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INFLUENCE OF SOIL MOISTURE AND TEMPERATURE ON PENDIMETHALIN DEGRADATION IN CULTIVATED AND FORESTED LANDS

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Abstract: Degradation of pendimethalin [N-(1-ethylpropyl)-2, 6-dinitro-3, 4-xylidine] was evaluated under varying environmental conditions by monitoring its residual concentration in soil at weekly interval during an incubation period from 0 to 11 weeks. A factorial arrangement of treatments of two soils differing in land use (cultivated and forested), two moisture regimes (30 and 80 %) and two temperatures (20 and 40°C) were examined. After 11 weeks of incubation, initial concentration of pendimethalin (8.00 µg g^{-1} soils) reduced to 2.00 and 1.40 µg g^{-1} soil in cultivated and forested lands, respectively. The mean per cent of pendimethalin degraded corresponded to 70.79 and 77.50 in cultivated and forested lands following the order: Forested land > Cultivated land, revealing the impact of land use. It is attributed to more organic C (3.25%) accumulated by regular and long-term addition of litter in soil under forests. Significant relationship (R^2 = 0.991^{**}- 0.997^{**}) was noticed linking pendimethalin degradation with incubation period. Rate of degradation was rapid at 30 % moisture and 40°C as evidenced by about 6 days advancement in half life (DT_{50}) due better adaptability of microbes to degrade pendimethalin under aerobic (30% moisture) and warmer conditions (40°C) as compared to moist (80 %) and cooler (20°C) conditions.

Keywords: pendimethalin degradation, soil moisture, temperature, cultivated and forested lands, half life

1. INTRODUCTION

Herbicides used to control weeds in crops have moderate to high soil persistence (Patzold & Brummer, 2003). The applied herbicides can enrich the environments by terrestrial runoff and leaching and to a lesser extent of direct application and aerial spraying (Ying & Williams, 2000). Consequently, it increases the risk of contaminating soil surface (Alister et al., 2009) and ground waters (Spalding et al., 2003) either in their original or transformed forms (Barbash & Resek, 1996).

Pendimethalin, N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) is a selective herbicide used to control most annual grasses and broad leaf weeds in potatoes, maize, rice, cotton, soybean, and tobacco both as pre-emergence and early post-emergence herbicide. It is highly hydrophobic and lipophilic and less volatile (Weber, 1990). It has potential to persist in the environment sufficient to affect small grain crops (Hermann et al., 2000) and reducing the nematodes, micro-organisms and plant-*Rhizobium* symbiosis (Strandberg & Scott-Fordsmand, 2004).

Soil physico-chemical properties and agro-climatic conditions regulate the movement and degradation of herbicides in agricultural fields. Therefore, an attempt was made to evaluate the degradation behavior of pendimethalin in two soils differing in land use, namely, cultivated and forested at two soil moisture regimes and two temperatures.

2. MATERIALS AND METHODS

2.1. Treatments

Degradation behavior of pendimethalin was evaluated by monitoring its residual concentration in soil over time under various environmental conditions. A factorial arrangement of treatments triplicated in a completely randomized design consisting of two soils differing in land use (cultivated and forested), two soil moisture regimes (30 and 80 %), two temperatures (20 and 40°C), and twelve incubation periods (0-11 weeks) at weekly interval was examined.

2.2. Collection and analysis of soil samples

Bulk surface samples (0-15cm) were collected from two soils differing in land use, namely, cultivated and forested from Bhot and Bilaspur, respectively, lying in Rampur district of Uttar Pradesh, northern India. The respective soils were classified as Alfisols and Mollisols. After processing, the pH of the soil samples was estimated by pH meter after equilibrating 10 g of the sample with 25 ml distilled water (1:2.5) for 30 min., organic carbon by Walkley and Black method (Walkley & Black, 1934) and soil texture by International pipette method (Page et al*.*, 1982).

