

## Influence of Organic Fertilizer Application on Pendimethalin Volatilization and Persistence in Soil

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Laboratory studies were undertaken to evaluate the influence of fertilizers on pendimethalin volatilization and persistence in soil. Various organic fertilizers such as liquid humic substances and urea were used at doses of 100 L/ha or 170 kg of N/ha, respectively. Herbicide residues were determined in air, soil solution, and soil samples by GC-ECD; the recovery of pendimethalin from spiked fertilized or control samples was found to be 81–103%. Liquid humic fertilizers increased pendimethalin dissipation during the first part of the assay, although 4 months after application, herbicide levels were similar to those observed in unfertilized soil. Fertilization of soil with urea decreased, in general, pendimethalin volatilization but increased herbicide levels in soil solution and persistence in soil, with a pendimethalin half-life ~70% higher than that found in unfertilized soil.

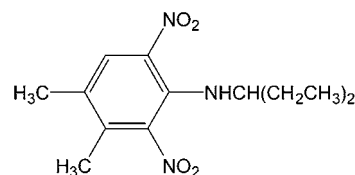
**KEYWORDS:** Organic fertilizer; urea; pendimethalin; volatilization; persistence

### INTRODUCTION

Pendimethalin [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] is a dinitroaniline herbicide used selectively for the control of weeds in many agronomic and horticultural crops such as cotton, wheat, maize, tomato, and onion. **Figure 1** shows the chemical structure of pendimethalin. This herbicide is a relatively volatile compound (vapor pressure of 4 mPa at 25 °C), has a low solubility in water [0.3 mg/L and a  $K_{ow}$  of 152000 (1)], is strongly adsorbed to soil, and does not leach (2, 3). It is a hydrophobic herbicide with a  $pK_a$  value of 2.8. Field studies have shown that this herbicide is persistent, and its residues are carried over to the next crop year (4–6).

Organic fertilizers are used in horticultural crops and applied at approximately the same time as herbicides. Fertilizer applications may affect the fate of herbicides in soil that is controlled by processes such as degradation, volatilization, and mobility. In the case of low solubility and hydrophobic organic compounds, it has been postulated that interactions between the dissolved organic matter (DOM) and the chemical occur (7, 8), favoring herbicide desorption and increasing its apparent water solubility (9–12). Ammonia-based fertilizers such as anhydrous ammonia and urea initially increase soil pH (13–15) and cause the release of organic matter from the soil matrix, increasing DOM in solution (14–16). Moreover, urea solutions at concentrations >2 M increase the solubility of pendimethalin in water (17). In the case of pendimethalin, information concerning the influence of organic fertilizers on the volatilization and persistence of this herbicide in soil is very scarce in the available literature.

The aim of this study was to determine the influence of fertilizer applications on pendimethalin volatilization and per-



**Figure 1.** Chemical structure of pendimethalin

sistence in soil. For this purpose, analytical procedures were developed to determine pendimethalin levels in air, soil, and soil solution. Various organic fertilizers, such as urea and liquid humic substances, were applied before pendimethalin treatment to study the influence of different sources of soil DOM on the herbicide behavior. In one case, an endogenous DOM source was produced by urea application, whereas in the others exogenous DOM was supplied by the application of liquid humic substances.

### MATERIALS AND METHODS

**Chemicals.** Pendimethalin was obtained from American Cyanamid (Princeton, NJ) as a commercial emulsifiable concentrate (EC) formulation, Stomp 330E, containing 330 g/L of active ingredient (ai).

Ethyl acetate and methanol, pesticide residue analysis grade, were obtained from Scharlau (Madrid, Spain). Florisil 60–100 mesh, activated by heating at 80 °C overnight before use, was purchased from Aldrich (Stainheim, Germany), and anhydrous sodium sulfate was obtained from Merck (Darmstadt, Germany).

