

Sorption and Leaching of Atrazine and MCPA in Natural and Peat-Amended Calcareous Soils from Spain

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The sorption and leaching of atrazine and MCPA (0.02 M CaCl₂ aqueous solution at 25 °C) by a calcareous soil from Southeastern Spain, after organic carbon (OC) amendment with a commercial peat (from 0.18% to 4.61% OC), were studied in batch and soil column experiments. Adsorption capacity (K_f) values, obtained by fitting the experimental data to the Freundlich equation, ranged from 0.24 mg kg⁻¹ for MCPA sorption on the original soil to 5.47 mg kg⁻¹ for atrazine sorption on the peat-amended soil containing 4.61% OC. The breakthrough curves obtained from the step-function soil column experiments indicated that the amount of herbicide adsorbed ranged from 17.5 mg kg⁻¹ for MCPA in the original soil to 331 mg kg⁻¹ for atrazine in the peat-amended soil containing 1.67% OC. The results obtained from the pulse experiments indicate that the mobility of MCPA is much greater than that corresponding to atrazine.

Keywords: Atrazine; MCPA; sorption; leaching; soil

INTRODUCTION

The leaching of pesticides into the groundwater from agricultural practices is receiving increasing attention. In this process, the physicochemical properties of the compounds used, as well as soil properties, play a decisive role (Sawhney and Brown, 1989). The participation of the individual factors in the possible displacement of pesticides to the groundwater can be determined fundamentally by adsorption and desorption studies using selected active agents and by percolation experiments in columns under saturated flow conditions (Hutson and Robert, 1990).

As a regional factor, the vulnerability of the groundwater has to be taken into account where geological formation has an influence on the possible contamination of groundwater by pesticides as well as texture, clay content, and content of organic carbon in the soil. It is generally accepted that adsorption of pesticides by soils is more closely related to the soil organic matter content than any other single property (Hutson and Roberts, 1990).

Correlation between sorption of pesticides and soil organic carbon content has been commonly reported (González-Pradas et al., 1992; González-Pradas et al., 1994a), but such relationships have not been usually reported for desorption and soil columns studies.

Atrazine [6-chloro-*N*²-ethyl-*N*¹-isopropyl-1,3,5-triazine-2,4-diamine] and MCPA [4-chloro-*o*-tolylxyacetic acid] are widely applied herbicides for general weed control (Tomlin, 1994). In addition, organic matter amendment of soils is a very common practice in areas of intensive horticultural production (based on plastic greenhouses) in the Almería region (Southeastern Spain),

where the native soils are of poor quality (Perez de los Cobos, 1960). So we have considered it appropriate to study the sorption–desorption and leaching processes of atrazine and MCPA by a calcareous soil from the Almería region, after organic matter amendment from 0.18% OC to 4.61% OC using a commercial peat. Peat amendment was applied to vary soil-inherent OC content since peat is generally used for organic matter amendment in this intensive horticultural production.

Taking into account the above, the main objective of this paper is to evaluate the sorption and mobility of the herbicides atrazine and MCPA in a peat-amended calcareous soil from Spain. This evaluation was carried out by studying the sorption process in batch experiments, to obtain the corresponding sorption isotherms and sorption capacities, as well as the mobility in step function and pulse column experiments, to determine the breakthrough curves and leaching of atrazine and MCPA, respectively. We compared the sorption and mobility of these herbicides by using soil samples of varied organic matter content.

MATERIALS AND METHODS

Chemicals. Analytically pure atrazine (98.0%) and MCPA (99.0%) (Riedel-de Haën, Seelze, Germany) were used as adsorbables.

Soil Samples Used as Adsorbents. The soil chosen was a calcareous soil (Camborthids) from Almería region (Southeastern Spain). Air-dried <2-mm samples were analyzed by standard methods. Soil pH was determined in a 1:2.5 soil–water suspension using a glass electrode (Jackson, 1982), organic matter content by the Walkley-Black method (Walkley and Black, 1934), clay content by the hydrometer method (Black et al., 1982), cation exchange capacity by the barium acetate method (Mehlich, 1948), and nitrogen total content by the Kjeldahl method (Jackson, 1982). The soil mineralogy was analyzed using an X-ray semiquantitative method. A more complete discussion about the characteristics of this soil is given in previous papers (Valverde-García et al., 1987; Socías-Viciano, 1990). This soil will be referred in the text as original soil, and will be labeled as T-0.

