LEACHING PATTERNS OF PESTICIDES AS RELATED TO SORPTION AND POROSITY PROPERTIES OF SOILS

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ABSTRACT

The influence of adsorption-desorption phenomena and distribution of pore sizes on the leaching behaviour of two herbicides, thiazafluron (highly polar, nonionic) and clopyralid (anionic) in three soils has been studied. Adsorption data, obtained by batch equilibrium, were fitted to Freundlich equation and Kf values calculated. Pore size distribution of the soils was studied by mercury porosimetry. Mobility has been studied by leaching in handpacked soil columns and the retardation factor (Rf) calculated as the pore volumes required for leaching 50 % of the applied herbicide. Rf and Kf values correlated directly in the case of thiazafluron. Rf and mean pore radius were inversely related in both cases.

INTRODUCTION

The study of pesticide movement throughout the soil profile is of great interest as far as biological performance and groundwater contamination are concerned (Bowman, 1989; Beck et al., 1993). Adsorption and mobility, in general, have been shown to be inversely related (Bilkert & Rao, 1985; Beck et al., 1993). Pore size distribution, as accounting for different pore water velocity, is also related to the transport of solute in soils (Ping et al., 1975).

The aim of this study was to compare the leaching patterns of two different adsorbing herbicides in three different soils with special attention to the influence of their adsorption capacity and pore size distribution.

MATERIALS AND METHODS

The herbicide thiazafluron (1,3-dimethyl-1-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)urea) used in this study was the high purity compound supplied by Ciba-Geiby. Thiazafluron is a non-selective herbicide used for industrial weed control and active mainly through plants roots. The herbicide clopyralid (3,6-dichloropicolinic acid) used was the high purity compound supplied by DOW Chemicals. Clopyralid is an herbicide of selective use in cereal crops, rangeland, grass pastures and turf (Worthing & Hance, 1991).

Soils were sampled, air dried, sieved to pass a 2 mm mesh and stored in a refrigerator. Their physico-chemical properties were determined by the usual methodology (Hermosin et al., 1987) and are given in Table 1.

Duplicate samples of 2.5 g of each soil sample were treated with 10 ml of thiazafluron and clopyralid initial solution concentrations (Ci) 0.05, 0.1, 0.3, 0.5, 0.8, 1, 1.5 and 1.8 mM using 0.01 M $CaCl_2$ as solvent. The suspensions were shaken at 20 ± 2 ^{0}C for 24 hours and then centrifuged at 12000 r.p.m. at the same temperature. Equilibrium concentration (Ce) was determined in the supernatant by UV spectroscopy (absorption maximum, 266 nm for thiazafluron and 280 nm for clopyralid). Previously, it was checked that equilibrium was reached before 24 hours and no significant degradation occurred during this period. Differences between Ci and Ce were assumed

to be adsorbed. Desorption was measured after adsorption using the 1 mM and 1.8 initial solution concentrations. After the samples were shaken and centrifuged, 5 ml of supernatant were removed and analyzed and 5 ml of 0.01 M CaCl₂ added to the centrifuge tubes. The samples were resuspended, shaken for other 24 hours and centrifuged and equilibrium concentration in the supernatant was determined. Desorption procedure was conducted three times for each soil sample.

Table 1. Physicochemical properties of the soils.

Soil property	Soil 1	Soil 2	Soil 3
% Organic Matter	0.99	2.24	2.54
pH	7.9	7.7	7.6
% Sand	70.7	12.1	11.9
% Silt	8.9	43.6	35.8
% Clay	20.4	44.3	52.3

The distribution of pore radii of soil samples from $4{\cdot}10^4$ to 3.7 nm was determined using a Carlo Erba 2000 mercury depression and intrussion porosimeter. The measurements were carried out on soils packed in the same way as the columns used for leaching experiments.

Leaching has been studied in 30 cm long metacrilate soil columns of 5 cm inner diameter. The first ring was filled with sea sand and the last ring was filled with sea sand and glass wool. The other four rings were handpacked with the soils. Leaching experiments were run in triplicates, and for every soil a blank column (without herbicide) was used. The amount of thiazafluron and clopyralid corresponding to the maximum application rate in soils (12 Kg/Ha and 100 g/Ha, respectively) was applied to the top of the columns. 50 ml of 0.01 M CaCl₂ were applied daily. In this way, water flow rates were 0.8 ml/min for soil 1 and 0.3 ml/min for soil 2 and 3. The total amount of CaCl₂ applied was 2,5 L. Leachates containing the herbicides were collected daily, filtered and analyzed by HPLC.

