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Movement of Pendimethalin in Soil of the South of France

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Pendimethalin belongs to the class of dinitroaniline herbicides. Several papers report degradation and persistence of pendimethalin in soil (Barua et al 1990; Copin and Deleu 1985; Sato et al 1990; Savage 1978; Savage and Jordan 1980; Singh and Kulshrestha 1991; Stahnke et al 1991; Sugjama et al 1990; Walter and Bond 1977; Zimdahl et al 1984) and about its photodecomposition in soil and water solution (Dureja and Walia 1989; Parochetti and Dec 1978). Although Gustafson (1989) classified pendimethalin as a nonleacher compound, few precise data have been published about its soil mobility. An approach to evaluate the migration of pendimenthalin in soil and to confirm the lack of risk for underground waters necessitates the determation of some parameters: Koc, desorption constant, degradation and vertical distribution of the pollutant in soil. Our purpose was to study its movement in PVC pipes filled with soil in conditions as similar as possible to natural ones.

MATERIALS AND METHODS

All chemicals and reagents used were analytical grade and redistilled or pesticide analysis grade. Analytical grade Pendimethalin (99.1%) was obtained from American Cyanamid Co. France and commercial formulation(40EC PROWL^{R}) bought from the market. Gas liquid chromatography was performed on a HP 5710A with ECD, Ni-63 or NPD and packed glass columns (2 m x 2 mm i.d - SP 2110-SP 2510). Oven temperature: 190°C.

From a cultural area (Lavalette, Montpellier), we selected a thin, brown soil with saturated mineral conplex and a calcareous tuff at 80 cm depth, classified as an *Eutrochrept*, inside the *Inceptisol* order (Duchaufour, 1983). Then we collected soil samples corresponding to 0 to 10, 10 to 50, 50 to 95 cm depth increments. These soil samples were air dried and crushed to pass through a 2 mm sieve. Simultaneously soil was submitted to complementary analysis, as presented in Table 1.

Adsorption of pendimethalin on the soil was evaluated from several aqueous PROWL solutions (0.5 to 20 mg of pendimethalin/L). 10 g of soil sample were introduced in a centrifuge tube and gently shaken with 25 mL water solution of pendimethalin for 4 hrs at 25 C using a rotary agitator. After centrifugation (at 2000 g for 20 min), the aqueous supernatants were extracted and analyzed. The sediment was kept for further desorption study, performed by shaking this soil residue for 4 hrs with 25 mL of 0.01 M $CaCl_2$ aqueous solution

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Table 1. Montpellier Soil Characteristics (*Eurochrept*)

depths cm	pH (H_2O)	sand %	silt %	clay %	CEC meq/100	organic C %
0-10	7.9	45.5	29.4	25.1	11.23	1.04
10-50	8.05	55.8	26.1	18.2	7.39	0.59
50-90	8.15	62.3	25.2	12.5	6.93	0.44

before centrifugation and GLC analysis.

Kinetics of adsorption was studied using 10 grams of soil sample shaken for 1/4, 1/2, 1, 2, 4, 6 and 24 hrs with 25 mL of a 5 mg/L aqueous suspension of pendimethalin, prior to analysis of the supernatant issued from centrifugation.

To evaluate the behaviour of Pendimethalin in soil columns, 10 PVC pipes were used. The lack of adsorption of the herbicide on PVC pipes was verified experimentally after soaking some pieces of PVC into 5 ppm aqueous solution. A perforated stopper was placed at the bottom of the columns to allow dripping of water. In order to reconstitute, as much as possible, the natural soil profile, each of 10 pipes (length 100 cm x 11.7 cm i.d.) was filled 15 days before treatment by introducing successively the 3 soil samples:

- 95-50 cm ("deep" soil) density 1.6
- 50-10 cm ("intermediate" soil) density 1.5
- 10- 0 cm (surface soil) density 1.5.
- 4 cm at the top of the pipe were kept for "irrigation".

For using pendimethalin dose comparable to these recommanded for tomatoes and green stuffs in field (1320 g a.i./ha), we have applied at the top of PVC columns, 270 µL of an appropriate PROWL dilution (1:70) corresponding to 1.6 mg of active ingredient. Five pipes (1-5) were watered twice before treatment (at day-10 and day-5) and not irrigated on the day of herbicide application. The 5 remaining pipes (6-10) were watered for the first time on the day of treatment. These columns have been kept vertically in the laboratory at room temperature (22±2 C). Further soil waterings and sample collection were realized as indicated in Table 2. For irrigation we tried to use water volume comparable to local rainfalls, calculated during a period of 61 years: March: 166 mm; April: 226 mm and May: 60 mm. The samples were collected 1, 3, 7, 14, 28, and 56 days after application of pendimethalin. At each sampling date, 13 samples were removed from column at different