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Table 1. Characteristics of the Peat and Soils^a

sample	pH	organic carbon (%)	cation exchange capacity (mequiv/100 g)	nitrogen total content (%)
T-0	7.60 (0.03)	0.18 (0.01)	2.06 (0.15)	0.045 (0.007)
T-1	7.43 (0.02)	1.67 (0.03)	6.39 (0.15)	0.070 (0.004)
T-2	7.10 (0.04)	4.61 (0.22)	15.90 (0.99)	0.115 (0.004)
peat	2.81 (0.01)	41.10 (0.71)	161.5 (2.48)	0.770 (0.021)

Texture and Soil Mineralogy							
	sand (%)	silt (%)	clay (%)	montmorillonite (g kg ⁻¹)	illite (g kg ⁻¹)	chlorite (g kg ⁻¹)	kaolinite (g kg ⁻¹)
T-0	63.0	29.0	8.00	13.4	62.2	25.6	13.4

Elemental Analysis and Total Surface Acidity				
	C (%)	H (%)	N (%)	total surface acidity (mequiv g ⁻¹)
peat	45.99	5.67	0.77	4.28

^a Standard deviation of three replicates shown in parentheses.

The commercial peat used for the soil amendment was obtained from NAVASA S.A. (Almeria, Spain). C, H, and N contents were determined by elemental analysis; cation exchange capacity and pH (1:5 peat-water suspension) were determined as above.

Neutralization of a solution of Ba(OH)₂ by the sample was used to determine the total surface acidity of the peat. In this procedure, a 100-mg sample was mixed with 0.02 L of a 0.25 N Ba(OH)₂ solution. The suspension was flushed with N₂ to remove O₂ present. After the suspension was shaken mechanically for 24 h, the supernatant liquid was back-titrated with hydrochloric acid (Schnitzer and Gupta, 1965; Black et al., 1982).

The above-indicated properties of the original soil and peat are given in Table 1.

Soil Amendments. The organic carbon (OC) amendment using the commercial peat was carried out by thoroughly mixing, 500 g of the original soil with 20 or 60 g of peat, for 1 h. The samples of the amended soil so obtained were also analyzed by standard methods; they are labeled in the text as T-1 and T-2, respectively. The properties of the modified soils after the indicated peat treatments are also given in Table 1.

Sorption Experiments. Experimental sorption data were obtained as follows: 3 g of each soil sample were weighed into conical flasks and shaken for 24 h until equilibrated with 0.025 L of 0.02 M CaCl₂ aqueous solutions of atrazine and MCPA containing initial pesticide concentrations (C₀) ranging between 2 and 14 mg L⁻¹. The experiments were all carried out in a thermostated shaker bath at 25 °C (New Brunswick Scientific Co.). After centrifugation, the concentrations of atrazine and MCPA in the supernatant solution, C_e, were determined by high-performance liquid chromatography (HPLC) using a diode-array detector and data station (Beckman Instruments España S.A., Madrid, Spain). The mobile phase was an acetonitrile-water mixture (60:40) for atrazine, and an acetonitrile-water (0.02% H₃PO₄) mixture (60:40) for MCPA. The analysis was performed by isocratic elution on a 150 mm × 3.9 mm i.d. Waters Nova Pack bonded-phase column-C₁₈ reversed-phase particle size 4 μm (Waters Co., Milford, MA). Atrazine and MCPA were analyzed at their wavelengths of maximum absorption, 222 and 228 nm, respectively. Solvents used for HPLC analysis were obtained from Riedel-de-Haën (Germany). The atrazine and MCPA adsorbed were calculated from the difference between the initial and final solution concentrations. Blanks containing no atrazine and no MCPA and two replicates of each adsorption point were analyzed for each series of experiments.

Column Experiments. Adsorption dynamics were determined using disturbed soil columns. Soil columns were constructed of PVC tubes (300 mm long and 44.0 mm i.d.). Nylon mesh with an effective pore diameter of 60 μm was placed on the base of each column, minimizing the dead-end volume.

