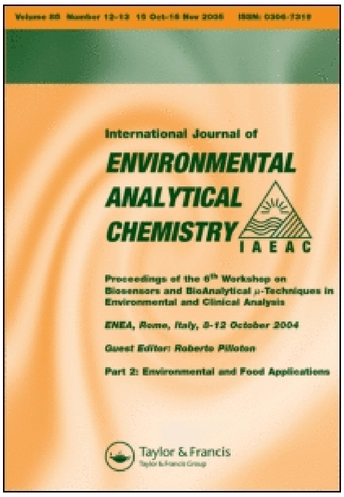


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Mobility of Terbacil as Influenced by Soil Characteristics

A. Mora[a]; M. C. Hermosin[a]; J. Cornejo[a]
[a] Inst. Recursos Naturales y Agrobiología de Sevilla-C.S.I.C., Sevilla, Spain

To cite this Article Mora, A. , Hermosin, M. C. and Cornejo, J.(1997) 'Mobility of Terbacil as Influenced by Soil Characteristics', International Journal of Environmental Analytical Chemistry, 66: 3, 149 — 161
To link to this Article: DOI: 10.1080/03067319708028359
URL: http://dx.doi.org/10.1080/03067319708028359

Intern. J. Environ. Anal. Chem., Vol. 66, pp. 149–161
Reprints available directly from the publisher
Photocopying permitted by license only

MOBILITY OF TERBACIL AS INFLUENCED BY SOIL CHARACTERISTICS

A. MORA, M. C. HERMOSIN and J. CORNEJO*

Inst. Recursos Naturales y Agrobiología de Sevilla-C.S.I.C. Aptdo. 1052, 41080 Sevilla, Spain

(Received 10 September 1995; In final form 15 November 1996)

Research efforts dealing with the parameters and processes affecting the transport of herbicides in soils are needed in order to prevent further damage of surface and groundwater reserves. The present study was designed to improve the knowledge of the terbacil behaviour in soils by integrating adsorption/desorption and mobility experiments as related to soil characteristics. Hand-packed soil columns were used for the mobility experiments and simultaneously the sorption of terbacil was examined by the batch procedure. Four soils were used: two clay soil, a sandy clay soil and a sandy soil. The sorption parameters from Freundlich equation showed weak sorption, although it was higher and partially irreversible in the clay soils. The herbicide was found very mobile in the sandy soils and mobile in the clay soils with a leachate herbicide recovery ranging from 100 to 87% for the sandy and clay soils respectively. The elution profile and cumulative curves showed differences among the soils related to organic matter and clay contents and the combined influence of sorption (adsorption/desorption) and degradation processes are suggested. The mobility index calculated from the residue distribution along the soil column showed that terbacil mobility was inversely related with soil organic matter and with soil clay content, being highly correlated with the soil water flow, which also relates to the soil texture.

Keywords: Adsorption; degradation; desorption; herbicide; leaching; mobility; soil; soil clay; soil organic matter; terbacil; water flow

INTRODUCTION

Pesticides play a major role in agriculture, helping to ensure high yields of food crops. However, pesticide contamination has become a world environmental concern because many herbicides have been used extensively for a number of years, and some of them are now found in surface and groundwaters.[1] Although some pesticides have been listed for restrictive use due to their potential

---

*Corresponding author. Fax: +34-5-4624002. E-mail: cornejo@irnase.csic.es.

leaching, research efforts dealing with the processes affecting the transport of pesticides in soils are needed in order to prevent further damage to surface and groundwater bodies.[2]

The risk of groundwater contamination from agricultural pesticide use is ultimately determined by the relative rates of percolation, sorption and degradation within the soil profile, and by factors controlling these processes. Soil/water partitioning coefficients have been used for predicting pesticide mobility in soils and also coefficients from some adsorption isotherm equations such as Freundlich and Langmuir. Herbicide mobility has been measured in the laboratory by using soil leaching columns[3] which allow to control the leaching conditions in order to compare different soils and pesticides.

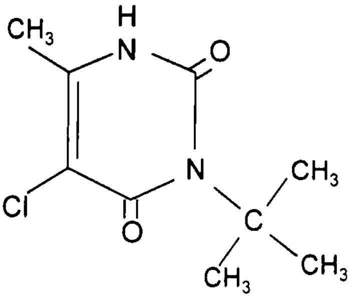
The soil organic matter has been recognized as the most important contributor to the retention of nonionic organic pesticides in soils[4–7] acting as a partitioning medium. However, for polar pesticides such as terbacil, specially in soils of low organic matter content, other factors as the clay fraction increase their role on the net sorption[8–13]. Despite such evidences not much work has been done on pesticide sorption by poor organic matter soils.

