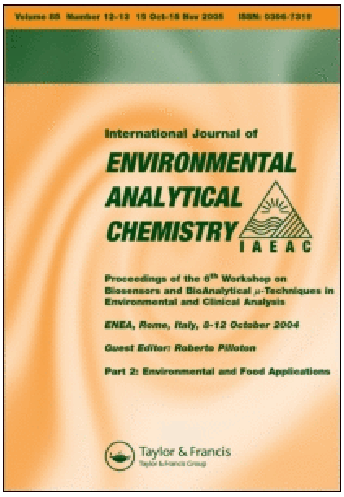

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Adsorption and Desorption of the Herbicide Thiazafluron as A Function of Soil Properties

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ADSORPTION AND DESORPTION OF THE HERBICIDE THIAZAFLURON AS A FUNCTION OF SOIL PROPERTIES

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The effect of soil composition on the adsorption and desorption of the herbicide thiazafluron [1.3-dimethyl-1-(5-trifluoromethyl-1,2,3-thiadiazol-2-yl) urea] by 20 soil samples of 13 selected soil profiles of southern Spain has been studied. The adsorption curves conformed the Freundlich equation and the values of the constants, Kf and nf, ranged from 0.13 to 4.64 and from 0.14 to 1.30, respectively. The simple and multiple regression analysis between Kf and soil properties revealed soil clay content, illite content and CEC as fundamental factors determining thiazafluron adsorption by soils. Unlike other substituted ureas, non significant correlation was found with soil organic matter. Desorption of thiazafluron was hysteretic in all cases, showing nfd values much lower than those for adsorption. Desorption kinetic indicated that this hysteresis is essentially due to irreversible adsorption, although some degradation seems also to occur. The Freundlich desorption Kfd values were closely related to the same factors as Kf: clay and illite contents and also montmorillonite content, suggesting that most of the hysteresis was due to thiazafluron irreversibly bound to soil clay mineral components.

KEY WORDS: Thiazafluron, soils, sorption isotherms.

INTRODUCTION

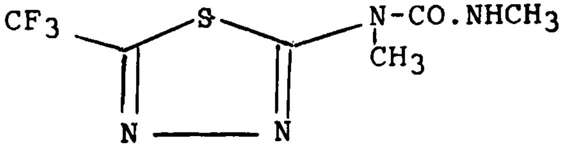
The study of adsorption-desorption phenomena of herbicides by soils is of great interest from an environmental and agricultural point of view. Herbicide adsorption affects other processes determining the final fate of these compounds in the environment (transport, degradation, volatilization, living organism uptake) and also controls the biological effectivity of the pesticide toward the target organism[1-4]. Thus, knowledge of the herbicide soil adsorption-desorption characteristics is useful in predicting mobility in soil-water systems and in making herbicide recomendations. The chemical nature of the pesticide and the characteristics of soils are the most important factors affecting adsorption-desorption behaviour. The organic matter content of soils has been emphasized as the most important factor determining the adsorption of pesticides or other organic chemicals by soils[5-10]; even an adsorption parameter based on organic carbon content (Koc) of the soils has been defined[5]. However soil clay content has been shown to be very important in pesticide-soil adsorption[11-16]. Furthermore, the mineral composition of the clay fraction appears to be fundamental in the retention of pesticides by soils[12,13,15].

Substituted urea herbicides are used in a variety of ways. At high rates, they are used as soil sterilants and at low to moderate rates as selective preemergent or postemergent herbicides in crop production[6]. In comparison with other herbicide families, substituted ureas are adsorbed by soils in low to moderate amounts[6,17-19] and generally, soil organic matter has been pointed out as the most important soil factor affecting their adsorption by soils[6,17-19]. However, a preliminary study on the distribution coefficient of thiazafluron in surface horizons of spanish soils showed the clay fraction as the most important soil property related to thiazafluron retention[20]. Chemical degradation of urea herbicides in soils has been reported[21] whereas biodegradation processes has been also shown to be important in the fate of these herbicides in soils[22].

The aim of this study was to examine the variability in the adsorption-desorption potential of the substituted urea herbicide thiazafluron [1,3-dimethyl-1-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl) urea] as a function of soil properties and to determine which are the most relevant soil characteristics related to its adsorption. For this purpose, 20 soil samples of different characteristics which correspond to 13 different soil profiles were selected.

EXPERIMENTAL

The herbicide thiazafluron is an urea derivative having an heterocyclic substituent. The thiazafluron used was the high purity compound supplied by Ciba-Geigy. This herbicide is a crystaline solid of melting point 136–137°C, v.p. 267 µPa at 20°C, M.W. 240.2 and water solubility at 20°C of 2.1 g/Kg[23]. Thiazafluron is a non-selective herbicide used for industrial weed control and active mainly through plant roots.



