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Persistence of Pendimethalin in/on Wheat, Straw, Soil and Water

Indu Chopra[1] · **Reena Chauhan**[1] · **Beena Kumari**[2]

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Abstract Pendimethalin, a dinitroaniline group of organic herbicide compounds used as pre emergence weed control in wheat, onion and soyabean crops in India. The experiments were designed to study the harvest time residues of pendimethalin in wheat grain and straw its dissipation behaviour in soil and water. At harvest time, the residues of pendimethalin in wheat grain and straw were found to be below determination limit of 0.001 mg kg^{-1} following single application of the herbicide at the rate of 1 (T_1/single dose) and 2 (T_2/double dose) kg a.i. ha^{-1}. Soil samples from the field were collected periodically and analysed by GC-ECD system. In soil, initial deposits of 4.069 and 10.473 mg kg^{-1} of pendimethalin persisted up to 90 days and dissipation followed first order kinetics with half life period of 12.03 days in T_1 and 13.00 days in T_2. Residues of pendimethalin studied in water under laboratory conditions at 0.5 (T_1) and 1.0 (T_2) mg L^{-1} levels persisted up to 90 days. Dissipation kinetics followed first order kinetics with half-life values of 12.70 and 13.78 days at single and double dose, respectively. Limit of determination in grain, straw and soil were 0.001 mg kg^{-1} and in water was 0.001 mg L^{-1}. Application of the herbicide is considered quite safe from consumer and environmental point of view.

Keywords Persistence · Pendimethalin · Water · Wheat · Dissipation · Half-life

✉ Beena Kumari
beena@hau.ernet.in; beenakumari.958@rediffmail.com

1 Department of Chemistry and Physics, CCS Haryana Agricultural University, Hisar 125004, India

2 Department of Entomology, CCS Haryana Agricultural University, Hisar 125004, India

Among the food grain crops of the world, wheat (*Triticum aestivum* L.) is prominent both in regards to its antiquity and its importance as a food of mankind. As per FAO (2011) India is the second largest producer of wheat, the world's major food staples. In 2012, total production of wheat was around 93.382 million tonnes from an area of about 30 million hectares (FAOSTAT 2012). It is one of the most important rich sources of carbohydrates and protein for mankind and its increased production is essential for food security (Devi et al. 2011).

North-West region of the country suffers a setback due to heavy infestations by several weeds and insects. The losses in wheat yield caused by weeds which depend upon weed species, density of weeds and the crop etc. Pesticide use has increased worldwide to secure the food supply of the swelling global population. An important role is played by herbicides in increasing the agricultural yield by protecting the crops from pests (Khalid et al. 2013). Excessive use of herbicides and other pesticides in agriculture causes serious environmental problems. These may remain to the soil surface and contaminate surface water as well as ground water and may also affect the yield of the next crop cultivated on the same land (Sondhia 2008; Jaźwa et al. 2009). As the movement of water through the soil is the principal mechanism for the pesticides to reach the surface and groundwater, there has been increased research interest aimed at understanding the process that controls the penetration of pesticides into the soil and their subsequent contamination of groundwater and surface water. Accumulation of these toxic pesticides in groundwater is influenced by the physical, chemical, and biological mechanisms.

Pendimethalin [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] belonging to dinitroaniline group of organic herbicidal compounds has long been used as a selective herbicide for wide spectrum weed control in crops such as corn, soybean, cotton, transplanted tobacco, peanuts, barley, rice, sunflower, potatoes, peas, onions, wheat, gram, lentil etc. Its persistence is influenced by cultivation practices, soil temperature and moisture conditions, as well as soil type (Lee et al. 2000; Stranberg and Scott-Fordsmand 2004). It is rapidly lost by photodecomposition, microbial degradation and volatilization (Kulshrestha et al. 2000; Sondhia 2012). It disrupts the mitotic sequence by inhibiting the production of the microtubule protein, tubulin (Tomlin 2000).

Herbicide residue estimation in wheat crop, soil and canal water is very essential to determine the duration of herbicide activity in soil, its effect on the crop and to analyze the quality of the food. Hence, present study was undertaken to observe the extent of persistence of pendimethalin in wheat crop, soil and canal water.

Materials and Methods

All the solvents were of analytical grade used for this study and redistilled before use in glass apparatus and their suitability was ensured by running reagent blanks along with actual analysis. The stock solution of the insecticide prepared at concentration of 1000 µg mL^{-1} in GLC-grade solvent and further diluted to prepare working standards.

