

Influence of Soil Moisture on Sorption and Degradation of Hexazinone and Simazine in Soil

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Sorption and degradation rates of hexazinone and simazine on soil were determined in a sandy loam soil incubated, during 44 days, at 25 °C with moisture contents ranging from 4% to 18%. Herbicide levels in soil solution were also measured, after extraction of this solution by a centrifugation method. All experiments were conducted with treated soil in plastic columns, and the results showed that this method is suitable for the simultaneous study of pesticide sorption and degradation in soil at different environmental conditions. In general, sorption of both herbicides was higher for aged herbicide residues compared to recently applied herbicides, and soil subjected to drying and rewetting cycles had the highest sorption values. K_f values ranged from 0.5 to 1.2 for simazine and from 0.2 to 0.4 for hexazinone. Degradation rates increased with soil moisture content for both herbicides, and drying–rewetting of soil yielded degradation rates slower than that obtained at 10% soil moisture content. Hexazinone concentration in soil solution decreased with incubation time faster than simazine.

Keywords: Sorption; degradation; soil solution; herbicides

INTRODUCTION

Simazine (6-chloro-*N,N*-diethyl-1,3,5-triazine-2,4-diamine) and hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-dione) are two triazine herbicides widely used to control herbaceous weeds in forestry. The persistence of herbicides in soil over the growing season is important for obtaining good control of weeds, but this may increase concerns over environmental contamination, especially in groundwaters and surface waters. Sorption and degradation are the main processes that affect the behavior of herbicides in soil, thereby determining their persistence and distribution in the field.

Herbicide sorption on soil can be measured by various laboratory methods, such as the batch-equilibration method, based on the shaking of a soil and a herbicide solution for a determined time, or the flow-equilibration method, in which a herbicide solution is passed through a soil column until the effluent has attained the same concentration as the input solution (Lechón et al., 1997). These laboratory measurements of herbicide sorption do not reflect field conditions properly. Under field conditions, herbicide residues are in contact with soil for longer periods of time, degradation can take place, and water:soil ratios may be limited by the field capacity of the soil.

The soil solution is the phase where chemical reactions mainly occur and pesticides dissolved in this phase move through the soil profile where they are available for plants and other organisms. It is very important to know the herbicide concentration in soil solution and how sorption and degradation processes can affect this concentration over the residence time of residues in soil. The extraction of soil solution has been carried out by several techniques, including suction (Green and Obien,

1969; Streibig, 1982), pressure (Scott and Lutz, 1971; Hance and Embling, 1979; Goetz et al., 1986; Shelton and Parkin, 1991), and centrifugation (Davies and Davies, 1963; Dao and Lavy, 1978; Adams et al., 1980; Duffy et al., 1993; Walker and Jurado-Exposito, 1998). All of these techniques have been found adequate for extracting soil solution, although relatively high moisture contents are normally used to obtain high enough solution volumes.

Different authors have pointed out an increase in sorption with aging of pesticide residues in soil (McCall and Agin, 1985; Lehmann et al., 1990; Pignatello and Huang, 1991). This increase in sorption may be explained by a preferential degradation in the soil solution together with a limited desorption from the soil (Duffy et al., 1993; Walker and Jurado-Exposito, 1998). The desorption-resistant fraction may result from the slow diffusion of organic compounds through the solid organic matter in soil or from the entrapment of these compounds within soil micropores (Hatzinger and Alexander, 1995; Pignatello and Xing, 1996). There is little information on the effects of drying and rewetting of soil on these processes. Previous laboratory studies have shown the decrease in bioavailability and extractability of some chemical compounds when soil was wet and dried during the incubation (Shelton et al., 1995; Goetz et al., 1986; White et al., 1998).

Reported values of simazine sorption in soil are higher than those of hexazinone (Wauchope et al., 1992) and half-lives of these herbicides varied, under field conditions, between 11 and 149 days for simazine and from 1 to 6 months for hexazinone, being soil moisture content an important factor for herbicide degradation (Walker et al., 1983).

