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ASSESSING HERBICIDE LEACHING FROM FIELD MEASUREMENTS AND LABORATORY EXPERIMENTS

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A b s t r a c t. Field and laboratory experiments with undisturbed soil columns were performed for assessing the mobility and persistence of chloridazon and lenacil in a clayey soil in the marshes of Lebrija, southwest Spain. In the laboratory we tried to evaluate the herbicides fate when applied with doses greater than normal, as it happens by overlap when spraying the herbicides. Thus, the herbicides doses in the field experiments were similar to those applied by the growers in the area, while the doses applied to the soil columns were four times greater. Apart from that, in the field experiments the herbicides were incorporated into the soil just after the application, by sprinkling irrigation, as it is usually made by the growers. Sometimes, however, there is a delay in irrigating after herbicide application, which may favour adsorption by the soil. To evaluate how this can influence the fate of the studied herbicides in the soil, in the soil columns water was applied for the first time one week after applying the herbicides. Both herbicides showed a low mobility, being the amounts of residues found in the top 0.05 m of soil several times greater than deeper in the soil. Negligible amounts of chloridazon were found at about 4 weeks after application, both in the field and in the soil columns. Lenacil showed a greater persistence, taking about 7 weeks after application for the herbicide to dissipate. The half-life values calculated from the field samples were 11 d for chloridazon and 16 d for lenacil. Calculations from the data of the soil column samples yielded half-life values of 4 d for chloridazon and 14 d for lenacil. The air temperature recorded in the laboratory during the experiments (18±2 °C) was greater than in the field (average maximim temperature = 17.2 °C; average minimum temperature = 8.7 °C; minimum temperature = 1.5 °C), which may explain the quicker dissipation of the herbicides in the soil columns. Also the higher herbicide concentration in column experiments could to have enhanced biodegradation process. For the studied conditions, neither chloridazon nor lenacil represent a serious risk of groundwater contamination. The values of the coefficient of variation of the herbicide residues in soil samples from the columns were similar to those from the field, suggesting that the technique for herbicide application in the soil columns should be improved to decrease variability.

K e y w o r d s: herbicides, leaching, clayey soil.

INTRODUCTION

Groundwater contamination by pesticide leaching has always been a matter of concern for researchers and environmentalists. Special attention is paid to herbicides, since they are applied directly to the soil surface and, in many cases, incorporated into it. The high volumes of irrigation water used in the cash crops extensively cropped in many semi-arid and arid Mediterranean areas increase pesticide-leaching potential, especially in soils with macropores, which allows for significant water movement due to preferential flow paths. This is the case of the cracking soils in many areas of the Guadalquivir river valley, in south Spain. The leaching phenomenon, as the vertical movement of a pesticide within the soil profile, influences its potential as a contaminant of ground and runoff water [1,3]. Pesticide movement has been studied under field conditions [2,15], as well as in laboratory experiments in which modified or undisturbed soil columns are used [8,12,16,18,]. Since field conditions cannot be easily standarized, laboratory experiments are more appropriate for studying the environmental behaviour of pesticides, specially when comparative results want to be obtained. The necessity of both types of experiments was already outlined in 1975 by Burkhard *et al.* [3], Later on, Cheng and Lehmann [10] remarked that specially when characterizing pesticide degradation, because of the complexity of the processes involved, a field study may not always be the most suitable approach. However, both approaches have been used at the same time in just a reduced number of cases [4]. In this work the mobility and persistence of chloridazon and lenacil in the soil of a reclaimed area of the marshes of Lebrija, in the Guadalquivir river valley was studied with field experiments reproducing the usual herbicide management of the growers in the area. Additional results were obtained from laboratory experiments with undisturbed soil columns, in which an irrational herbicide management, sometimes occurring in commercial farms, was studied. Results from both approaches were compared to evaluate to what point they can complement each other.

