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Persistence and degradation of propineb in soil

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SUMMARY

A laboratory experiment was conducted to study the persistence and degradation of propineb in soils from Malur and Hassan (sandy clay loamy) at 25 and 50 µg g^{-1} with field capacity and half-field capacity moisture regimes. The degradation pattern followed the first order kinetics. Degradation of propineb was faster under field capacity than half-field capacity moisture regimes at both rates in both the soils. Higher degradation was noticed in Malur soil than Hassan soil at both the rates of application and moisture regimes. The half-life values ranged from 6.5 to 7.1 days for Malur soil and 6.9 to 7.1 days for Hassan soil when applied at 25 and 50 µg g^{-1} of propineb under field capacity. Under half-field capacity the half-life ranged from 7.1 to 7.9 days for Malur soil and 9.1 and 9.8 days when applied at 25 and 50 µg g^{-1} of propineb, respectively.

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KEY WORDS : Persistence, Degradation, Propineb, Sandy clay loam

Potato (*Solanum tuberosum* L.) is one of the prime remunerative crop of southern Karnataka, which are mainly attacked by several fungal diseases. Research recommendations of chemical control of pest are considered as incomplete if data on toxic residue of pesticides are not available. Antracol 70WP (Propineb) is a newly introduced broad spectrum contact dithiocarbamate fungicide (Polymeric) in Indian market by Bayer (India). It is also called as methylzineb or mezineb or LH 30/Z or Bay 46131. Its closely related compounds are zineb, mancozeb, metiram, etc., which contain zinc in their structure. Propineb, PBDC (Propylene bis dithiocarbamate), a propylene analogue of zineb, has moderate acute toxicity. It degrades to propylene thiourea (PTU) in the environment. It is used as a protective treatment on several crops for the control of various fungi belonging especially to Oomycetes, Ascomycetes, Basidiomycetes and Fungi imperfect. Propineb controls blight on potatoes and tomatoes, downy mildew on hops and vines, apple scab, blue mould on tobacco and sigatoka disease of banana. It can also be used on gooseberries, black currants, celery and cereals to control many fungal diseases. 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 per cent WP, which belongs to the group of propylene-bis-dithiocarbamates, can be used as a substitute for the control of several fungal diseases of potato. It is widely used as foliar application against blight disease of potato, tomato and paddy. Present investigation was under taken to evaluate the persistence and degradation pattern of propineb in two soils of potato growing areas of Karnataka.

EXPERIMENTAL METHODS

The experiment on the influence of moisture regimes (field capacity and half field capacity) and rate of application (25 and 50 µg g^{-1}) on the persistence and degradation of propineb was studied in two (Malur and Hassan) potato growing soils of Karnataka with sandy

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Table A : Physical and chemical properties of incubated soils

Sr. No.	Parameters	Malur (Kolar)	Hassan
1.	Particle size distribution		
	Sand (%)	64.1	72.8
	Silt (%)	10.6	10.9
	Clay (%)	25.3	16.3
	Textural class	Sandy clay loam	Sandy clay loam
2.	pH (1:2.5)	7.3	5.4
3.	Electrical conductivity(dS m^{-1})	0.15	0.07
4.	Organic carbon (g kg^{-1})	8.03	6.04
5.	Moisture at field capacity (%)	24.5	23.6
6.	Cation exchange capacity [cmol (p+) kg^{-1}]	10.1	8.2
7.	Zn (µg g^{-1})	0.76	1.02
8.	Cu (µg g^{-1})	0.93	1.89
9.	Fe (µg g^{-1})	10.15	24.48
10.	Mn (µg g^{-1})	8.04	29.28

clay loam texture. Twenty gram of each soil samples were weighed in to 300 ml incubation bottles. The propineb was added to each incubation bottles at 25 and 50 µg g^{-1}, respectively for all the treatments. After thoroughly mixing soil with fungicide, the moisture level was maintained at field capacity and half field capacity. Each treatment was replicated thrice. The moisture lost from each bottle was maintained everyday by adding water throughout the incubation period. The evaporated moisture was added by keeping initial soil moisture weight and balancing it every day. At regular intervals (0, 3, 7, 14, 21, 30, 45, 60 and 90 days after treatment), the incubation bottles were drawn and entire quantity of the soil contained in the bottles (20 g) was used for estimation of propineb remained in the soil.