2.3. Fortification of soils with pendimethalin and treatments imposition

Both soils were fortified with technical grade (90% pure) pendimethalin (active ingredient, 2 mg ml^{-1}) stock solution prepared in water-methanol (1:10). Then 20 ml of the stock solution was added to 5 kg of each soil to have a pendimethalin concentration of 8 µg g^{-1} soil. After thorough mixing, the soil samples were stored in polythene bags. Then from each soil, 350 g oven dried soil was weighed in 12 separate flasks of 500 ml capacity.

Soil moisture treatments of 30 and 80 % were imposed on fortified soil samples by adding suitable volumes of water to bring each sample to specific soil water content. Temperature treatments were imposed on soil samples by placing the flasks in the dark incubators either at 20°C or 40°C. Untreated soil samples were also maintained under identical conditions. Each treatment was triplicated in a completely randomized arrangement. Samples were incubated for 11 weeks. Foil-lined caps were placed on flasks, but slightly turned to maintain air contact with the outside environment and prevent the loss of soil moisture. Distilled water was added to samples weekly to maintain appropriate soil moisture level. After incubation for the desired time interval, samples were air dried for 24 h, weighed and then stored at - 20°C until analyzed. Data were corrected for the percentage water in each soil sample.

2.4. Extraction and estimation of pendimethalin in soils

Extraction of pendimethalin from each fortified soil was conducted by shaking 10 g soil of each sample with 50 ml methanol for 1 h in a flask, centrifuged for 10 min at 3500 rpm, and the supernatant transferred into a flask. The remaining soil in centrifuged tubes was again treated with 25 ml methanol, and the whole procedure repeated twice. Methanol extracts were pooled and filtered through Whatman No. 42 filter paper. Similarly, the untreated soil was also extracted. Combined methanol extracts were evaporated to dryness on water bath (70°C). Residue was dissolved in 20ml distilled water and filtered through Whatman No.42 filter paper. The filtrate was transferred to 250 ml separatory funnel and solutions were extracted with chloroform (20 ml x 4). After 2 min shaking, the layers were allowed to separate and the equipoise layers were drawn off. The extracted fractions were combined and evaporated to dryness on water bath (70°C). Residue was dissolved in 10 ml of 0.1 N HCl and filtered. Extracts of unfortified soil were also treated under similar conditions.

Pendimethalin concentration in the aqueous acid extracts was estimated on UV-VIS double beam absorption spectrophotometer at 250 nm (^max) using unfortified soil extract as blank. Pendimethalin concentration was estimated from calibration curves linking absorbance with varying pendimethalin concentrations.

2.5. Evaluation of degradation behavior of pendimethalin

The degradation behavior of pendimethalin was evaluated using linear semi log regression equation in terms of first order reaction (Timme & Frehse, 1980):

$$\log Y = \log a - \log (b) X \qquad (1)$$

Taking log a = A and log b = B

$$\log Y = A - BX \qquad (2)$$

Where, Y = pendimethalin residue (µg g^{-1} soil)

X = incubation time (days)

A or log a = intercept at X = 0

B or log b = regression coefficient

Degradation rate constant (K_{deg}) was computed from equation (2) as K_{deg} = -2.303 regression coefficient (B) and half life (DT_{50}) from rate constant as:

$$DT_{50} = \ln 2 / K_{deg} \qquad (3)$$

3. RESULTS AND DISCUSSION

3.1. Physicochemical characteristics of the soils

The pH, organic C (%), texture and order of the soils used were 7.4, 0.45, sandy loam and Alfisols for the cultivated and 7.6, 3.25, clay loam and Mollisols for the forested lands, respectively. The physico-chemical characteristics of the soils used represented a wide variation in organic matter, texture and soil taxonomy.