RESULTS AND DISCUSSION

Thiazafluron adsorption isotherms in the soils studied are shown in Figure 1. Adsorption coefficients, K_f and n_f, obtained by fitting adsorption isotherms to Freundlich equation, are given in Table 2, together with desorption percentages after three succesive dilutions. Higher adsorption was found for soil sample 3, of higher organic matter and clay content. The last has been shown to be the most important single factor affecting the adsorption of this highly polar herbicide in soils (Cox et al., 1994-a,b). Desorption percentages indicate that only a small amount of the herbicide adsorbed is released after three desorption cycles. This has been attributed to irreversible binding of thiazafluron molecules to soil clay (Cox et al., 1994-b). The herbicide clopyralid did not adsorb on the soils studied. Adsorption studies at the µM range gave the same results. This could be due to the low pKa of the herbicide (pKa= 2.33), which indicates that at the pH of the soils (Table 1) the molecule would be in the anionic form. The low content of the soils in organic matter, which has been shown to adsorb this herbicide (Pik et al. 1977), would also contribute to these results.

Cumulative and differential mercury porosimetry curves of the three soils are shown in Figure 2. The volume of greater pores (r> 1 µm) for soil samples 1 and 2 are nearly the same, but soil 1 has a lower volume of smaller pores (r< 1µm). Pore size distribution of soil 3 is characterized

by a great volume of pores in the lower limit of pore radius studied (about 0.03 μm). Thus, the mean pore radius, r_m, for the three soil samples decreases in the order $r_m(3) < r_m(2) < r_m(1)$.

Table 2. Thiazafluron adsorption coefficients (K_f and n_f) calculated from Freundlich equation and desorption percentages (D) calculated at 1 mM and 1.8 mM thiazafluron initial solution concentrations after three desorption cycles.

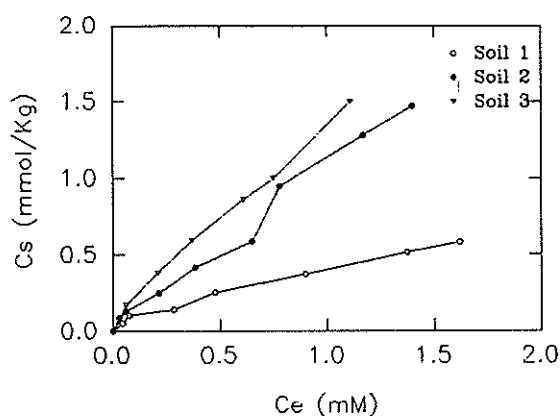| Soil	K_f	n_f	r	% D
1	0.41	0.73	0.97	14.5
2	1.00	0.76	1.00	14.5
3	1.33	0.80	1.00	10.5

Figure 1. Thiazafluron adsorption isotherms on soils studied.

Figure 3a shows thiazafluron BTCs in the three soils studied. Recovery percentages of the applied thiazafluron were 88.4, 67.7 and 65.1 % for soils 1, 2 and 3, respectively. Thiazafluron BTC in soil 1 has a higher concentration peak when compared with the curves for soils 2 and 3, indicating that thiazafluron moves more rapidly in this soil. All BTCs showed solute concentration peaks to the right of one pore volume, which result from solute adsorption (Beck et al., 1993). Although BTCs for thiazafluron were not symmetrical, a retardation factor Rf was calculated as the pore volumes required to leach 50 % of the applied herbicide (Brusseau and Rao, 1989). Rf values (Table 3) correlated directly with adsorption coefficients Kf, indicating that adsorption and mobility of thiazafluron in soils are inversely related and that the different shape of thiazafluron BTCs can be explained considering the different adsorption capacity of the soils. The assymmetry ("tailing effect") observed in the BTCs can also be attributed to the low desorption rate of thiazafluron found in batch studies, as shown in Table 2.

