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Dissipation kinetics and residues analysis of pendimethalin in soil and maize under field conditions

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ABSTRACT

Herbicides play an important role in the production of crops, but their residues may cause numerous human/environmental problems. Dissipation kinetics of pendimethalin and residues in soil, maize straw and cobs in winter maize under field conditions were studied by gas chromatograph-electron capture detector (GC-ECD). Dissipation followed the first order kinetics and accounted by a biphasic pattern. The half-life for initial phase and later phase was 11.70 and 34.13 days for recommended and 9.19 and 46.81 days for double dose, respectively. Percent recovery from cobs, straw and soil samples varied from 76.2–88.5, 76.6–84.4, and 85.0–89.5%. The limit of quantification was 0.001 μg/g of sample. At harvest pendimethalin residues were below detectable limit in soil, maize cobs and maize plant at both application rates (1 and 2 kg/ha). Pendimethalin is safe for use and does not appear to pose any health hazard to consumers or harm to the environment.

Keywords: herbicide; *Zea mays*; persistence; DT_{50}; chromatography

Due to scarcity and non availability of labour at the peak period, herbicides are gaining importance for weed control in major crops. Weeds seriously reduce yield or quality of products by competing with the crop for available moisture, nutrients and light. Maize is one of the staple foods of Asians and also utilized in starch, oil and food and feed industries. In India, it is grown round the year in an area of 6.56 million hectares with production of 12 million tonnes. The winter maize (rabi season) with its high productivity potential has opened up a viable alternative (Mishra et al. 2001). Weeds cause heavy losses to maize yield to the extent of 32.4–42.3% (Sharma et al. 2000).

Pendimethalin [N-(1-ethylpropyl)-3, 4-dimethyl 2, 6-dinitro benzenamine], a member of the group 2, 6 dinitroaniline herbicides commercially available as Prowl, Stomp, Panida etc. has selective pre-emergence characteristics. It has a widespread usage for selective control of wide variety of grasses and broadleaved weeds in several crops. Pendimethalin disrupts the mitotic sequence by inhibiting the production of the microtubule protein, tubulin (Tomlin 2000).

Pendimethalin was determined to be a systemic toxicant. In recent years, this compound has been 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 (Dimitrov et al. 2006). Degradation, leaching and adsorption of pendimethalin herbicide in soil and crops had been the subject of many studies (Kulshrestha et al. 2000, Liu et al. 2004, Lin et al. 2007, Tandon 2008, Bandyopadhyay and Choudhury 2009, Shah et al. 2011, Sondhia 2012, 2013). 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, Srivastava et al. 2006, Sondhia 2012). Pendimethalin degrades slowly in aerobic soil and rapidly in anaerobic soil conditions. Field dissipation studies revealed that pendimethalin is persistent herbicide, with its half-life of 98 days at 30°C (Kolberg and Wiles 2002). Due to injudicious use of pesticides, the

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lack of a pesticide usage database and improper monitoring systems, it is always difficult to carry out risk assessment and environmental monitoring studies in developing countries. On account of its wide applicability and potential health hazards, the present study was undertaken with objective to analyse residue and kinetics of corn herbicide (pendimethalin) in soil and winter sown maize crop in field conditions under subtropical climate.

MATERIAL AND METHODS

Hewlett Packard-5890 series-II gas chromatograph equipped with μ-ECD (Ni^{63}) and HP (model-3396) series-II integrator (Santa Clara, USA). Analytical grade pendimethalin (99.0% pure) was obtained by courtesy of M/s American Cyanamid Company, Wayne, USA (now BASF). Formulation was obtained from M/s Gharda Chemicals, Mumbai Pendiguard 30 EC.

Field trials on winter maize (cv. K-55) were conducted during the winter season at the N.E. Borlaugh Crop Research Center, G.B. Pant University of Agriculture and Technology, Pantnagar, India. Pendimethalin formulation (Pendiguard 30EC) was applied as pre-emergent herbicide in plots at 1 and 2 kg a.i./ha doses. A control plot was also maintained where no pendimethalin was sprayed. The plot size was 6 × 5 m. The experiment was laid in RBD fashion and all treatments were replicated thrice. All other crop management practices were followed except weed management.