3.2. Pendimethalin degradation in soils

Pendimethalin degradation was different among the two soils. After 11 weeks of incubation, its initial concentration (8μg g^{-1} soil) reduced to 2.30 and 2.00 at 30 %, and 2.60 and 2.45 μg g^{-1} soil at 80 % soil moisture at 20° and 40°C, respectively, in cultivated land (Table 1). In terms of its per cent initial concentration, it corresponded to 28.75 and 25.00 at 30 %, and 32.50 and 30.62 at 80 % moisture at the respective temperatures. Whereas, in forested land, initial concentration of pendimethalin declined to 1.60 and 1.40 at 30 %, and 2.20 and 2.00 μg g^{-1} soil at 80 % soil moisture at 20° and 40°C, respectively; corresponding to 20.00 and 17.50 at 30% and 27.50 and 25.00 at 80 % soil moisture as percent of initial pendimethalin left at the respective temperatures.

After 11 weeks of incubation, cultivated land had more of pendimethalin residue left to the tune of 0.70 and 0.60 μg g^{-1} soils at 30 % and 0.40 and 0.45 μg g^{-1} soils at 80 % soil moisture compared to forested land at 20 and 40°C, respectively (Table 1). These data show that the mean per cent of pendimethalin degraded irrespective of moisture and temperatures in two soils corresponded to 70.79 and 77.50 for cultivated and forested lands, respectively. It suggested that degradation of pendimethalin in soils followed the order:

Forested land > Cultivated land.

The possible differences in microbial action under two soils of varying characteristics and environmental conditions might have influenced the availability of herbicide for degradation (Hermann et al., 2000). It may be ascribed to higher organic C (3.25%) in forested land having more than 7-times organic matter than the cultivated land (0.45 %). Regular addition of forest litter over long - term led to enhanced level of organic matter in soil under forests leading to higher microbial action to degrade pendimethalin. Consequently, least pendimethalin residue was left in soil of forested land in comparison to that of cultivated land. Microbial activities for biodegradation of pendimethalin are often higher in organic matter rich soils (Singh & Kulshreshtha, 1991). In addition, Garcia-Valcarcel & Tadeo (2003) also reported enhanced pendimethalin dissipation with liquid humic fertilizers.

Table 1. Effect of soil moisture and temperature on pendimethalin degradation in soils

Incubation period (weeks)	**Pendimethalin residue in soil (*μg g^{-1}*)**				**Percent initially added pendimethalin left in soil**			
	30 % moisture		**80 % moisture**		**30 % moisture**		**80 % moisture**	
	20°C	**40°C**	**20°C**	**40°C**	**20°C**	**40°C**	**20°C**	**40°C**
Cultivated land								
0	8.00	8.00	8.00	8.00	100.00	100.00	100.00	100.00
1	7.50	7.20	7.60	7.40	93.75	90.00	95.00	92.50
2	6.70	6.25	6.90	6.80	83.75	78.12	86.25	85.00
3	5.90	5.80	6.30	5.90	73.75	72.50	78.75	73.75
4	5.00	4.90	5.40	5.20	62.50	61.25	67.50	65.00
5	4.50	4.40	5.20	4.60	56.25	55.00	65.00	57.50
6	4.00	3.80	4.50	3.90	50.00	47.50	56.25	48.75
7	3.35	3.40	4.00	3.70	41.87	42.50	50.00	46.25
8	3.00	2.80	3.50	3.30	37.50	35.00	43.75	41.25
9	2.55	2.40	3.00	2.85	31.87	30.00	37.50	35.62
10	2.45	2.20	2.80	2.60	30.62	27.50	35.00	32.50
11	2.30	2.00	2.60	2.45	28.75	25.00	32.50	30.62
Forested land								
0	8.00	8.00	8.00	8.00	100.00	100.00	100.00	100.00
1	7.10	7.00	7.30	7.20	88.75	87.50	91.25	90.00
2	6.30	6.00	6.60	6.50	78.75	75.00	82.50	81.25
3	5.60	5.30	6.00	5.50	70.00	66.25	75.00	68.75
4	4.70	4.50	5.40	4.80	58.75	56.25	67.50	60.00
5	4.20	4.00	4.70	4.20	52.50	50.00	58.75	52.50
6	3.50	3.25	4.10	3.70	43.75	40.62	51.25	46.25
7	3.00	2.80	3.70	3.40	37.50	35.00	46.25	42.50
8	2.60	2.45	3.00	2.80	32.50	30.62	37.50	35.00
9	2.30	2.20	2.60	2.40	28.75	27.50	32.50	30.00
10	1.80	1.65	2.30	2.20	22.50	20.62	28.75	27.50
11	1.60	1.40	2.20	2.00	20.00	17.50	27.50	25.00

