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Dissipation of Pendimethalin in Soybean Crop Under Field Conditions

Shishir Tandon[1]

Abstract Persistence of pendimethalin was studied in soil, soybean pods, straw and water under field conditions. Pendimethalin was applied at 1 and 2 kg a.i. ha^{-1}. Residues in soil were detected up to 60 and 90 days at the recommended and double dose, respectively. Dissipation followed first order kinetics and was accounted for by a biphasic pattern. The half-life for the initial phase and later phase was 12.73 and 26.60 days, respectively, for recommended and 7.25 and 37.91 days, respectively, for double dose. The limit of quantification was 0.005 μg g^{-1} of sample. Percent recovery from soil, oil, defatted cake, straw and water samples fortified with 0.01–1.0 mg kg^{-1} varied from 84.5 %–89.6 %, 84.6 %–88.7 %, 79.4 %–86.0 %, 78.2 %–85.6 % and 90.2 %–93.0 %, respectively. At harvest, pendimethalin residue in soybean pods, straw, and soil were below detectable limits. No residues of pendimethalin were detected in ground water. Current application of pendimethalin in the environment is not expected to cause adverse health effects form the consumption of soybeans.

Keywords Residue analysis · HPLC · *Glycine max* · Soil · Persistence

Pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl 2,6-dinitro benzenamine], a member of the dinitroaniline herbicides is commercially available as Prowl^{TM}, Stomp^{TM} and Panida^{TM}. It interferes with the microtubule system and thereby inhibits cell mitosis, cell elongation and finally plant growth. This herbicide has widespread usage for selective pre-emergent control of a wide variety of grasses and broadleaved weeds in several crops including soybean (Street and Lanham 2003). Soybean [*Glycine max* (L.) Merr.] is an important pulse and oilseed crop (Tandon and Dubey 2015). Reduction in soybean yields due to weed infestation varies from 20 % to 77 % depending on the type of soil, season and intensity of weed infestation.

In recent years, pendimethalin was subjected to increased toxicological and environment assessments because of various physiological changes and endocrine effects in animal studies including liver, kidney damage, and number of mutagenic effects (Dimitro et al. 2006). Degradation, leaching and adsorption of pendimethalin in soil and crops has been examined by others (Lin et al. 2007; Tandon 2008, 2015; Bandyopadhyay and Choudhury 2009; Shah et al. 2011; Sondhia 2012, 2013). Herbicide residues may persist in the environment, posing environmental pollution and health hazards to consumers. Therefore, herbicide residue estimation in soybean crop, soil and water is essential to determine the duration of herbicide activity in soil, its effect on the crop and to analyze the quality of the food. The current study examined dissipation kinetics and residues of pendimethalin in ground water, soil and soybean crop under sub tropical conditions.

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Materials and Methods

The present investigation was carried out at the NEB Crop Research Centre, G. B. Pant University of Agriculture and Technology, Pantnagar. Analytical grade pendimethalin (99.0 % pure) and the formulation Pendiguard 30 EC were

obtained courtesy of M/s BASF, India and M/s Gharda Chemicals, India, respectively. Three treatments (control, 1 and 2 kg a.i. ha^{-1}) of pendimethalin were applied as pre-emergent herbicide. Treatments were in randomized block design with three replicates of each treatment. Soil samples (0–15 cm) were collected from each control and treated plots at different time intervals (0, 1 h, and 1, 3, 5, 7, 10, 15, 30, 45, 60, 75, 90 and 105 days after herbicide application) and finally on the harvesting day, while soybean crop samples were collected from all plots at harvest time. Ground water was collected from nearby borewells of treated plots after 3, 7, 10, 15, 30, 60, and 90 days after herbicide application and again at harvest. Soybean variety used during investigation was 1045 and the plot size was 7 × 3 m.

Soil was shade dried and processed, while soybean pods were weighed and crushed using mortar and pestle and subjected for removal of soybean oil and defatted cake. For percent recovery, soil, soybean oil, defatted cake straw and water were fortified with 0.01–1.0 mg kg^{-1} of standard pendimethalin.