Table 2.Schedule of Irrigation and Soil Sampling

Date (day)	Humid Columns Irrigation cm	Sample No.	Dry Columns Irrigation cm	Sample No.
D-10	40		0	
D-5	30		0	
D0(treat)	0		30	
D+1	0		0	column 6
D+3	0	column 1	0	
D+7	25	column 2	25	column 7
D+14	25	column 3	25	column 8
D+18	40		40	
D+25	25		25	
D+28		column 4		column 9
D+38	25		25	
D+56		column 5		column 10

depth: 0 to 3, 3 to 6, 6 to 9, 9 to 15, 15 to 21, 21 to 27, 27 to 33, 33 to 39, 39 to 50, 50 to 60, 60 to 70, 70 to 80, 80 to 95 cm. Samples were submitted immediately to analysis or stored by congelation.

Analytical metholoqy included soil and water extraction, clean up and gas-liquid analysis. Soil extraction was performed on 10.0 g of sample placed in a 125 mL mixer cup, blend for 15 min with 80 mL of a mixture of petroleum ether-acetone was filtered under vaccuum, transferred into a 500 mL separatory funnel, containing 200 mL of distilled water and 25 mL NaCl saturated solution. The soil was extracted again with 40 mL of petroleum ether-diethyl ether (PE-EE 1+1), then trasferred in the same separator. After shaking for 1 min and separation, the aqueous layer was reextracted by 30 mL PE-EE and then discarded. The organic layers were dried, combined and concentrated to 2-3 mL. Then the extract can be directly analyzed by GLC or submitted to clean up by column chromatography.

For water extraction, solution (supernatant after centrifugation from adsorption-desorption study) was pourred into a separatory funnel and extracted with 2x40 mL of mixture PE-EE. The combined organic layers were dried by anhydrous sodium sulphate and concentrated, prior to direct GLC analysis.
If necessary, clean up was performed into a glass chromatographic column (25x1.0 cm i.d.) containing 5 g of 5% water desactivated Florisil and 1 cm of anhydrous sodium sulphate. After washing the column with 30 mL petroleum ether, the extract was transferred to the column and eluted with 30 mL of PE (E1) which are discarded, then with 50 mL PE:EE (E2). This eluate (E2 contains 95 % of pendimethalin) is concentrated to 2-3 mL prior to its GLC analysis.

In the previously described GLC conditions, retention time was 2.72 min. The detection of 0.15-0.20 ng of pendimethalin after an injection of 4 μL of an extract concentrated to 3 or 4 mL allows a sensitivity of 0.01 mg/kg of soil. The percent recovery of pendimethalin was 87-94% in all soil samples, after addition of a.i at 3 different levels.

RESULTS AND DISCUSSION

After agitation and analysis, concentration of equilibrium solutions was reported to initial concentration to allow the calculation of quantities adsorbed by mass of soil. Adsorption isotherms can be traced from these data (Figure 1). This could be described reasonably by the Freundlich equation :

$Q_{ads} = K_{fa} C_e^n$ (1) or $\ln Q_{ads} = \ln K_{fa} + n \ln C_e$ (2)

where Q_{ads} is the equilibrium content of compound sorbed to soil (in μg/g), K_{fa} is the Freundlich coefficient in μg L^{-n} mL ^{n} g^{-1}, Ce is the equilibrium concentration of the compound in the liquid phase in μg/mL and n is the Freundlich exponent. Values of K_{fa} and n (Table3) were estimated by linear regression after log-log transformation. Table 3. shows that the adsorption coefficient K_{fa} decreased with soil depth. Due to the importance of organic matter content on pesticide adsorption (Calvet 1980) the distribution coefficient must be correlated by this organic matter content as given by this relationship: $K_{oc} = K_{fa}/W_{oc}$(3) where W_{oc} is the mass fraction of organic content in dry soil. In our study K_{oc} values were comparable for 0-10, 10-50, and 50-95 cm depth(respectively 65, 80 and 74). Perhaps granular matter and chemical soil

