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Dissipation of Pendimethalin in Soil and Its Residues in Chickpea (*Cicer arietinum* L.) Under Field Conditions

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Abstract Disappearance of pendimethalin in the soil of chickpea (*Cicer arietinum* L.) at 0–110 days, and terminal residues in plant samples have been studied under field conditions. Pendimethalin was applied as pre-emergence herbicide at 750, 350 and 180 g a.i. ha^{-1} in winter, in chickpea crop. The dissipation of pendimethalin in the chickpea field soil conditions followed first order kinetics showing a half-life of 11.23 days averaged over all doses. Low pendimethalin residues were found in plant samples. 0.025, 0.015, <0.001 μg g^{-1} residues of pendimethalin were found in grains at 750, 350 and 185 g a.i. ha^{-1} treatments, respectively. Much lower pendimethalin residues were found in straw viz. 0.015 to <0.001 μg g^{-1} at 750, 350 and 185 g a.i. ha^{-1} treatments, respectively.

Keywords Pendimethalin residues · Chickpea (*Cicer arietinum* L.) · Soil · Dissipation

Herbicides play an important role in the production of vegetables but their residues may cause numerous environmental problems. They may contaminate surface and groundwater through leaching and run-off. Herbicides may also remain on the soil surface due to adsorption process and potentially affect quality and yield of the next crop cultivated on the same field. Stable herbicides may be taken up by a plant forming unwanted residues (Sondhia 2008, 2009a; Jaźwa et al. 2009). Herbicides when applied to the crop undergo transformation under the influence of environment. The persistence of herbicides causes health hazards and affects non-target organisms. The fate of herbicides applied in the soil is governed by various processes such as adsorption, transformation and transportation in addition to the influence of factors such as herbicide application rate, crop type, agricultural practices and climatic conditions (Arnold and Briggs 1990; Cheng 1990; Sondhia 2009b, 2010; Sondhia and Varsheney 2010). Therefore, the use of persistent herbicides requires a thorough understanding of their dissipation and movement under field conditions. Unfortunately, little research has been undertaken on the behaviour of some herbicides.

Pendimethalin (N-(1-ethylpropyl)-2, 6-dinitro-3, 4-xylidine) (Fig. 1) is rapidly lost by photodecomposition, microbial degradation and volatilization (Gasper et al. 1994; Schleicher et al. 1995; Tsiropoulos and Miliadis 1998; Tomlin 2000; Kulshrestha et al. 2000; Sondhia 2007). Pendimethalin disrupts the mitotic sequence by inhibiting the production of the microtubule protein, tubulin (Appleby and Valverde 1989). Adsorption and degradation of pendimethalin and other dintroaniline herbicide in soil has also been the subject of many studies (Zheng et al. 1993; Kulshrestha et al. 2000; Sondhia and Dubey 2006; Sondhia and Varsheney 2010). Pendimethalin adsorbs rapidly and strongly to soil because of its high potential for hydrogen bonding. Its persistence in the soil is affected by cultivation, soil temperature, and moisture conditions (Gasper et al. 1994; Schleicher et al. 1995). Pendimethalin is a low-volatile and low-mobile dinitroaniline containing low water solubility properties (Schleicher et al. 1995; Sondhia 2007). Pendimethalin is most persistent in silty clay soil and persists longer when it is soil incorporated rather than applied to the surface (Zimdahl et al. with a recovery of 1984; Lee et al. 2000). Field dissipation studies have revealed that pendimethalin is persistent, and its half life is 98 days at 30°C (Kol et al. 2002). Pendimethalin degrades slowly

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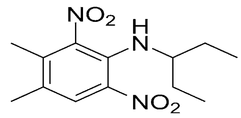

Fig. 1 Chemical structure of pendimethalin (N-(1-ethylpropyl)-2, 6-dinitro-3, 4-xylidine)

in aerobic soil and rapidly in anaerobic soil conditions. Pendimethalin is classified as a non-leaching compound (Kaleem et al. 2006) and has been used as herbicide for controlling weeds in crop fields in our country that are used in daily food plans (Hurley et al. 1998). In recent years, the compound is subjected to increase toxicological and environment concerns, e.g., to cause various physiological changes and endocrine effects in the animal studies including liver, kidney damage, and number of mutagenic effects (Dimitro et al. 2006).