The aim of this work was to study the effect of soil moisture and drying–rewetting cycles on sorption and degradation of hexazinone and simazine in soil. Specifically, the objectives of this study were (1) to assess

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sorption of these herbicides by soil as a function of soil moisture and residence time, (2) to determine the effect of soil moisture on the degradation of these herbicides in soil, and (3) to compare herbicide levels in soil solution and their changes with time at different soil moisture contents.

EXPERIMENTAL PROCEDURES

Soil and Herbicides. The soil used in the experiments, sampled from the top layer (0–10 cm), was a xerofluent sandy loam with 64.8% sand, 23.9% silt, 11.5% clay, and 1.75% organic matter, pH 6.68, and a water field capacity of 20% w/w. Particle size distribution was determined by the pipet method, and organic matter, by the Walkley–Black method; pH was measured in a mixture soil–distilled water (1:2.5); and field capacity was determined in a pressure chamber using a ceramic plate (MAPA, 1994). Soil moisture content was determined by drying a soil subsample for 24 h at 110 °C.

The commercial formulations of the two triazine herbicides used in the experiments were a wettable powder of simazine (6-chloro-*N,N*-diethyl-1,3,5-triazine-2,4-diamine) with 50% active ingredient and a suspension concentrate of hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione) with 90% active ingredient that were provided by Cyba-Geigy (Switzerland) and DuPont (Wilmington, DE), respectively.

Incubation Studies. Freshly collected samples of soil were air-dried and sieved to pass a 2 mm mesh. Soil samples (800 g) were treated with an aqueous solution of the herbicide using an adequate volume of solution in order to obtain a soil moisture content of 4% and herbicide contents of 4 or 2 µg/g (soil dry wt) for simazine and hexazinone, respectively. Each treated soil was passed four times through a 2 mm mesh sieve and allowed to equilibrate for 24 h at 4 °C. After this time, the moisture content and the herbicide concentration in soil were determined. Soil subsamples (6 g) were transferred to tared polypropylene syringes (20 mL) with nonadsorbent polyethylene frits and filters at the end. To each soil subsample was added an adequate amount of water, determined by weighing, to give a soil moisture content of 4, 10, or 18% (g/g soil dry wt), corresponding to 20, 50, and 90% of the soil field capacity, respectively, before they were submitted to the incubation procedure.

Two types of incubation assays were carried out at a constant temperature of 25 ± 1 °C:

(a) *Incubation at a Constant Soil Moisture Content.* Soil samples with 4, 10, or 18% soil moisture content were placed in a glass desiccator with water at the bottom, to avoid drying of soil during the incubation period. Four replicates per herbicide and soil moisture content were sampled at 0, 15, 30, and 44 days of incubation.

(b) *Incubation with Drying–Rewetting Cycles.* Soil samples with 18% soil moisture content were placed in a glass desiccator with silica gel at the bottom, which allowed the drying of soil from 18% to 4% soil moisture content in about a week period. After this time, samples were removed from the glass desiccator and an adequate amount of water, determined by weighing, was added to the soil to obtain 18% of soil moisture content. Syringes were then replaced in the glass desiccator. This drying–rewetting period, considered a cycle, was repeated several times and four replicates per herbicide were sampled after two, four, and six cycles.

At each sampling time, for both incubation studies described above, water was added to all soil samples to raise soil moisture content to field capacity, and samples were placed in a chamber at 25 °C for 48 h to allow equilibration. Additionally, four nonincubated replicates per herbicide were used to determine the initial herbicide concentration in soil solution and soil.

Extraction and Analysis of Herbicides. After 48 h of equilibration at field capacity, the syringe was weighed and its outlet inserted into a previously tared vial, which was enclosed in the receptacle of a centrifugation tube. The whole

Table 1. Parameters of the Freundlich Isotherm and Derived K_{oc} Values Obtained by the Centrifugation Method^a

herbicide	K_f	$1/n$	r^2	K_{oc}
simazine	0.499 (0.561–0.445) ^b	1.556 ± 0.154 ^c	0.9190	46
hexazinone	0.206 (0.222–0.190)	1.047 ± 0.093	0.9263	19

^a Soil solution was obtained after equilibration at field capacity for 48 h. ^b Numbers in parentheses are standard errors about the K_f values. ^c Numbers are $1/n$ values ± standard errors. Confidence limit: 95%.

unit was centrifuged at 4000 rpm (2930g) for 1 h at 18 °C, and then the vial with the soil solution and the syringe with the soil were weighed separately.