Terbacil is a relatively mobile herbicide in comparison with other frequently used herbicides[14,15], but there are few studies about its behaviour in soils specially dealing with mobility as related to soil processes and characteristics, and none in Spanish soils most of which have a low organic matter content. The present work deals with the study of terbacil mobility in typical southern Spanish soils from an intensive agricultural area surrounding Doñana National Park. The reported data on the presence of other pesticides in this important European Wild Life Reserve lead[16,17] the interest to improve knowledge of the soil factors controling pesticide transport in this area. The main objective of the present work was to ascertain the soil processes and parameters implied in the mobility of the herbicide terbacil.

MATERIALS AND METHODS

Pesticide and Reagents

Terbacil (3-tert-butyl-5-chloro-6-methyluracil) is a uracil herbicide widely used for the selective control of many annual and some perennial weeds in crops as citrus, apples, peaches, alfalfa and blueberries. Pure terbacil has a vapour pressure of 0.0625 mPa (29°C) and a water solubility of 710 mg/1, its water solution are stable, even in alkali conditions and undergoes microbial degradation in moist soil[18–20]. It is marketed as a wettable powder containing 80% active ingredient under the trade name Simbar by E. I. du Pont. Its molecular structure is shown below:



Pure terbacil (99%) obtained from Riedel-de Haën was used in all the experiments. All other chemicals were analytical or HPLC grade.

Soils

The soils were selected on the basis of previous work done in our laboratory, which allowed us to select sampling points at the intensive cultivation zone surrounding Doñana National Park. The samples used in this study originated from the upper layer of two clay soils classified as Xerofluvent (P-1) and Entic Pelloxerert (P-7), a sandy-clay soil as Typic Rhodoxeralfs (P-2) and a sandy soil as Fragixeralf Grosarenico (P-13). They were taken from the field, air-dried, mixed, sieved through a 2 mm mesh screen, and stored in polyethylene bottles at 5°C. Selected properties are shown in Table I.

Adsorption/Desorption Assays

Equilibrium adsorption isotherms for all soils were measured using the batch procedure at six terbacil concentrations ranging from 5 to 24 μM. Equilibrium was achieved by shaking at 22°C duplicate samples of soil (5 gr) with aqueous

TABLE I Some physicochemical characteristics of the soils used

Soil	*Sand*	*Silt*	*Clay*	*O.M.*	*pH*
		%		%	
P-1	12.1	43.6	44.3	2.24	7.7
P-2	70.7	8.9	20.3	0.99	7.9
P-7	11.9	35.8	52.3	2.54	7.6
P-13	90.1	6.7	3.2	0.55	5.8

TABLE II Some physical characteristics of the soil columns

Soil	*P-1*	*P-2*	*P-7*	*P-13*
Dry Bulk Density (g/cm^3)	1.010	1.094	1.010	1.389
Particle Density (g/cm^3)	2.465	2.567	2.437	2.619
Porosity	0.410	0.426	0.414	0.530
One Pore Volume	194.8	202.4	196.7	251.9
Water Flow (cm^3/h)	11.5	49.3	14.7	116.4
Soil Water Content (%)	28.20	25.32	31.31	16.46

terbacil solution (20 mL) in 0.01 M $CaCl_2$ for 24 hours; it has been previously checked this time long enough to reach the equilibrium and no degradation of terbacil was detected. The adsorbed terbacil was calculated from the difference between concentrations in the aqueous phase before and after interaction with soil. The concentrations were measured by liquid chromatography according to a method previously developed by us for this purpose[21].

Desorption was measured after adsorption from the initial adsorption concentration of 24 μM using the consecutive dilution method. After the adsorption soil suspension was centrifuged and 10 mL of the supernatant solution were replaced by 10 mL of 0.01 M $CaCl_2$ solution. The soil was resuspended, shaken for 24 hours, centrifuged and terbacil equilibrium concentration determined in the supernatant, as in the adsorption test. This desorption procedure was conducted four times.

