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Influence of Soil Moisture and Microbial Activity on Pendimethalin Degradation

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Pendimethalin, N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline, is a selective pre-emergence herbicide used extensively for control of large variety of grasses and broadleaf weeds in several crops including wheat (Triticum aestivum L.), soybean (Glycin max(L) Marr), peas (Pisum sativum) and various vegetable crops (Sprankle 1974).

Persistence of herbicides, in general, is influenced by soil type, soil temperature, soil moisture and cultivation practices. It was observed (Zimdahl et al 1984) that under identical conditions of soil moisture and temperature, effect of soil type on pendimethalin persistence was rather small. The persistence of this herbicide in a sandyloam soil with moisture at 75 per cent field capacity was inversely related to temperature, the half lives being 98 and 409 days at 30 and 10°C, respectively (Walker and Bond 1977). Pendimethalin showed half life ranging between 58 and 63 days in IARI sandyloam soil when applied at 1.5 kg a.i./ha in wheat crop under Indian tropical climate (Kulshrestha and Yaduraju 1987). The present study was undertaken to investigate the influence of soil moisture and microbial activity on degradation of pendimethalin in soil.

MATERIALS AND METHODS

Pendimethalin (90% purity) was provided by Cyanamide India Ltd., Bombay, India. Sandyloam soil under investigation had composition of 60.2% sand, 18.6% clay, 21.2% silt and 0.35% organic carbon with pH of 8.2. The air dried soil was screened through a 2 mm sieve before use.

To study effect of moisture and role of microorganisms in the degradation of pendimethalin, 10 g sieved soil

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Send reprint request to G. Kulshrestha at the above address was weighed in Erlenmeyer flask and 1.2 ml sterile distilled water was added to each flask to provide 80% field capacity. The soil was sterilized by autoclaving at 121°C for 1 h for three consecutive weeks. To each of the 36 flasks of one set containing autoclaved and nonautoclaved soil, 1.2 mL sterile water was added to provide non-flooded condition and to each flask of the other set containing equal number of soil samples, 12 mL sterile water was added to create flooded condition. The flasks were incubated in dark at 30±1°C for one week. Then 1 mL of pendimethalin (100 µg) solution was added to each flask and again incubated at 30±1°C. At periodic intervals, duplicate soil samples were extracted and analysed by gas chromatography (GLC).

To investigate degradation products of pendimethalin, 1 kg sandyloam soil and 20 g ground straw were placed in glass bottle (2.25 L). After contents were mixed 100 mL distilled water was added to soils in one set of samples to create non-flooded condition and 1 L distilled water to the other set of samples to provide flooded condition. Bottles containing flooded soil were tightly closed with corks and kept in dark. After two days, 1 mL solution of pendimethalin (20 mg) was added to each bottle and incubated in dark at 30±1°C together with blank soil. After four days flooded soil and after one month non-flooded soil was extracted and analysed by GLC and thin layer chromatography (TLC).

For residue extraction, 50 mL of solvent (hexane and ethylacetate, 1:1) and 20 g of anhydrous sodium sulfate were added to the flasks. To extract degradation products, 200 mL of the same solvent mixture and 50 g of anhydrous sodium sulfate were added to the bottles containing soil. The contents were shaken for 1 h. Pendimethalin and the degradation products in solvent fraction were analysed in a Hewlett Packard gas chromatograph model 5890 equipped with a Ni^{63} electron capture detector using 3% OV-17 in a stainless steel column; column, injector and detector were maintained at 210, 230 and 275°C, respectively. Analysis by TLC was done using silica gel G (Merck Type 60) plates (0.25 mm), solvent mixture of benzene and ethylacetate (3:2) and iodine as chromogenic reagent. The degradation products were detected on Varian nuclear magnetic resonance (NMR) model Em-360 L (60 MHz) and mass spectra (MS and GCMS) model Jeol JMS-D 300.