Four hundred grams of each soil (T-0, T-1, and T-2) were added in small increments to the tubes to minimize particle size segregation. The columns were packed to an appropriate bulk density ($\rho = 1.28, 1.22, \text{ and } 1.14 \text{ kg L}^{-1}$ for T-0, T-1, and T-2 samples, respectively). The liquid-filled pore volume (V_p) was determined as the difference between the mass of the soil in the column, after excess water has been added and drainage had effectively ceased, and the oven-dried mass of soil. The values so obtained were V_p = 0.125, 0.154, and 0.208 L for T-0, T-1, and T-2, respectively. The upper part of the column was uniformly covered with glass wool and acid-washed sand over the whole of the surface of the column to facilitate the distribution of the atrazine and MCPA solutions as well as minimize surface disturbance (Bolan et al., 1986; Garmerdinger et al., 1991; Goicolea et al., 1991).

Two types of columns experiments were carried out. One involving a step-function experiment in which an aqueous solution with a constant concentration of pesticide was passed through the soil column to obtain the corresponding breakthrough curves and related parameters. The other involving a pulse experiment in which a pulse of active ingredient was added to the top of the column, leached with a known amount of 0.02 M CaCl₂ solution, and its distribution in both the column and the leachate was measured. The objective of this experiment is to determine the mobility and leaching potential of atrazine and MCPA in the soils used. Two replicates were used for each column experiment; prior to conducting the experiments, the columns were saturated with 0.02 M CaCl₂ aqueous solution from the bottom via capillarity (Achik et al., 1988).

For the step-function experiments, a 0.02 M CaCl₂ aqueous solutions of atrazine (C_i = 24.2 mg L⁻¹) or MCPA (C_i = 26.1 mg L⁻¹) were each passed through the columns at 0.025 L h⁻¹ using a peristaltic pump. The leachates were collected in 0.25 L aliquots for atrazine and 0.025 L for MCPA, and the pesticide content (C) was analyzed as indicated above. When C equaled to C_i, a 0.02 M CaCl₂ solution was again applied to the columns to initiate desorption, and then the process was repeated. Blank columns were leached with 0.02 M CaCl₂ aqueous solution, and the dissolved organic matter was measured in the effluents by using a Total Organic Carbon Analyzer, Shimadzu 5050A (IZASA S.A., Spain).

For the pulse experiments, 50 g of the different soils were inoculated with 0.01 L of a methanol solution containing 4 mg of pesticide (dose equivalent to 26 kg ha⁻¹). This rate was required to achieve adequate surface coverage. The soils were then thoroughly mixed and air-dried (Thomas and Barks, 1991). The spiked soils samples were then added to the top of each column, which already contained 350 g of uncontaminated soil, and the columns were saturated with 0.02 M CaCl₂ solution from bottom. Next, the columns were eluted with 2.0 L of 0.02 M CaCl₂ solution by using a peristaltic pump, and the leachate was collected. The columns were then sectioned in 5-cm-deep portions; each soil fraction was dried at room temperature and homogenized. Subsamples of soil were extracted in conical flasks, placed in a shaker bath for 24 h with 25 mL of HPLC grade methanol, filtered through Whatman no. 42 paper, and analyzed by HPLC as described above. Atrazine and MCPA determination limits were 0.05 and 0.07 mg L⁻¹, respectively. The extraction efficiencies for atrazine were 90.0, 88.2, and 87.7% for T-0, T-1, and T-2 respectively and approximately 75% in T-0, T-1, and T-2 for MCPA.

RESULTS AND DISCUSSION

Sorption Experiments. Sorption isotherms of atrazine and MCPA in T-0, T-1 and T-2 are shown in Figure 1 and Figure 2. According to Giles classification (Giles et al., 1960), the experimental sorption isotherms for atrazine and MCPA show an evolution from S type for T-0 soil to L type for T-2 soil. It is also noted an increasing slope of the initial part of the curve from the T-0 to the T-1 and T-2 samples. This fact indicates an increasing affinity for atrazine and MCPA due to increased OC.