Column Setup and Characterization

Methacrylate cylinders were used to hold the soil columns. Preliminary experiments determined that the cylinders and others pieces do not adsorb herbicide or it was negligible. Columns 30 cm long × 5.5 cm i.d. were constructed of 6 segments, each 5 cm long, with silicone adhesive sealant, in such a way that a small portion of silicone ring remained inside the column each 5 cm to prevent preferential movement of water and chemical down the walls. Finally, a Büchner funnel was glued to the bottom of each column.

The lowest 5 cm over the Büchner funnel were filled with glass wool and coarse quartz sand to retain the soil. After that the soils were added to the columns in portions (between 60 and 80 g dry soil each) in order to uniformly pack the soil columns up to a depth of 20 cm. Bulk densities (ρ) of the soil columns resulted ranging from 1.010 to 1.389 g/cm^3 (Table II). The particle density (Table II) of the soils were measured by the helium pycnometer method.

Leaching Experiment

The upper 10 g of soil from each column were removed and mixed with 1.00 mg of terbacil in approximately 2.5 ml of methanol, after that 10 ml of water were added and equilibrated during 24 hours at room temperature in the dark. A separate study showed that no herbicide loss occurs during this process. The soil was then returned to the column which at the same time had been saturated with water (0.01 M $CaCl_2$) and allowed to drain for 24 hours. Finally, a 3 cm layer of coarse quartz sand was placed on the top covering the soil surface of each column to prevent soil disturbance during the water application and water evaporation and terbacil volatilization from the top of the columns.

The water (0.01 M $CaCl_2$) was added on the top of the column and allowed to percolate through the soil by gravity in saturated/insaturated non-continuous flow conditions. It was done with a daily application of 25 cm^3 (13 mm) all at once, during a period of 11 days; after that, daily 50 cm^3 (26 mm) until the end of the test. Several times in the course of the experiment the water outflow (Jw) througth the soil was determined from the column cross-sectional area by measuring in a graduated cylinder the volumetric outflow rate. The leachates were daily collected and an aliquot from each of them was analyzed by the HPLC method mentioned above[21]. Experiments were conducted at room temperature (22°C) and in triplicate.

After no terbacil was any longer detected in the leachates, the columns were allowed to drain for 36 hours, and the 5 cm column segments were then carefully disassembled and the corresponding soil layer was withdrawn. Water content of soil (θ) was determined by oven-drying 20 g samples at 110°C until constant weight. The rest of each soil fractions was mixed thoroughly, placed into plastic bags, labeled and sealed. Samples not analyzed immediately were stored at -5°C. The soils were extracted according to a method previously developed by us and which guarantees a terbacil recovery greater than 95%. The solvent used is methanol: water 60:40 v/v. In separate columns terbacil content in the soils were determined after a cumulative leaching of 275 and 450 cm^3 of eluent. Thus, we achieved a terbacil leachate curve and two different terbacil distributions through the column depth for each soil type. From the depth residue distribution a mobility index (M.I.) was calculated according to Weber et al. 1993[22].

RESULTS AND DISCUSSION

Adsorption/Desorption

The adsorption isotherm data are shown in Figure 1 being this process described by the Freundlich equation:

$$Cs = K_F \cdot Ce^{n_F} \qquad (1)$$

where K_F and n_F are constants and Cs and Ce are adsorbed (µmol Kg^{1}) and solution (µmol L^{-1}) concentrations, respectively. The values of the Freundlich adsorption constants K_F and n_F were obtained using a least-squares fit to the linearized form of the equation [1]. These values are summarized in Table III.[4]

The K_F constant is the value of Cs when Ce is 1, and it is considered as a measure of the relative sorption capacity. The n_F value in the Freundlich equation is an index of linearity of the isotherm and the obtained values of this index are very close to unity, the lowest one corresponding to the P-13 soil (Table III). Since Eq. [1] for $n_F = 1$ resulted in the linear adsorption equation:

$$Cs = K_d \cdot Ce \qquad (2)$$

where K_d is a distribution coefficient, the adsorption isotherms data were fitted to Eq. [2] and the computed values for K_d are included in Table III.