Chickpea (*Cicer arietinum* L.) is one of the important vegetable crops of winter season. Pendimethalin as pre-emergence herbicide found effective for the control of annual weeds in leguminous and other field crops (Sinha et al. 1996; Tsiropoulos and Miliadis 1998; Sondhia and Dubey 2006; Lin et al. 2007). Behaviour of pendimethalin deposits in soils of cotton fields indicates that the compound is more persistent than trifluralin (Tsiropoulos and Lolas 2004). The experimental results of Jaźwa et al. (2009) indicated that pendimethalin is quite stable compound and may cause problems with follow-up crops. Dissipation and residues studies of pendimethalin in field crop especially in vegetables/pulses is lacking hence current studies were taken to understand dissipation of pendimethalin in soil of chickpea (*Cicer arietinum* L.) growing under field conditions and finally terminal residues in plant samples (grains and straw).

Materials and Methods

The field experiment was conducted at Directorate of Weed Science Research (DWSR), Jabalpur, India during Rabi season in a randomized block design with three replications. Residues analysis was conducted in residue laboratory of DWSR. Soil of experimental field was sandy clay loam having Clay 35.49 %, Silt 12.33 % and sand 52.19 %, Organic carbon (OC) 0.85 %, EC (mmhos cm^{-1}) 0.35 and pH 7.3.

Commercial available formulation of pendimethalin as Stomp30 EC was applied at 750, 350, and 185 g a.i. ha^{-1} in chickpea crop on 6 November as pre-emergence herbicide. Pendimethalin residues in soil were monitored from 0, 15, 30, 60, 90, and harvest (110 days) from a depth of 0–20 cm after herbicide application. Five soil cores were randomly taken for residue studies from each treated and untreated plot avoiding the outer 20 cm fringes of the plots using a soil auger up to a depth of 20 cm. The cores (0–20 cm depth) were bulked together from each plot, air-dried, powdered and passed through a 2 mm sieve to achieve uniform mixing. Pebbles and other unwanted materials were removed manually. The mature chickpea plant samples were collected from the pendimethalin treated plots at 110 days.

Pendimethalin from soil and pea were extracted following the method of Sondhia (2007) and Jaźwa et al. (2009) with a recovery of 80 %–88 % for soil and 80–82 % for pea at 0.5 and 1.0 μg g^{-1} fortification level. Homogeneous plants samples (each 20 g) viz grains and straw were macerated in 50 mL acetone for 1 min with a homogenizer. The extract was separated from plant fiber by filtration, and transferred into a 500 mL Erlenmeyer flask and extracted with acetone: water (9:1) on horizontal mechanical shaker for 1 h. This process repeated twice and filtrates were pooled together, concentrated to approximately 10 mL and diluted with 5 % NaCl in water (20 mL) and partitioned with n-hexane (20 mL) (repeated twice) and n-hexane layer was concentrated to approximately 5 mL in a rotary vacuum evaporator.

Soil samples (10 g) were extracted with acetone: methanol (9:1) on horizontal mechanical shaker for 1 h, which were filtered this process was repeated twice. Filtrates of same sample were pooled together and partitioned with n-hexane (50 mL) (repeated twice) and n-hexane layer was collected and concentrated to approximately 5 mL in a rotary vacuum evaporator.

Extracted soil and plant samples containing pendimethalin residues were passed on a pre-conditioned glass column packed with silica gel (6 g) and anhydrous sodium sulphate. Elutes were collected and concentrated to dryness in a rotary vacuum evaporator and made volume of 2 mL in acetonitrile for analysis.

Pendimethalin in soil and plant samples were determined by HPLC following of method of Jaźwa et al. (2009) and Triantafyllidis et al. (2005) using a Shimadzu HPLC with Photo Diode Array Detector (PDA). A C-18 column (ODS) (250 mm × 4.6 mm i.d.) was used. The mobile phase used was acetonitrile: water (70:30) with flow rate 1 mL/min. For the detection of pendimethalin 240 nm wavelength was used. All the samples were filtered through 0.20 μm membrane filter and 20-μL aliquots of sample extracts were injected in HPLC column along with standard solution. The method detection limit was 0.001 μg mL^{-1}. The retention time and peak area of the samples and standard were recorded and pendimethalin in the samples was quantified.

Pendimethalin reference analytical standard of 99.9 % purity were obtained from ACCU standard, USA. All the other chemicals and solvents used in the study were analytical grade reagent (E Merck).