**Soil.** Soil was collected from the top 20 cm of a field located in Madrid, air-dried, and sieved to pass a 2 mm mesh. Its principal physical and chemical properties were the following: sand, 64.5%; loam, 23%; clay, 11.5%; pH 7.5; and organic matter, 2.0%. The soil texture was determined using the pipet method (18). Soil pH was measured in slurries made up at 1:1 soil/water, and organic matter was determined by a modified Walkley–Black method (19).

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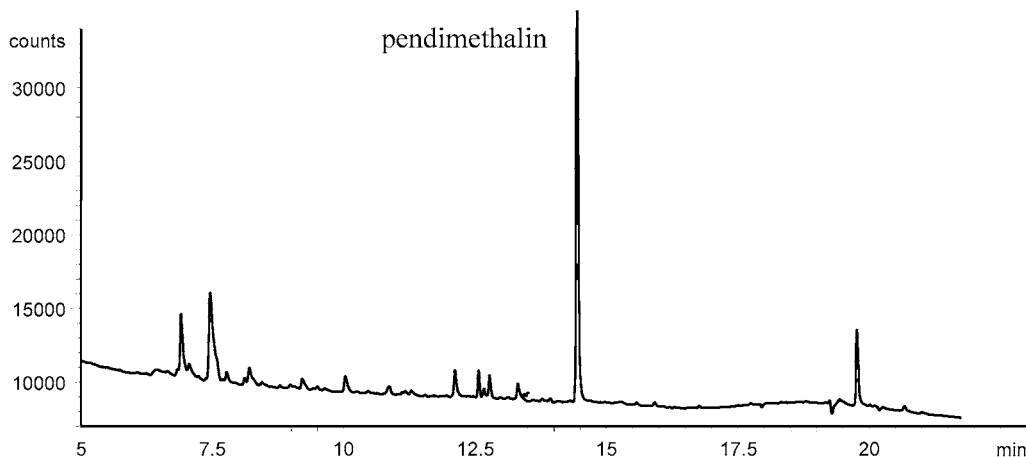


Figure 2. GC-ECD chromatogram of pendimethalin (0.5  $\mu\text{g}$ ) in air.

Table 1. Characteristics of Control and Fertilized Soils<sup>a</sup>

fertilizer	dose	OM (%)	pH
control		2.0	7.5
Liqui-Mat	100 L/ha	2.05	7.6
Humisol	100 L/ha	2.05	7.6
urea	170 kg of N/ha	2.0	8.5

<sup>a</sup> Values were obtained 4 days after fertilizer application.

**Fertilizers.** Two commercial liquid humic fertilizers from Agro-águilas (Águilas, Murcia) were employed: Liqui-Mat, with a total humic extract content of 13.56% (fulvic acid content of 13.56%), a pH of 7.2, and a density of 1.18 g/mL; and Humisol USA extra, with a total humic extract content of 16.95% (fulvic acid content of 1.7% and humic acid content of 15.25%), a pH of 13, and a density of 1.18 g/mL.

The other fertilizer employed was urea from Fertusa (Silla, Valencia) with a nitrogen content of 46%.

Soil was divided into four parts; one was used as control (unfertilized soil), and the other three parts were treated with the fertilizers Liquid-Mat, Humisol, and urea applied to the soil at a dose of 0.1% w/w, equivalent to 100 L/ha for liquid organic fertilizers and 170 kg of N/ha for urea.

Unfertilized and fertilized soils (120 g) were transferred to glass jars (four by treatment and assay type) and kept in a refrigerator for 4 days to allow for homogenization. After this time, organic matter and pH were measured, and values obtained are shown in Table 1.

**Volatilization Assay.** Soil (120 g) placed into a jar (6.5 cm i.d.  $\times$  10.5 cm length) was surface treated with a Stomp solution (3 mL of 12.1 mg/mL) to obtain a pendimethalin concentration equivalent to 3.4 kg/ha. Air entrance to the chamber was located on the center of the cap by placing a 5.2 cm diameter glass funnel. Air entered the chamber through the funnel located at 2.1 cm up to the soil surface and exited through a hole on the cap of the glass jar. Volatilized pendimethalin was trapped in a Florisil column placed in the exit hole. Florisil (2 g) was sandwiched between two polyethylene frits. A Q-Max sampling pump, purchased from Supelco, was connected to the head of the Florisil column, through a perforated silicone septum, to produce a constant airflow of 1 L/min during the experiment.