Soil samples (1.0 kg) of 0–15 cm depth were collected from five randomly selected spots at different time intervals i.e. 0 (1 h), 1, 3, 5, 7, 15, 30, 45, 60, 75, 90, 105 and 120 days after herbicide application and finally on the harvesting day (160 days after treatment (DAT)). Maize (cobs) (0.5 kg) and straw samples (0.2 kg) were collected from all plots i.e. control and treated (at two rates) at harvest time. Seeds of maize were removed from the cobs and were crushed using pestle and mortar, while straw was chopped into small pieces using knife. Soil was analyzed for pH, organic carbon percentage and proportion of sand, silt and clay fraction by standard analytical procedure.

Extraction of pendimethalin from soil, maize cobs and straw. Extraction and clean-up of pendimethalin from soil (20 g), maize cobs (20 g) and straw (10 g) were done according to Tandon (2008). The residue obtained was dissolved in 2 mL n-hexane (GC grade) and filtered through 0.22 μm Millipore filter before subjection to gas chromatograph (GC) analysis.

GC condition. The following gas chromatographic conditions were optimized to achieve proper separation for determination of pendimethalin at trace levels using Equity-5 micro-capillary column (30 m length, 0.25 mm ID and 0.25 μm film thickness), flow rate 1 mL/min, and μ-ECD (Ni^{63}) detector. The oven, injector and detector temperatures were maintained at 250, 275 and 300°C, respectively. GC was operated in splitless mode. The sample injection volume was 1 μL and total run time was 20 min. Pendimethalin was identified by comparing the retention time of the peak present in the extracts of the samples with the retention time of the standard.

Recoveries studies of pendimethalin. For determination of the percent recovery of pendimethalin for soil, cobs and straw 100 g of soil sample, 50 g of cobs and 25 g of straw was fortified with 0.05–2 μg/g of standard pendimethalin and was replicated thrice. Extraction, clean-up and analysis were done in the same way as given above for soil, cobs and straw.

Kinetics of pendimethalin. The amount of pendimethalin recovered from soil at different time intervals for both application dosages fitted in the first order kinetic equation according to Eq. 1:

$$C = C_0 e^{-\lambda t} \quad (1)$$

Where: C – amount of pendimethalin recovered from soil at time t; C_0 – amount of pendimethalin recovered at $t = 0$ interval; λ – degradation constant; t – time in days.

RESULTS AND DISCUSSION

The general physico-chemical properties of soil samples taken in the study showed the soil was clay loam type with sand:clay:silt in the ratio of 30:27:43%, organic content in soil was 1.68% and pH was 8.02. The temperature range (minimum to maximum) and rainfall during the experimental period was 4.4–35.5°C and 90 mm, respectively. Retention time for pendimethalin was 15.48 min. The limit of detection was 0.0003 μg/g while, the limit of quantification was 0.001 μg/g for the samples. The percent mean recovery of pendimethalin

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Table 1. Percent recovery of pendimethalin from fortified samples of straw, cobs and soil

Soil No.	Sample	Amount (μg/g)	Mean percent recovery (± SD)
1	straw	0.05	76.6 ± 0.2
		0.5	79.4 ± 0.2
		1.0	81.8 ± 0.4
		2.0	84.4 ± 0.3
2	cobs	0.05	76.2 ± 0.6
		0.5	78.6 ± 0.4
		1.0	82.0 ± 0.4
		2.0	88.5 ± 0.4
3	soil	0.05	85.0 ± 0.4
		0.5	87.5 ± 0.2
		1.0	88.6 ± 0.2
		2.0	89.5 ± 0.6

Average of three replicates. SD – standard deviation

from cobs, straw and soil samples fortified with herbicide varied from 76.2–88.5, 76.6–84.4, and 85.0–89.5%, respectively (Table 1).

Dissipation studies of pendimethalin. Persistence/dissipation studies of pendimethalin in soil at two different concentrations were performed. Percent persistence values at different time intervals were calculated considering the amount of herbicide recovered on 0^{th} day (1 h after application) as 100%. The persistence of herbicide in soil treated at 1 kg/ha decreased from 100–82.79% from 0^{th} day to 3^{rd} day and then it gradually fell up to 51.72% till 15^{th} day. On 45^{th} day of application, the persistence decreased to 21.42% and then to 16.16 on 60^{th} day and persisted up till 75^{th} day after application (5.10%). However, no detectable residue (< 0.001 μg/g) was found after 90^{th} day of application. The dissipation pattern of the herbicide at 1 kg/ha was faster for the first seven days but got slower up till the next 90^{th} day thereafter it became non-detectable. The persistence of pendimethalin applied at 2 kg/ha in soil decreased from 100–78.54% from 0^{th} day to 3^{rd} day and then it gradually fell up to 41.06% till 15^{th} day, on 45^{th} and 90^{th} day of application, the persistence decreased to 25.57% and 5.28%, respectively, and persisted up till 105^{th} day after application. No detectable residue (< 0.001 μg/g soil) was observed on 120^{th} day of application. Similar trend of dissipation at 2 kg/ha application rate was observed.