MATERIALS AND METHODS

Field experiments

The field experiments were carried out in a commercial 12.5 ha plot located in a reclaimed area of the marshes close to the city of Lebrija, southwest Spain (37° 1' N, 6° 8' W, 2 m a.s.l.). The soil type is Fluvaquent (USDA). The soil texture is

clayey, with about 69% clay and 30% silt. The mineralogical composition of the clay fraction (70% altered illite; 15% smectite; 10% kaolinite; <1% interstratified) is very homogeneous throughout the profile. More details are given by Moreno *et al.* [13]. The plot has a drainage system consisting on ceramic pipes buried at 1 m depth and spaced at intervals of 10 m. Irrigation in the area is made with fresh water, to wash out the excess of salts through the drainage system. The climate of the area is typically Mediterranean, with an average rainfall of 550 mm falling mainly from November to March. Average annual potential evapotranspiration (ET_o) is about 1000 mm. During the field experiments, meteorological records were taken from an automatic weather station close to the plot. Sugar beet was sown on 9 November 2000. Herbicides application (1290 g a.i. ha^{-1} of chloridazon, plus 500 g a.i. ha^{-1} of lenacil) was made the day after sowing, using a standard spraying machine mounted on a vehicle. The amount of herbicide solution applied was about 150 l ha^{-1}. The plot was sprinkled irrigated (30 mm) just after the herbicide application, and a total of 15 mm of rain fall on the 13^{th} and 14^{th} of November. The soil, therefore, was at around field capacity soon after the herbicide application. The rain supplied most of the water needed to avoid excessive water stress to the crop at the beginning of the crop season. Sprinkling irrigation was applied from 11 April 2001, to keep the soil wet during the dry period. The crop management was representative for the area. No tillage operations were made during the experiments.

Before the herbicide application, we took soil samples for reference. In each of six locations randomly chosen within the plot, we took samples at the depths of 0.00-0.05, 0.05-0.10, 0.10-0.20, 0.20-0.30, 0.30-0.60 and 0.60-0.75 m. After the herbicide application we sampled in eight locations, also randomly chosen, at the depths of 0.00-0.05, 0.05-0.15, 0.15-0.30 and 0.30-0.60 m. Samples were taken once a week in the 1^{st} month after applying the herbicides. In the 2^{nd} month after the application, samples were taken once every 15 days; we sampled again at the end of the 3^{rd} month after the herbicide application. On the same days that we sampled the soil we also took samples of the water coming out of the drainage pipes.

Laboratory experiments

Five undisturbed soil columns (PVC cylinders, diameter 0.2 m, height 0.2 m) were taken from the plot before field herbicide application. The columns were taken to the laboratory after covering their bottom with a nylon mesh and glass wool. Then they were matched to plastic pots where the elution water was collected. Before applying

the herbicide, enough water was added to the columns to reach field capacity conditions. The amounts of herbicides applied to the columns were 5191 g a.i. ha^{-1} of chloridazon and 2006 g a.i. ha^{-1} of lenacil, four times more than in the field. Water was added weekly to the columns from one week after the herbicide application. The amounts of added water (Table 1) matched those of the field.

Table 1. Water (ml) applied to the columns (col.)

Time (d*)	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
7	800	800	800	800	800
14		800	800	800	800
21			800	800	800
28				1200	1200
35				1200	1200
Total	800	1600	2400	4800	4800

*Days after the herbicide application.

Water leached from the columns (Table 2) was collected for assessing the columns porosity, and samples were taken every week for analysis. Fifteen days after the herbicide application, five replicates of soil samples were taken in column 1, at the depths of 0.00-0.05, 0.05-0.10, 0.10-0.15 and 0.15-0.20 m. The same was made in column 2, three weeks and one day after the herbicide application. At the beginning of the 5^{th} week soil samples were taken in column 3, and at the beginning of the 6^{th} week in column 4. Column 5 was sampled 6 weeks and one day after the herbicide application.

Table 2. Water (ml) drained from the columns (col.)

Time (d*)	Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
8	600	611.5	570.2	562.0	670.5
15		662.0	674.0	671.0	642.5
22			672.0	646.5	650.0
29				1010.5	1045.0
36				1045.0	1055.0
Total	600	1273.2	1916.2	3935.0	4063.0

*Days after the herbicide application.