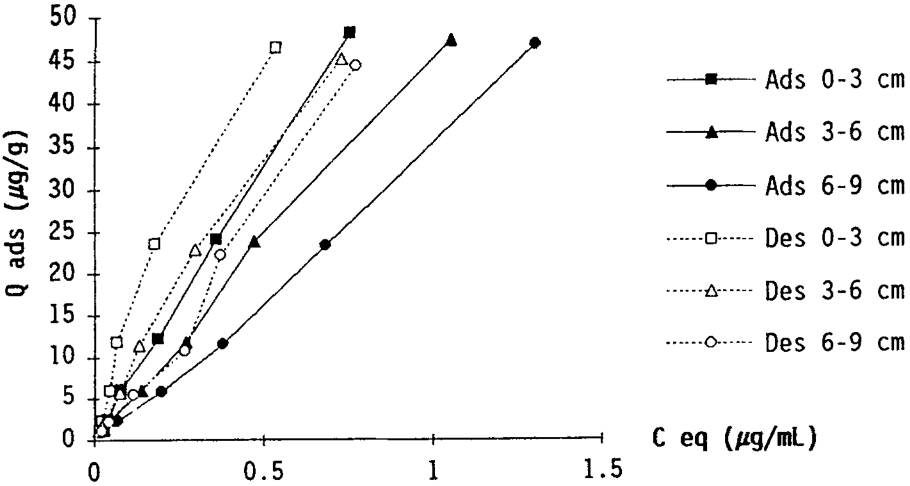

Figure 1. Adsorption and desorption of pendimethalin in three soil depths

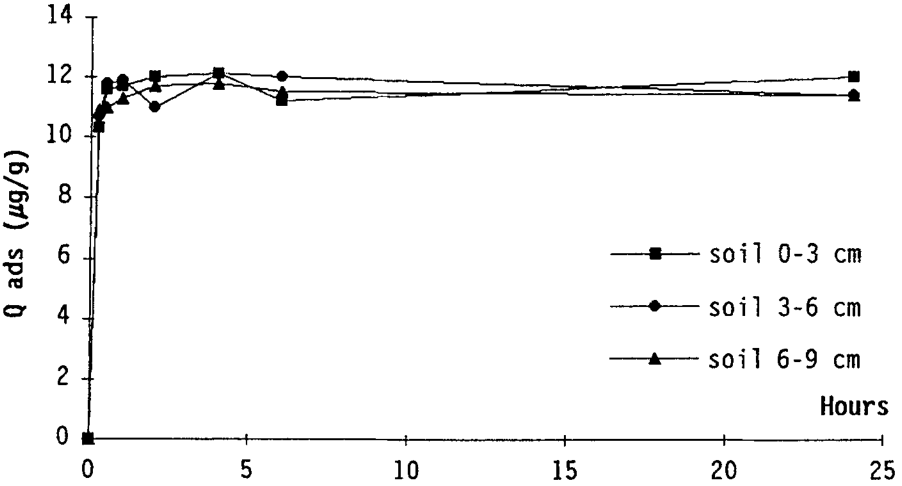

Figure 2. Adsorption kinetics of pendimethalin in sois from 3 depths intervals

composition can intervene on these small differences. Nevertheless, these K_{fa} and K_{oc} values can be considered as high comparatively to data published for other pesticides (Gustafson, 1989). Pendimethalin, a very hydrophobic molecule, is strongly adsorbed by the three types of soil: 96% of the herbicide was sorbed for a ratio soil-water of 1:1.25 and a range of concentration 0.5-20 mg/L.

Table 3. Adsorption Parameters as Found for Pendimethalin in Montpellier soil (*Eurochrept*).

depth	K_{fa}	K_{oc}	n	r^2
0-10 cm	68±5	65±5	1.02	0.996
10-50 cm	47±3	89±6	1.03	0.997
50-90 cm	33±3	74±7	0.98	0.994

Kinetics of adsorption of pendimethalin in soil is illustrated in Figure 2. The equilibrium between liquid and solid phases was practically reached in 30 min, without significative differences between the three samples. Adsorption of pendimethalin in these soils seems to be a very rapid phenomenon.

The three curves presented in Figure 1 show the pendimethalin desorption isotherms with 0.01M $CaCl_2$ aqueous solutions. These curves practically straight seem to be in accordance with Freundlich equation:

$$Q_{ads} = Q_{ads0} - Kf_d \, [C_0 - C_e]^{nd} \quad (4)$$

in which Q_{ads} is a quantity remaining adsorbed , K_{fd} is a constant of desorption and nd is an index of intensity of desorption. These parameters (K_{fd} and nd) have been calculated (Table 4) and were practically similar for the three soil samples. As K_{fd} was very low and nd close to 1, its appears that pendimethalin desorption is very difficult from soil with $CaCl_2$ 0.01M aqueous solution, according to its hydrophobic molecule structure. Car pendimethalin is very slightly solubility in water the studies of adsoption and desorption seem very difficuty. Add few organic solution as methnol or acetone was also importent for environnment.

