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Dissipation Behavior of a Mancozeb Residue (Dithiocarbamate Fungicide) in Tomato Under South Moroccan Climatic Condition

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ABSTRACT

Dissipation behavior of mancozeb, a widely used dithiocarbamte fungicide, applied under field condition on tomato at recommended dose was undertaken under greenhouses and open field during October and March in Souss-Massa area (south of Morocco) climatic condition. Residue levels of mancozeb were determined by using a simple method consisting in a hot acid digestion of the whole sample to evolve carbon disulfide (CS_2), which is further quantified by spectrophotometry. Degradation rate in both open field and greenhouse followed first order kinetic. 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 harvested interval of at least three days after pesticide application at recommended dose may be suggested.

Key words: Mancozeb, Dissipation, Tomato, Souss-Massa

1. INTRODUCTION

In Morocco, tomatoes are considered to be high value cash crops for farmers and they are also a source of hard currency. The annual production of these crops is over 600000 tons, of which about 80% is exported from Souss-Massa area.

Long-cycle tomatoes grown develop throughout autumn and part of spring. Fruits ripen gradually and are usually harvested weekly. Therefore, to protect tomato from pathogens, such as grey mold, pesticides with a short pre-harvest interval (PHI) of one week or less are required. Conventional fungicides have shown resistance phenomena due to their extensive use [1,2]. As a result, these compounds do not give sufficient protection and the PHI of most of these pesticides is too long.
Dithiocarbamate, a non-systemic group of pesticide, is one of the major fungicide groups used in the production of agricultural crops and the most frequently detected pesticides in food monitoring programs in many countries [3-7]. In addition, Fungicides of the dithiocarbamate group are much better at controlling fungal pathogens of Solanaceous crops and vegetables [8]. To sustain the quality and productivity of the crops mancozeb, the ethylene-bis-dithiocarbamate (EBDC), is recommended but it was considered to be a multipotent carcinogenic agent in a long-term rat study [9].

The methodology most commonly used by monitoring laboratories to analyze dithiocarbamates in natural food products relies on the detection of CS_2 generated after acid digestion of any dithiocarbamates present in the crop [3-7]. Spectrophotometry [10-11] or gas chromatography [12-14] can be used for detection of these compounds, but the origin of the CS_2 generated cannot be determined by these methods.

With the intensive use of pesticides, residues may be accumulated at levels higher than those permitted by the EU or international MRLs. The dissipation rate of a pesticide after application is a useful tool for the assessment of the behaviour of its residues. Additionally, residues dissipation curves can be used to estimate the time required for decreasing the residues levels below MRLs [15-17]. To the best of our knowledge, there is limited data in the literature concerning the dissipation rate of the mancozeb in tomato.

Tomato crop is highly remunerative and sprayed heavily with fungicides close to harvest, which may leave harmful residues in fruits. The present investigation was conducted to determine the dissipation pattern as well as the residue level of Mancozeb, when applied recommended doses, in tomatoes fruits in two different growing locations: under greenhouses and in open field during two periods: October and March under Souss-Massa area (south of Morocco) climatic conditions.

2. MATERIALS AND METHODS

Chemicals

In the present study, Mancozeb, an analytical standard purity 98.97%, was purchased from Sigma Aldrich and the carbon disulfide CS_2 was purchased from Fluka, Swisserland.

Commercial mancozeb (Ditham M45) was purchased from local distributors.
Hydrochloric acid, Potassium iodide, Tin (II) chloride, Sodium hydroxide, diethanolamine, ethanol and cupric acetate monohydrate were purchased from Panreac, Spain.

Design of Field Experiment
The study was carried out at orchard located in the Souss-Massa area (south of Morocco). Four field experiments were conducted to study the residues of Mancozeb in Tomatoes fruits.
The first trial was conducted under greenhouse (Location-I) with Tomatoes. On the contrary, the second trial was conducted in open field (Location-II) with the same variety. The trials were conducted during October (Period-I) and during March (Period-II) at both location. The tomatoes varieties were sown with a spacing of 40 cm x 100 cm and the plot size was 9 m x 9 m (81 m^2) in open field. However, under greenhouse the tomato planting density was 20000 plants/ha.