The volatilization chamber was mounted inside an incubator chamber maintained at 25 °C during the assay. The Florisil column was removed and trapped herbicide analyzed at 1, 3, 24, 48, 72, 96, and 168 h after herbicide application. A new Florisil column was placed after each measurement time. Initial soil moisture content (8%) was restored after those times by adding water to soil.

**Persistence Assay.** Fertilized and unfertilized soils (120 g) were surface treated with a water/Stomp solution (3 mL of 12.1 mg/mL) to obtain an initial pendimethalin concentration of 10  $\mu\text{g/g}$  of ai (equivalent to 3.4 kg/ha) at a soil moisture content of 8%. The treated soil was incubated at 25 °C, in darkness. Jars were opened periodically during the incubation for aeration and soil moisture adjustments.

Sampling from control soil and fertilized soil began immediately after herbicide application and continued periodically, each 30 days, until 4 months. One soil core (1.5 cm i.d.) was taken from each treatment.

**Analytical Procedure. Volatilization.** The trapped pendimethalin was extracted by adding ethyl acetate (3 mL  $\times$  2) to the Florisil column, assisted by sonication in an ultrasonic bath (15 min  $\times$  2). The extract was collected in a graduated tube, and an aliquot was analyzed by gas chromatography (GC) under the conditions described below.

**Soil.** Extraction of pendimethalin residues from soil was carried out using low volumes of organic solvent (20). Soil cores were placed into a tared plastic column, containing sodium sulfate (2 g) at the bottom, and extracted with 5 mL of a methanol/ethyl acetate (50:50) mixture during sonication in an ultrasonic bath (15 min). This extraction step was repeated with another 5 mL of the mixture. Organic extracts were separated from soil in a multipoint vacuum manifold and collected in graduated tubes, and pendimethalin was analyzed by GC as described below.

**Soil Solution.** Soil cores were placed into tared centrifuge tubes, water was added (1:2.5 w/w; soil/water), and the mixture was agitated during 20 h in a wrist-shaker at 630 rpm. The slurry was centrifuged at 4300 rpm during 30 min. Soil solution was transferred to a tube and pendimethalin extracted with ethyl acetate (5 mL  $\times$  3). The ethyl acetate phase was separated from the aqueous phase and concentrated under vacuum at 40 °C. The extract residue was dissolved with a suitable volume of ethyl acetate, and pendimethalin was analyzed by GC under the conditions described below.

**Recovery Assays.** Assays were conducted to study the recovery of pendimethalin from air, soil, and soil solution samples. Fortification of the different matrices was carried out with a water solution of Stomp, and the analytical procedure was performed as described above, except for herbicide extraction from soil. In this case, pendimethalin recovery from fertilized and control soils was assayed with various solvents.

**Gas Chromatographic Analysis.** A Hewlett-Packard model 5890 gas chromatograph equipped with an electron-capture detector and a fused silica capillary column, HP-1 (30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness), was used. The following operating conditions were employed: carrier gas (helium) flow, 1 mL/min; injector temperature, 270 °C; and detector temperature, 300 °C. The oven temperature program used was as follows: 120 °C (1 min) to 230 °C (1 min) at 8 °C/min, programmed to 270 °C (2 min) at 20 °C/min.

The detector response was linear in the range of concentrations studied, and the method detection limits, considered to be 3 times the background signal, were 1 ng, 0.01  $\mu\text{g/g}$ , and 0.01  $\mu\text{g/mL}$  in air, soil, and soil solution, respectively.

A representative chromatogram is shown in Figure 2.