Fungicide residue analysis:

The method used for this purpose was as described by Keppel (1969, 1971) with slight modifications. Dithiocarbamate residues in substrates (soil, crop and water sample) were decomposed by refluxing with boiling hydrochloric acid. The evolved CS_2 is carried by gas stream which is purified from H_2S or other interferences by passing through lead acetate (30 %) and sodium hydroxide (10 %) solution and finally trapped in 15 ml of the colour reagent (0.012 g of cupric acetate + 25 mlof diethanolamine and diluted to 250 ml with ethanol) to form the cupric salt of N,N-bis-(2-hydroxy) dithiocarbamic acid which is immediately measured by spectrophotometer at 435 nm. The carbon disulphide was used as a standard for estimation of propineb residues.

Carbon disulphide standard preparation:

To accurately weighed 25 ml volumetric flask containing 5 ml ethanol, about 0.1 ml CS_2 was added and closed with stopper, reweighed and volume made to 25 ml with ethanol. From this 2 ml aliquot of solution was diluted with 100 ml ethanol. CS_2 was calculated in µg per ml.

EXPERIMENTAL FINDINGS AND ANALYSIS

Degradation of fungicides added to the soil is mediated purely as result of volatilization from soil surface, chemical hydrolysis and microbiological actions. The rate of degradation is dependent upon the soil clay content, moisture content, rate of application and nature of the compound (Bailey and White, 1970). It was difficult to mention one or two factors for degradation and persistence of propineb under environment. Hence, there are several factors which act together. However, the persistence and degradation of propineb under field capacity and half-field capacity with two soils (Malur and Hassan) of Karnataka at 25 and 50 µg g^{-1} are presented in Tables 1 and 2.

The present investigation reveals that the degradation of propineb was faster under field capacity than at half-field capacity with both application rates. This can be attributed to propineb chain structure which has hydrogen atoms attached to nitrogen atoms. Where the chain structure with hydrogen atoms easily breakdown than the structure with halogen atoms (chlorine, bromine and fluorine), since the hydrogen bonding is weak in nature and can be easily broken down (Connel, 1993).

The persistence of propineb was higher under moisture regime of half-field capacity than at field capacity which was observed in both soils of Malur and Hassan at both application rates. Among the soils, the degradation was less (6 to 67 %) in Hassan soil than in Malur soil (5 to 70 %) within 14 days after incubation from the initial concentration at both the application rates. However, the

Table 1 : Dissipation of propineb in Malur (Kolar) soil at different day's as affected by concentration and moisture regimes under laboratory conditions

Moisture regimes	Propineb added (µg g^{-1})	Residue (µg g^{-1}) at different intervals								
		0	3	7	14	21	30	45	60	90
Field capacity	25	20.2 ±0.59	19.1 ±0.15 (5.5)	11.3 ±0.21 (43.9)	6.0 ±0.16 (70.3)	3.9 ±0.14 (81.0)	1.1 ±0.01 (94.7)	BDL	BDL	BDL
	50	40.0 ±0.23	39.3 ±0.54 (1.85)	23.8 ±0.43 (40.58)	12.8 ±0.14 (68.11)	7.5 ±0.17 (81.37)	2.5 ±0.13 (93.67)	0.3 ±0.13 (99.21)	BDL	BDL
Half field capacity	25	21.7 ±0.30	20.9 ±0.19 (3.6)	13.8 ±0.21 (36.5)	7.6 ±0.05 (65.1)	4.8 ±0.11 (77.9)	2.2 ±0.12 (90.0)	0.2 ±0.08 (98.9)	BDL	BDL
	50	43.7 ±0.57	41.3 ±0.26 (5.6)	27.8 ±0.36 (36.4)	14.6 ±0.23 (66.7)	9.8 ±0.11 (77.5)	4.1 ±0.13 (90.7)	0.8 ±0.13 (98.1)	BDL	BDL