The 20 soil samples selected for this study are different horizons of 13 soil profiles located in southern Spain, most of them in a wide zone surrounding Doñana National Park. The soil samples were air dried at room temperature, sieved to pass a 2 mm mesh and stored in a refrigerator. Their physico-chemical properties were determined by the usual soil lab methodology[12] and the clay mineralogy by X-ray diffraction procedure on oriented specimen[12]. Physico-chemical properties, clay mineralogy and classification are given in Table 1.

Adsorption studies were performed using batch equilibration procedure. Duplicate samples of 2.5 g of soil were treated with 10 ml of thiazafluron initial solution concentrations (Ci) 0.05, 0.10, 0.30, 0.50. 1.00 and 1.80 mM. This range of thiazafluron concentration was used because in the lower range (10^{-3} to 5×10^{-2} mM) no differences were found between soil adsorption isotherms. Aqueous 0.01 M $CaCl_2$ was used as solvent in order to minimize

Table 1 Physicochemical properties, clay mineralogy (I= Illite, M= Montmorillonite and K= Kaolinite) and classification of the soils studied.

Sample	*Depth*	*Soil Type*	*pH*	*% O.M.*	*% Clay*	*% I*	*% M*	*% K*	*% Fe_2O_3*	*C.E.C.**
1	0-20	Salorthidic fluvaquent	7.5	0.83	67.7	37.2	11.5	16.9	1.07	24.1
2	120-160		7.3	0.99	62.7	34.5	11.3	10.6	1.00	18.4
3	0-20	Xerofluvent	7.6	1.62	57.0	31.9	14.2	10.8	1.11	19.6
4	50-80		7.6	0.62	32.3	16.1	4.8	11.0	0.94	18.8
5	5-20	Xerofluvent	7.7	2.24	44.3	29.2	8.0	7.1	1.17	19.2
6	70-90		7.9	0.48	29.9	17.0	7.8	5.1	0.57	10.1
7	90-110		8.1	0.40	15.6	8.9	4.1	2.6	0.51	7.6
8	5-20	Typic Rhodoxeralfs	7.9	0.99	20.4	12.4	3.5	4.5	1.40	9.0
9	30-		7.5	0.58	37.5	15.0	15.0	7.5	2.37	19.6
10	50-100	Palexeralf	5.3	0.12	24.1	19.1	0.0	5.0	1.75	5.7
11	0-30		6.6	1.30	12.4	2.6	0.0	9.8	1.63	4.2
12	115-250		5.1	0.27	17.7	3.5	0.0	14.2	1.07	3.6
13	0-30	Mollic Haploxeralf	8.1	0.86	15.0	9.0	2.2	3.7	1.00	8.5
14	0-30	Chromoxerert	7.7	1.92	49.7	14.4	24.8	9.9	1.60	21.5
15	0-25	Entic Pelloxererts	7.6	2.54	52.3	18.8	17.8	15.7	0.71	28.5
16	0-25	Typic Chromoxerert	7.8	1.68	21.6	17.3	1.1	3.2	0.58	11.9
17	0-20	Fragixeralf	7.2	0.99	22.5	11.2	7.8	3.3	0.87	11.9
18	20-50	Typic Pelloxererts	7.1	1.14	65.1	22.1	35.8	2.3	0.92	32.0
19	0-30	Fragixeralf	5.8	0.37	3.2	0.8	0.1	2.3	1.11	1.7
20	0-30	Fragixeralf	5.9	0.49	20.0	17.0	1.0	2.0	8.46	2.8

* meq/100 g

ionic strength changes and to promote floculation. The suspensions were shaken at 20 ± 2°C for 24 h in polypropylene centrifuge tubes and centrifuged at 12000 rpm at the same temperature. The supernatants were filtered through Dynagard (0<2 µm) filters and the equilibrium concentration (Ce) was determined by UV spectroscopy at 266 nm. Previously it was checked that equilibrium was reached within 24 h and no significant degradation occurred, as monitored by HPLC analysis using the following conditions: Nova-Pak-C18 column (150×3.9 mm); eluent system, 60/40 methanol:water; flow rate, 1 ml/min; wavelength, 266 nm. Differences between Ci and Ce were assumed to be adsorbed. Both methods were checked to work properly by determining 10 times the thiazafluron concentration of a standard in soil solution. Two controls or blank samples of soil with 0.01 mM $CaCl_2$ solution and thiazafluron solution in 0.01 mM $CaCl_2$ were used to correct for background effects in both methods. The linear range of thiazafluron concentration was 0.02 to 0.1 mM for UV spectroscopy and HPLC.