Table 2. Regression equations and coefficients of determination (R^2) for pendimethalin residue

Soil moisture (%)	Temperature (°C)	Regression equation log Y=	R^2 value
Cultivated land			
30	20	0.9239-0.0078 X	0.994^{**}
	40	0.9157-0.0081 X	0.996^{**}
80	20	0.9272-0.0067 X	0.992^{**}
	40	0.9130-0.0070 X	0.995^{**}
Forested land			
30	20	0.9257-0.0092 X	0.995^{**}
	40	0.9197-0.0096 X	0.994^{**}
80	20	0.9280-0.0077 X	0.991^{**}
	40	0.9112-0.0081 X	0.997^{**}

Y = Pendimethalin residue (µg g^{-1} soil); X = Incubation time (days)

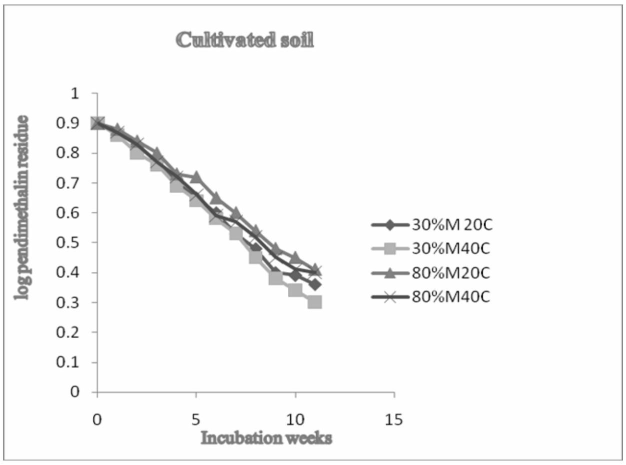
Table 3. Degradation rate constant (K_{deg}) and half life (DT_{50}) of pendimethalin

Land use	Soil moisture (%)	Temperature (°C)	K_{deg} (day^{-1})	DT_{50} (days)
Cultivated land	30	20	0.0179	38.71
		40	0.0186	37.25
	80	20	0.0154	45.00
		40	0.0164	43.00
Forested land	30	20	0.0211	33.00
		40	0.0221	31.25
	80	20	0.0177	39.15
		40	0.0186	37.25

The mean per cent of pendimethalin degraded irrespective of the soils corresponded to 77.19 and 71.10 at 30 and 80 % soil moisture and 72.82 and 75.47 % at 20 and 40°C, respectively. Relatively faster degradation at 30 % soil moisture and 40°C temperature resulted in the least pendimethalin left in soil under these environmental conditions. Favorable aerobic and warmer conditions might have accelerated better microbial activity to degrade pendimethalin (Weber, 1990).

3.3. Pendimethalin degradation kinetics

The kinetics of pendimethalin degradation was interpreted by linear regression analysis on logarithmically transformed data of pendimethalin residue (µg g^{-1}soil) presented in table 1. The regression analysis demonstrated highly significant coefficients of determination (R^2) ranging from 0.992^{**} to 0.996^{**} in cultivated and from 0.991^{**} to 0.997^{**} in forested lands for pendimethalin degradation (Table 2). The relationship revealed that pendimethalin degradation followed first order kinetics (Allen & Walker, 1987).The negative values of the regression coefficients inferred that pendimethalin left declined as the incubation period progressed. The linear degradation trends of pendimethalin (Fig. 1) in terms of log of pendimethalin residue in soil (µg g^{-1}) with incubation time (weeks) revealed that degradation followed first order kinetics.