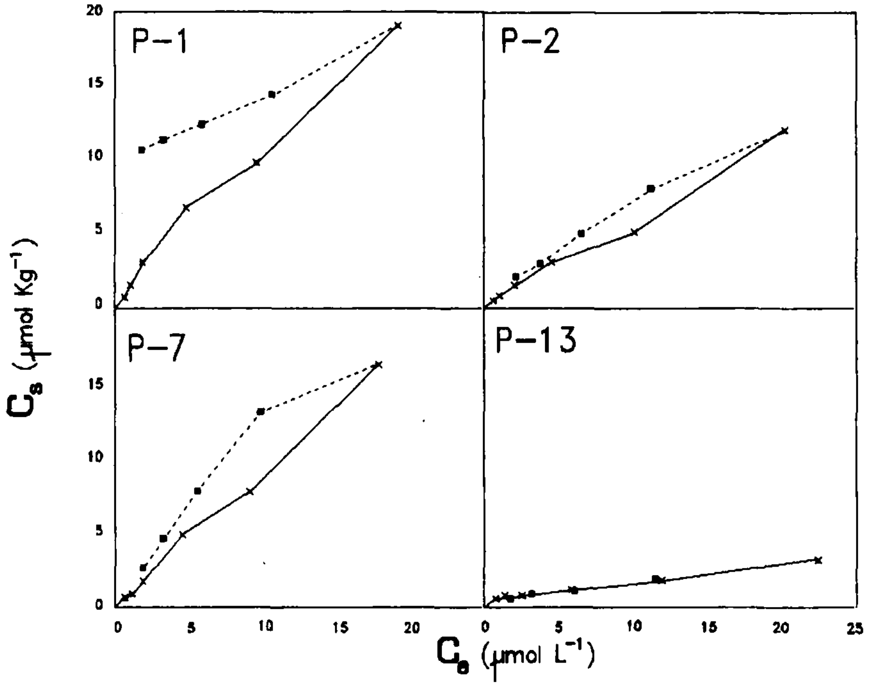


FIGURE 1 Terbacil adsorption (cross, solid line) and desorption (full square, dotted line) isotherms in the soils.

TABLE III Freundlich adsorption (K_F,n_F) and desorption ($K_{F,d}$,$n_{F,d}$) constants, distribution coefficients (K_d) and fitting coefficients (r^2)

Soil	K_F	n	r^2	K_d	r^2	$K_{F,d}$	$n_{F,d}$	r^2
P-1	1.085	1.04	0.9455	1.038	0.9745	8.736	0.23	0.8565
P-2	0.804	0.87	0.9955	0.584	0.9894	0.799	0.92	0.9968
P-7	0.595	1.19	0.9832	0.898	0.9914	1.566	0.87	0.9744
P-13	0.248	0.75	0.9858	0.129	0.9841	0.153	0.96	0.9665

The K_F values of terbacil indicated very weak adsorption as compared with other herbicides studied in these same soils[12,13]. In our experimental isotherms, the K_F coefficient is the amount of adsorbed terbacil when the equilibrium concentration is 1 μM which corresponds to lowest measured data (Figure 1). Thereafter we will use the distribution coefficient K_d as a measure of the soil adsorption capacity as representing the whole range of experimental data. The K_d values show (Table III) the highest sorption in soils P-1 and P-7, having the highest content in organic matter (OM) and clay and the lowest sorption corresponds to P-13 having the lowest OM and clay contents. However P-7 having the highest organic matter and clay contents did not show the highest distribution coefficient. A parallel study with 19 soil samples belonging to the same region showed that terbacil sorption depended on OM/illite+smectite ratio, being controlled by OM when this ratio is higher than 0.0420, suggesting a combined contribution of these two soil components. The soil clay fraction has been found to be a controling sorption factor for diverse polar pesticides, specially in soils with low organic matter content.[8–13]

Desorption isotherms, which provide information on the release of sorbed molecules, are shown in Figure 1 and they develop the non-singularity of adsorption/desorption process except in the case of P-13. P-1, P-7 and P-2 showed hysteresis, cycles decreasing in that order, which indicate some irreversibility in the adsorption process. The existence of hysteresis cycles is of great importance for transport phenomena because adsorption/desorption controls the terbacil available for participation in these processes. As a general rule, for equal adsorption, a higher hysteresis leads to a lower mobility.[24] However, sometimes part of this hysteresis could be due to experimental errors associated with desorption procedure and to biodegradation losses.[25] The desorption data were fitted to the Freundlich Eq. 1 and the corresponding parameters K_{Fd} and n_{Fd} are summarized in Table III.