Preparation of Standard Solution

A standard stock solution of pendimethalin having a concentration of 1 mg mL^{-1} was prepared in acetone. The standard solutions required for constructing a calibration curve (2.00, 1.50, 1.00, 0.50, 0.25 and 0.10 µg mL^{-1}) were prepared from stock solution by serial dilution using *n*-hexane and were stored at −4°C.

Analysis of the pendimethalin in wheat straw, grain, soil and water was carried out on gas liquid chromatography (GLC, model Shimadzu 2010, equipped with ^{63}Ni electron capture detector (ECD) and capillary column HP-1 (30 m × 0.32 mm i.d × 0.25 µm film thickness of 5 % diphenyl and 95 % dimethyl polysiloxane) with split ratio 1:10.

Wheat (*T. aestivum*) variety C-306 was raised during *Rabi* season at Research Farm of the Department of Soil Science, Chaudhary Charan Singh Haryana Agriculture University (CCSHAU), Hisar using randomized block design (RBD) with a plot size of 25 m^2, following the recommended agronomic practices. There were three replications for each treatment (i.e. control, single and double the application dose). The soil (sandy loam) under crop was of light texture with low content of organic matter; other relevant properties of the soil were EC 2dSm^{-1}; K 10.08, P_2O_5 15 kg ha^{-1} with pH 7.6 and organic carbon 0.67 %.

Under laboratory conditions, degradation kinetics of pendimethalin was studied in canal water at room temperature. The physico-chemical characteristics of canal water were as follows: EC × 10^{-6} (µ S m^{-1}), 240; HCO_3^{-1} (meql^{-1}), 1.2; Cl^{-1} (meql^{-1}), 0.5; Ca^{2+} (meql^{-1}), 1.0; Mg^{2+} (meql^{-1}), 2.2 and pH 7.7.

The pendimethalin (Stomp 30EC) was applied in the field manually along with the sowing at two different doses. The treatment one (T_1) consisted of 1 kg a.i. ha^{-1} and treatment two (T_2) consisted of 2 kg a.i. ha^{-1}. In control plots, only water was sprayed.

Water sample (200 mL) replicated thrice was treated with pendimethalin at the rate of 0.5 mg L^{-1} (T_1) and 1.0 mg L^{-1} (T_2) and kept in 54 brown colour bottles excluding untreated control samples.

Residues of pendimethalin were estimated in soil under the cover of wheat crop drawn from top 15 cm of soil profile on 0 (1 h after treatment), 1, 3, 7, 15, 30, 60, 90 days of treatment and in straw and wheat grains at the time of harvest. The samples from each treatment and each plot were collected separately, packed in polyethylene bags and brought to the laboratory for processing. The soil samples were shade dried, crushed in pestle mortar and sieved through 2 mm sieve. The treated water samples were processed for pendimethalin residues on 0 (l h after treatment), 1, 3, 7, 15, 30, 60 and 90 days after treatment (DAT).

The samples of wheat were processed and analyzed at the Pesticide Residue Laboratory, Department of Entomology, CCSHAU, Hisar. From each sample after quartering, representative sample of 5 g straw and 10 g of grains was extracted with methanol on mechanical shaker for 1 h by using the method of Sondhia and Dubey (2006). The contents were filtered through 2–3 cm pad of anhydrous sodium sulphate and concentrated the extracts to 50 mL using a rotary vacuum evaporator. The extract was diluted with 10 % sodium chloride solution and partitioned twice with hexane (50, 50 mL) by vigorous shaking. The organic layer was collected each time and passed through the pad of anhydrous sodium sulphate and pooled together. The pooled organic layer was concentrated to 10 mL. For clean up, the extracts were passed through column containing adsorbent mixture (neutral alumina: Florisil: activated charcoal, 1:2:0.5 w/w) between two layers of anhydrous sodium sulphate. The column was eluted with 100 mL solution of hexane. The clean extract was evaporated to dryness and finally dissolved in 2 mL *n*-hexane for GC analysis.

Soil samples were extracted as per method of Kumari et al. (2007). A representative soil sample of 15 g mixed with 0.5 g each of activated charcoal and Florisil was filled in a 60 cm long glass column having 22 mm i.d. between two layers of anhydrous sodium sulphate. The residues were eluted with 125 mL of hexane: acetone (9:1 v/v). The organic layer was concentrated on rotary vacuum evaporator and final volume was made to 2 mL in *n*-hexane for GC analysis.