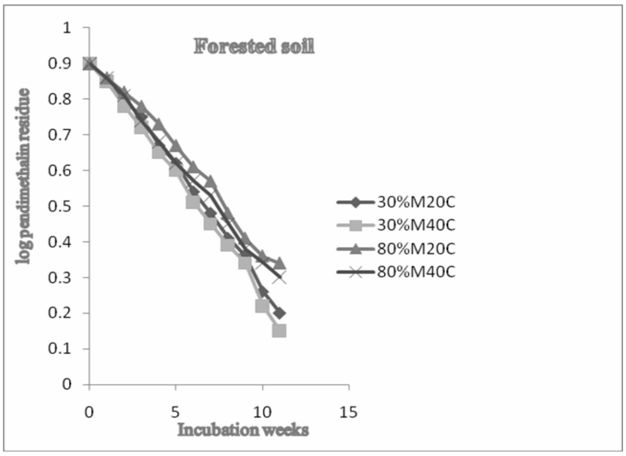


Figure 1. Degradation trends of pendimethalin in cultivated and forested soils

3.4. Rate constant and half-life of pendimethalin degradation

Rate constant (K_{deg}) and half life (DT_{50}) of pendimethalin degradation were computed from the semi log linear regression equations (Table 2). At the same soil moisture and temperature, pendimethalin degradation enhanced in forested land as compared to cultivated land, which is evident by its higher rate constant and shorter half life (Table 3). Moreover, pendimethalin degraded rapidly at 30% soil moisture and 40°C than at 80 % soil moisture and 20°C in both soils.

The rate constant (K_{deg}) ranged from 0.0154 to 0.0186 in cultivated and from 0.0177 to 0.0221 day^{-1} in forested lands; showing slightly rapid degradation in forested land on accounts of its high organic matter (3.25% Organic C) accumulated over the years under forests. Half life (DT_{50}) of pendimethalin ranged from 37.25 to 45.00 in cultivated and 31.25 to 39.15 days in. forested lands. The mean of half life (DT_{50}) for pendimethalin degradation was 41 and 35 days in cultivated and forested lands, 35 and 41 days at 30 and 80 % soil moisture, and 39 and 37 days at 20 and 40°C , respectively. These DT_{50} values are within the range of 23 to 62 days reported for pendimethalin degradation under agricultural field conditions (Kewat et al., 2001 and Tsiropoulus et al., 2004).

In both soils, the DT_{50} advanced by about 6 days at 30 % moisture and 40°C revealing rapid degradation of pendimethalin in comparison to 80% moisture and 20°C. This shortening in half life is attributed to the better adaptability of aerobic microbes to degrade pendimethalin. Kulshreshtha et al., (2000) also showed enhanced degradation of the herbicide only in surface soil, which could be due to aerobic environment for micro-organisms to degrade pendimethalin. Hermann et al., (2000) while studying pendimethalin and flumetralin degradation under controlled conditions found encouraged herbicide degradation at higher temperature. The increase in DT_{50} values at 80 % moisture could be explained because of an increase in soil moisture could avoid photodecomposition and volatilization.

4. CONCLUSION

The study has revealed the effect of land use pattern on degradation of pendimethalin following the order: Forested land > Cultivated land at the same soil moisture and temperature. It is ascribed to more accumulation of organic matter (3.25% Organic C) as a result of regular addition of forest litter over long time in this soil as it had more than 7-times organic matter than that of cultivated land (0.45% Organic C). It might have accelerated the higher microbial action to degrade pendimethalin.

Rate constant (K_{deg}) and half life (DT_{50}) showed rapid pendimethalin degradation under aerobic (30% soil moisture) and warmer temperature (40°C) due to creation of aerobic environment for microbes to degrade pendimethalin. The DT_{50} values varying between 31 to 45 days were within the reported half lives for pendimethalin degradation under agricultural field conditions. The results suggested that under normal field condition prevailing in plains of northern India pendimethalin would normally not persist to injurious levels in soils from crop-rotation perspective because of its faster degraded under such climatic conditions.

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