Figures in the parenthesis indicate the dissipation (%)
BDL = below detectable limit (<0.01 µg g^{-1})

Table 2 : Dissipation of propineb in Hassan soil at different days as affected by concentration and moisture regimes under laboratory conditions

Moisture regimes	Propineb added (µg g^{-1})	Residue (µg g^{-1}) at different intervals								
		0	3	7	14	21	30	45	60	90
Field capacity	25	21.2±0.4	19.8±0.13 (6.4)	12.0±0.17 (43.5)	6.9±0.09 (67.2)	4.4±0.04 (79.3)	1.3±0.07 (93.9)	0.25±0.07 (98.8)	BDL	BDL
	50	43.7±1.4	40.1±0.18 (8.3)	24.2±0.23 (44.7)	14.2±0.15 (67.6)	8.6±0.13 (80.3)	3.0±0.10 (93.1)	1.0±0.09 (97.6)	0.2±0.08 (99.6)	BDL
Half field capacity	25	23.3±0.2	20.4±0.14 (12.4)	13.9±0.04 (40.3)	8.1±0.06 (65.3)	5.7±0.10 (75.6)	2.9±0.07 (87.5)	0.7±0.06 (96.9)	BDL	BDL
	50	45.6±1.1	41.8±0.13 (7.9)	28.3±0.35 (37.8)	15.8±0.06 (65.3)	10.9±0.10 (76.1)	5.4±0.07 (88.2)	2.2±0.16 (95.1)	0.6±0.09 (98.6)	BDL

Figures in the parenthesis indicate the dissipation (%), BDL = below detectable limit (<0.01 µg g^{-1})

persistence of propineb in Malur soil was found only upto 45th day, whereas in the Hassan soil it persisted upto 60th day after incubation. This can be attributed to higher copper content in Hassan soil (Table 3) in than Malur soil. This study corroborates the findings of Weissmahr and Sedlak (2000), who reported that the applied dithiocarbamate fungicide forms a complex with copper and can slow down the transformation very effectively by inhibiting acid hydrolysis. However, trace amounts of copper (Cu^{2+}) content in soil yielded half-life of fungicide

Table 3 : Equations explaining the kinetics degradation of propineb in Malur soil as influenced by application rate and moisture regimes

Moisture regimes	Propineb added (µg g^{-1})	Exponential equation		$K_{(deg)}$ (10^{-3} day^{-1})	Half-life $t_{1/2}$ (days)	R^2
Field capacity	25	Overall	$C=23.15e^{-0.0968x}$	96.8	7.2	0.9816
		I Phase	$C=22.11e\text{-}^{0.0919x}$	91.9	7.5	0.9732
		II Phase	$C=3.85e^{-0.1829x}$	182.9	3.8	1.0
	50	Overall	$C=52.65e^{-0.1074x}$	107.4	6.5	0.984
		I Phase	$C=44.41e^{-0.0873x}$	87.3	7.9	0.9644
		II Phase	$C=15.26e^{-0.1217x}$	121.7	5.7	0.9894
Half-field capacity	25	Overall	$C=28.18e^{-0.0975x}$	97.5	7.1	0.9727
		I Phase	$C=23.75e^{-0.0796x}$	79.6	8.7	0.9701
		II Phase	$C=9.531e^{-0.1127x}$	112.7	6.1	0.9714
	50	Overall	$C=51.39e^{-0.088x}$	88.0	7.9	0.9917
		I Phase	$C=47.96e^{-0.0825x}$	82.5	8.4	0.9735
		II Phase	$C=16.77e^{-0.0942x}$	94.2	7.4	0.9898

$K_{(deg)}$ =Rate of residue degradation, $t_{1/2}$ =Half-life, R^2 =Determination co-efficient,
I Phase: < 14 days, II Phase: > 14days, Overall: 0 – 90 days

greater than in 2 weeks, irrespective of pH and organic matter in soil.