Herbicide residue extraction and analysis

The soil residue samples were extracted by placing 10 g of soil samples in plastic centrifuge tubes and adding 24 ml of methanol and 6 ml of water. After shaking 24 h, all samples were centrifuged (12 min at 1200 r.p.m. and 23 °C). The

soil extracts were analysed by high performance liquid chromatography (HPLC). A gradient analysis method (0-5 min mobile phase 80:20 water:acetonitrile; 5-15 min mobile phase 50:50 water:acetonitrile) was used with a Waters Multisolvent System, using a Waters-Novapack C-18 cartridge of 150 mm 3.9 mm and a photodiode array detector, performing the analyses at 275 nm. Water samples were analysed by HPLC after filtration.

RESULTS

Soon after the herbicide application, lower amounts of chloridazon and lenacil, as compared to the applied doses, were found in the field samples (Fig. 1) than in the samples from the soil columns (Fig. 2). Negligible amounts of chloridazon

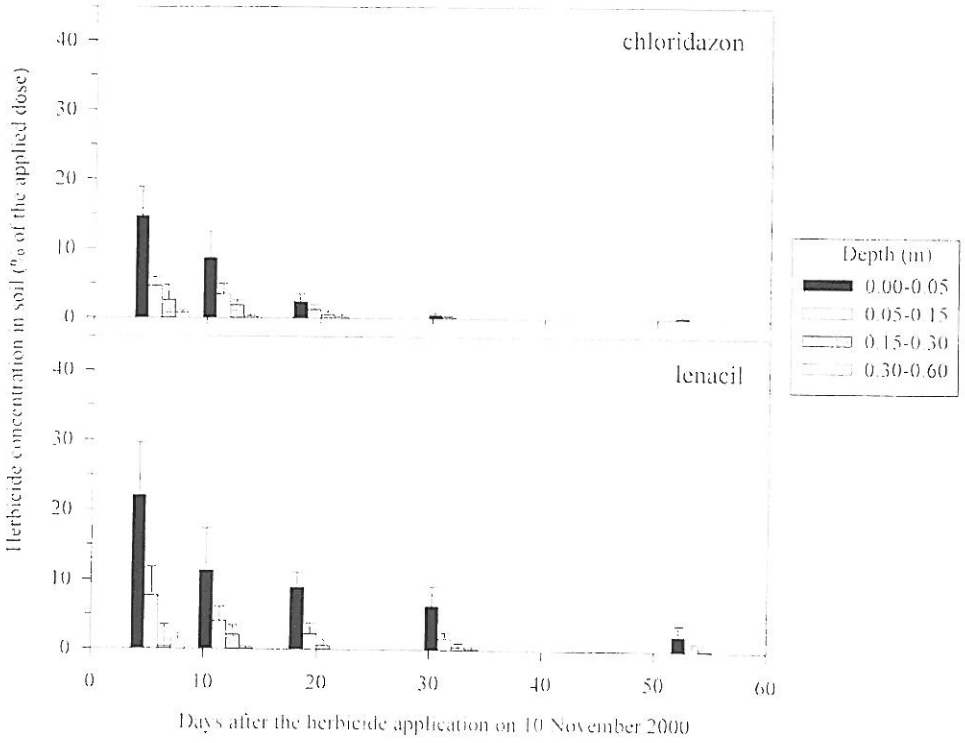

Fig. 1. Distribution of chloridazon and lenacil in the field (n=8; vertical bars = standard deviation).

were found in the field at about 4 weeks after herbicide application (Fig. 1). This was also the time for the herbicide dissipation in the soil columns, despite of the greater amount applied (Fig. 2). In the case of lenacil, the amounts of residue, expressed as percentage of the applied dose, found in the samples from the soil columns 29 d after the herbicide application were much greater than those found in the field samples 32 d after application. It can be seen in Fig. 2, however, that the data on lenacil residues in the soil columns 29 d after the herbicide application were unexpectedly high, being perhaps biased by the high variability found in the experiments (Table 3). The half-life ($t_{1/2}$) values of the two studied herbicides, calculated from the amounts of residues found in the soil samples, are shown in Fig. 3. Figures 1 and 2 show that both chloridazon and lenacil moved little in the soil, being the amounts of residues found in the top 0.05 m several times greater than in deeper layers and no residues were detected in the leachates. The mobility of both herbicides was greater in the field (Fig. 1) than in the soil columns (Fig. 2). No cracks were present during the experiments, neither in the field nor in the soil