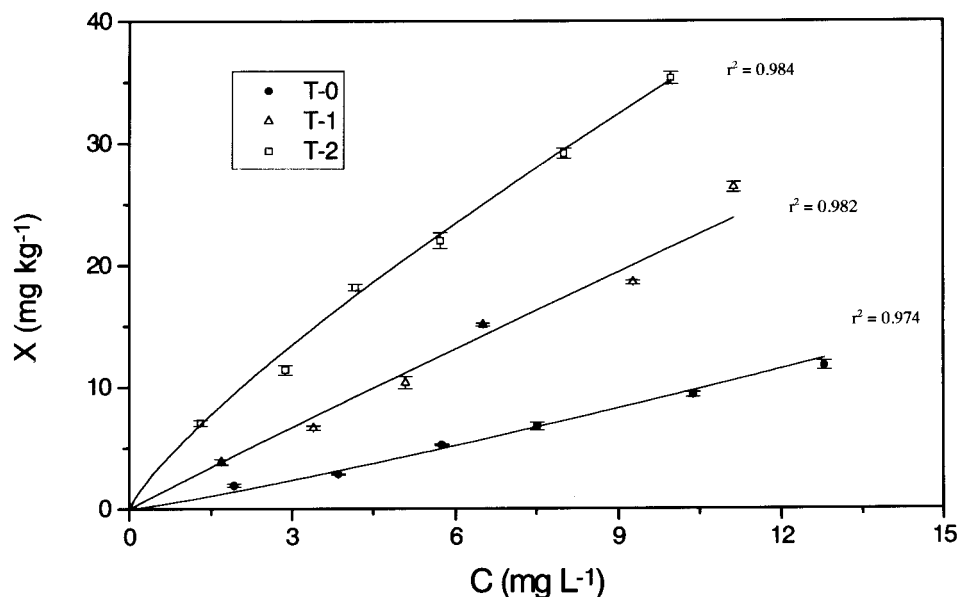


Figure 1. Sorption isotherms of atrazine on the soils.

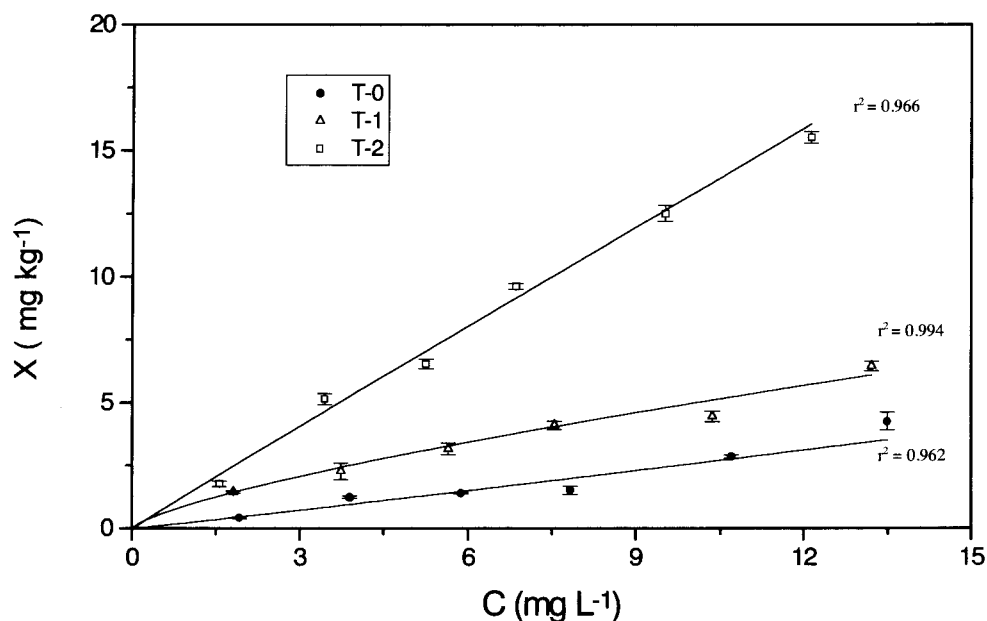


Figure 2. Sorption isotherms of MCPA on the soils.

The sorption isotherms were compared using the K_f parameters of the Freundlich's adsorption equation (Adamson, 1976). The linear form of this equation is

$$\log X = \log K_f + n \log C \quad (1)$$

where X is milligrams of pesticide sorbed per kilogram of soil, C the equilibrium solution concentration (mg L^{-1}), and K_f and n are constants that characterize the sorption capacity for the pesticide. The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1 mg L^{-1} and n is a measurement of the intensity of sorption and reflects the degree to which sorption is a function of concentration (Calvet et al., 1980; Sánchez and Sánchez, 1984). The K_f and n values were calculated from the least-squares method applied to the linear form of the Freundlich equation, and their values are summarized in Table 2. The correlation coefficients were in all cases greater than 0.98, the correlation being significant at the 0.001 probability level in all cases (degrees of freedom = 6).