## RESULTS AND DISCUSSION

**Herbicide Determination. Air.** Recovery of pendimethalin from air samples was evaluated by means of recovery and

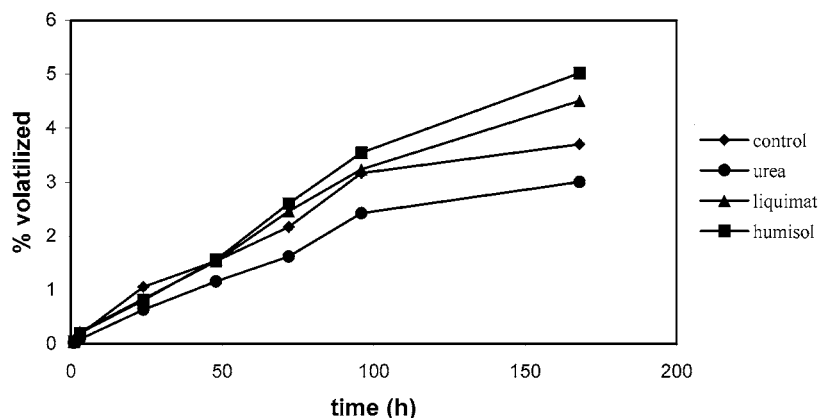


Figure 3. Volatilization of pendimethalin from soil, expressed as a percentage of the initial herbicide amount.

Table 2. Pendimethalin Recovery from Air, Soil, and Soil Solution Samples

sample	pendimethalin added	recovery (%)	retention (%)
air	0.1 $\mu\text{g}$	101 $\pm$ 1.4	101 $\pm$ 2.1
	0.5 $\mu\text{g}$	103 $\pm$ 6.5	98 $\pm$ 0.7
soil	1 $\mu\text{g/g}$	75 $\pm$ 3 <sup>a</sup>	
	10 $\mu\text{g/g}$	82 $\pm$ 14 <sup>b</sup>	
soil solution	0.2 $\mu\text{g/mL}$	60 $\pm$ 7 <sup>a</sup>	
	0.5 $\mu\text{g/mL}$	81 $\pm$ 5 <sup>b</sup>	
	0.5 $\mu\text{g/mL}$	100 $\pm$ 6.4	90 $\pm$ 6.2

<sup>a</sup> Extraction with ethyl acetate. <sup>b</sup> Extraction with ethyl acetate/methanol (50:50).

retention studies. Florisil columns, such as those employed in the assay of volatilization, were fortified in the range of 0.1–0.5  $\mu\text{g}$  of pendimethalin and analyzed following the procedure described above. Mean recoveries obtained were  $\sim$ 102% (Table 2).

To determine the retention efficiency, Florisil columns were fortified at the same pendimethalin levels used above, a pump was attached at the end of the column, and air was pumped at a rate of 1 L/min. Retention efficiencies of those columns for pendimethalin, after 24 h of air sampling, ranged from 98 to 101% (Table 2).

The results obtained indicate that the method proposed to study pendimethalin volatilization provides a rapid and sensitive procedure to determine this compound in air using a low volume of solvent. Previous published methods are often based in the use of solid adsorbents, although pesticide extraction is generally more time-consuming and higher volumes of organic solvent are required (21, 22).

**Soil.** Fertilized and unfertilized soils were fortified with a water/Stomp solution in the range of 1–10  $\mu\text{g/g}$ . Ethyl acetate or a mixture of ethyl acetate/methanol (50:50) was employed for soil extraction by the procedure described above. Recoveries obtained were higher when the ethyl acetate/methanol mixture was used, with mean values  $>$ 80%, whereas recoveries using ethyl acetate ranged from 60 to 75% (Table 2). Values obtained using ethyl acetate as extracting solvent were lower than those reported previously (20). These authors employed an organic solvent solution of a pendimethalin standard for soil fortification. In the present study, a water solution of a commercial formulation was used, and the presence of additives in the pendimethalin formulation may have an effect on the herbicide extraction by ethyl acetate. The use of a more polar solvent, as the methanol mixture, improved pendimethalin extraction from soil samples

