of mancozeb in tomato under both open field and greenhouse condition followed first order kinetics. Half-lives were 1.77

and 1.3 days in open field and in greenhouse were 2.0 and 1.8 days, for October and March period respectively. Based on the observation reported, a pre-harvest interval of at least three days after pesticide application at recommended dose was suggested. Devi PA *et al.* (2015) reported average initial deposition of mancozeb in mango in the range of 2.25 to 2.71 and 4.17 to 5.96 mg/kg at respective doses. Residues of mancozeb were dissipated to the below detectable limit of 7 days after spray at recommended dosage in all the locations. The fungicide degradation followed a first order kinetics with half-lives of 1-3 days, for mancozeb. Ritu Rani *et al* (2013) [9] estimated the dissipation of mancozeb and metalaxyl in tomato by following four applications of a combination formulation Ridomil MZ (mancozeb 64% + metalaxyl 8%) at 0.25 and 0.50% at 10 days interval. They further reported half-life periods for mancozeb as 3.7 6 and 4.1 4 days, at single and double the application rates, respectively. Residues of mancozeb dissipated below limit of quantification (LOQ) of 0.25 mg kg after 1 0 and 1 5-day s at single and double the application dosage, respectively. All these reports lend support to the present findings.

**Table 2:** Residues of mancozeb in/on onion

Days after treatment	Dosage			
	Mancozeb @1500 g a.i. /ha		Mancozeb @ 3000 g a.i. /ha	
	Residues (mg/kg) Mean* ± SD	Dissipation (%)	Residues (mg/kg) Mean* ± SD	Dissipation (%)
0	3.444 ± 0.131		5.893 (±0.266)	
3	2.100 ± 0.015	39.24	4.630 (±0.012)	21.39
5	1.190 ± 0.019	43.33	2.178 (±0.101)	52.91
7	0.232 ± 0.022	80.50	1.081 (±0.014)	50.45
10	BLQ	--	0.336 (±0.021)	68.52
15	BLQ	--	BLQ	--
Mature onions without leaves at harvest	BLQ	--	BLQ	--
Soil at harvest	BLQ		BLQ	
DT <sub>50</sub> (Days)		1.91		2.33

Astrisk represents the mean of three replications



**Fig 2:** Dissipation curves of mancozeb at recommended dose on onion

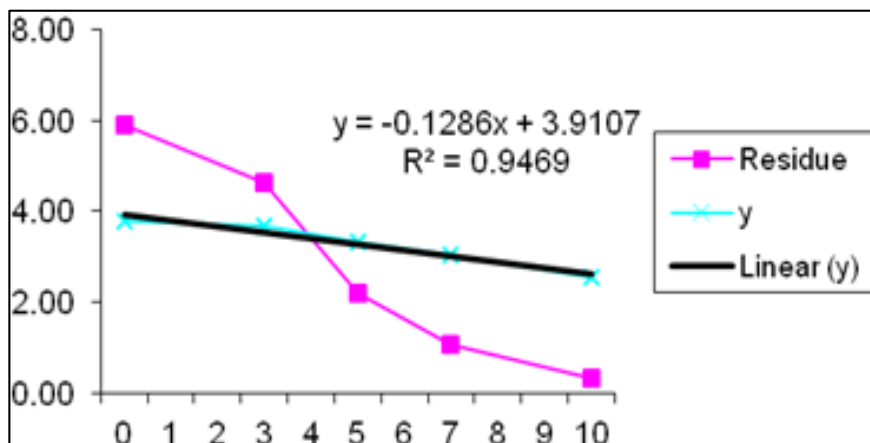


Fig 3: Dissipation curves of mancozeb at double the recommended dose on onion

#### 4. Acknowledgement

Authors are thankful to the Network Coordinator, AINP on Pesticide Residues, ICAR, New Delhi for providing the financial support to undertake the studies.

Application of Confounded Factorials. Journal of Agricultural Science. 2013; 5(1):17-22 doi:10.5539/jas.v5n1p17

#### 5. References

1. Anonymous, Horticulture Statistics at a glance. 2018, 197.
2. Arun Kumar GS, Kamanna BC, Benagi VI. Management of Chrysanthemum leaf blight caused by *Alternaria alternata* (FR) Keissler under field condition. Plant Arch. 2011; 11(1):553-555.
3. Chethana BS, Kachapur MR. Field evaluation of Fungicides, Bioagent and Plant extract against purple blotch of onion. Geobias. 2010; 37(4):253-261.
4. Devi PA, Paramasivam M, Prakasam V. Degradation pattern and risk assessment of carbendazim and mancozeb in mango fruits. 2.15; Environ Monit Assess. Vol. 187(1):4142.
5. El Habib Ait Addi. Dissipation Behavior of a Mancozeb Residue (Dithiocarbamate Fungicide) in Tomato under South Moroccan Climatic Condition. IRA-International Journal of Applied Sciences. 2017; 07(02):62-68.
6. Gevens A. Fungicide updates in onion. WPVGA Ed Conference, 2011.
7. Jagadish GK, Jayalakshmi SK, Sreeramulu K. Persistence and dissipation of mancozeb residues in/on tomato in Bidar District of Karnataka State, India. Issues in Biological Sciences and Pharmaceutical Research. 2015; 3(9):94-99, September 2015.
8. Marmath KK, Giri P, Sharma S, Taj G, Kumar A. In-silico interaction studies of *Alternaria brassicae* toxin destruxin B and potential partners of MAPK4 cascade. Int J Agric Environ Biotechnol. 2003; 6(2):203-210.doi: 10.5958/j.2230-732X.
9. Ritu Rani, Vineet K, Sharma GS, Rattan, Balwinder Singh, Neeraj Sharma. Dissipation of Residues of Mancozeb and Metalaxyl in Tomato (*Solanum lycopersicum* L.). Bulletin of Environmental Contamination and Toxicology. 2013; 90(2):248-251 |
10. Sarkar MA, Raktim Pal, Piw Das, Chaowdhury A. Studies on residues and persistence/dissipation of Mancozeb in whole onion plant (*Allium cepo*) and soil following application of 75 WP formulations. 2005; 29: 17-20.
11. Shahnaz VK, Razdan SEH, Rizvi TR, Rather, Sachin Gupta, Muneeb Andrabi. Integrated Disease Management of Foliar Blight Disease of Onion: A Case Study of