Table 2. Parameter of the Freundlich Equation, K_d , and Corresponding Coefficients^a

soil	K_f (mg kg^{-1})	n	r	K_d (L kg^{-1})	K_{OC}	r
Atrazine						
T-0	0.94 (0.09)	0.97 (0.05)	0.987	0.92 (0.02)	511.0	0.997
T-1	2.24 (0.37)	0.98 (0.07)	0.991	2.23 (0.06)	133.5	0.992
T-2	5.47 (0.39)	0.80 (0.04)	0.992	3.46 (0.11)	75.0	0.995
MCPA						
T-0	0.24 (0.06)	1.05 (0.02)	0.981	0.28 (0.03)	155.5	0.983
T-1	0.90 (0.15)	0.75 (0.08)	0.997	0.48 (0.02)	28.7	0.989
T-2	2.21 (0.16)	0.75 (0.05)	0.983	1.24 (0.02)	26.9	0.994

^a Standard errors shown in parentheses. Abbreviations: K_f , Freundlich coefficient; n , Freundlich parameter related to linearity of the sorption; r , correlation coefficient; K_d , distribution coefficient; K_{OC} , organic carbon distribution coefficient.

As can be seen from Table 2, the K_f values ranged between 0.94 mg kg^{-1} for the T-0 sample and 5.47 mg kg^{-1} for T-2 sample, for atrazine, and between 0.24 mg kg^{-1} for T-0 sample and 2.21 mg kg^{-1} for T-2 sample

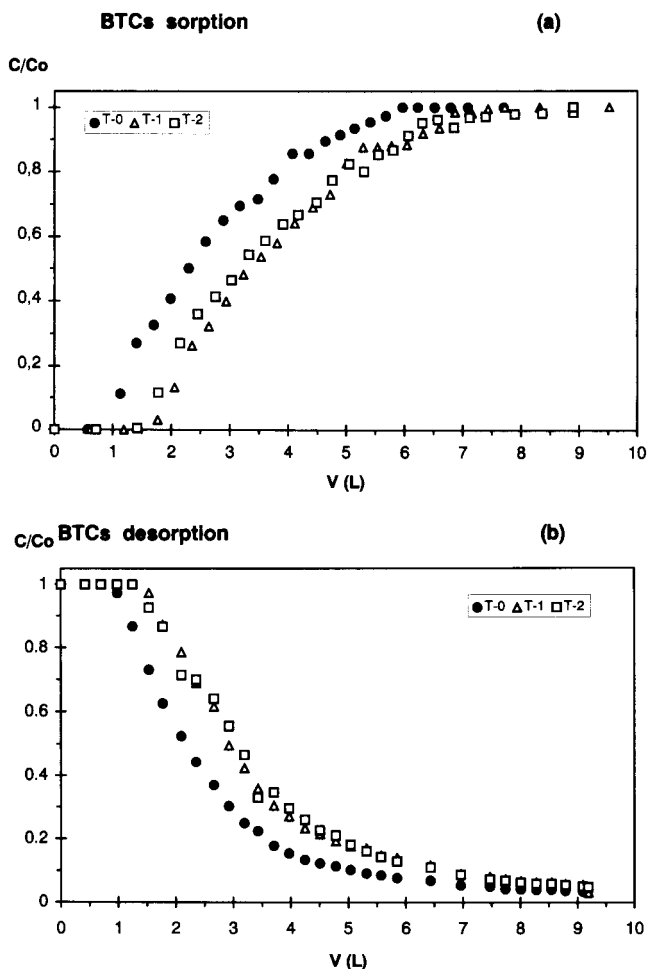


Figure 3. Breakthrough curves of atrazine obtained from the step-function-type experiments: (a) sorption and (b) desorption.

for MCPA. In both cases the increasing order of the K_f values are T-0 < T-1 < T-2.

This variation order of K_f values is according to the increasing organic matter content of the soil samples (0.18%, 1.67%, and 4.61% OC for T-0, T-1, and T-2, respectively). Similar results have been obtained when the calcareous soil was amended with humic acid; that is, the higher organic matter content, the higher sorption capacity (González-Pradas et al., 1994a).

In Table 2 also appear the K_d values which have been calculated from the fit of the experimental sorption isotherms ($X = K_d C$). From K_d and the organic matter content of the soil samples, the $K_{O.C.}$ constants were calculated for the herbicides and the three soils studied [$K_{O.C.} = (K_d/\% \text{OC})100$]. The average of the values were 239.8 L kg⁻¹ for atrazine and 70.4 L kg⁻¹ for MCPA which revealed higher sorption of atrazine than MCPA in these soils. This fact suggests that atrazine has a higher potential sorption than MCPA on this type of soils (Madhun et al., 1986a).