Table 3. *K* Values, Correlation Coefficients, and Total Amount Volatilized of Pendimethalin from Soil

days after treatment	fertilizer	<i>K</i> (days <sup>-1</sup> )	<i>r</i>	amount volatilized <sup>a</sup> (%)
4	control	0.03094	0.9936	3.167 ab
	Liqui-Mat	0.03287	0.9988	3.235 ab
	Humisol	0.03619	0.9976	3.547 b
	urea	0.02425	0.9968	2.423 a
7	control	0.02276	0.9637	3.705 ab
	Liqui-Mat	0.02736	0.9888	4.504 a
	Humisol	0.03082	0.9909	5.023 a
	urea	0.01873	0.9760	3.003 b

<sup>a</sup> In each column, values followed by the same letter are not significantly different ( $p < 0.05$ ).

and, therefore, the ethyl acetate/methanol mixture (50:50) was selected as the extraction solvent.

**Soil Solution.** Samples of soil solution (10 mL), obtained as indicated under Materials and Methods, were fortified in the range of 0.2–0.5  $\mu\text{g/mL}$ , and determination of pendimethalin was carried out following the procedure described above. The average recoveries obtained varied from 90 to 100%, with relative standard deviations (RSDs) of  $<$ 10% (Table 2).

**Volatilization.** Volatilization of pendimethalin from soil, expressed as a percentage of the initial amount of pendimethalin, is summarized in Figure 3. Values are the mean of four replicates and represent the accumulated amount measured at the end of each sampling period. During the first 4 days (96 h), volatilization is more rapid than during the following 3 days. The decrease of the volatilization rate of a herbicide with time may be explained by the increase of the herbicide adsorption to soil that takes place with the residence time (23–25).

A linear model was used, as a simple approximation, to compare volatilization of pendimethalin from unfertilized or fertilized soils. Linear kinetics represent well the experimental data obtained during the first 4 days of volatilization, with correlation coefficients of  $>$ 0.99 (Table 3). During that time period, the volatilization rates were similar for the unfertilized soil and the soil treated with Liqui-Mat. The slowest rate obtained was for the soil treated with urea and the quickest for the soil treated with Humisol. An ANOVA analysis ( $p < 0.05$ ) of the obtained data showed differences between treatments (Table 3). The amount of pendimethalin volatilized was  $\sim$ 46% higher for the soil treated with Humisol than for the soil treated with urea, whereas the control soil and the soil treated with Liqui-Mat showed similar volatilization losses of pendimethalin.

Data obtained during the 7 day period were also fitted to a linear regression analysis. In this case, the correlation coef-

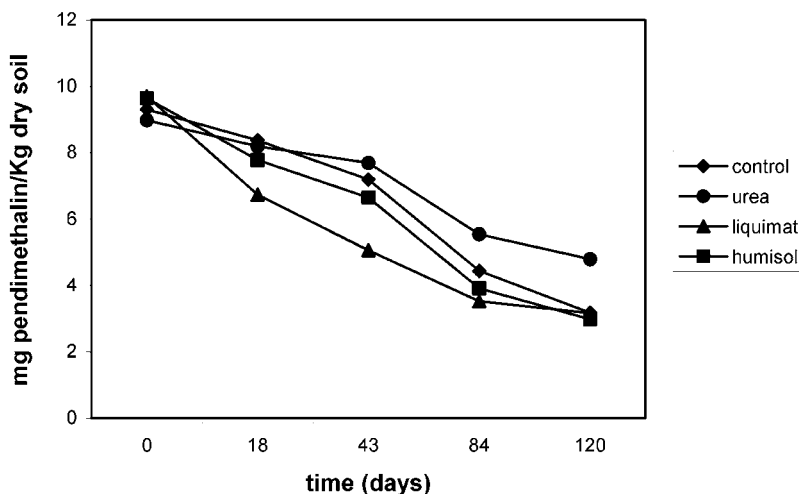


Figure 4. Pendimethalin concentration in soil during the incubation assay at 25 °C and 8% of soil moisture content.