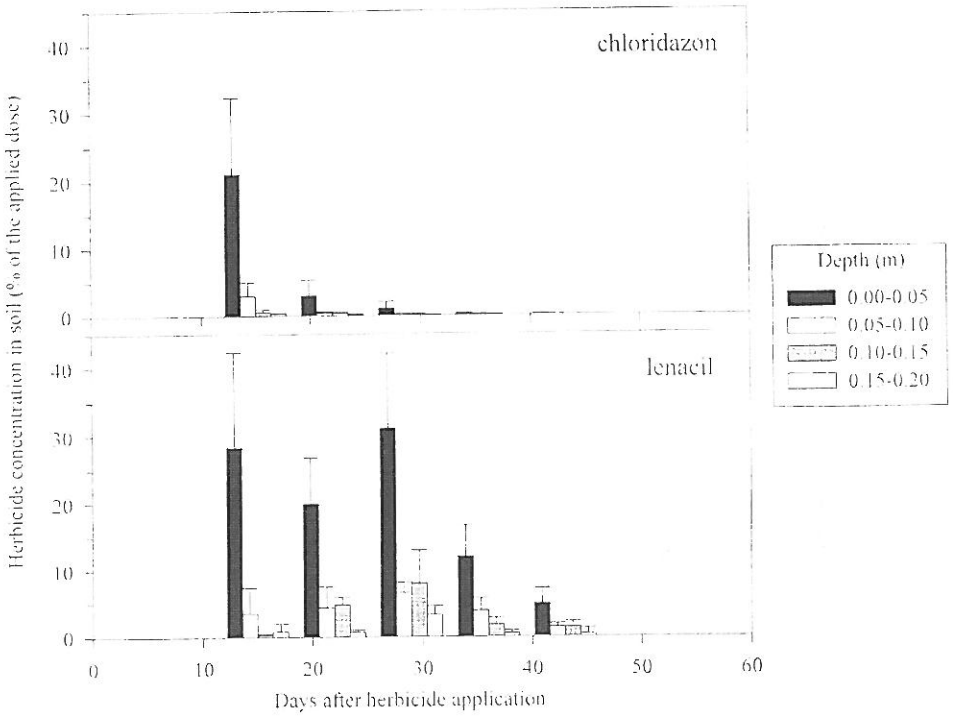

Fig. 2. Distribution of chloridazon and lenacil in soil columns (n=5; vertical bars = standard deviation).

columns, because the high soil water contents avoided the soil shrinkage. Little differences on the coefficient of variation (*CV*) were found between field and soil columns when analysing the data on herbicide residues in the soil samples (Table 3). No herbicide residues were detected neither on the soil samples taken on the 3rd month after the application nor in the water samples. We believe that the differences on porosity between columns, as calculated from the data on Tables 1 and 2, were not big enough to greatly influence the results.

Table 3. Values of the coefficients of variation (*CV*) for the concentrations of chloridazon and lenacil in the soil samples taken at different depths from the field (n = 8) and from the soil columns (n = 5), on different days after the herbicides application

Days after herbicide application	FIELD SAMPLES							
	CV (%) for chloridazon				CV (%) for lenacil			
	0.00-0.05 m	0.05-0.15 m	0.15-0.30 m	0.30-0.60 m	0.00-0.05 m	0.05-0.15 m	0.15-0.30 m	0.30-0.60 m
6	28.6	28.6	82.7	50.0	34.0	53.5	89.2	54.2
12	15.5	43.5	42.6	117.1	52.9	52.2	62.8	283.3
20	47.6	59.3	80.0	120.8	23.5	66.7	142.1	
32	63.8	110.5			42.9	56.6	111.5	183.3
54	86.9				71.4	95.2	289.5	
	COLUMN SAMPLES							
	CV (%) for chloridazon				CV (%) for lenacil			
	0.00-0.05 m	0.05-0.15 m	0.15-0.30 m	0.30-0.60 m	0.00-0.05 m	0.05-0.15 m	0.15-0.30 m	0.30-0.60 m
15	53.4	72.5	83.3	36.4	49.2	110.1	50.0	140.4
22	82.2	49.2	26.7	46.5	34.3	74.9	24.9	50.0
29	100.0	25.4	26.7	137.6	35.6	23.9	61.7	40.4
36	53.2	100.0	22.7		40.0	49.0	58.5	103.6
43	26.2	223.9			48.4	39.5	59.7	224.5