Column Experiments. Breakthrough curves (BTCs) for the step-function-type experiments are shown in Figure 3 for atrazine and in Figure 4 for MCPA.

The amounts of pesticide adsorbed (X_C) or desorbed (X_B) during each experiment were calculated by measuring the area above the experimental curve [$C = f(V)$], where C is the concentration of pesticide in the eluent fractions and V is the volume of solution passed through the column. These data are given—together with the

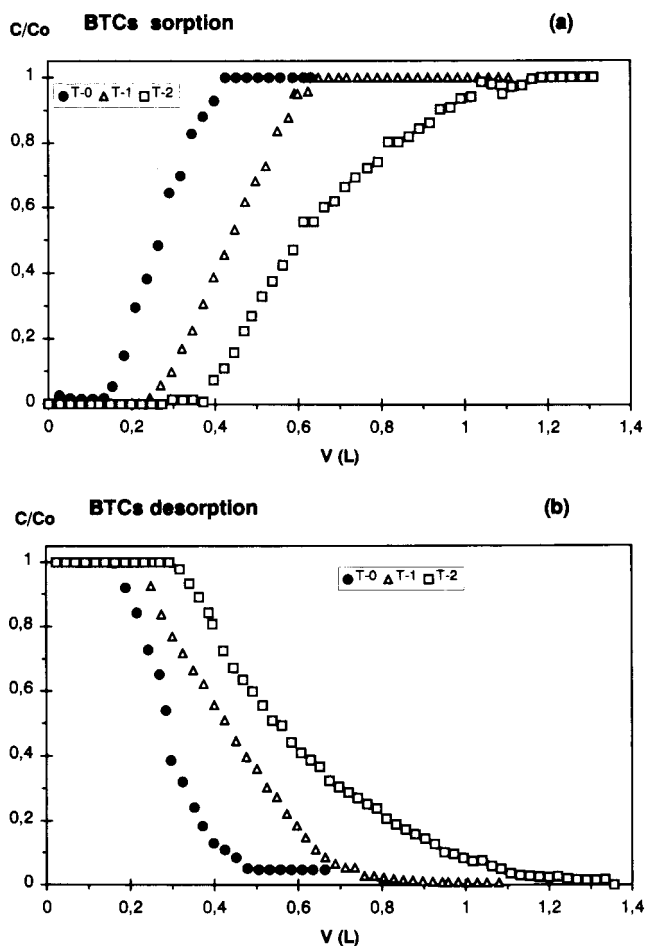


Figure 4. Breakthrough curves of MCPA obtained from the step-function-type experiments: (a) sorption and (b) desorption.

breakthrough volume (V_B) and percentages of atrazine and MCPA desorbed—in Table 3.

As can be seen from Table 3, the V_B values corresponding to atrazine range between 0.710 L for the T-0 soil column and 1.768 L for the T-1 soil column, V_B value for T-0 soil being intermediate between those obtained for the other soils and slightly close to the obtained for the T-2 soil. The values of the amount of atrazine retained (X_C) range between 165.9 mg kg⁻¹ for T-0 soil column to 331.3 mg kg⁻¹ for T-1 soil column, showing the next variation order T-0 < T-2 < T-1.

The retention data for column experiments reveal an unexpected behavior compared to the retention data obtained from the sorption isotherms: the amount of atrazine adsorbed in T-1 soil column is higher than the amount adsorbed in T-2 soil column. This fact may be due to the effect of dissolved organic matter on the atrazine mobility in these conditions. This could be explained considering the nature of the herbicide which would bind to the organic matter by means of a hydrophobic mechanism, then moving through the column together with the dissolved fraction of the organic matter (Lee and Farmer, 1989; Khan and Thompson, 1990; Barriuso et al., 1992a). This is also in accordance with the V_B values obtained which are less for T-2 soil column than for T-1 soil column. The results obtained from measurements of the dissolved organic matter (DOM) in the column effluents confirm this fact; that is, DOM was detected in all eluent fractions for T-2 soil column (from 250 mg L⁻¹ for the first fraction