Results and Discussion

Immediately after 2 h (0-day) of treatment, the average pendimethalin residue in the soil at 0–20 cm depth was found 0.626, 0.760 and 0.773 μg g^{-1} at 185–750 g a.i. ha^{-1} dose with low variation coefficient (Relative Standard Deviation, RSD) indicating that Stomp 30 EC was evenly distributed on field surface (Table 1). With passage of time pendimethalin residues decreased successively and reached the level of 0.370 and 0.050 μg g^{-1} after 15 and 30 days in 185 g a.i. ha^{-1} treatment respectively. Dissipation of pendimethalin was continued with time and by 60 and 90 days residues were found 0.020 and 0.019 μg g^{-1} in 185 g a.i. ha^{-1} treatment, respectively. The pendimethalin residues in different matrix at different time interval are presented in Table 1.

However 0.450, 0.040, 0.023 and 0.020 μg g^{-1} pendimethalin residues were detected in soil at 15, 30, 60 and 90 days after pendimethalin application at 350 g a.i. ha^{-1}. Residues of pendimethalin were found 0.470, 0.052, 0.041, and 0.023 μg g^{-1} after 15, 30, 60 and 90 days in the soil samples collected where pendimethalin was applied at 750 g a.i. ha^{-1} rate.

Pendimethalin is known for its high adsorption onto the soil and organic matter (Sondhia and Dubey 2006; Sondhia 2007). Pendimethalin adsorbs strongly to topsoil's and has reported soil–water partition coefficients (Kd values) ranging from 99.8 (0.59 % organic carbon) to 1638 (16.9 % organic carbon) (Zheng and Cooper 1996). Increasing soil organic matter and clay content is associated with increased soil binding capacity (EXTOXNET 1996). Based on the strong affinity for the soil, pendimethalin was not expected to be transported in significant amounts in the traditional perception of dissolved species transport. In spite of high adsorption of pendimethalin to soil several reports indicated long persistence of pendimethalin. Jaźwa et al. (2009) reported half-lives of pendimethalin 60–62 days in the soil of funnel field. Triantafyllidis et al. (2005) reported residues of pendimethalin up to 129 days after the treatment in the top soil of tobacco field with a half life of 23–27 days.

Therefore, some disappearance parameters for pendimethalin residues were calculated in the soil of chickpea on the basis of first order kinetics and regression equations. The disappearance trends of initial deposits of pendimethalin residues on soil surfaces, determination coefficients, and half-life times are shown in Table 2. By this time, pendimethalin residues decreased according to equations: $y = -0.029x + 1.664$ (linear) in soil treated with 185 g a.i. ha^{-1} pendimethalin in chickpea field. However dissipation of pendimethalin in soil at 350 g a.i. ha^{-1} according to equations: was $y = -0.024x + 1.684$ (linear) (Fig. 2). Whereas dissipation of pendimethalin in chickpea soil treated with 750 g a.i. ha^{-1} pendimethalin was found according to equation $y = -0.027x + 1.757$ (linear) with excellent coefficient of determination.

Half-lives of pendimethalin in chickpea field soil from those linear equations were 10.4–12.5 days obtained at 350 and 185 g a.i. ha^{-1} treatments, whereas half-life of pendimethalin at 750 g a.i. ha^{-1} treatments was found 11.2 days. Pendimethalin disappeared according to the linear equations, the initial residues of this herbicide lowered by half after 11–12 days from the application date of the pendimethalin (Stomp30 EC). Raj et al. (1999) reported that organic matter content of the soil is responsible for high adsorption of pendimethalin.

The other aim of the study was to estimate residue levels resulting from pendimethalin residues in plant samples at mature stage. Analyses of chickpea samples indicated that despite of high level of pendimethalin residues present in soil surface, less terminal residues of pendimethalin viz. 0.025, 0.015 and <0.001 μg g^{-1} were found in chickpea (grains) collected at mature stage at 750, 350 and 185 g a.i.