Kinetics. The computed values of degradation constant, coefficient of determination (R^2) for the first order dissipation kinetics and half-lives of pendimethalin under field conditions at two different fortification levels are depicted in Table 2. Dissipation followed the first order kinetics as highly significant R^2 values indicated that the dissipation of pendimethalin conformed to the first order kinetics. Dissipation of pendimethalin in clay loam soil accounted by a biphasic pattern in both the application doses. It is evident from Table 2 that degradation of pendimethalin during 0–7 days was many folds higher than the later phase of degradation. The half-life calculated for initial phase and later phase was 11.70 and 34.13 days for recommended and 9.19 and 46.81 days for double dose respectively. The slower dissipation of pendimethalin in the present investigation in the latter phase might be due to strong binding of herbicide with soil colloids minimizing its losses and also rendering the chemical less prone to

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

Computed value		1.0 kg/ha	2.0 kg/ha
Initial phase (0–7 days)	degradation rate constant	0.057	0.080
	half-life days	13.959	9.198
	coefficient of determination	0.9229	0.9501
	regression equation	$Y = -0.0593x - 0.1452$	$Y = -0.0791x + 0.1814$
Later phase (7 days – onwards)	degradation rate constant	0.020	0.061
	half-life days	31.254	46.818
	coefficient of determination	0.9155	0.9005
	regression equation	$Y = -0.3027x - 0.0615$	$Y = -0.2415x + 0.1143$

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physical and bio-chemical modes of degradation. Biphasic dissipation pattern for pendimethalin was also reported by Srivastava et al. (2006). Soil factors like availability of soil moisture, organic carbon content and pH plays an important role in dissipation of pesticides from soil (Tandon 2014, Tandon and Singh 2015). In low organic matter the content in soil pendimethalin persisted for longer period as compared to high organic matter (Berayon 1987). Manish and Kewat (2002) found that pendimethalin dissipated fast in the first phase i.e. about 64% and after 90 days only 3–15% persisted in soil; as opposed to that other workers reported half-life of pendimethalin during initial (2–5 days) and later (12 days) phase for the sampling period of 6 and 27 days, respectively (Savage and Jordan 1980). Half-life of pendimethalin varied from 28.1–31.7 days in soil and the residue was not detected in onion at harvest (Diwan et al. 1999). Dissipation of pendimethalin varied from 5.78–77.08% in six different soils in 120 days and rate of dissipation of pendimethalin was influenced by organic matter, soluble salt content and other soil factors (Pai et al. 1999). In red sandy loam soil pendimethalin did not persisted for more than 60 days (Devi et al. 2000). In a sandy loam soil pendimethalin half-life ranged from 10.5–31.5 days, and was affected mainly by the time interval between irrigation application and the first rain event (Alister et al. 2009).

Harvest residue studies in maize cobs and straw. Pendimethalin residues in maize cobs and straw for both the treatments (1 and 2 kg/ha) were below detectable amount at harvest time. In pea, pendimethalin dissipated about 86.86% in 60 days after application and was not detected in soil and pea at harvest (Srivastava et al. 2006). Tandon (2008) reported that residues of pendimethalin persisted for more than 90 days in soil and were below the maximum residue limit in potato tubers and soil at harvest of crop. Similar results were obtained by Sondhia (2012, 2013) where residues were below maximum residue limit (MRL) limit in chick pea, onion, tomato, radish and radish at harvest.

In conclusion, based on the results obtained in the present investigation, it can be concluded that the use of pendimethalin as a herbicide in winter maize crop is safe from environmental aspects and human/animal feed as the residues of pendimethalin were not detected in soil, maize cobs and straw from treated fields at harvest and maize crop and straw was also safe for consumption as residues were below MRL as set by EU (0.05 μg/g). Degradation of herbicide primarily depends on the soil microbes population and their activity, soil constituent e.g. organic matter and clay. Apart from these, factors like soil pH, temperature and other environmental conditions, play equally an important role in pesticide degradation.

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