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Persistence and Dissipation of Propineb-A Dithiocarbamate Fungicide in Potato under East-Indian Climatic Conditions

Md. Wasim Aktar[1]*, M. Paramasivam[1] and Dwaipayan Sengupta[2]

ABSTRACT

A two season study (Season-I: October, 2005 January, 2006 and Season-II: October, 2006 January, 2007) on the persistence of propineb (Propineb® 70% WP) was undertaken with potatoes at two different locations having two different types of soil: new alluvial and old alluvial, respectively. Two dosage rates were applied: 2.5 and 5.0 kg ai ha^{-1} twice with a 15-day interval. More than 94% of the initial residues of propineb in the potato tubers dissipated within 15 days after application irrespective of dose, season and location. The residue was detectable up to 20 days after the last application of the fungicide. Assuming first order kinetics, the half-life values varied from 2.59 to 3.48 days. A safe waiting period of 10 days is recommended for potatoes.

Key words: dissipation, residues, propineb, potato, degradation dynamics

INTRODUCTION

Propineb [polymeric zinc propylene-bis-(dithiocarbamate)] $[(C_5H_8N_2S_4Zn)_x]$ is a polymeric dithiocarbamate fungicide. A new, commercially-available fungicide formulation, Propineb® 70% WP, belonging to the group of propylene-bis-dithiocarbamates, can also be used as a substitute for the control of numerous fungal diseases of potato (Anon,1971; Sharma *et al*., 1994).

Dithiocarbamates are widely-used chemicals that display high, broad-spectrum activity against fungal plant diseases (Tomlin, 1994). Disulfiram, the thiuram disulfide of diethyldithiocarbamate (DDTC), also has clinical applications, having been used for almost 50 years in alcohol-aversion therapy (Brewer, 1993). Furthermore, dithiocarbamates are presently receiving attention as potential adjuncts to traditional oncological chemotherapy, due to their "immune restorative" effect, along with protection against the tissue toxicity of cisplatin treatment and the potentiation of tumoricidal therapies (Cohen and Robins, 1990). Although dithiocarbamates are known to display low acute and chronic toxicities in human and experimental animals (Liesivuori and Savolainen, 1994), the extreme reactivity mainly related to their metal-chelating ability (Allain and Krari, 1991), and high affinity for proteins containing the -SH group, underlies the wide range of their adverse effects. These include neurotoxicity (Miller, 1982), a sympathetic vascular-asthenic syndrome, antithyroid

1 Pesticide Residue Laboratory, Department of Agricultural Chemicals, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur-741252, Nadia, West Bengal, India.

2 Department of Agricultural Chemistry and Soil Science, Institute of Agricultural Science, University of Calcutta, Kolkata, West Bengal, India.

* Corresponding author, e-mail: wasim04101981@yahoo.co.in

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properties, skin sensitization and teratogenesis (Hayes, 1991). Furthermore at low doses, DDTC provokes cytotoxicity, both in human cell lines of lymphoid origin (Cohen and Robins, 1990) and in serum-free, dissociated mesencephalic-striatal cocultures (Soleo *et al*., 1996).

Potato is a principal crop of eastern India and is attacked by a number of diseases, such as potato scab (*Venturia inaequalis*) and early and late blight among others. To sustain the quality and productivity of the crops, mancozeb (a dithiocarbamate fungicide) is recommended. Fungicides of the dithiocarbamate group are much better at controlling fungal pathogens of *Solanaceous* crops and vegetables (Ahuja and Pande, 2006; Kumar, 1989).

A potato crop is highly remunerative and is sprayed heavily with fungicides close to harvest, which may leave harmful residues in the tuber. Since there are no data available on the persistence of propineb in potatoes, the present investigation was conducted to determine the dissipation pattern, as well as the residue level of propineb in potato tubers at two different locations for two consecutive seasons in West Bengal (East India) when applied at 2.5 kg ai ha^{-1} (T_1) and 5.0 kg ai ha^{-1} (T_2), along with an untreated control (T_3).

