

Photolysis of pretilachlor on soil surface

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ABSTRACT

Pretilachlor (2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetanilide) is a soil-applied post-emergent herbicide selectively used in rice. Photolysis of pretilachlor was studied on soil surfaces under UV light and sunlight. The rates of photodegradation of pretilachlor on different solid surfaces followed first-order rate kinetics, with half-lives of 7.2 min, 31.0 min, 30.1 min and 10 h, 30.1 h, 30.0 h for glass surface, black cotton soil and alluvial soil under UV and sunlight, respectively. Pretilachlor was stabilized on soil surface by organic and inorganic constituents.

Key words : Pretilachlor, Photolysis, Soil, Sunlight, UV light

Phototransformation is one of the important pathways for the degradation of organic pollutants to non-toxic or less toxic components on the soil surface. Previous studies have demonstrated that many organic pollutants could be phototransformed on soil surface through direct photolysis (Choudhury and Dureja 1997, Romero *et al.* 1998) or indirect photolysis by reaction with reactive oxygen species (Gohre and Miller 1986, Misra *et al.* 1997, Konstantinou *et al.* 2001). Herbicides, being important agricultural chemicals, are surely one of the targets of environmental concern. To be more effective, an herbicide needs to kill more weed species and stay in the soil for a longer period of time. A soil applied herbicide must be able to maintain an effective concentration when weed control is necessary for proper crop growth. But it should not persist for a long time as it may pose a threat to the non-targets. Hence, a longer dissipation period of an herbicide may raise problems for its environmental safety. Therefore, it is important to determine the rate of photolysis of soil acting herbicides on soil surface. Pretilachlor (2-chloro-2',6'-diethyl-N-(2 propoxyethyl) acetanilide) was developed for the selective control of some annual weeds in low land rice including barnyardgrass (Murakami and Ebner 1983, Quadranti and Ebner 1983). Pretilachlor disappears from paddy water at moderate rate with half-life of 3.0 to 3.6 days (Fajardo *et al.* 2000). But in general, the half-life of pretilachlor in soil is 20 to 50 days (Worthing and Hance 1991). The higher rate of degradation in different soils with half-life ranging

from 2.6 to 10 days was also observed under the differential influence of temperature and moisture (Handah 1999). This loss of pretilachlor from soil is due to different forces including microbial action, photoreaction, adsorption on clay and organic macromolecules, leaching, etc. But the sole influence of light on the degradation of pretilachlor on soil surface is yet not investigated. This present experiment will provide the result found from the interaction between light and pretilachlor.

MATERIALS AND METHODS

Chemicals

An analytical grade pretilachlor sample was procured from AccuStandard Inc., USA. Laboratory grade reagents and solvents were procured locally. All the solvents were dried and distilled before use.

Soil characteristics

The alluvial and black cotton soils used in this study were collected from the field surfaces of IGFR, Jhansi and DWSR, Jabalpur, respectively. The soils were air-dried and sieved through a 2 mm sieve. The properties of the soils after sieving were listed in Table 1.

Preparation of standard solution of pretilachlor

An analytical sample of pretilachlor (10 mg) was added to 10 mL of distilled acetone in 10 mL volumetric flask to get a 1000 ppm standard solution. Solutions of required concentration were prepared from this stock.

Table 1. Physicochemical properties of different soils

Soil	Soil class	pH	EC (dS/m)	Clay (%)	Organic carbon (%)
Alluvial	Clay loam	7.4	0.60	30.0	0.73
Black -cotton	Sandy clay loam	6.8	0.38s	35.5	0.75

Photolysis on solid surface

Soil thin-layer plates were prepared from soil sieved to 2 mm. Soil thin-plates were prepared from a slurry of 1 g of soil in 1 mL of water (1 mm thickness). These plates were air-dried. Thin-films were then uniformly treated with 1 mL of 10 mg/L solution of pretilachlor. Similarly, thin-films of pretilachlor (1 mL of 10 mg/L per plate) on glass surface were also prepared. These plates were exposed to UV-light or sunlight. The UV light was supplied by a 30-W UV lamp held 30 cm above the test substrate. The light produced by this lamp was rich in irradiation at wavelength 254 nm. Tests with sunlight were run during cloudless sunny days of April month between 10 am and 5 pm (7 h per day) on an area of a roof protected as much as possible from the wind. The temperature varied at the test surface between 30 and 38°C in the sunlight and between 25 and 30°C under ultraviolet light. Thin-film samples in triplicate for each treatment were taken at 0, 7, 14, 21 and 28 h from the plates exposed to sunlight and 0, 10, 20, 30, 40 and 60 min from those under sunlight. Only the sampling of the thin films on glass surface exposed to UV light was done on 0, 2, 4, 6, 8, and 10 min due to its fast degradation.

Extraction and clean-up of samples

Soil samples from each plate were scratched and collected in a 50 mL Erlenmeyer flask together with 15 mL acetone. It was then shaken for 30 minutes and filtered using a 60 μ m/m filter paper and the filtrate collected in 100 mL round bottom flask. This was repeated twice with the remaining soil in the Erlenmeyer flask and the filtrate was added to the previous one. The filtrate was then concentrated under vacuum to a 2 to 3 mL portion. It was then poured into a 25 mL separatory funnel containing 5 mL of 5% NaCl solution. The round bottom flask was washed with 10 mL of hexane that was added into the separatory funnel. It was then shaken vigorously for about 2 minutes. The hexane layer was collected in round bottom flask. It was repeated twice. The collected hexane was evaporated at around 45°C and collected in volumetric flask. The sample from glass surface was directly taken in hexane.