Water samples were extracted as per method of Kumari et al. (2007). Treated water samples (200 mL) at different time intervals were taken in a separatory funnel and 10 g of sodium chloride was added to it. The pendimethalin residues were extracted by liquid–liquid partitioning thrice with 15 % dichloromethane in hexane (50, 30, 20 mL). The organic layers were combined and concentrated to near dryness on a rotary vacuum flash evaporator followed by gas manifold evaporator. The process was repeated thrice after adding 5 mL hexane in order to eliminate the traces of dichloromethane. Final volume (2 mL) was made in *n*-hexane for analysis.

Residues of pendimethalin were estimated by GC (GLC, Model Shimadzu 2010). GC parameters were as follows: Temperature (°C): oven: 150 (5 min) → 8 min^{-1} → 190 (2 min) → 15 min^{-1} → 280 (10 min). Injection port, 280 °C, detector, 300 °C; carrier gas (N_2) flow was maintained at 30 mL min^{-1}, 2 mL min^{-1} through column with split ratio 1:10. Before use, the column was primed with several injections of a standard solution of pendimethalin until a consistent response was obtained. Retention time (R_t) for pendimethalin was 14.601 min under these operating conditions.

In the present study, recovery experiments for wheat grain and straw were performed at 0.50 and 1.0 mg kg^{-1} spiking levels to check the validity of analytical method and to know the efficiency of extraction and clean-up procedures. Average recoveries obtained in wheat grains were 90.74 % and 85.53 % while in straw were 85.80 % and 82.46 %. Soil and water sample were fortified at 0.25 and 0.50 mg kg^{-1} and at limit of detection level of 0.001 mg kg^{-1}. Average percent recoveries in case of soil were 95.8 and 94.0, respectively and in canal water were 98.80 and 99.10, respectively.

Results and Discussion

The results of analysis of wheat grains and straw following application of pendimethalin at the rate of 1 and 2 kg a.i. ha^{-1} showed that residues dissipated almost completely at harvest time and reached below detectable/determination level of 0.001 mg kg^{-1} in both the doses. Thus the results indicated either complete degradation or non translocation of the herbicide from soil into the wheat plants. Various factors leading to complete degradation/dissipation of the translocated herbicide in plants may be enlisted as relatively low dose of the herbicide, long duration (131–137 days) of the crop and climatic conditions. Dilution due to plant growth leading to enhanced enzymatic degradation may have played a significant role in overall dissipation of the herbicide. Sondhia (2013a) revealed that at harvest, 0.008, 0.001, and 0.014 µg g^{-1} residues of pendimethalin were found in tomato, cauliflower, and radishes, respectively when pendimethalin was applied pre-emergently at 1 kg a.i. ha^{-1}. Terminal residues of pendimethalin in green and mature pea were studied under field conditions by Sondhia (2013b) by applying pre-emergence herbicide at 750, to 185 g a.i. ha^{-1} in winter, in field peas. Low pendimethalin residues were found in mature pea grain (0.004, 0.003, <0.001 µg g^{-1}), and straw (0.007, 0.002, <0.001 µg g^{-1}) at 750, 350 and 185 g a.i. ha^{-1} treatments, respectively. Sondhia and Dubey (2006) reported that application of pendimethalin as pre emergent herbicide at the rate of 1 kg a.i. ha^{-1} did not leave detectable residues in onion at the time of harvest. Tandon and Tripathi (2008) found no residues of pendimethalin in maize cobs and maize plants at the time of harvest applied at the doses of 1 and 2 kg a.i. ha^{-1}. Keeping all these factors in consideration, absence of detectable residues in wheat straw and grains at the tested doses appeared to be justified and logical.