MATERIALS AND METHODS

Design of field experiment

Four field experiments were conducted to study the residues of propineb in/on a potato crop. The first field trial was conducted during rabi (Winter), October, 2005 January, 2006 (Season I) with the potato variety Kufri Chandramukhi. The second trial was conducted during rabi (Winter), October, 2006 January, 2007 (Season II) with the variety Kufri Jyoti. The trail was replicated at two different locations: Location I, on a new alluvial soil (Baruipur, District-North 24 Parganas); and Location II, on an old alluvial soil (Balarampur, District-Hooghly) in west Bengal. Both field trials were laid out using a randomized complete block design (RBD) with three replicated plots. The potato varieties were sown with a spacing of 30 cm × 40 cm and the plot size was 6 m × 6 m (36 m^2).

Climatic conditions

The climatic parameters for Season I (October, 2005 January,2006) were: minimum temperature 21.04°C, maximum temperature 27.50°C, relative humidity 86.71%, rainfall 164 mm for Location I; and minimum temperature 14.60°C, maximum temperature 22.70°C, relative humidity 84.00%, rainfall 233.10 mm for Location II. For Season II (October, 2006 January, 2007), the climatic conditions were: minimum temperature 17.40°C, maximum temperature 25.60°C, relative humidity 85.23%, rainfall 185.65 mm for Location I; and minimum temperature 20.80°C, maximum temperature 29.90°C, relative humidity 75.36%, rainfall 75.20 mm for Location II.

Application of fungicide

Propineb (zinc propylene-bis-dithiocarbamate) containing 70% active ingredient (a.i.) was obtained from a local dealer in Kolkata. It was sprayed by knapsack twice on the potatoes with an interval of 15 days. Propineb® 70% WP @ 2.5 and 5.0 kg a.i. ha^{-1} was sprayed at both locations. Identical portions of plants were maintained as controls and were sprayed with water.

Collection of samples

Tubers of potato were collected randomly from each treatment replication after the last foliar application at intervals of 0 (2 hrs after application), 1, 3, 5, 7, 10, 15, 20 and 30 days. Soil samples were also collected on the same basis.

Extraction and clean up

A representative 100 g slurry sample

from each plot was processed for the estimation of propineb residue as per the method of Dubey and Nath, 1991. Potato tuber and soil samples were taken separately. The crop matrices and soil samples were decomposed separately by refluxing with dilute acid (30 ml hydrochloric acid). The evolved CS_2 was trapped in an H_2S trap containing 10 ml of 10% NaOH solution overlaid with 5 ml benzene. The final CS_2 trap contained 15 ml of chromogenic reagent, made up from 25 mg of cupric acetate monohydrate and 25 g diethanolamine in 250 ml ethanol (Dubey and Nath, 1991).

Estimation of residues

The CS_2 on reaction with chromogenic reagent yielded a yellow-coloured complex of cupric salt of N, N-bis (2 - hydroxy) dithiocarbamic acid which was measured immediately by spectrophotometer at 435 nm. The level of residues in the samples was expressed as mg of carbon disulfide (CS_2) per g tuber or soil. The half-life and waiting periods were calculated (Hoskins, 1961) on the basis of the maximum residue limit of CS_2 per kg of fruit or soil (Anon, 1971). The limit of detection (LOD) and limit of quantification (LOQ) were 0.01 μg g^{-1} and 0.03 μg g^{-1}, respectively.

Recovery experiment

In order to estimate the efficiency of the method, a recovery experiment was conducted by fortifying untreated samples of potato tuber and soil with propineb (analytical standard, purity 98.97%, Sigma Aldrich) @ 0.25, 0.50 and 1 μg g^{-1} level. The fortified samples were analyzed and estimated following the method described earlier.

RESULTS AND DISCUSSION

Average recoveries of propineb from different substrates fortified @ 0.25, 0.50 and 1.00 μg g^{-1} ranged from 90-96% and 88-98% for soil and potato tuber, respectively (Table 1).