The soil solution was transferred to a 10-mL tube, combined with acetone, and vacuum evaporated to dryness. The residue was dissolved in an adequate volume of ethyl acetate (2 mL), and the herbicide concentration was determined by GC-NPD under the conditions described below.

The soil remaining in the syringe after centrifugation was extracted by a previously reported method (Pérez et al., 1998). Small volumes of ethyl acetate for simazine and acetone:water (90:10) for hexazinone were used in an ultrasonic water bath, followed by solvent filtration on a multiport vacuum manifold. Herbicide concentration was determined by GC-NPD under the conditions described below. Blank samples were used and no interference was found in the determination of herbicides. The adsorbed triazine, x/m (µg/g soil dry wt), was calculated as

$$x/m = (R - VC)/W \quad (1)$$

where R is the total herbicide (sorbed plus dissolved in the solution) remaining in the soil (micrograms), V is the volume of soil solution retained in the soil after centrifugation (milliliters), C is the herbicide concentration in the soil solution (micrograms/milliliters), and W is the dry weight of soil (grams).

A Hewlett-Packard model 5890 gas chromatograph equipped with a nitrogen–phosphorus detector and automatic injector was used for the analysis of herbicides. A fused silica capillary column, HP-1 (12.5 m × 0.20 mm i.d.) and 0.33-µm film thickness, was employed with helium as carrier gas at 1 mL/min. The column temperature was maintained (1 min) at 100 °C for simazine and at 120 °C for hexazinone, then programmed at 20 °C/min to 180 °C held 0.5 min, and then programmed at 10 °C/min to 230 °C and held 1 min. Injector port and detector temperatures were 270 °C and 300 °C, respectively.

RESULTS AND DISCUSSION

Influence of Soil Moisture on Herbicide Sorption. Herbicide levels were determined in soil solution and in soil after treatment with simazine to be 1–4 µg/g and with hexazinone to be 0.5–2 µg/g. Soil solution was obtained by centrifugation of moist soil placed in plastic columns following the procedure described above, which is similar to the method used by other authors (Dao and Lavy, 1978; Adams et al., 1980; Duffy et al., 1993; Walker and Jurado-Exposito, 1998). The herbicide concentrations in soil and soil solution were fitted to the linearized Freundlich sorption isotherm

$$\log x/m = \log K_f + 1/n \log C \quad (2)$$

where x/m is the concentration of the herbicide adsorbed in soil (micrograms/grams of soil dry weight); C is the concentration of the herbicide in soil solution (micrograms/milliliter); and $1/n$ and K_f are constants. Table 1 shows the values of K_f , $1/n$, the determination coefficient (r^2), and the K_{oc} calculated from the obtained K_f value

Table 2. Apparent Sorption Parameters of the Freundlich Isotherm Obtained for Simazine and Hexazinone at 25 °C and Different Soil Moisture Contents

herbicide	moisture	K_f	$1/n$	r^2
simazine	10%	0.900 (1.024–0.806) ^a	0.922 ± 0.139 ^b	0.7590
	18%	0.848 (0.934–0.770)	1.001 ± 0.131	0.8053
	4–18%	1.215 (1.292–1.142)	0.753 ± 0.080	0.8632
hexazinone	10%	0.366(0.383–0.350)	0.572 ± 0.046	0.9150
	18%	0.376 (0.389–0.364)	0.486 ± 0.034	0.9365
	4–18%	0.422 (0.439–0.405)	0.446 ± 0.042	0.8887

^a Numbers in parentheses are standard errors about the K_f values. ^b Numbers are $1/n$ values ± standard Confidence limit: 95%.

and the corresponding soil organic carbon content, for the determination carried out at field capacity of soil with nonincubated samples.