Representative soil samples (20 g) were weighed, and 50 mL of acetone: hexane (1:3 v/v) solution was added. Samples were shaken for 30 min on an orbital shaker and centrifuged for 15 min at 5000 rpm. Clear supernatant was filtered through Whatman filter paper in round bottom flasks. The same procedure was repeated twice with fresh 25 mL of acetone: hexane solution. Filtered clear supernatants were pooled and evaporated under reduced pressure at 45 ± 2°C using a flash evaporator. Residue obtained was dissolved in 2 mL acetonitrile (HPLC grade). The dissolved residue was filtered through a 0.22 μm Millipore filter before analysis by HPLC.

Ground soybean pod samples (50 g) were subjected to Soxhlet extraction with 200 mL of hexane for 6 h. The hexane fraction was collected, and the rest (de-oil cake) was kept separately. The hexane fraction was partitioned thrice (50 + 50 + 50 mL) with acetonitrile. The acetonitrile fraction was dried over anhydrous Na$_2$SO$_4$ and concentrated on a rotary vacuum evaporator at 45 ± 2°C and subjected to column cleanup. The oil sample was cleaned up using a florisil column conditioned with *n*-hexane. The sample was eluted with 50 mL *n*-hexane, which was discarded. Then, 100 mL acetone:*n*-hexane (5:1 v/v) was passed through, and the fraction was collected and concentrated on a rotary vacuum evaporator at 45 ± 2°C. Finally, it was reconstituted with acetonitrile and followed the same procedure for the final analysis by HPLC.

Plant samples were chopped and ground into small pieces. Chopped samples (10 g) were weighed and 50 mL of acetone:hexane (3:1 v/v) were added, followed by shaking for 30 min and centrifuged for 30 min at 5000 rpm. The clear supernatant was decanted in a conical

flask, and the whole procedure was repeated twice using fresh acetone:hexane mixture. The combined supernatant was reduced to 2 mL by drying under reduced pressure at 45 ± 2°C and subjected to column cleanup. A 2 cm bed of charcoal and sodium sulphate was packed at the base over glass wool in the columns. They were then packed with silica gel (100–200 mesh size) in wet form in hexane solvent. Residue was loaded onto the column and eluted with 5 mL hexane, after which the eluent was discarded. The residue was finally eluted with 20 mL acetone: hexane (4:1 v/v) mixture. The collected elute was dried on a flash evaporator at 45 ± 2°C to dryness. Residues were re-dissolved in 2 mL acetonitirle (HPLC grade) and filtered through a 0.22 μm Millipore filters before being analyzed by HPLC.

The deoil cake (10 g) extraction was done by following the same procedure as described for plant samples, while the cleanup procedure was done similar to oil. Groundwater (100 mL) was partitioned with dichloromethane thrice (100 + 75 + 50 mL). The organic phase was collected, dried over anhydrous sodium sulfate, and concentrated to dryness over a flash evaporator at 45 ± 2°C. Residues were re-dissolved in 2 mL HPLC grade acetonitirle.

A Beckmann HPLC system equipped with selectable wave length detector, Kipp and Zonen BD-40 recorder, Rheodyne injector with 20 μL loop, 100 A pump and 5 μm C$_{18}$ column (250 mm × 4.5 mm i.d.) was used for residue analysis. Specific parameters included: mobile phase: acetonitrile:water [80:20 v/v]; mode: isocratic, flow rate 1 mL min^{-1}, detector UV at 239 nm, injection volume 20 μL, range 0.02 aufs and chart speed 1 cm min^{-1}. The mobile phase was degassed and filtered through a 0.45 μm PTFE disc filter prior to use. The pendimethalin limit of detection was 0.001 μg g^{-1}, while limit of quantification was 0.005 μg g^{-1} for the samples.
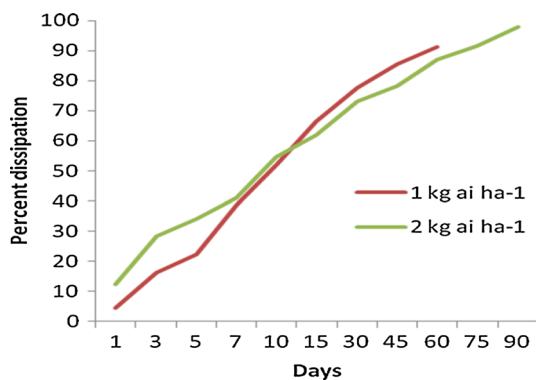
Results and Discussion