The residues in μg g^{-1} (CS_2) of propineb in the potato tubers at different days after application and the corresponding half-life values by season are represented in Tables 2, 3 and 4. The residue was below the detectable limit in the untreated control (T_3), as well as in the cropped soil with time irrespective of any dose and season. It was also observed from the study that the dissipation rate was very fast.

The initial deposits of Propineb (0 day) in potato tubers were found to be fairly uniform (6.95-12.81 μg g^{-1}) in both seasons at both locations (Tables 2 and 3). The residue of the fungicide had dissipated to the extent of 67.84-83.27 % by the fifth day after application at the two locations irrespective of the dosage. However, there were significant differences in the rates of dissipation, not only season-wise, but also

Table 1 Results of method validation by recovery analysis of propineb (analytical grade) from test samples.

Substrates	Amount fortified (μg g^{-1})	Amount recovered (μg g^{-1})	Recovery of propineb (%)	Avarage recovery of Propineb (%)
Soil	0.25	0.225	90	
	0.50	0.47	94	93.33
	1.00	0.96	96	
Potato tuber	0.25	0.22	88	
	0.50	0.48	96	94.00
	1.00	0.98	98	

Table 2 Dissipation of propineb in/on potatoes at Location I in 2005 and 2006.

Sampling interval (in days)	Residues (in μg g^{-1}) M*± SD (% of Dissipation)			
	T_1 (2.5 kg ai ha^{-1})		T_2 (5.0 kg ai ha^{-1})	
	Season I	Season II	Season I	Season II
0	8.13 ± 0.13	7.37 ±0.17	12.81 ±0.19	11.76 ±0.23
	(-)	(-)	(-)	(-)
1	5.15 ±0.15	4.62 ±0.13	8.27 ±0.16	8.29 ±0.12
	(36.65)	(37.31)	(35.44)	(29.51)
3	2.88 ±0.21	2.85 ±0.18	5.19 ±0.15	5.37 ±0.05
	(64.58)	(61.33)	(59.48)	(54.34)
5	1.36 ±0.17	1.41 ±0.11	4.12 ±0.21	3.54 ±0.13
	(83.27)	(80.87)	(67.84)	(69.90)
7	0.78 ± 0.09	0.53 ±0.15	2.66 ±0.13	2.64 ±0.17
	(90.41)	(92.81)	(79.23)	(77.55)
10	0.35 ±0.07	0.31 ±0.14	1.13 ±0.11	1.36 ±0.09
	(95.69)	(95.79)	(91.18)	(88.44)
15	0.11 ±0.04	0.13 ±0.03	0.53 ±0.06	0.64 ±0.05
	(98.65)	(98.24)	(95.86)	(94.56)
20	0.05 ± 0.06	0.03 ± 0.05	0.11 ± 0.07	0.17 ± 0.09
	(99.38)	(99.59)	(99.14)	(98.55)
30	BDL	BDL	BDL	BDL

BDL = Below detectable limit (<0. 01 μg g^{-1})
M* = Mean of three replicates

Table 3 Dissipation of propineb in/on potatoes at Location II in 2005 and 2006.