Simazine adsorption to soil (based on K_f and K_{oc}) was higher than hexazinone, and showed an exponent $1/n$ higher than 1, indicating that simazine sorption was dependent on the herbicide concentration (Table 1). The $1/n$ value close to 1 for hexazinone indicates a constant partitioning of the herbicide between soil and solution at the concentration levels used in this study. Values of K_{oc} reported in the literature ranged from 46 to 181 for simazine (Reddy et al., 1992; Rao et al., 1985; Wauchope et al., 1992; García-Valcárcel et al., 1998) and from 4 to 54 for hexazinone (Wauchope et al., 1992). In a previous study in our laboratory with the soil used in this work, K_{oc} values of 56 and 26 were obtained for simazine and hexazinone, respectively, using a flow method to determine sorption coefficients (García-Valcárcel et al., 1998). The K_{oc} values shown in Table 1 are somewhat lower than those previously obtained in our laboratory and in the lower end of the range of those reported in the literature. This may be explained by the influence of factors such as shaking in the slurry technique or soil:solution ratio in the flow method that make sorption sites more available to the herbicide (Walker and Jurado-Exposito, 1998; Shelton and Parkin, 1991). Moreover, the slurry or flow methods usually employ technical or analytical grade herbicides while, in this study, formulated herbicides were used. Thus, this may affect sorption by interaction or competition between the formulating agent and the active ingredient, and also by increasing the water solubility of the active ingredient (Smith and Bayer, 1967; Hance and Embling, 1979).

Herbicide levels in soil and soil solution were determined at different times after treatment in soil incubated at 25 °C and various moisture contents. Apparent sorption coefficients for simazine and hexazinone (Table 2) were obtained by fitting the amount of herbicide adsorbed by the soil and the concentration of herbicide in the soil solution obtained by centrifugation into the Freundlich equation (eq 2). In the case of incubation at 4% soil moisture content, K_f sorption coefficients were not obtained due to the small variation of concentration with time and consequently the poor fitting to the Freundlich isotherm. Distribution coefficients (K_d) were then calculated as the herbicide concentration in soil divided by its concentration in soil solution at each sampling time. K_d values for simazine were similar over the incubation time, with a mean value of 0.813 ± 0.073 , while for hexazinone the obtained average value was 0.218 ± 0.028 , except for the last sampling where an increase was observed to a K_d value of 0.379 ± 0.03 . These K_d values together with the K_f values shown in Table 2 indicate an increase in the sorption coefficient and a decrease in the exponent $1/n$ for aged herbicide residues with respect to the corresponding values for

the recently applied herbicide (Table 1). Sorption of herbicides in soil was apparently similar at 10 and 18% of soil moisture content, although a small decrease of $1/n$ was observed for hexazinone with the increase in soil moisture content, indicating a greater curvature of the isotherm (Graham-Brice, 1967), which would suggest an increase in sorption. This increase in sorption may be explained by the pesticide partitioning into soil organic matter or by diffusion to more inaccessible sites with the residence time and entrapment of compounds in micropores (White et al., 1997; Walker and Jurado-Exposito, 1998).

The soil subjected to drying and rewetting cycles gave the greatest K_f values, which is in agreement with the results reported by Shelton et al. (1995) in an atrazine sorption study. Different explanations have been given to account for this increase in sorption. Drying and wetting cycles cause shrinkage and swelling of the soil structure that result in a decrease of surface area, which may enhance the pesticide diffusion into the soil matrix (White et al., 1998). Moreover, it has been observed higher pesticide sorption to dry than wet soil (Goetz et al., 1986).

Influence of Soil Moisture on Degradation.

Changes of simazine and hexazinone levels in soil were detected during the incubation period. It was assumed that the degradation of these herbicides in the different incubation conditions followed first-order kinetics. Data were then plotted as total herbicide concentration, in logarithmic scale, against time of incubation, and first-order rate constants, half-lives of herbicides at various soil moisture contents and determination coefficients were calculated.

Simazine was more persistent than hexazinone except when soil was incubated at 4% soil moisture content, where hexazinone levels remained almost unchanged during the incubation period (Table 3). Results obtained at 4% soil moisture content showed a poor fit to the linear regression analysis, as half-lives were clearly longer than the time of the assay.

The simazine half-lives are similar to those previously reported. Under field conditions, simazine half-life varied between 11 and 149 days (Wauchope et al., 1992). Walker et al. (1983) reported a considerably lower loss of simazine in dry soil than in moist soil under controlled laboratory conditions, which is consistent with the large differences in half-lives between simazine incubated at 4% of soil water content and those of the other soil moisture conditions. Simazine can be degraded in soil by biotic and abiotic processes, being chemical hydrolysis the predominant way of degradation at low soil pH (Dao et al., 1979; Burkhard and Guth, 1981; Walker et al., 1983).