Table 1 Residues of pendimethalin in the soil of chickpea at 0–110 days

Days after application	Pendimethalin residues (μg g^{-1})[a]		
	Treatments (g a.i. ha^{-1})		
	185	350	750
0	0.626 ± 0.049[b]	0.760 ± 0.026	0.773 ± 0.047
15	0.370 ± 0.020	0.450 ± 0.015	0.470 ± 0.034
30	0.050 ± 0.006	0.040 ± 0.004	0.052 ± 0.001
60	0.020 ± 0.002	0.023 ± 0.001	0.041 ± 0.001
90	0.019 ± 0.001	0.020 ± 0.001	0.023 ± 0.002
110	<0.001	<0.001	<0.001

[a] Mean of three replications

[b] Standard deviation, this is a measure of the dispersion of a set of replicated residues data from its mean

Table 2 Regression equation, K, R^2 and half-life of pendimethalin in field soil

Treatment (g a.i. ha^{-1})	Equation	K	R^2	$t_{1/2}$
185	$y = -0.029x + 1.664$	0.029	0.90	10.38
375	$y = -0.024x + 1.684$	0.024	0.85	12.54
750	$y = -0.027x + 1.385$	0.027	0.84	11.15

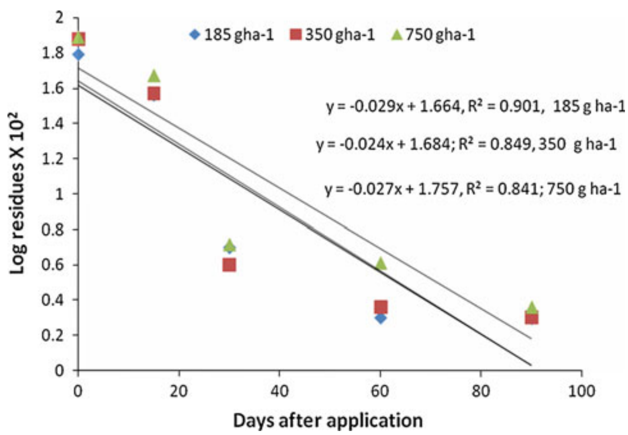

Fig. 2 Dissipation kinetics of pendimethalin residues in soil (*linear regression line*)

Table 3 Residues of pendimethalin in plant samples

Matrix	Pendimethalin residues ($\mu g\ g^{-1}$)[a]		
	Treatment (g a.i. ha^{-1})		
	185	350	750
Straw	<0.001	<0.001 ± 0.001	0.015 ± 0.007[b]
Mature grains	<0.001	0.015 ± 0.001	0.025 ± 0.006

[a] Mean of three replications

[b] Standard deviation, this is a measure of the dispersion of a set of replicated residues data from its mean

ha^{-1} treatments, respectively. Much lower pendimethalin residues were found in straw viz. 0.015 to <0.001 $\mu g\ g^{-1}$ at 750, 350 and 185 g a.i. ha^{-1} treatments, respectively (Table 3). The dissipation of pendimethalin in the chickpea field soil conditions followed first order kinetics showing a half-life of 11.23 days averaged over all doses.

Jaźwa et al. (2009) reported 0.017 $\mu g\ g^{-1}$ residues of pendimethalin in funnel. They emphasized that the rate of the pendimethalin disappearance was slow ($t_{1/2} = 60$ days) and its residues in the soil can be locally toxic for the follow-up plants as residues in the soil was 0.221 $\mu g\ g^{-1}$, and were 3 times higher than in other samples of the soil taken in the period of crops. Lazic (1995) reported that pendimethalin residues decreased during the onion crop vegetative stage, and 50 % of the herbicide degraded in an average of 50 days. Pendimethalin residues in young onion were 0.239 $\mu g\ g^{-1}$ and in ripe onion 0.113 $\mu g\ g^{-1}$ (Lazic et al. 1997). Sinha et al. (1996) reported that pendimethalin residues in the soil were taken up by the onion plants and persisted up to 45 days at 1.0 kg ha^{-1}, and beyond 60 days at 2.0 kg ha^{-1}.

Residues found on crops that had direct contact with soil could result from pendimethalin present in the crop matrix or from soil adhering to the crop material. Sharma and Mehta (1989) reported 0.103 $\mu g\ g^{-1}$ residues in onion at harvest when the pendimethalin treatment was 2.0 kg ha^{-1}. Tsiropoulos and Miliadis (1998) reported 0.054 $\mu g\ g^{-1}$ residues in onions treated at 2.0 kg ha^{-1}. As discussed previously, soil contact, microbial action, soil moisture, and photodecomposition can affect pendimethalin residue levels found in the harvested crop.

A high level of persistence in the soil during the initial days of the crop growth would ascertain effective weed control during the most critical period of crop-weed competition and safety to rotational crops as the residues dissipate to a very low level of activity by 90 days after treatment. In the current studies the residues of pendimethalin in chickpea were found below the maximum residue limit set by EPA (0.05 $\mu g\ g^{-1}$).

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