Table 3. Amounts of Pesticide Adsorbed (X_C) and Desorbed (X_D) Obtained from the BTCs^a and Related Parameters

parameter	atrazine			MCPA		
	T-0	T-1	T-2	T-0	T-1	T-2
X_C (mg kg ⁻¹)	165.9 (6.5)	331.3 (6.2)	228.3 (5.2)	17.5 (0.4)	28.4 (0.6)	42.0 (0.7)
X_D (mg kg ⁻¹)	148.8 (2.7)	200.5 (6.0)	180.3 (4.7)	17.3 (0.3)	27.6 (0.2)	38.3 (0.4)
V_B (L)	1.125 (0.018)	1.768 (0.022)	0.710 (0.031)	0.026 (0.002)	0.217 (0.015)	0.297 (0.011)
V_C (L)	5.959 (0.082)	7.717 (0.058)	8.893 (0.080)	0.425 (0.007)	0.649 (0.020)	1.186 (0.031)
% desorbed	89.66 (1.50)	60.53 (1.91)	78.98 (1.61)	99.02 (0.28)	97.35 (0.19)	91.31 (0.20)
Q (mg)	144.2 (4.37)	186.8 (9.57)	215.2 (7.31)	11.09 (0.28)	16.94 (0.25)	30.95 (0.35)

^a Standard deviation for three replicates shown in parentheses. Abbreviations: X_C , amount of pesticide adsorbed; X_D , amount of pesticide desorbed; V_B , breakthrough volume; V_C , volume passed through the columns to reach the initial concentration (C_i) in the eluent; $Q = C_i V_C$.

up to 70 mg L⁻¹ for the 27th one), only detected in the first six fractions for T-1 soil column (60 mg L⁻¹ – 10 mg L⁻¹), and in no appreciable amount in T-0 soil column eluents.

As can also be seen from Table 3, the V_B values corresponding to MCPA range from 0.026 L for the T-0 soil column to 0.297 L for the T-2 one, the amount of MCPA retained increasing from 17.5 mg kg⁻¹ for T-0 soil column to 42.0 mg kg⁻¹ for T-2 soil column; in other words, the higher organic matter content in soil, the higher V_B and the higher amount of MCPA retained; these retention data being in accordance with those obtained from the sorption isotherms.

The comparison of the sorption parameters obtained from the sorption isotherms (K_f and K_d) as well as from the BTC (X_C), clearly showed that the data corresponding to atrazine are higher than those corresponding to MCPA. This difference could be probably due to the following factors: (i) MCPA has a higher water solubility than atrazine (825 mg L⁻¹ for MCPA and 30 mg L⁻¹ for atrazine) and (ii) the K_{OW} value for MCPA is smaller than that corresponding to atrazine (12.0 and 123.0 for MCPA and atrazine, respectively) (Tomlin, 1994); moreover, given that MCPA is a weakly acidic chemical ($pK_a = 3.07$) and atrazine a basic one ($pK_a = 1.7$), atrazine is more readily adsorbed onto organic matter by hydrophobic interaction (Barriuso et al., 1992b). As a result of all factors, atrazine is more strongly adsorbed than MCPA (González-Pradas et al., 1994b).

On the other hand, the amount of atrazine and MCPA adsorbed calculated from the batch experiments is less than that obtained from the column experiments. Agreement between K_f and X_C values obtained by these two quite independent measurements is not expected due to the fact that (i) the initial concentrations are different and (ii) the different chemical and physical conditions persist, particularly the different soil/solution ratios (Jamet and Hoyoux-Roche, 1988).

With regard to the results obtained from desorption experiments (Figures 3b and 4b), which are also shown in Table 3, it can be seen that the amount of herbicide desorbed decreases from 89.66% for T-0 soil column to 60.53% for T-1 soil column in the case of atrazine, and from 99.02% for T-0 to 91.31% for T-2 for MCPA. In both cases the same behavior is observed: the higher soil sorption capacity in dynamic conditions the less percentage of desorption obtained.

From Table 3, it is noted that the MCPA present, in all cases, higher values of desorption percentage than those obtained for atrazine. The reason could be due to the different solubility and K_{OW} parameters of these herbicides as discussed above.