Hydraulic Properties of the Soils

Herbicide transport can not be separated from water movement; therefore, it was necessary to adequately define some soil hydraulic properties. Important parameters are water outflow (Jw) and water soil content (θ). Although Jw has not a constant value throughout the day, we can considere it constant until 80% of the water added was recuperated as leachate. Daily average of Jw within the replicates remained relatively constant in the course of the experiment showing that the soil columns keep their hydraulic properties during the experiment and also that the soils were equally packed.

The average daily values of Jw differed greatly from one soil to another, being the minimun for P-1 (11.5 $cm^3 h^{-1}$) and the maximun for P-13 (116.4 $cm^3 h^{-1}$), although the amount of water daily applied to the columns were the same 25 (first 10 days) and 50 ml (from 11th day). The water flow were closely related to the texture of the soils, increasing as the sand proportion increases (Table I and II).

Water contents were very similar between replicates and water profiles were different from a soil to other as shown in Figure 2. The water contents of the soils (Table II) were also directly related to their clay content (Table I).

Mobility

The concentration leachate curves obtained from daily analyzed leachates and the cumulative leachate losses obtained in the experimental soil columns are illustrated in Figure 3 a and b respectively. The concentration vs. cumulative water applied plots show well-defined single peaks or maximum which differ in their residence times and in their shape for the four soils studied. The appearing of the terbacil maximum concentration (peak) increases from 200 ml (8 days)

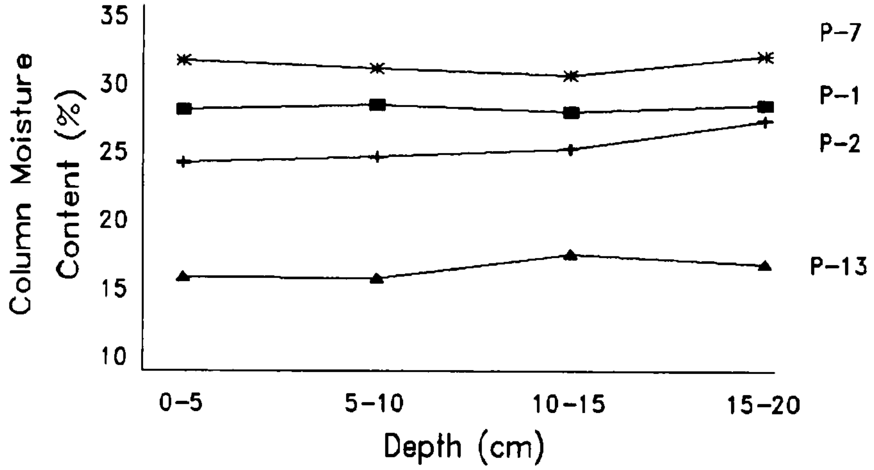


FIGURE 2 Moisture contents of the four soil columns at different depth.

for P-13, 350 ml (12 days) for P-2, 400 ml (13 days) for P-1 and 500 ml (14 days). Effluent terbacil concentrations decrease rapidly after the solute front or maximum reached the column outlet in the P-2 and P-13 soils, with concentrations approaching zero after 1575 and 975 cm^3 of cumulative water applied, respectively. Terbacil concentration leachate curves of soils P-1 and P-7 exhibit tails and also longer residence times and water volumes are needed up to no longer terbacil was detected in the leachates. These curves suggest the mobility order: P-13 > P-2 > P-1 > P-7. This order is the same as the K_d increase (Table III) except that P-1 and P-7 are in an inverse order.

Transport models commonly include the adsorption process by assuming equilibrium conditions between the solution and adsorbed phases and describing the relationship with a linear or Freundlich-type equation. Thus, adsorption can be incorporated into the classical convective-dispersive equation[23] for chemical transport in the form of a dimensionless equation:

$$R_{cal} = 1 + \frac{\rho \cdot K_d}{\theta}$$

where ρ is the bulk density of the soil, θ is the volumetric water content corresponding to that soil water which is assumed to be actively participating in solute transport, and $\rho\ K_d/\theta$, represents the apparent increase in pore volume resulting from the adsorption process. The experimental distribution coefficient K_d (Table III) was used to calculate R_{cal} for terbacil movement to obtain a quantitative expression of the extent to which the terbacil peak would be retarded by adsorption relative to water movement. The results listed in Table IV show that terbacil movement appears more retarded on soil P-1 and less on P-13, being the mobility in the order P-13 > P-2 > P-7 > P-1. This mobility order is not according to that observed in the leachate concentration curves (Figure 3b), indicating that other processes besides sorption are contributing to the transport of terbacil in the soils studied.