Information concerning half-lives of hexazinone under controlled laboratory conditions is scarce in the available literature. Reported half-lives of hexazinone varied from 1 to 6 months under field conditions (Rhodes, 1980;

Table 3. Degradation Constants (K), Half-Lives ($t_{1/2}$) with 95% Confidence Limit and Determination Coefficients (r^2) of Simazine and Hexazinone in Soil Incubated at 25 °C and Different Soil Moisture Contents

herbicide	moisture	K	$t_{1/2}$, days	r^2
simazine	4%	-0.00502	125.9 (165.7–101.6)	0.5544
	10%	-0.02098	33.0 (35.0–31.2)	0.9566
	18%	-0.02513	27.6 (29.1–26.2)	0.9638
	4–18%	-0.01874	37.0 (40.6–34.0)	0.9008
hexazinone	4%	-0.00121	572.1 (907.3–417.8)	0.3436
	10%	-0.02997	23.1 (24.3–22.2)	0.9728
	18%	-0.03516	19.7 (20.4–19.1)	0.9836
	4–18%	-0.02012	34.5 (38.6–31.1)	0.8623

Table 4. Observed Soil (x/m) and Solution (C) Concentrations of Simazine in Relation to Its Calculated Equilibrium Concentration in Solution (C_e)

moisture	15 days				30 days				44 days			
	x/m	C_e	C	C/C_e	x/m	C_e	C	C/C_e	x/m	C_e	C	C/C_e
4%	2.915	3.110	3.262	1.049 ± 0.047	2.308	2.675	2.935	1.098 ± 0.076	2.125	2.538	2.800	1.103 ± 0.022
10%	2.109	2.525	3.014	1.193 ± 0.065	1.494	2.022	1.914	0.946 ± 0.022	1.079	1.642	1.222	0.743 ± 0.066
18%	1.917	2.375	2.777	1.168 ± 0.067	1.143	1.703	1.497	0.879 ± 0.066	0.941	1.502	1.074	0.716 ± 0.066
4–18%	2.519	2.831	3.008	1.063 ± 0.106	1.609	2.122	1.538	0.725 ± 0.065	1.346	1.892	1.177	0.621 ± 0.067

Table 5. Observed Soil (x/m) and Solution (C) Concentrations of Hexazinone in Relation to Its Calculated Equilibrium Concentration in Solution (C_e)

moisture	15 days				30 days				44 days			
	x/m	C_e	C	C/C_e	x/m	C_e	C	C/C_e	x/m	C_e	C	C/C_e
4%	0.888	4.307	3.809	0.943 ± 0.070	0.804	3.671	4.033	1.106 ± 0.150	1.107	4.985	2.933	0.558 ± 0.049
10%	0.692	3.181	2.572	0.810 ± 0.051	0.513	2.390	1.914	0.633 ± 0.066	0.300	1.434	0.839	0.587 ± 0.033
18%	0.555	2.577	2.372	0.934 ± 0.121	0.381	1.799	0.947	0.526 ± 0.063	0.282	1.350	0.580	0.439 ± 0.123
4–18%	0.669	3.080	2.311	0.750 ± 0.039	0.452	2.118	1.442	0.684 ± 0.082	0.506	2.359	1.378	0.583 ± 0.026

Wauchope et al., 1992) and a value of 43 days under summer conditions (Roy et al., 1989). These authors identified metabolites that involved biotic and abiotic hexazinone degradation.

Degradation rate increased with soil moisture content for both herbicides, which is in agreement with the results of Walker and Blacklow (1994) for atrazine and simazine and those of Bowmer (1991) for atrazine. Drying and rewetting cycles of soil produced a herbicide degradation rate slower than that obtained at a medium soil moisture content (10%). Information regarding the effect of wetting and drying on the degradation of pesticides in soil is very scarce. The decrease in herbicide degradation caused by wetting and drying soil can be explained by the observed increase in sorption, which makes herbicide less bioavailable. This effect on degradation was more important for hexazinone according to its predominant biotic pathway of degradation. Our results agree with those of White and co-workers (1998) who observed that subjecting soil to wetting and drying cycles during periods of aging lower than 60 days decreased the bioavailability of phenanthrene.