ficients are somewhat lower than those obtained during the first 4 days of the volatilization assay, particularly those of the soil fertilized with urea and the unfertilized soil, due to a decrease in the slope of the volatilization rate for those soils at the end of the assay (Figure 3). Nevertheless, the volatilization rate, although somewhat slower, follows the same pattern as that obtained during the first 4 days. The cumulative amount of herbicide volatilized was higher when pendimethalin was applied to soils fertilized with liquid organic fertilizers (5–4.5%) and lower for soil treated with urea (3%), whereas unfertilized soil presented an intermediate value (Table 3). These results are comparable to the ones obtained for other dinitroanilines (24). These authors reported cumulative vapor losses of 6.5% for ethalfluralin and 8% for trifluralin, over a 7 day period under field conditions. These herbicides have vapor pressures of the order of  $10^{-4}$  mmHg, a little higher than that of the pendimethalin ( $10^{-6}$  mmHg), and similar water solubility values (0.3 mg/L).

The smaller volatilization of pendimethalin in soil treated with urea versus the other treatments may be explained by the capability of the basic urea to move rapidly through the soil profile and to mobilize the organic matter, including pendimethalin. Therefore, the amount of pendimethalin in the soil surface will decrease and the herbicide volatilization rate will be slower. This fact is in accordance with the results obtained by Liu et al. (26), who found a reduction in the amount of atrazine in the soil surface when the soil was fertilized with ammonia in comparison with unfertilized soil.

In addition, the application of organic fertilizers to soil may change its physicochemical properties, which in turn may influence herbicide behavior. Soil organic matter content and pH were measured after fertilizer application and gave the following values: 2.0% and 7.5 for the unfertilized soil; 2.05% and 7.6 for the soil fertilized with Liqui-Mat; 2.05% and 7.6 for the soil fertilized with Humisol; and 2.0 and 8.5 for the soil fertilized with urea (Table 1). No significant differences were found in the organic matter content of soils, but the initial pH was somewhat higher in the soil fertilized with urea. In this case, the pH decreased with time and reached values similar to the other soils ~1 month after herbicide treatment.

**Persistence.** Pendimethalin levels in soil solution during the assay are shown in Table 4. The herbicide concentration in soil solution decreases with the incubation time in all of the soils studied. In general, pendimethalin levels in soil solution are higher for the soil treated with urea during the entire assay.

Table 4. Levels of Pendimethalin in Soil Solution at Different Times after Pendimethalin Application<sup>a</sup>

fertilizer	0 days	18 days	43 days	84 days	120 days
control	0.213 a	0.134 a	0.134 a	0.146 ab	0.087 a
Liqui-Mat	0.242 ab	0.175 ab	0.134 a	0.127 ab	0.090 a
Humisol	0.240 ab	0.171 ab	0.123 a	0.108 a	0.079 a
urea	0.347 b	0.212 b	0.255 b	0.181 b	0.173 b

<sup>a</sup> Expressed as  $\mu\text{g/g}$  of soil dry weight. In each column, values followed by the same letter are not significantly different as determined by least-square means test ( $p < 0.05$ ).

Table 5. Disappearance Rate Coefficients ( $K$ ) and Half-Lives for Pendimethalin in Soils Incubated at 25 °C and 8% Soil Moisture Content

fertilizer	$K$ (days <sup>-1</sup> )	half-life (days)	$r$
control	0.00923235	75	0.9514
Liqui-Mat	0.00967280	72	0.9698
Humisol	0.00991863	70	0.9604
urea	0.00546285	127	0.9595

These higher levels of the herbicide may be explained by the nature of the soluble organic matter that may interact with pendimethalin. When applied to the soil, urea causes the release of organic matter from the soil matrix and the DOM is endogenous, whereas when Liqui-Mat and Humisol fertilizers are applied, the DOM is exogenous. This different type of soluble organic matter may influence the behavior of pendimethalin in the soils studied.