DISCUSSION

The greater amounts of herbicide residues found in the soil columns, specially in the first 5 cm layer, (Figs. 1 and 2) can be explained by the fact that in those experiments water was not added until one week after the herbicides were applied (Table 1). This delay, as compared to the field conditions, might have allowed for a greater adsorption of the herbicides by the soil of the columns. Smectite and montmorillonite, two clay minerals abundant in the experimental soil, have been

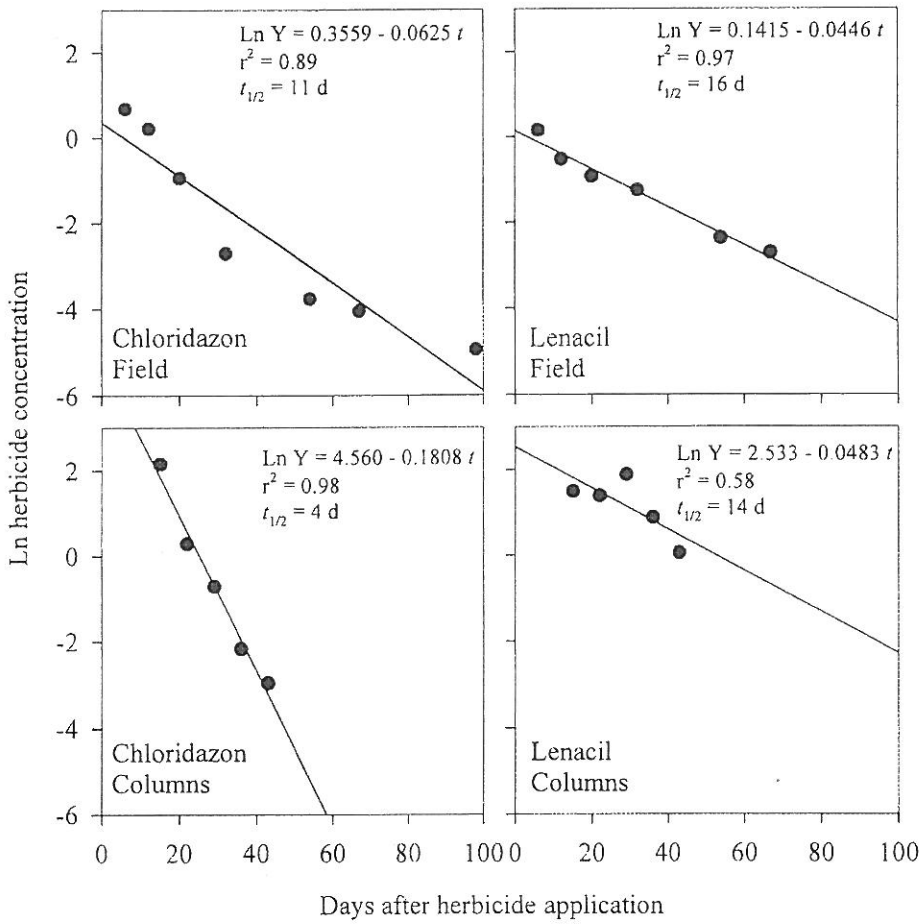

Fig. 3. Chloridazon and lenacil dissipation calculated with data from the field experiments and from the experiments with the undisturbed soil columns. The vertical axis (Y) refers to the Napierian logarithm (Ln) of the herbicide concentration in μg herbicide g^{-1} soil. $t_{1/2}$ = half-life. Each point represents the average of 8 replicates in the field and 5 replicates in the columns.