Table 4. Desorption Parameters as Found for Pendimethalin in Montpellier soil (*Eurochrept*)

depth	K_{fd}	nd	r^2
0-10 cm	2.54	1.011	1.000
10-50 cm	2.49	0.999	1.000
50-90 cm	2.50	1.003	1.000

Behaviour of Pendimethalin in soil columns was evaluated after collection of samples at different dates after treatment and at different depths. At the beginning, soil humidity was about 14%. After watering as described in Table 2, wetness increased in all columns to reach 17-19% in the upper layers, and 35% at 80 cm depth. Results obtained in columns 1-5 and 6-10 are shown respectively in Figures 3 and 4. For dry soil (columns 6-10), 90% of remaining pendimethalin has been found in superficial layer (0-3 cm). No residue was detected below 9 cm. For moist soil (columns 1-5), 70% of the herbicide stayed in surface layer, the rest being distributed lower, respectively 20%, 7% and 2% in the 3-6, 6-9 and 9-15 cm strata. After this two months study, Pendimethalin migration seems limited in soil; it depends on soil humidity and is rather effective on the first days after application.

On each soil column (1-5 and 6-10), pendimethalin levels found in the different layers were added together (Figures 3 and 4). The total was compared to the quantity once applicated at the top of column, evaluated to c.a 3 mg/kg in the upper soil layer. An approach to describe this degradation rate may be a first order kinetics, as previously indicated by Savage (1978) : $Q=Q_0e^{-kt}$ (5) with k=0.021 and r^2 = 0,98 for moist soil, k=0.022 and r^2 = 0,92 for dry soil at 22°C±2°C. The half life of the herbicide has been estimated to about 35 days. Of course, complementary studies with different experimental conditions (application dose, temperature...) would be necessary to support this approach, which does not agree with Zimdahl theory (1984), who preferred to describe Pendimethalin degradation with a quadratic model.

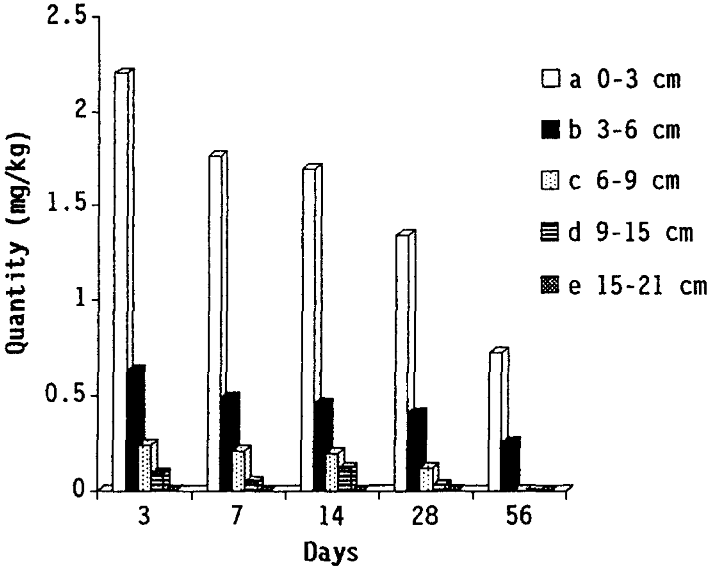

Figure 3. Movement of pendimethalin in humid soil columns

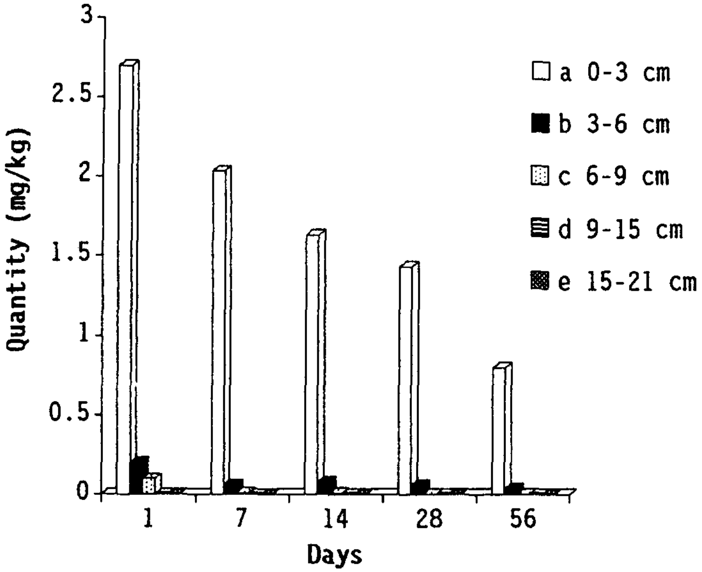

Figure 4. Movement of pendimethalin in dry soil columns

This study showed a rapid and strong adsorption of pendimethalin on the available samples of soil, its desorption being very difficult. Correspondingly, downward movement was very limited in soil columns. Pendimethalin remains in superficial layers during the degradation process .

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