Application of Fungicides
The treatment was carried out with Ditham M45 (Mancozeb 80%) as a commercial formulation applied at the dose recommended by the manufacturer (200 g/hL) with a portable motor sprayer. The pesticide was applied as a single application only. Identical portions of trees were maintained as controls.

Collection of Samples
Fruits of Tomato were collected randomly at intervals of 0 (2 hrs after application), 1, 3, 5, 7, 9, 14, 15, 16 days after spraying with pesticide. Each sample consisted of 10 pieces of tomatoes. The samples were collected, sealed in labelled polyethylene bags with a unique sample identity, stored at 4 °C and transported to the laboratory. The samples were deep-frozen until analysis was carried out.

Extraction and Clean up
The digestion/distillation apparatus was used for the determination of CS_2 from residues of dithiocarbamate fungicides. The Representative 100 g sample of crop matrices, with 10g of KI, 2g of SnCl2 and 200 ml of distilled water, were decomposed by refluxing with dilute acid (30 mL hydrochloric acid). Released CS_2 is pushed through the entire system by applying slight vacuum. The evolved CS_2 was trapped in trap containing 10 mL of 15% NaOH solution. The final CS_2 trap contained 15 mL of Cullen reagent, made up from 25 mg of cupric acetate monohydrate and 25 g diethanolamine in 250 ml ethanol. The solution of the complex formed from the reaction between CS_2 and the copper (II) acetate monohydrate was measured at 435 nm in a Agilent 8453 UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

Analytical procedure

Estimation of Residues
The level of residues in the samples was expressed as mg of carbon disulfide (CS_2) per kg fruits. The limit of detection (LOD) and limit of quantification (LOQ) were 0.01 µg/g and 0.03 µg/g, respectively.

Recovery Experiment
In order to estimate the efficiency of the method, recovery experiment was conducted by fortifying untreated samples of Tomato fruits with Mancozeb at 0.1, 0.25, 0.50 and 1 mg/kg level. The fortified samples were analyzed and estimated following the method as described earlier. Average recoveries of Mancozeb from different substrates fortified ranged from 86-94% (Table-1).

Disappearance of Mancozeb from tomatoes:
The residue data, including mean values, standard deviations and % dissipation obtained in the decline study after treatment of Mancozeb are summarized in Table 2 and 3.
The residue was found below the detectable limit in the untreated control.

The results obtained shows that the initial deposits of mancozeb (0 days) in tomatoes fruits were found to be fairly uniform (6.16-6.28 mg /kg) independently of the period and the location. However, there were significant differences in the rates of dissipation not only according to the location but also according to the period. In general, by comparing the rates of dissipations we notice that residues dissipated at faster rate in the case of the open field than in the case under greenhouse. It was also observed from the study that the dissipation rate was faster in period 2 than period 1. But, in all cases, residues were detected until the 14^{th} day, beyond that no residues were detected. The only exception was observed in trial carried out in period 2 at location 2, where more than 99% reduction was achieved 9 days after spraying. We note that a rainfall was happened shortly after the application during this period.

The faster rate of dissipation can be attributed to the differences in the dilution due to the growth of tomato fruits and the excessive rains. The results are comparable with other works [8,18-19].
The growth dilution factor is important in reducing the residue levels in tomato as the fruit on which pesticides are applied is in different stages of growth. The immature fruits by the time attain the size and the coloration required; the residue of applied pesticides on them will undergo a growth dilution. Xue and Chen reported that the dissipation of pyrithyroid residues had been due to growth dilution factor[20]. A rainfall shortly after the application plays a significant role in washing of applied pesticides and might be the major reason for faster dissipation of residue in period 2 at location 2 as observed in the present study [21].

Since a strong correlation co-efficient (0.9583 - 0.9927) was obtained between residue dissipation and time it was concluded that the dissipation rate followed the first order kinetics at both periods and in both locations. The reaction rate constant was calculated from the slope of the linear regression line. Following the first order reaction, the half life of adsorption could be determined from: $\ln C/C_o = -kt$ where Co and C were the initial concentration and concentration of mancozeb at time t and k was the reaction rate constant.