Study soil was sandy clay loam, with sand:silt:clay percentage of 48:22:30. The soil had a pH of 8.11, organic carbon content of 1.21 %, electric conductivity 0.3139 dS m^{-1} and 0.493 % CaCO$_3$. The temperature range (minimum to maximum) and rainfall during the experimental period was 13.1–34.6°C and 1771.4 mm, respectively.

Recovery of pendimethalin from soil, oil, defatted cake straw and water samples fortified with 0.01–1.0 ppm of the herbicide varied from 84.5 %–89.6 %, 84.6 %–88.7 %, 79.4 %–86.0 %, 78.2 %–85.6 % and 90.2 %–93.0 %, respectively (Table 1). Percent dissipation values at different time intervals were calculated considering the amount of herbicide recovered on 0 days (1 h after

Table 1 Percent recovery of pendimethalin from fortified samples of soybean straw, de-oil cake, soil, oil, and water

Samples	Amount fortified (ppm)	Mean percent recovery ($\pm$ SD)
Straw	0.01	77.2 ± 0.1
	0.1	80.5 ± 0.3
	1.0	85.6 ± 0.4
De-oil cake	0.01	79.4 ± 0.6
	0.1	82.3 ± 0.3
	1.0	86.0 ± 0.4
Soil	0.01	84.5 ± 0.2
	0.1	87.7 ± 0.4
	1.0	89.6 ± 0.2
Oil	0.01	84.6 ± 0.4
	0.1	86.8 ± 0.6
	1.0	88.7 ± 0.5
Water	0.01	90.2 ± 0.2
	0.1	91.8 ± 0.2
	1.0	93.0 ± 0.4

$n = 3$

Fig. 1 Percent dissipation of pendimethalin in soil planted with soybean in Pantnagar, India

application) as 0 %. Dissipation of herbicide in soil treated at 1 kg ha^{-1} increased from 0 % to 16.36 % from 0 days (1 h after application) to 3 days, then gradually increased up to 66.44 % on 15 days. On 45 days, the dissipation increased to 85.64 % and on 60 days 91.15 % dissipated. However, no detectable residue (<0.005 µg g^{-1}) was found after 90 days. The dissipation pattern of the herbicide at 1 kg ha^{-1} was faster for the first 7 days but slowed until it became non-detectable (Fig. 1). At 2 kg ha^{-1} application rate, dissipation of pendimethalin in soil increased from 0 % to 12.25 % from 0 days (1 h after application) to 1 days, then it gradually increased up to 54.74 % till 10 days. On 30 days, dissipation enhanced to 73.11 % and dissipated until 90 days (98.07 %). No detectable residue (<0.005 µg g^{-1} soil) was observed on 105 days. At 2 kg ha^{-1} application rate, the herbicide degradation pattern behaved similar as the lower rate (Fig. 1).

The amount of pendimethalin recovered from soil at different time intervals for both application dosages fit the first order kinetic equation

$$C = C_0 e - \lambda^t$$

where C is amount of pendimethalin recovered from soil at time t. C_0 is amount of pendimethalin recovered at t = 0 interval, λ is the degradation constant and t is time in days.

The calculated values of the degradation constant, coefficient of determination (R^2) for first order dissipation kinetics and half-lives of pendimethalin under field conditions at two different fortification levels are depicted in Table 2. Dissipation followed first order kinetics as strong R^2 values indicated the dissipation of pendimethalin conformed to first order kinetics. Dissipation of pendimethalin in sandy clay loam soil demonstrated a biphasic pattern in both application doses. Degradation of pendimethalin during 0–7 days was higher than the later phase of degradation (Table 2). The half life calculated for the initial phase and later phase was 12.73 and 26.60 days for

Table 2 Computed values of degradation rate constant, half life and coefficient of determination of pendimethalin