The cumulative curves in Figure 3a showed that P-1 and P-7 reversed after 800 cm3 of water had been applied to the soil columns, in such a way that recovered terbacil in the soil leachate result in the order P-13 (100.7%) > P-2 (99.6%) > P-7 (92.4%) > P-1 (87.0%). The lowest terbacil recovery correspond to soils P-7 and P-1, showing also tails in their concentration profiles (Figure 3b) as due to the hysteresis in desorption which was found to be important in these two soils (Figure 1, Table III). However, when no more terbacil was detected in leachates, residues were determined in the columns and terbacil was not found in any soil suggesting some degradation might have occurred specially in soils P-1 and P-7[19-20]. Moreover, as terbacil is a relatively non-volatile herbicide

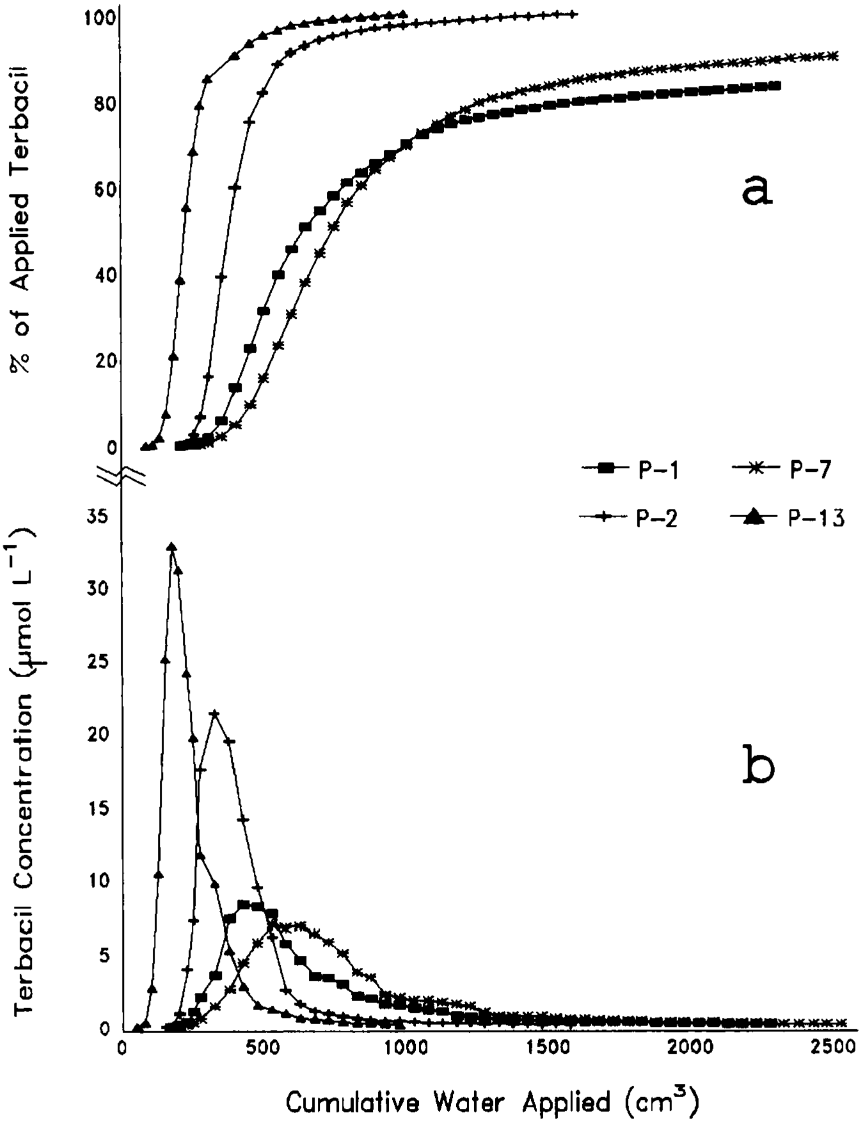


FIGURE 3 Cumulative curves of terbacil leachate losses (a) and terbacil leachate concentration curves (b).

TABLE IV Values of the retardation factors (R_{cal}) and the mobility indexes (M.I.) obtained.

Soil	R_{cal}	*M.I.*	
		275 cm^3	450 cm^3
P-1	4.74	1165	1680
P-2	3.56	1653	2175
P-7	3.93	1086	1437
P-13	2.12	2229	2243

and the volatilization process is limited by the sand layer on the column top, the loss of terbacil can not be due to this process.