A separate set of extraction and clean-up of samples was carried out with the pretilachlor fortified sample of alluvial and black-cotton soil and glass surface to judge the suitability of the extraction procedure. Pretilachlor had a 89.2% recovery from alluvial soil and 86.3% from black-cotton soil. The recovery of pretilachlor from glass surface was 96.6%.

Chromatographic analysis

The quantity of pretilachlor from each thin film was estimated on gas liquid chromatograph, Chemito, Model

GC-1000 equipped with ⁶³Ni electron captured detector fitted with capillary column SPB-1 (30 m X 0.32 mm id, 0.25 μ m film thickness). N₂ was used as carrier gas at a linear gas velocity of 2 mL/min and make up gas 60 mL/min. The injection port, oven and detector were maintained at 220°C, 200°C and 300°C, respectively.

RESULTS AND DISCUSSION

The rate of photodegradation of pretilachlor applied on the surface of alluvial soil, black-cotton soil and glass surface under UV light (Table 2) and sunlight (Table 3) was studied. The rate of photolysis on soil surface is slower than that on inert glass surface. On glass surface pretilachlor degrades very fast, around 78% within 10 minutes under UV light and about 86.7% within 20 h under sunlight; whereas, during that period pretilachlor degrades only 12 to 13% under UV light and 25 to 32% under sunlight on soil surfaces.

The log percentage concentration of pretilachlor, plotted against time, resulted in straight line (Fig. 1 and 2), suggesting first-order rate kinetics with a statistically

Table 2. Pretilachlor remaining on solid surfaces after exposure to UV light

Time (min)	Pretilachlor remaining (%)*		
	Glass surface	Alluvial soil	Black-cotton soil
0	100	100.0	100.0
2	65.7	-	-
4	52.4	-	-
6	44.2	-	-
8	34.5	-	-
10	22.0	88.0	87.8
20	¹ BDL	77.3	74.0
30	-	51.9	51.5
40	-	41.8	42.3
60	-	38.3	27.3

*Mean of three replicates; ¹Below Detectable Limit

Table 3. Pretilachlor remaining on solid surfaces after exposure to sunlight

Time (h)	Pretilachlor remaining (%)*		
	Glass surface	Alluvial soil	Black - cotton soil
0	100	100.0	100.0
7	43.8	90.7	79.5
14	34.1	82.3	70.7
21	22.4	75.2	68.65
28	13.84	62.3	54.3

*Mean of three replicates

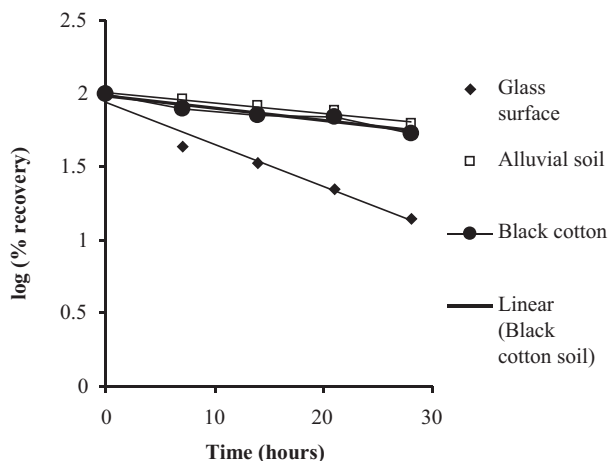


Fig. 1. Linear plot for first-order degradation of pretilachlor on solid surfaces under sunlight

significant rate constant with high R^2 values. The photolytic half-lives were 7.2 min, 31.0 min, 30.1 min and 10 h, 30.1 h, 30.0 h for glass surface, black cotton soil and alluvial soil under UV and sunlight, respectively (Table 4). Pretilachlor on glass surface undergoes direct photolysis.

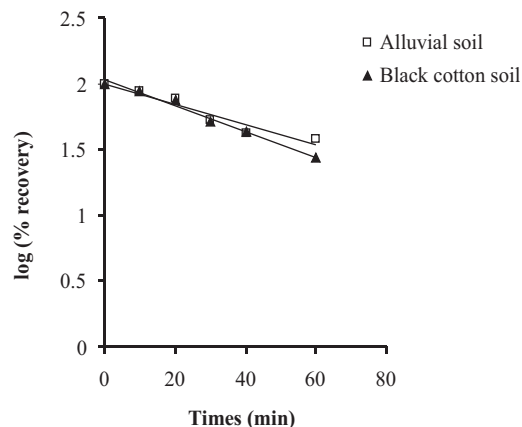


Fig. 1. Linear plot for first-order degradation of pretilachlor on solid surfaces under UV light

But on soil surface the photoreaction is quenched due to the presence of organic matter. Clay content may also interfere in the quenching process. Thus, on soil surface pretilachlor gets stabilized either by organic constituents or by inorganic fractions, or by their joint influence.

Table 4. Rate equations and half-lives of pretilachlor under the influence of UV light and sunlight on different solid surfaces

Surface	Type of irradiation	Rate kinetic equation	R^2	Half - life
Glass	UV light	$Y = 1.90 - 0.04 X$	1.00	7.2 min
Black cotton soil	UV light	$Y = 2.04 - 0.01 X$	0.96	31.0 min
Alluvial soil	UV light	$Y = 2.06 - 0.01 X$	0.92	30.1 min
Glass	Sunlight	$Y = 1.90 - 0.71 X$	0.95	10.0 h
Black cotton soil	Sunlight	$Y = 2.01 - 0.18 X$	0.95	30.1 h
Alluvial soil	Sunlight	$Y = 2.00 - 0.11 X$	0.89	30.0 h

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