Based on the first-order rate constants obtained, the fungicides dissipated in the following sequence (Table 4): OFP2 (0.52 d^{-1}) > OFP1 (0.39 d^{-1}) > GHP2 (0.37 d^{-1}) > GHP1 (0.34 d^{-1}).
On the basis of data generated the half-life values were calculated and found as 2.11; 2.28 days at location I and 1.77; 2.03 days at location 2. The pre-harvest intervals (PHI) were also calculated at MRL of 3 mg/ kg and found to be 2.21-3.0 days irrespective of periods and locations. The results are comparable with earlier studies [19,22-23].

When compared with the proposed MRL of 3.0 mg/kg on Tomato, the residues of mancozeb reached below MRL in 2.8-3.0 days and 2.21-2.69 days for location I and location-II, respectively. The pre-harvest intervals (PHI) of mancozeb in the present investigations are in agreement with the reports of earlier workers with values of 2.02-4.85 days for propineb in tomato [8,24].

Therefore it is recommended that Tomatoes fruits may be harvested 3 days after spraying of mancozeb at the recommended doses in accordance with good agricultural practices.

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Table 1. Results of method validation by recovery analysis of Mancozeb from test samples.

Substrate	Amount fortified (mg/kg)	Amount recovered (mg/kg)	Recovery of Mancozeb (%)	Average recovery of Mancozeb (%)
Tomatoes	0.1	0.088	88	90
	0.25	0.22	88	
	0.5	0.48	90	
	1	0.94	94	

Table 2. Dissipation of mancozeb in/on Tomato at Location-I: under Greenhouse (GH)

Sampling Interval (in days)	October (Period1) GHP1		March (Period2) GHP2	
	Residue (mg/kg), **M± SD**	**% of Dissipation**	Residue (mg/kg), **M± SD**	**% of Dissipation**
0	6.25±0.04	-	6.28±0.06	-
1	4.81±0.08	**23.04**	4.67±0.02	**25.64**
3	2.84±0.05	**54.56**	2.73±0.08	**56.53**
5	1.52±0.09	**75.68**	1.38±0.04	**78.03**
7	0.88±0.03	**85.92**	0.56±0.07	**91.08**
9	0.3±0.05	**95.20**	0.2±0.08	**96.82**
14	0.059±0.09	**99.06**	0.041±0.08	**99.35**
15	ND	-	ND	-
16	ND	-	ND	-

ND: not detected, ≤limit of detection (LOD)

Table 3. Dissipation of mancozeb in/on Tomato at Location-II: Open Field (OF)

Sampling Interval (in days)	October (Period1) OFP1		March (Period2) OFP2	
	Residue (mg/kg), **M*± SD**	**% of Dissipation**	Residue (mg/kg), **M*± SD**	**% of Dissipation**
0	6.16±0.04	-	6.17±0.06	-
1	4.31±0.08	**30.03**	3.07±0.02	**50.24**
3	2.48±0.05	**59.74**	1.44±0.08	**76.66**
5	1.22±0.09	**80.19**	0.52±0.04	**91.57**
7	0.60±0.03	**90.26**	0.31±0.07	**94.98**
9	0.16±0.05	**97.40**	0.035±0.08	**99.43**
14	0.031±0.09	**99.50**	ND	-
15	ND	-	ND	-
16	ND	-	ND	-

ND: not detected, ≤limit of detection (LOD)

Table 4. Regression equation, Determination Coefficient, Degradation rate constant k, half-life and Pre-harvest interval for the dissipation of mancoczeb in Tomatoes at different Location and period.

Period	Location	Determination coefficient (R^2)	Degradation rate constant k ($days^{-1}$)	Half life (days)	Pre-harvest interval (days)
October	Open field OFP1	$R^2 = 0.9895$	0.39	1.77	2.69
	Green house GHP1	$R^2 = 0.9914$	0.34	2.03	3.0
March	Open field OFP2	$R^2 = 0.9583$	0.52	1.33	2.21
	Green house GHP2	$R^2 = 0.9927$	0.37	1.86	2.8