The distribution profiles of terbacil in the soil after the application of two cumulative volumes of water (250 and 475 cm^3) to the soil columns are shown in Figure 4, expressed as the fraction of herbicide present at each depth. According to Weber et al. (1993)26 a herbicide mobility index (M.I.) was calculated for each soil column using the equation:

$$M.I. = \sum_{i=1}^{5} D \cdot F$$

where D is the mean depth of each soil layer, in cm; and F is the fraction of herbicide present at each layer normalized to 100% recovered for each column. Note that lost terbacil in leachates was considered as present in a column segment below the soil column and having the same length. The calculated M.I. (Table IV) values were in the following order: P-13 > P-2 > P-1 > P-7 both when 275 as 475 cm^3 were added, being this mobility order in agreement with that observed in the elution curve profiles (Figure 3b).

The discrepancy between the experimental mobility (M.I. and Figure 3a and b) and that calculated from the retardation factors (R_{cal}) is due to the influence of some soil parameters in the sorption (adsorption/desorption) and degradation processes behavior during the leaching experiment. This suggestion seems to be confirmed by the linear regression analyses where the terbacil mobility (M.I.) at 275 cm^3 water applied in the four soils was found highly and inversely correlated with the clay content ($r = -0.986$, significant at $\alpha = 0.02$ level) and with the organic matter content ($r = -0.976$, $\alpha = 0.05$) and directly related to Jw ($r = 0.987$, $\alpha = 0.02$). Although Jw was not constant in our experiment, it is a measure of the time that water is moving through the soil column and hence it influences in the terbacil dynamic/static sorption process, even in the terbacil degradation occurring in soils. Terbacil distribution on soil after a cumulative irrigation of 450 cm^3 originates a M.I. values with similar correlations as above but with lower significance.

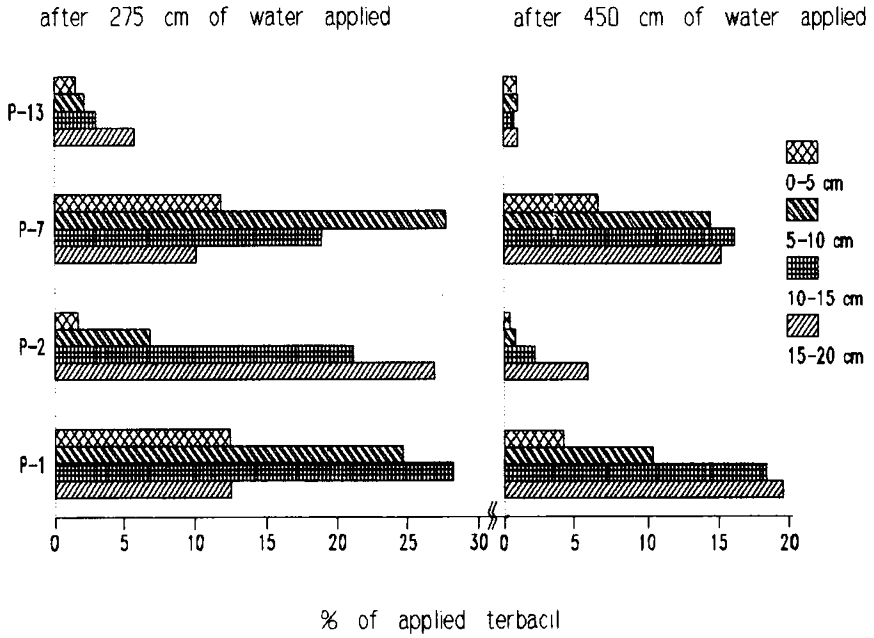


FIGURE 4 Terbacil distribution as a function of column depth in the selected soils after application of 250 and 475 ml of water.

CONCLUSIONS

The present results on adsorption/desorption, leaching and residue distribution in the four selected soils showed a combined contribution of the sorption (adsortion/desorption) and degradation processes in the mobility of the terbacil in soils. The simultaneous influence of some soil components such as clay and organic matter content and the soil property of water flow allowed to pass by the soils, which in its turn depends of the soil texture, is also revealed. According to these results terbacil mobility decreases as soil clay and organic matter contents increase.

Acknowledgements

This work has been supported by the projects: CICYT AMB93-0081 and AMB96-445-C02-02 and EU EV5V-CT94-0470.