Sampling interval (in days)	Residues (in μg g^{-1}) M*± SD (% of Dissipation)			
	T_1 (2.5 kg ai ha^{-1})		T_2 (5.0 kg ai ha^{-1})	
	Season I	Season II	Season I	Season II
0	7.62 ±0.17	6.95 ±0.13	12.34 ±0.21	11.29 ±0.19
	(-)	(-)	(-)	(-)
1	4.76 ±0.13	4.23 ±0.15	7.23 ±0.12	8.13 ±0.15
	(37.53)	(39.14)	(41.41)	(27.99)
3	2.69 ±0.16	3.12 ±0.12	4.97 ±0.17	5.28 ±0.11
	(64.70)	(55.11)	(59.72)	(53.23)
5	1.83 ±0.18	1.45 ±0.11	2.99 ±0.14	3.41 ±0.19
	(75.98)	(79.14)	(75.77)	(69.80)
7	0.62 ±0.11	0.56 ±0.09	1.93 ±0.06	2.38 ±0.12
	(91.86)	(91.94)	(84.36)	(78.92)
10	0.35 ±0.03	0.28 ±0.13	1.04 ±0.04	1.27 ±0.07
	(95.41)	(95.97)	(91.57)	(88.75)
15	0.14 ±0.04	0.11 ±0.08	0.32 ±0.02	0.45 ±0.09
	(98.16)	(98.42)	(97.41)	(96.01)
20	0.06 ± 0.05	0.04 ± 0.03	0.18 ± 0.07	0.21 ± 0.09
	(99.21)	(99.42)	(98.54)	(98.14)
30	BDL	BDL	BDL	BDL

BDL = Below detectable limit (<0.01 μg g^{-1})
M* = Mean of three replicates

Table 4 Regression equation, correlation coefficient and half-life for the dissipation of propineb in potato tubers at different locations and in different years.

Location	Season	Treatments (kg ai ha^{-1})	Regression equation	Correlation co-efficient	Half-life (days)	Safe waiting period (days)
Location I (Baruipur)	I	T_1 (2.5)	y = 3.7735-0.1114x	0.982	2.70	3.89
		T_2 (5.0)	y = 3.7532-0.1161x	0.981	2.59	3.36
	II	T_1 (2.5)	y = 4.0672-0.0974x	0.990	3.09	6.47
		T_2 (5.0)	y = 4.0219-0.0871x	0.994	3.46	6.81
Location II (Balarampur)	I	T_1 (2.5)	y = 3.7431-0.1054x	0.972	2.86	3.84
		T_2 (5.0)	y = 3.7308-0.1128x	0.978	2.67	3.23
	II	T_1 (2.5)	y = 3.9713-0.0916x	0.986	3.29	6.71
		T_2 (5.0)	y = 3.9935-0.0865x	0.996	3.48	6.65

location- wise. In Season II, the residues dissipated to about 98% within 20 days of application at Location I and no residues could be detected thereafter, whereas in Season I the residues were detected up to the 20th day of the second application at the double dosage rate (T_2). At Location II, the residues dissipated at a slower rate during Season I compared to the dissipation at Location I. During the same season, the residues were detected up to the 20th day for both dosage rates. The faster rate of dissipation could be attributed to the differences in the dilution effect due to the growth of the potato tubers and excessive rain. The results were comparable with earlier works (Ahuja and Pande, 2005; Liesivuori and Savolainen, 1994).

Using the data collected, the half-life values were calculated and found to be in the range of 2.59 to 2.86 days at Location I and 3.09 to 3.48 days at Location II on the presumption of a first order rate of dissipation. The waiting periods were also calculated at an MRL of 3 mg kg^{-1} and found to be 3.36 to 6.81 days irrespective of dosage rate, season and location. Since a strong correlation co-efficient (0.972-0.996) was obtained between the residue dissipation and the time, it was concluded that the dissipation rate followed first order kinetics in both the seasons and at both locations. The results were comparable with earlier studies (Ahuja and Pande, 2004; and Kumar, 1989).

When compared with the proposed MRL of 3.0 mg/kg for potato tubers, the residues of propineb were below the MRL after 3.36-6.81 days and 3.23-6.71 days for Location I and Location II, respectively. The waiting periods of propineb in the present investigations were in agreement with the reports of earlier workers with values of 5.78 to 8.13 days for potato tubers (Sarkar *et al*.,1998).The waiting periods of mancozeb (EBDC fungicide) for different crops were different depending upon the type and texture of the crop (Sharma *et al*.,1994). Therefore it is recommended that potatoes may be harvested 10 days after the second application of propineb to satisfy the recommended doses for consumption.

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