Computed value	1.0 kg ha^{-1}	2.0 kg ha^{-1}
Initial phase (0–7 days)		
Degradation rate constant (λ)	0.0560	0.1002
Half life ($T_{1/2}$) days	12.73	7.25
Coefficient of determination (R^2)	0.9329	0.9793
Regression equation	Y = $-0.0516x - 0.1513$	Y = $-0.058x + 0.1099$
Later Phase (7 days onwards)		
Degradation rate constant (λ)	0.0261	0.0205
Half life ($T_{1/2}$) days	26.60	37.91
Coefficient of determination (R^2)	0.9967	0.8751
Regression equation	Y = $-0.1839x - 0.3386$	Y = $-0.2051x + 0.0681$

recommended and 7.25 and 37.91 days for double dose, respectively. Slower dissipation of pendimethalin in the present investigation in the latter phase might be due to strong binding with soil colloids rendering the chemical less prone to physical and bio-chemical modes of degradation. Biphasic dissipation pattern for pendimethalin has been reported in several studies. Srivastava et al. (2006) reported dissipation of pendimethalin was higher in initial than later phase with a half-life of 5.13 and 23.34 days at a 2 kg ha^{-1} application rate, while Manish and Kewat (2002) reported pendimethalin in soil degraded faster in the first phase (about 64 %) and after 90 days with 3 %–15 % remaining afterward. In red sandy loam soil, pendimethalin did not persist for more than 60 days (Devi et al. 2000). When applied in different doses, the half life of pendimethalin varied from 28.1 to 31.7 days (Diwan et al. 1999). Dissipation of pendimethalin occurred from 5.78 %–77.08 % in six different soils in 120 days, and the rate of dissipation was influenced by organic matter, soluble salt content and other soil factors (Rai et al. 1999). Savage and Jordan (1980) reported a pendimethalin half-life of 6 and 27 days for initial and later periods, respectively. In a sandy loam soil pendimethalin half-life ranged from 10.5 to 31.5 days and was mainly affected by the time interval between irrigation application and the first rain event (Alistera et al. 2009).

Soil factors (soil moisture, organic carbon content, temperature and pH) play an important role in dissipation of pesticides from soil (Sachan et al. 2007; Tandon et al. 2015). Pendimethalin persisted for a longer period in low organic matter containing soils (Berayan 1987). Zimdahl and Gwynn (1977) found pendimethalin half-lives in a clay loam at 75 % field capacity increased from 54 days at 30°C to 101 days at 10°C. Pendimethalin is degraded rapidly in vitro by several soil fungi (*Aspergillus, Fusarium, Penicillium, Paecilomyces, Rhizoctonia*). The identified degradates under aerobic and anaerobic conditions and fungi were 2,6-dinitro-3,4-xylidine, 4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitrobenzyl alcohol, *N*-(1-ethylpropyl)-2-amino-6-nitro-3,4-xylidine, *N*-propyl 3-methyl 4-hydroxy–2,6-dinitroaniline, *N*-(1-ethylpropyl)-6-amino-2-nitro 3,4 xylidine, 4-[(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid and benzimidazole (Roberts et al. 1998).

Pendimethalin residue analysis was done for soybean oil, defatted cake and straw for both the treatments and all were below detection at harvest time. Diwan et al. (1999) found pendimethalin residues were not detected in onions at harvest. Sondhia (2012, 2013) reported residues were below the MRL limit in chick pea, onion, tomato and radish. Similar results were obtained by Tandon (2008) in potato. In groundwater samples, no residues of pendimethalin were detected on any sampling day. Since pendimethalin is not mobile in soil, chances of it leaching are remote.

Pendimethalin degraded moderately in soil under sub tropical conditions. Residues of pendimethalin were not detected at harvest in soil, soybean oil, defatted cake, and straw from treated fields. Pendimethalin residues were below MRL in soybean as set by the EU (0.05 μg g^{-1}; ESFA 2014). Groundwater was not contaminated with pendimethalin residues. Persistence of pendimethalin depends on various factors such as organic content, soil pH, soil microflora and other biotic and abiotic components. These factors would be responsible for rapid degradation of pendimethalin in soil.

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