The results of the pulse experiment showed that MCPA was completely leached in the three soil columns used in this study. Nevertheless, the percentage of

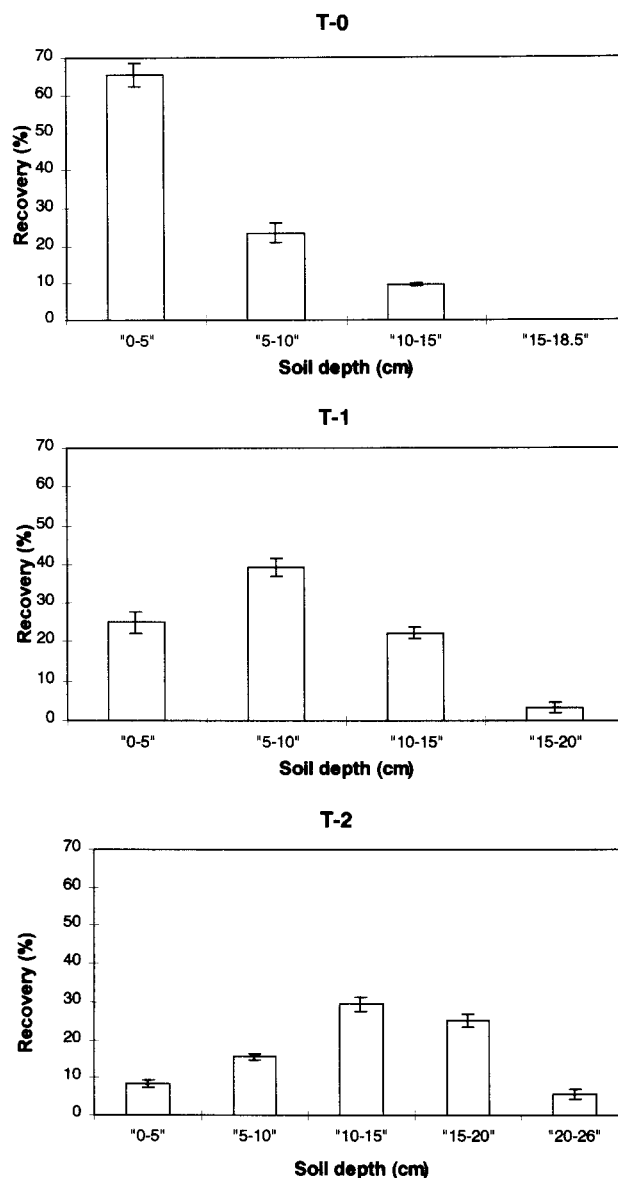


Figure 5. Distribution of atrazine in the soil columns of pulse type experiments.

herbicide collected in the leachate was 99% when 0.6, 0.75, and 0.9 L of 0.02 M CaCl₂ solution was passed for T-0, T-1, and T-2 soil columns respectively; that is, the volume of solution necessary to obtain this percentage was higher when the OC content of the soil increases.

The results of the pulse experiment for atrazine are shown in Figure 5. It can be seen that percentage of atrazine recovered in the first 5 cm of the column decreases from 65.5% for T-0 soil column to 8.5% for T-2 soil column. On the other hand the active ingredient

only reached the last 5 cm of the column for T-1 (3.25%) and T-2 soil column (5.75%). The reason could be due that atrazine binds to the dissolved organic matter, then moves through the column and reaches the deeper layers of the soil column; even atrazine was recovered from the leachate fractions for T-1 (10.4%) and T-2 (13.1%) soil columns. So, the leaching of atrazine could be enhanced by means of the dissolved soil organic matter. Similar results have also been shown by other authors in similar experiments (Stevenson, 1982; Madhun et al., 1986b; Liu and Amy, 1993).

CONCLUSIONS

Considering the above and taking into account that K_{OC} values are generally used for predicting the fate of pesticides in the environment (Hutson and Roberts, 1990), the results obtained could be useful to complete the knowledge about the fate of atrazine and MCPA, and other similar herbicides, in regions such as South-eastern Spain, in which due to the poor organic matter content, organic matter amendment of soils is a normal practice. So, if we consider the different characteristics of both herbicides studied, fundamentally the K_{OW} and the K_{OC} values, and the water solubility, MCPA would be expected to leach, as can also be deduced from the column experiments carried out. On the other hand, atrazine is not expected to leach significantly in the soils studied. Nevertheless, soil column studies such as those performed are also necessary, since if the organic matter amendment is increased, atrazine might bind to the dissolved organic matter and then move through the soil, with the possibility of reaching and contaminating the groundwater resources.

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