The residue data in Table 1 revealed that at 1 kg a.i. ha^{-1} (T_1), average initial deposits on 0 (1 h after treatment) were 4.069 mg kg^{-1} which dissipated to 3.713, 2.852 and 1.706 mg kg^{-1} in 1, 3 and 7 days, respectively in soil. The per cent dissipation was recorded to be 8.74, 29.90 and 58.07, respectively in this period. The residues dissipated by 99.90 % leaving 0.004 mg kg^{-1} residues 90 days after treatment. At the time of harvest (150 DAT) residues found were below detectable level (BDL) showing 100 % dissipation of pendimethalin in the soil. At T_2 i.e. at 2 kg a.i. ha^{-1}, the initial residues were found to be 10.473 mg kg^{-1} on 0 (1 h after treatment) days. After 1 day of treatment, the residues declined to 9.700 mg kg^{-1} indicating per cent dissipation of 7.38. The residues further declined to 7.462, 4.638 and 2.219 mg kg^{-1} after 3, 7 and 15 days of treatment indicating 55.71 %, 78.81 % and 95.81 % dissipation respectively. At the time of harvest (150 DAT), the residues were found to be 0.002 mg kg^{-1} with per cent dissipation of 99.98. The dissipation of pendimethalin residues in soil followed first order kinetics with half-life value of 12.03 days at T_1 and 13.0 days at T_2. Statistically analyzed data showed that the interaction between days and treatment was found to be 2.246 and critical difference ($p = 0.005$) for treatments was found to be 0.7942 while for days it was 1.5883. The dissipation can be considered to have been rapid and almost complete in T_1 but slightly slow in T_2 dose. Various factors, which appeared to have played role in dissipation/degradation of pendimethalin in

Table 1 Persistence and dissipation of pendimethalin residues in soil at two doses

Days after treatment	Residue (mg kg^{-1})			
	T_1 (1 kg a.i. ha^{-1})		T_2 (2 kg a.i. ha^{-1})	
	Average	% Dissipation	Average	% Dissipation
0	4.069	–	10.473	–
1	3.713	8.74	9.700	7.38
3	2.852	29.90	7.462	28.75
7	1.706	58.07	4.638	55.71
15	0.825	79.72	2.219	78.81
30	0.135	96.68	0.438	95.81
60	0.098	97.59	0.325	96.89
90	0.004	99.90	0.161	98.46
150 (Harvest)	BDL	100	0.002	99.98
Rate constant k ($days^{-1}$) = 0.05760			Rate constant k ($days^{-1}$) = 0.05330	
Correlation coefficient r = −0.9710			Correlation coefficient r = −0.9721	
Regression equation = 3.3789 + 0.02501x			Regression equation = 3.8223 + 0.02315x	
$t_{1/2}$ = 12.03 days			$t_{1/2}$ = 13.00 days	
BDL – below determination level: 0.001 mg kg^{-1}				

CD (p = 0.05) for treatments = 0.07942; for days = 1.5883; for days × treatment = 2.246

soil under the cover of wheat crop, can be considered as favourable climatic factors like high temperature couples with high humidity. Rapid degradation of pesticides under hot and humid conditions has been known for the consequence. Other factors such as volatilization, leaching and uptake by the crop can also be considered to have played some role leading to complete dissipation of herbicide by the harvest of crop.

Sondhia (2013a) reported that at harvest, the pendimethalin residues in the soil of tomato cauliflower and radish field were 0.02, 0.023 and 0.019 µg g^{-1} at 1000 g a.i. ha^{-1} dose, respectively indicating that with passage of time residues decreased in the soil successively. Sondhia (2012) studied disappearance of pendimethalin in the soil of chickpea, and terminal residues in plant samples under field conditions and found that dissipation of pendimethalin in the chickpea field soil conditions followed first-order kinetics showing a half-life of 11.23 days which are in agreement with the present study. Half-lives of pendimethalin in pea field soil from those exponential and linear equations were 20.0–15.0 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 to be 27.36–25.1 days. The residues of pendimethalin disappeared according to the equations reported by Sondhia (2013b). Tandon and Tripathi (2008) reported that dissipation of pendimethalin in soil applied at the rate of 1 and 2 kg a.i. ha^{-1} followed biphasic first order kinetics. The half life values for initial phase and later phase was 10.12 and 55.65 days for single and 7.16 and 65.58 days for double dose, respectively. Present results are in conformation of these results.