The predicted degradation products N-(1-ethylpropyl)-3,4-dimethyl-2-nitrobenzene-1,6-diamine (II, Figure 1) and 3,4-dimethyl-2,6-dinitroaniline (III) were prepared as described earlier (Singh and Kulshrestha 1991). For preparing N-(1-ethylpropyl)-5,6-dimethyl-7-nitrobenzimidazole (IV), a mixture of 6-amino pendimethalin (II,200 mg),trimethylorthoformate (3 mL) and triflouroacetic acid (2 drops) in benzene (20 mL) was refluxed until the bright red colour turned to a medium yellow. The compound was extracted in hexane. On removal of solvent, a brownish mass obtained which when crystallized with methanol-water yielded yellow plates, m.pt. 96-97°C.

RESULTS AND DISCUSSION

Pendimethalin and its predicted degradation products were resolved on GLC and TLC with distinct Rt and Rf values, respectively (Table 1). Recoveries of the herbicide from six freshly spiked soil samples using GLC technique were more than 95%.

Table 1. Retention time(Rt) and Retardation factor(Rf) values of pendimethalin and its analogues

No.	Compound	GLC (Rt)	TLC (Rf)
I	Pendimethalin	3.45	0.75
II	6-Amino pendimethalin	3.03	0.67
III	Dinitroaniline derivative	1.83	0.11
IV	Benzimidazole	3.80	0.34

Results of the laboratory persistence studies with pendimethalin are summarised in Table 2. There was gradual dissipation of pendimethalin in soil under different moisture conditions. Semilog plots of the data of nonsterile non-flooded and flooded soils revealed that herbicide dissipation followed first order rate kinetics which was also evident from the significant correlation coefficient. Pendimethalin persistence was quite high (half life, 52 days) in non-flooded soil with about 24% remaining in soil after 90 days. Moisture appeared to alter the persistence of pendimethalin in sandyloam soil. Degradation of the herbicide was rapid in flooded (half lives, 33 and 45 days) than in non-flooded (half lives, 52 and 67 days) conditions in nonsterile and sterile soils, respectively. Faster degradation of other dinitroaniline herbicides in flooded compared to non-flooded soil was reported earlier (Helling 1976).

Influence of microbial activity in the degradation of pendimethalin was examined by comparing its dissipation

Table 2. Persistence of pendimethalin in nonsterile and sterile non-flooded and flooded sandyloam soil

Incubation Days	Residues in ug/g soil			
	Non-flooded		Flooded	
	Sterile	Nonsterile	Sterile	Nonsterile
0	9.8 ± 2.1	9.7 ± 1.72	9.5 ± 2.3	9.9 ± 1.01
15	8.32 ± 1.61 (16.8)*	8.12 ± 2.10 (18.8)	7.92 ± 1.97 (20.8)	7.15 ± 2.51 (27.8)
30	7.25 ± 0.97 (27.5)	6.88 ± 1.82 (31.2)	5.81 ± 2.16 (41.9)	5.23 ± 1.92 (47.2)
45	6.32 ± 1.35 (36.8)	5.98 ± 0.58 (40.2)	4.67 ± 1.65 (53.3)	4.14 ± 2.16 (58.2)
60	5.41 ± 1.93 (45.9)	4.79 ± 0.83 (54.9)	3.72 ± 1.83 (62.8)	2.41 ± 1.49 (75.7)
90	3.84 ± 0.68 (61.6)	2.41 ± 1.51 (75.9)	2.68 ± 0.77 (73.2)	1.75 ± 0.83 (82.0)
Half life (days)	66.9	52.2	44.9	33.4
Correlation coefficient (r)	-0.999	-0.983	-0.998	-0.988

* Figures in parentheses indicate per cent dissipation

in sterile and nonsterile soil under different moisture conditions. The herbicide was more persistent in sterile than in nonsterile soil. In 90 days 11 to 14% degradation of pendimethalin could be attributed to microbial transformation which was only a small fraction of the total loss of the herbicide from soil. Similar observation was made (Messersmith et al 1971) for trifluralin breakdown in soil.