Figure 3b shows clopyralid BTCs in the three soils studied. Recovery percentages were higher than 80 % for the three soils. Although no adsorption of clopyralid had been detected, differences in clopyralid BTCs for the three soils studied were observed. Rf values for clopyralid (Table 3) were found around one pore volume, indicating the low influence of adsorption in leaching of this herbicide. Differences between the BTCs and Rf values for the different soils can

be explained considering the different pore size distribution of the soils. Clopyralid BTC in soil 1 showed higher concentration peak than in soils 2 and 3 and, thus, lower retardation factor Rf. Soil 1, as mentioned above, has the highest mean pore radius (r_m) and, consequently, water flow rate, which can give rise to earlier breakthrough (Van Genutchen et al., 1990). Broadening of the leaching curves observed in soils 2 and 3 during flow reflects the combined influence of diffusion and hydrodynamic dispersion processes (Biggar & Nielsen, 1962), the first more likely to occur in these heavier soils of lower mean pore radius and water flow rate. In soil 3, of a higher clay content and higher volume of small pores than the others, there would be a greater tendency for clopyralid to diffuse into stagnant or relatively non-conducting pores causing the BTCs to become more diffused and broadened and to have lower peak concentrations. The different porosity of the soils should also contribute to the extend of adsorption processes in the case of thiazafluron.
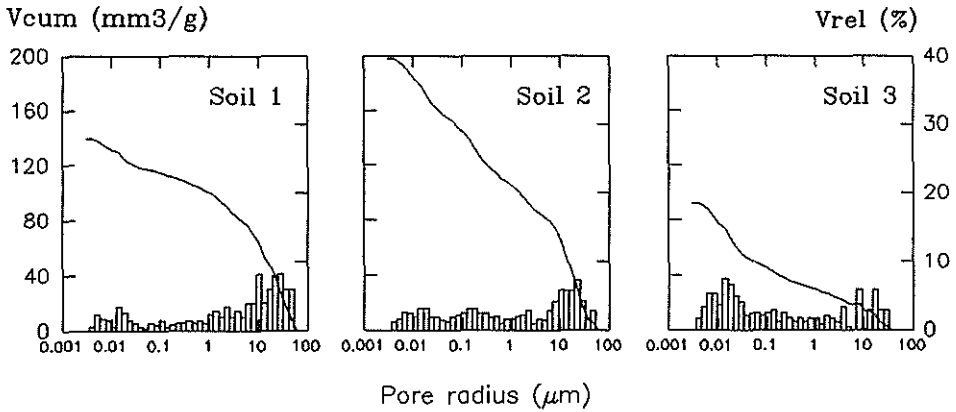

Figure 2. Differential and cumulative mercury pore volume for the three soil samples as a function of calculated pore radius.
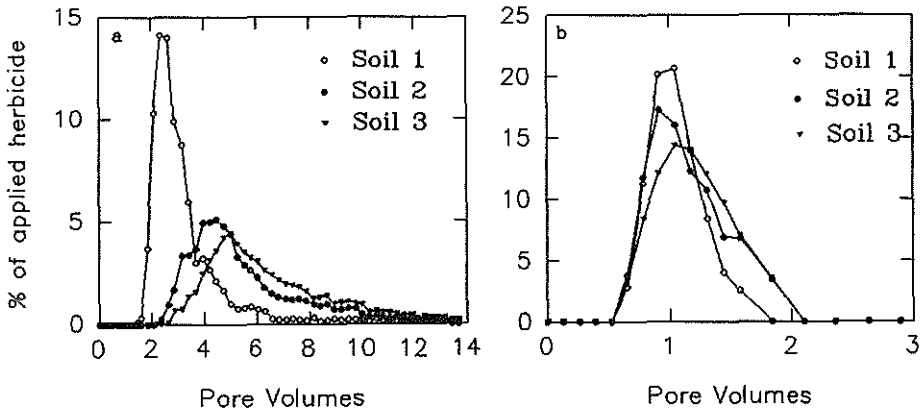

Figure 3. a) Thiazafluron BTCs. b) Clopyralid BTCs

Table 3. Retardation factors, Rf (pore volumes) calculated from thiazafluron and clopyralid BTCs.

Soil	$Rf_{Thiazafluron}$	$Rf_{Clopyralid}$
1	4.7	0.9
2	6.3	1.0
3	7.9	1.2

CONCLUSIONS

The herbicide thiazafluron moves more slowly in soils than clopyralid, due to adsorption of thiazafluron on soil clay, as confirmed by previous studies. The different porosity of the soils affects the leaching of these herbicides in soil columns, since it controls water movement. This different porosity might also affect adsorption processes by determining the permanence of the herbicide in the column in contact with soil components.

ACKNOWLEDGEMENTS

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