observed to favour chloridazon adsorption [14]. The altered illite present in this soil, has been shown to behave in herbicide adsorption in similar way to smectite [6,7]. Specifically the illite of this soil has been shown to largely adsorb metamitron [9] a herbicide similar to chloridazon. The greater adsorption of the herbicides by the soil in the columns can also explain their mobility being lower than in the field. The fact that chloridazon dissipated quicker in the soil of the columns than in the field, may be due to the temperature conditions. The air temperature (T_a) in the field was significantly lower than in the laboratory where the

experiments with the soil columns were carried out. Thus, the average T_a in the laboratory was 18±2 °C. In the field the average maximum T_a for the studied period was 17.2 °C, and the average minimum T_a was 8.7 °C, with a minimum value of T_a of 1.5 °C. No differences due to the soil humidity were expected, because the soil was around field capacity throughout the experiments, with no great differences between the field and the columns. In addition, the higher amount (4 times) of herbicides applied in the column experiments could also to contribute to an enhancement of the biodegradation process.

The results both from the field experiments (Fig. 1) and from the soil column experiments (Fig. 2), together with the calculated half-life values (Fig. 3), show that the dissipation of lenacil in the soil was slower than that of chloridazon. Dahms [11] found a half-life value for chloridazon of 10 d for a loam soil at 20 °C, similar to what we have found. Capri *et al.* [5] studied the influence of soil temperature on the half-life of the herbicide, finding that $t_{1/2}$ varied from 76 d to 14 d when temperature changed from 10 to 30 °C. For lenacil, Zhang *et al.* [19] found half-life values between 150 d and 81 d, depending on the soil type (silty soils showed lower $t_{1/2}$ values than sandy soils).

The *CV* values for data on soil residues of both herbicides agree with those shown in other reports [17]. The lack of substantial differences on the *CV* values obtained from the laboratory experiments as compared to those calculated from the field data is striking. We expected greater *CV* values in the field experiments than in the column experiments, due to the greater variability of driving variables normally found in the field. The herbicide solution was randomly distributed in the surface of the soil columns with a micropipete. The *CV* values for the soil columns seem to indicate that this technique could not be appropriate for a uniform herbicide distribution.

CONCLUSIONS

It is unlikely that the use of chloridazon and lenacil in the marshes soils of the Guadalquivir river valley may represent a serious risk of groundwater contamination, due to the low mobility and quick dissipation shown by both herbicides. The experiments with columns provided useful information on the herbicides fate in the experimental soil. These laboratory experiments were easier to make than the field experiments, and allowed for a more accurate control of the environmental conditions. However, differences on temperature and on herbicide management between the field and the laboratory experiments with soil columns caused significant differences on

the results from both approaches. This shows that results from experiments with soil columns can be used to assess the fate of herbicides in the field only if the field environmental conditions are adequately reproduced in the laboratory.

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OKREŚLENIE WYMYWANIA HERBICYDÓW NA PODSTAWIE POMIARÓW POLOWYCH I DOŚWIADCZEŃ LABORATORYJNYCH

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S t r e s z c z e n i e. Przeprowadzono polowe i laboratoryjne doświadczenia z nienaruszonymi kolumnami glebowymi w celu określenia ruchliwości i trwałości chloridazonu i lenacilu w glebie ilastej bagien Lebrii w południowo-zachodniej Hiszpanii. W laboratorium próbowano określić los herbicydów w przypadku zadania dawki większej niż normalna jak to ma miejsce w przy zachodzeniu na siebie warstw w trakcie rozpylania herbicydu. Tak więc, dawki herbicydów w eksperymentach polowych były zbliżone do zadawanych przez farmerów na tym obszarze, podczas gdy dawki zadawane w kolumnie glebowej były cztery razy większe. Oprócz tego w eksperymentach polowych herbicydy były wprowadzane do gleby bezpośrednio po nawodnieniu gleby zraszaczem, jak to jest zwykle robione przez farmerów. Dla badanych warunków, ani chloridazon ani lenacil nie przedstawiały poważnego zagrożenia zanieczyszczeniem wody gruntowej. Wartości współczynnika zmienności pozostałości herbicydu w próbkach glebowych z kolumn były podobne do tych z pola, co sugeruje, że technika zadawania herbicydu w kolumnach glebowych powinna być udoskonalona aby zmniejszyć tę zmienność.

S ł o w a k l u c z o w e: herbicydy, przesączanie, gleby gliniaste.