Degradation studies in nonsterile non-flooded soil showed formation of two major and two minor metabolites of pendimethalin. The major products were isolated by column chromatography. The fraction eluted with hexane-benzene (4:1) gave solid mass on removal of solvent which when crystallized with benzene resulted in deep red crystals. The mass spectral analysis of this compound showed a peak at m/e 251. By comparison of Rt and Rf values with the authentic sample, the product was characterised as N-(1-ethylpropyl-3,4-

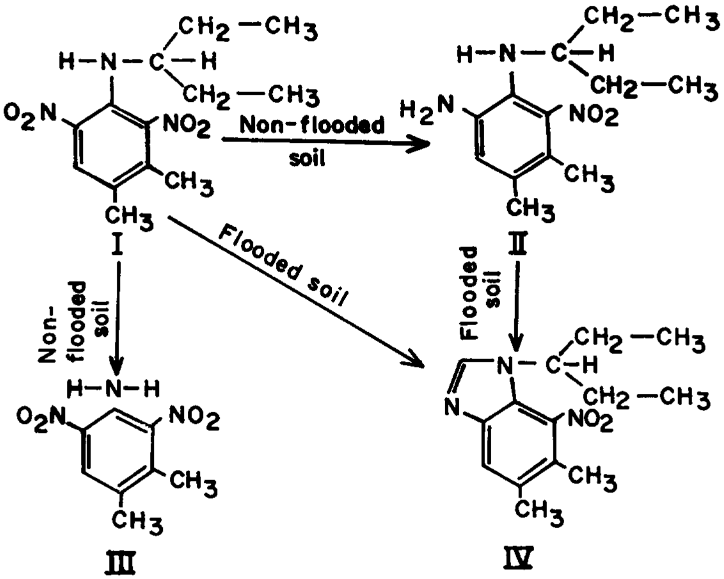

Figure 1. Transformation of pendimethalin

dimethyl-2-nitrobenzene-1,6-diamine (II).

The benzene fraction from column gave a deep brown mass which was purified by preparative TLC to give orange-yellow solid. Mass spectra of this compound showed parent peak at m/e 211. The product was identified as 3,4-dimethyl-2,6-dinitroaniline (III), by further comparing its chromatographic properties with that of the synthetic sample. The minor products were obtained in too small quantities to characterise.

Formation of products II and III in nonsterile non-flooded soil indicated two major mechanisms of transformation of pendimethalin in aerobic condition, N-dealkylation and reduction of less hindered nitro group in the molecule. The degradation of the herbicide could either be chemical or microbial in nature.

Analysis of soil incubated under flooded conditions indicated formation of a single major metabolite. The compound was isolated by preparative TLC and crystallised to a yellow solid. The mass spectrum of this product showed parent peak at m/e 261. By comparison of its spectral properties and chromatographic mobility with that of the synthetic sample, it was identified as N-(1-ethylpropyl)-5,6-dimethyl-7-nitrobenzimidazole (IV).

Interestingly there was complete degradation of pendimethalin in flooded soil in four days. Subsequent studies with shorter incubation periods revealed that herbicide was quantitatively transformed to the cyclised product (IV) within one day. When 6-amino pendimethalin (II) treated soil was incubated under similar flooded condition, once again benzimidazole (IV) was isolated after one day as the only metabolite without a trace of the parent compound. It was, therefore, concluded that under anaerobic conditions pendimethalin was first degraded to 6-amino pendimethalin which in presence of carbon of organic matter got cyclised to benzimidazole.

The practical significance of this study lies in the fact that such type of anaerobic state may exist, though for a short time, under conditions of excessive rainfall with poor drainage and may result in unexpected rapid dissipation from soil of a herbicide which otherwise under normal conditions remains quite stable.

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REFERENCES

Helling CS (1976) Dinitroaniline herbicides. J Environ Qual 3 : 1-15.
Kulshrestha G, Yaduraju NT (1987) Persistence of pendimethalin in soil following pre-emergence application to wheat. Indian J Agron 32 : 271-274.
Messersmith CG, Burnside OC, Lavy TL (1971) Biological and non-biological dissipation of trifluralin from soil. Weed Sci 19 : 285-289.
Singh SB, Kulshrestha G (1991) Microbial degradation of pendimethalin. J Environ Sci Health B26(3) : 309-321.
Sprankle PL (1974) AC-92,553 a selective herbicide for weed control in cereals and other crops. Proc 12th Brit Weed Control Conf 2 : 825-830.
Walker A, Bond W (1977) Persistence of the herbicide AC-92,553, N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine in soils. Pestic Sci 8 : 359-369.
Zimdahl RC, Catizone P, Butcher AC (1984) Degradation of pendimethalin in soil. Weed Sci 32 : 408-412.

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