Herbicide Levels in Soil Solution. Changes with time of herbicide content in soil solution, as well as those of total and sorbed herbicide content, are shown in Figure 1 expressed as percentages of the initial herbicide content. In general, herbicide levels in soil and soil solution decreased with time as a function of soil moisture content, although the behavior of simazine and hexazinone was somewhat different. Decline of total hexazinone content in soil was similar to that of hexazinone content in soil solution, while decline of total simazine content was similar to that of adsorbed simazine in soil. This decline was clearly less pronounced, or in some cases nonexistent, at low soil moisture content (4%) with both herbicides, especially with hexazinone. The percentage of simazine in soil solution was lower than that of hexazinone, irrespective of soil moisture content, and simazine level in soil solution

showed a decrease with time less marked than that of the hexazinone level. This is in accord with results of Hance and Embling (1979), who found little changes with time of simazine concentration in soil solution, while with metribuzin, a more water-soluble and less sorbed herbicide than simazine, the concentration in soil solution decreased with time.

The expected herbicide concentration in aqueous phase at equilibrium (C_e) can be calculated by means of the values of K_f and $1/n$ of sorption equilibrium isotherms (Table 1) for the corresponding adsorbed concentration in soil (x/m) measured at the different times. These values are pointed out in Tables 4 and 5 for simazine and hexazinone, respectively, and show, in general, that the C/C_e ratio decreased with the incubation time for both herbicides, indicating a decrease with time of the herbicide available in soil solution. This is in accord with the increase in sorption indicated before and with the increased resistance to desorption that occurs with longer contact times (Loehr and Webster, 1996).

An exception is the incubation at 4% soil moisture content with simazine where C/C_e is always near 1.0, indicating equilibrium conditions. This fact is consistent with the low degradation rate and the unchangeable K_d value with time observed at those conditions. At the end of the period studied, the C/C_e ratio obtained for simazine (Table 4) was lower than 1.0, except for incubation at 4% soil moisture content as indicated before. This ratio was similar for the other soil moisture contents assayed, although the decrease in the C/C_e ratio was observed earlier with the soil subjected to drying–rewetting cycles.

Data obtained for hexazinone (Table 5) also showed this early decrease in the C/C_e ratio for the soil submitted to drying–rewetting cycles. At the end of the assay, all hexazinone incubation treatments presented similar C/C_e values, which could be explained by the similar sorption coefficients obtained for this herbicide at the