References

[1] A. M. A. van der Linden, in: *Environmental Behaviour of Pesticides and Regulatory Aspects* (A. Copin, G. Honins, L. Pussemier, and J. F. Salembier, eds. European Study Service, Brussels, 1994) pp 299–305.

[2] D. Barceló, *J. Chromatogr.*, **643**, 117–143 (1993).

[3] J. B. Weber, L. R. Swain, H. J. Strek and J. L. Sartori, in: *Research Methods in Weed Science* (N. D. Camper, ed. Southern Weed Science Society, Champaign, IL. 1980) pp 189–200.

[4] S. W. Karickhoff, *Chemosphere* **10**, 833–846 (1981).

[5] C. T. Chiou, L. J. Peters and V. H. Freed, *Science* **206**, 831–832 (1979).

[6] J. J. Hassett, and W. L. Wanwart, in *Reactions and Movement of Organic Chemicals in Soils* (B. L. Sawhney et al. eds. SSSA Special Publication 22, ASA and SSSA: Madison, WI, 1989), pp 31–44.

[7] U. Mingelgrin and Z. J. Gerstl, *J. Environ. Qual.* **12**, 1–11 (1983).

[8] J. B. Weber, D. H. Shea and S. B. Weed, *Soil Sci. Soc. Am. J.* **50**, 582–588 (1986).

[9] M. C. Hermosín, and J. Cornejo, *Soil Science*, **144**, 453–456 (1987).

[10] I. Roldan, M. C. Hermosín and J. Cornejo, *Sci. Total Environ.* **132**, 217–228 (1993).

[11] M. C. Hermosín and J. Cornejo, in: *Environmental Behaviour of Pesticides and Regulatory Aspects* (A. Copin, G. Honins, L. Pussemier, and J. F. Salembier, eds. European Study Service, Brussels, pp 206–207 (1994).

[12] L. Cox, M. C. Hermosin and J. Cornejo, *Intern. J. Environ. Anal. Chem.* **58**, 305–314 (1995).

[13] L. Cox, M. C. Hermosin and J. Cornejo, *Chemosphere* **32**, 1391–1400 (1996).

[14] C. S. Helling and B. C. Turner, *Science* **162**, 562–563 (1968).

[15] R. C. Rhodes, I. J. Belasco and H. L. Pease, *J. Agric. Food Chem.* **18**, 524–528 (1970).

[16] G., Baluja, M. J. Gonzalez, M. C. Rico, and L. M. Hernandez, *Bull. Environ. Contam. Toxicol.* **35**, 482–486 (1985).

[17] J., Albaiges, J., Algaba, P. Arammbarri, F. Cabrera, G. Baluja, L. M. Hernandez and J. Castroviejo, *Sci. Total Environ.* **63**, 13–28 (1987).

[18] C. R. Worthing and R. J. Hance, In *The Pesticide Manual*, BCPC, Farham, UK, pp. 794 (1991).

[19] D. C. Wolf and J. P. Martin, *Soil Sci. Soc. Am. Proc.* **38**, 921–925 (1974).

[20] R. L. Zimdahl, V. H. Freed, M. L. Montgomery and W. R. Furtick, *Weed Res.* **10**, 18–26 (1970).

[21] A. Mora, M. C. Hermosín and J. Cornejo, *Fresenius Environ. Bull.* **3**, 679–684 (1994).

[22] H. J. Weber, Strek and J. L. Sartori, *Pestic. Sci.* **39**, 39–46 (1993).

[23] A. Mora, M. C. Hermosín and J. Cornejo, In *Pesticides in Soil Environment* Abstracts, Stradford-upon-Avon, HRI, Wellesbourne, pp. 73–74 (1996).

[24] C. R. Leake and E. W. Gatzweiler, in: *Pesticide Movement to Water* (A. Walker et al. eds. BCPC Monograph No 62. UK, 1995).

[25] W. C. Koskinen and H. H. Cheng, *J. Environ. Qual.* **12**, 325–330 (1983).

[26] J. A. Gardiner, R. C. Rhodes, J. B. Adams Jr and E. J. Soboczenski, *J. Agric. Food Chem.* **17**, 980–986 (1969).26. J.B.

[27] M. Th. van Genuchten, J. M. Davidson and P. J. Wierenga, *Soil Sci. Soc. Am. Proc.* **38**, 29–35 (1974).