Dissipation of pendimethalin in water at two different doses is given in Table 2. Initial residues of 0.180 mg L^{-1} from T_1 at 0 (1 h after treatment) day dissipated to 0.154, 0.120 and 0.094 mg L^{-1} in 1, 3 and 7 days after treatment, respectively thereby recording 14.44 %, 33.33 % and 47.77 % dissipation in this period. Residues further declined to 0.059 mg L^{-1} in 15 days after treatment followed by 0.013 mg L^{-1} in 30 days after treatment. The corresponding figures of per cent dissipation were 67.72 and 92.77. The residues further dissipated to 95.55 % and 99.44 % after 60 and 90 days of treatment with the average value of 0.008 and 0.001 mg L^{-1}, respectively. At T_2, initial residues of 0.347 mg L^{-1} dissipated to 0.300, 0.235 and 0.185 mg L^{-1} in 1, 3 and 7 days after treatment with per cent dissipation of 13.54, 32.27 and 46.68, respectively in this period. After 15 days of treatment, the residues were 0.120 mg L^{-1} showing 65.41 % dissipation followed by 0.030 mg L^{-1} after 30 days of treatment with per cent dissipation of 91.35. Residues of pendimethalin were found to be 0.018 and 0.003 mg L^{-1} after 60 and 90 days of treatment recording 94.81 % and 99.13 % dissipation, respectively. Statistically analyzed data showed that the interaction between days and treatment was significant with the value of 0.033 and critical difference (p = 0.005) for treatments was found to be 0.0117 while for days it was 0.0233.

The result showed that 99 % dissipation occurred at both doses in a period of 90 days. Residue half-life was observed to be 12.70 days at T_1 and 13.78 days at T_2 dose. The degradation of pendimethalin was observed to be faster at lower dose (T_1) than T_2 in canal water. Vidotto

Table 2 Dissipation of pendimethalin residues (μg mL^{-1}) in canal water at two doses

Days after treatment	Residue (μg mL^{-1})			
	T_1 (0.5 mg L^{-1})		T_2 (1.0 mg L^{-1})	
	Average	% Dissipation	Average	% Dissipation
0	0.180 ± 0.0081	–	0.347 ± 0.0236	–
1	0.154 ± 0.0015	14.44	0.300 ± 0.0127	13.54
3	0.120 ± 0.0134	33.33	0.235 ± 0.0255	32.27
7	0.094 ± 0.0243	47.77	0.185 ± 0.0322	46.68
15	0.059 ± 0.0166	67.72	0.120 ± 0.016	65.41
30	0.013 ± 0.0029	92.77	0.030 ± 0.010	91.35
60	0.008 ± 0.0008	95.55	0.018 ± 0.0066	94.81
90	0.001 ± 0.0008	99.44	0.003 ± 0.0014	99.13
Rate constant k ($days^{-1}$) = 0.0545			Rate constant k ($days^{-1}$) = 0.0503	
Correlation coefficient r = −0.9826			Correlation coefficient r = −0.9831	
Regression equation = 2.146 + 0.0237x			Regression equation = 2.4305 + 0.0218x	
$t_{1/2}$ = 12.70 days			$t_{1/2}$ = 13.78 days	

et al. (2004) reported the behaviour of pretilachlor in water and sediment of a rice field in his 2-year field study (2001–2002) carried out in N-W Italy. The amount of the herbicide in the paddy water gradually fell to levels below the sensitivity of the analytical method when water circulation was re-established. The average half-life in water was 6.77 and 28.76 days in 2001, 4.68 and 15.01 days in 2002, respectively. Watanabe et al. (2007) studied the fate of three herbicides (simetryn, mefenacet and thiobencarb) applied as a granular formulation at a rate of 10 kg ha^{-1}, 21 days after transplanting. Dissipation of the herbicides appeared to follow first order kinetics with the half-lives (DT_{50}) of 1.6–3.4 days and the DT_{90} (90 % dissipation) of 7.4–9.8 days. Earlier results do not corroborate with the present results may be due to climatic conditions and standing water in paddy crop.

Conclusion

The herbicide did not translocate in edible portion of the wheat crop (grain and straw). Therefore, food commodities may be considered safe for human and animal consumption. Pendimethalin persisted in soil up to 90 days, therefore, can be considered effective almost throughout the crop period of wheat. The degradation of pendimethalin in water under field conditions can be expected still faster because of favorable degrading factors normally existing there. Therefore, pendimethalin at the tested doses i.e. 0.5 and 1.0 mg L^{-1} in water system can be considered safe from point of view of hazards due to its residues. Application of the herbicide is considered quite safe from consumer and environmental point of view.

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Compliance with Ethical Standards

The work is original research and has not submitted for publication in whole or in part and has never been published in any form elsewhere. The authors along with all co-authors are in agreement for the work being peer reviewed and possibly published and we have no undeclared competing financial interests. We are responsible for the accuracy of the facts presented.

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