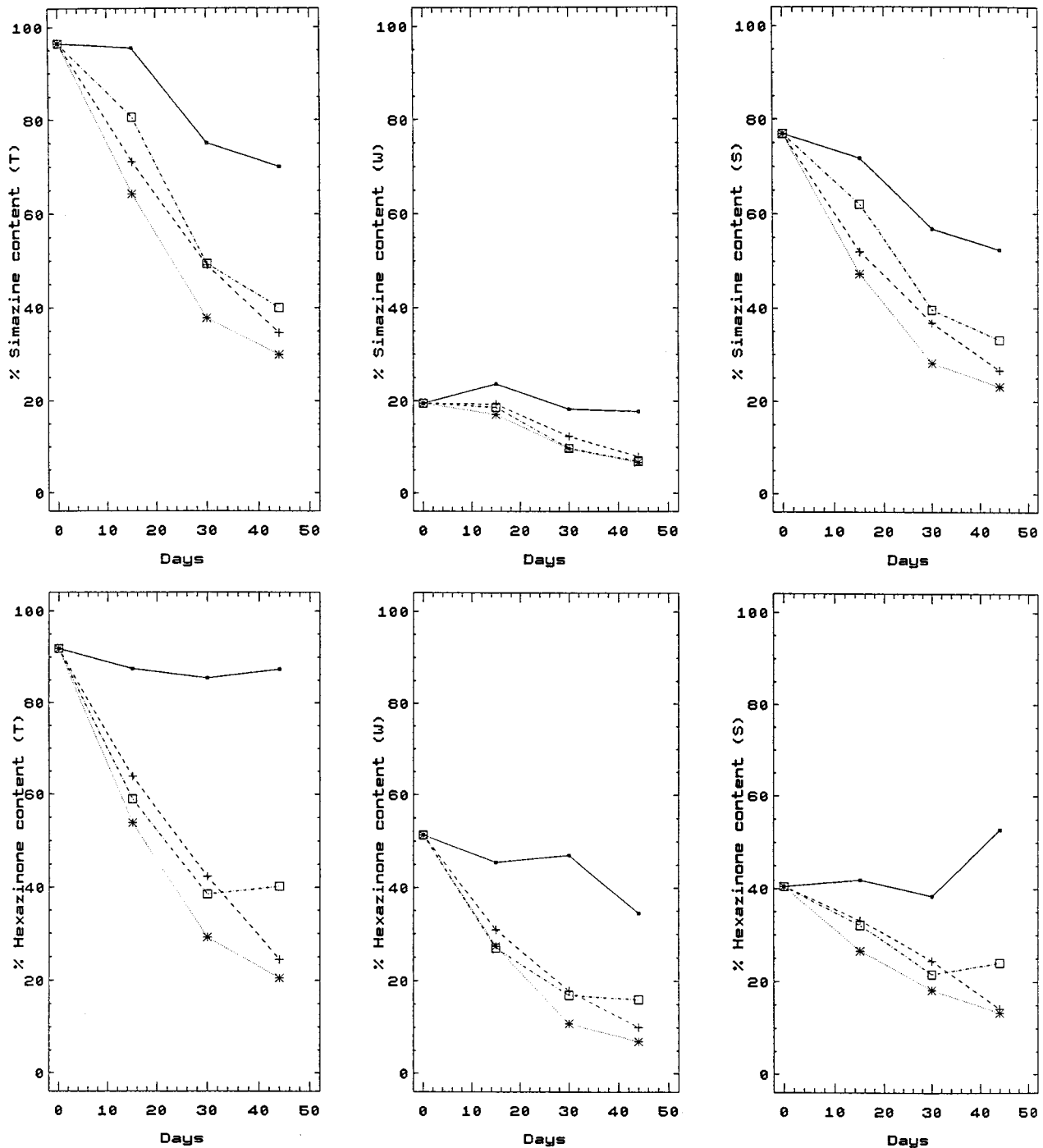


Figure 1. Changes in total herbicide content (T), soil solution content (W) and soil content (S) in soil incubated at the following soil moisture contents: 4% (—), 10% (+), 18% (*), and 4–18% (□). Values are the mean of four moisture replicates expressed as percentages of the initial herbicide content.

different soil moisture contents assayed. Scribner et al. (1992) studied the behavior of simazine in soil under field conditions and observed that the fractional equilibrium values (C/C_0) decreased from 1 at the time of field application to less than 0.1 after 3 months. They suggested that desorption of simazine becomes slower over time, due to herbicide entrapment in soil micropores that are less accessible. This in turn may reduce herbicide degradation in soil.

CONCLUSIONS

The results presented in this work show that the method proposed for the extraction of soil solution, by means of centrifugation of treated soil samples placed

in small plastic columns, is suitable for the simultaneous study of pesticide sorption and degradation at different environmental conditions. In addition, the analysis of pesticide residues in soil can be carried out in the same column, after obtaining soil solution. The method is rapid, with good sensitivity for residue analysis and uses small volumes of organic solvents. Moreover, this procedure allows the determination of pesticide levels at conditions that are closer to field conditions than those used in the conventional sorption studies.

An increase in sorption with time was observed for aged herbicide residues incubated at various soil moisture contents with respect to freshly applied herbicides.

Half-lives of herbicides were obtained at the different conditions assayed, and an increase of the degradation rate with soil moisture content was observed. Drying and rewetting cycles of soil produced a lower degradation rate, in comparison with soil incubated at constant moisture content in the same range, and samples subjected to drying-rewetting cycles showed the highest increase in sorption. In accordance with these findings, herbicide levels in soil solution declined with the incubation time, and this decline was faster for hexazinone than for simazine.

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