Values of pendimethalin concentration in soil throughout the incubation assay at 25 °C and 8% of soil moisture content are shown in Figure 4. Disappearance of pendimethalin from the soil generally did not conform totally to a first-order kinetics, because the disappearance rate during the first period is higher than that at the end part of the experiment. However, that kinetics law may be used as a first approximation (27), and linearization was accomplished by transformation of soil levels into the corresponding logarithms. Half-lives of pendimethalin in each soil, treated or not with fertilizer, were calculated from the slope of the regression equation, and the obtained results are shown in Table 5. Values of pendimethalin half-lives in soil obtained in this work are similar to the results obtained in other studies (4, 5, 28).

Pendimethalin dissipation rates and half-lives are similar in soil treated with organic humic substances and in unfertilized



control soil (Table 5). This is in concordance with the results obtained by Moorman et al. (29), who pointed out that fertilization with organic matter at rates of 0.5% w/w, after herbicide treatment, had no effect on the degradation of trifluralin, a herbicide belonging to the same chemical class as pendimethalin. The application of urea to soil retarded the herbicide dissipation and caused a pendimethalin half-life in soil longer than that obtained with the other treatments.

Nevertheless, pendimethalin losses after an incubation period of 43 days were generally more important in soil fertilized with liquid organic matter (48% for Liqui-Mat and 31% for Humisol) than in unfertilized soil (23%) (Figure 4). This may be explained by an interaction of pendimethalin with the soluble organic matter of the fertilizer that originates a higher concentration in the soil solution of the herbicide, which in turn is more bioavailable to degradation during the incubation period. This is in concordance with data in Table 4, where the herbicide level in soil solution is somewhat higher during the first weeks in soil treated with liquid humic substances than in unfertilized soil, although these differences decreased with the incubation time. The application of liquid humic substances to soil with a humified part in solution would interact to form micelles, which are able to retain nonpolar molecules inside through hydrophobic interactions and then increase the apparent water solubility or decrease the adsorption of pendimethalin to soil (30). This effect will decrease with the incubation time, due to the mineralization of the liquid organic matter that would cause pendimethalin degradation by soil microorganisms (31, 32).

At the end of the persistence assay (120 days), pendimethalin residues in soil fertilized with liquid humic substances and those of control soil were similar, with values of 34% of that applied for control soil, 33% for the soil fertilized with Humisol, and 31% for the soil fertilized with Liqui-Mat. These values are of the same order as those reported by Smith et al. (6), ranging from 31 to 41% after 4 months of pendimethalin application under field conditions.

On the other hand, pendimethalin dissipation in soil treated with urea was slower in comparison to the other fertilized and unfertilized soils (Table 5). Urea applications, as discussed above, raised soil pH and DOM content. This may cause the decrease of pendimethalin adsorption to soil (33), leading to higher pendimethalin levels in soil solution, as can be seen in Table 4. However, the urea N can inhibit pendimethalin degradation by some fungi and bacteria as reported by Entry (34). This author found that addition of N to soil decreased atrazine and 2,4-D degradation after 10–15 weeks of incubation.

The application of organic fertilizers to soil before pendimethalin treatment may influence the fate of this herbicide in the environment. Liquid organic fertilizers increased, during the first part of the assay, pendimethalin dissipation and herbicide levels in solution and in air, but no differences were found at the end of the experiment (4 months) in soil and soil solution levels in comparison with unfertilized soils. In general, the application of urea to soil decreased pendimethalin degradation and herbicide residues in air and increased, during the entire assay, pendimethalin levels in solution and herbicide half-life in soil, which is ~70% higher than in unfertilized soil.

The results presented in this work show that organic fertilizers may influence pendimethalin behavior in soil according to the nature of the organic matter used, and this fact should be considered in the evaluation of the environmental fate of pendimethalin.

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