The faster degradation was also influenced by the soil pH. Under higher pH, there was a faster degradation noticed than under lower pH. Therefore, the degradation was more in Malur soil (pH 7.3) compared to that of in Hassan soil (pH 5.4), which can be attributed to more micronutrient availability and/or and even can observe the micronutrient toxicity which will definitely form complex with dithiocarbamate. The findings of present study are also in confirmation with the findings of Weissmahr and Sedlak, (2000), where they tried with different micronutrients and found that copper can complex with dithiocarbamate fungicide. These observations are similar to the results found under different pH by Richardson and Munnecke, (1964) and Edward (1964). Contradictorily, Vandana and Chaube (2002) observed that alkaline soils (pH 9.0 and 11.0) favoured the persistence of mancozeb as compared to acidic soils (pH 3.0 and 5.0). Neutral soils (pH 7.0) also favoured persistence but less than the alkaline soils.

However, faster degradation of propineb was also attributed to the organic matter and clay content which play important role in propineb persistence. The destabilization and breakdown of polymeric structure of propineb occurs due to, adherence and complexation of zinc ions in propineb with soil organic matter and clay content. Due to more organic matter content, low recovery test of propineb was observed under Malur soil than Hassan soil. Similar observations were also recorded by Edward (1964) and Vandana and Chaube (2003).

The degradation of propineb in both soils, with both moisture regimes and under two soils fitted into first order kinetic reaction. The propineb degraded very fast in the initial days (before 14 days), then degraded at slower rate (beyond 14 days) with determination coefficient of $R^2 > 0.964$. Increased rate of application increased the persistence of propineb in both the soils irrespective of moisture regimes. However, slightly higher values of half-life and lower degradation rate constants were noticed for higher rate of application in soil. Similar results were also reported by Hanumantharaju and Awasthi (2003) who noticed higher half-life and lower degradation rate constants for higher rate of application of mancozeb in soil.

As discussed earlier, the degradation was faster in Malur soil as compared to Hassan soil and degradation varied with rate of applied concentration and also moisture regimes. It was observed that field capacity moisture regime favours the faster degradation when compared to half-field capacity. Under field capacity, the degradation was more mainly due hydrolysis of propineb structure where it splits the larger molecule into smaller one. The chemical hydrolysis of propineb can be expected in soil solution by reacting with H^+ ions in soil solution or water molecule. This can be combined with the sulphur atom in the terminal end of chain structure of propineb, thereby releasing H_2S and also producing carbon disulphide in soil.

The study corroborated with the findings of Vandana and Chaube (2003) who found that the field capacity moisture level showed lowest persistence of mancozeb in soil followed by saturation point and wilting coefficient level. Ahuja and Pande (2005b) reported increased dissipation with increased moisture up to 80 per cent field capacity.

In Hassan soil the higher rate of degradation was

Table 4 : Equations explaining the kinetics degradation of propineb in Hassan soil as influenced by application rate and moisture regimes

Moisture regimes	Propineb added (µg g^{-1})	Exponential equation		$K_{(deg)}$ (10^{-3} day^{-1})	Half-life $t_{1/2}$ (days)	R^2
Field capacity	25	Overall	$C= 25.74e^{-0.0995x}$	99.5	6.9	0.9887
		I Phase	$C= 22.66e^{-0.0844x}$	84.4	8.2	0.9738
		II Phase	$C=7.87e\text{-}^{0.1106x}$	110.6	6.3	0.9921
	50	Overall	$C=49.69e^{-0.0915x}$	91.5	7.6	0.9957
		I Phase	$C=46.30e^{-0.0849x}$	84.9	8.2	0.9771
		II Phase	$C= 15.24e^{-0.0949x}$	94.9	7.3	0.9947
Half-field capacity	25	Overall	$C=24.70e^{-0.0757x}$	75.7	9.1	0.9938
		I Phase	$C= 24.23e^{-0.078x}$	78.0	8.9	0.9919
		II Phase	$C=9.11e^{-0.0791x}$	79.1	8.8	0.9876
	50	Overall	$C= 47.12e^{-0.0709x}$	70.9	9.8	0.9971
		I Phase	$C= 48.88e^{-0.079x}$	79.0	8.8	0.9818
		II Phase	$C=16.90e^{-0.0698x}$	69.8	9.9	0.9951

$K_{(deg)}$ =Rate of residue degradation, $t_{1/2}$ =Half-life, R^2 = Determination co-efficient,
I Phase: < 14 days, II Phase: > 14days, overall: 0 – 90 days

observed under field capacity ($K_{(deg)}$ = 99.5x10^{-3} day^{-1}) than at half-field capacity ($K_{(deg)}$ =75.7x10^{-3} day^{-1}) at 25 µg g^{-1}.

At higher rate under field capacity, higher rate of degradation ($K_{(deg)}$ = 91.5 x 10^{-3} day^{-1}) was found when compared to half-field capacity ($K_{(deg)}$ =70.9x10^{-3} day^{-1}). For Malur soil, the rate of degradation was lower at field capacity ($K_{(deg)}$ =96.8x10^{-3} day^{-1}) than under half-field capacity ($K_{(deg)}$ =97.5 x10^{-3} day^{-1}) at 25 µg g^{-1} and at higher rate the rate of degradation $K_{(deg)}$ =107.4x10^{-3} day^{-1} was found in field capacity, but under half-field capacity it was $K_{(deg)}$ =88.0 x10^{-3} day^{-1}. The rate of degradation with different moisture regime and with different concentration was more in Malur soil than in Hassan soil. Similar results were recorded by Chakpram *et al*. (2008), who reported that the degradation constants were higher at lower rates compared to higher rates of application and *vice versa* in case of submergence and field capacity moisture regimes.

The half-life values for Hassan soil were 6.9 and 9.2 days when incubated at 25 µg g^{-1} under field capacity and half-field capacity moisture regimes, respectively, whereas at higher rate (50 µg g^{-1}) the half-life value were 7.6 and 9.8 days at field capacity and half-field capacity moisture regimes, respectively. However, for Malur soil the half-life values were 7.2 and 7.1 days at 25 µg g^{-1} with field capacity and half-field capacity, whereas at higher rate (50 µg g^{-1}) the values were 6.5 and 7.9 days with field capacity and half-field capacity moisture regimes, respectively. These findings corroborated with the findings of Ahuja and Pande (2005a) where half-life values of propineb ranged from 5.9 to 6.3 days under field capacity following application of 5 µg g^{-1} CS_2. These findings are substantiated by the findings of Ahuja and Pande (2005b) who reported that half-life values of propineb were in the range of 6.5 to 7.3 days when soil moisture was maintained at 20, 50 and 80 per cent of the field capacity.

The present investigation reveals that propineb with different moisture regimes under field capacity showed more degradation and less persistence compared to half-field capacity. This can be attributed to more period of complexation of fungicide and copper in soil, due to less water availability which actually breaks down the complexation by acid hydrolysis reaction. Similar results were recorded by Weissmahr and Sedlak (2000).

Among the Malur and Hassan soils, more degradation and less persistence was found in Malur soil than in Hassan soil, which is because of lesser amount of copper content in Malur (0.93 µg g^{-1}), neutral pH (7.3), high organic matter content (8.03 µg g^{-1}) and high clay content (25.3 %) than Hassan soil. Similar results were also observed by Edward (1964) where high pH and clay content decreased the persistence of fungicide. Weissmahr and Sedlak (2000) observed that copper content of soil increases the persistence of dithiocarbamate irrespective of soil pH and organic matter content of soil.

Conclusion:

Degradation of propineb was faster under filed capacity than at half-field capacity moisture regimes at both rates in both the soils. Higher degradation was noticed in Malur soil (clay 25.3 %) than Hassan soil at both the rates of application and moisture regimes. Application of propineb even at higher dosage under field capacity will reduce phytotoxicity for the on growing and subsequent crop.

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