Desorption of thiazafluron was measured after adsorption from the initial adsorption concentration of 1.0 and 1.8 mM using the consecutive dilution method. After the adsorption samples were shaken and centrifuged, 5 ml of the supernatant solution were replaced by 5 ml of 0.01 M $CaCl_2$. The soil sample was resuspended, shaken for 24 h, centrifuged and thiazafluron equilibrium concentration determined in the supernatant, as in adsorption. This desorption procedure was conducted 3 times. The desorption kinetic was also monitored by HPLC in some soils.

Adsorption and desorption isotherms were obtained by plotting the amount of thiazafluron adsorbed (Cs, mmol/Kg) versus equilibrium concentration (Ce, mmol/l). These adsorption and desorption isotherms were fitted to the linear form of the Freundlich equation:

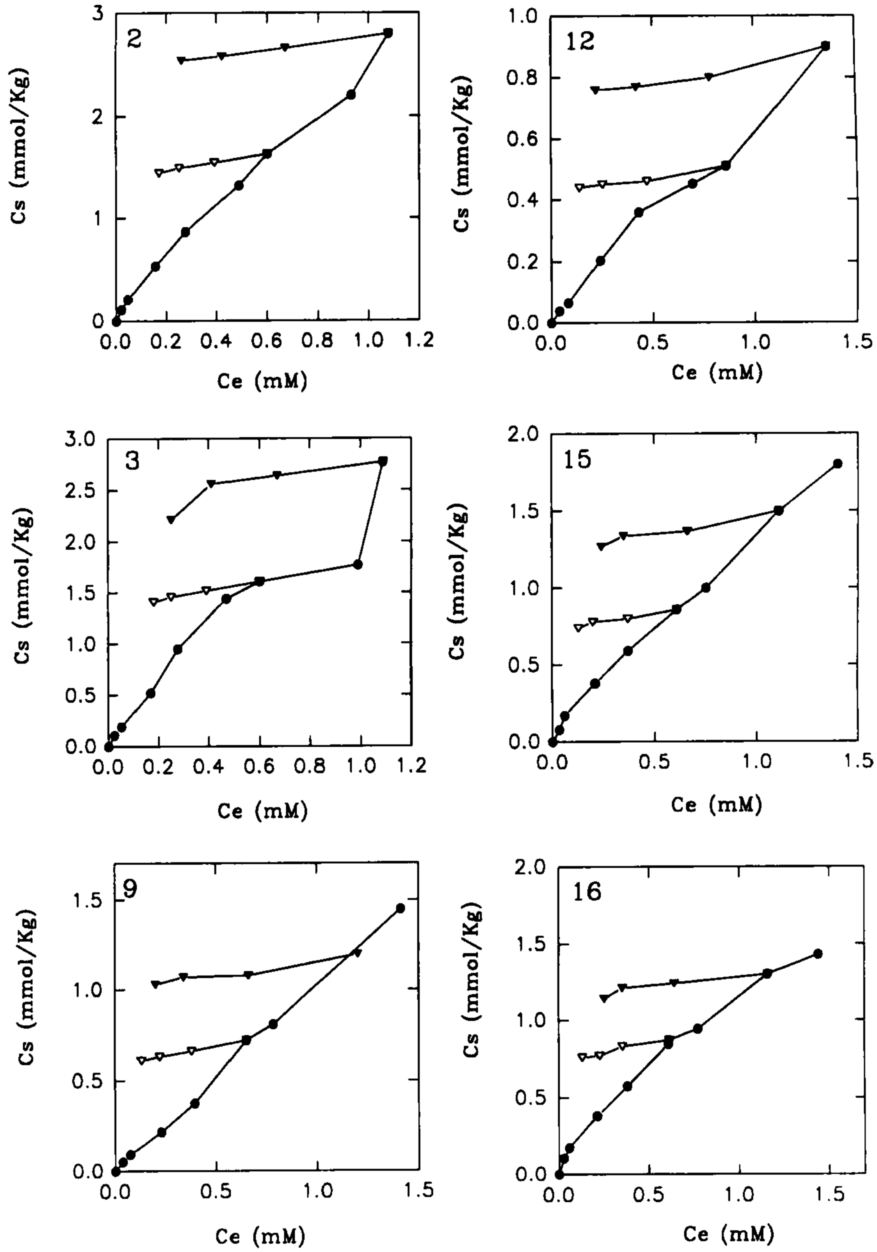


Figure 1. Adsorption and desorption isotherms for selected soil samples.

$$\log Cs = \log Kf + nf \log Ce$$

where Kf is the adsorption capacity evaluated at Ce = 1 and nf is the intensity factor, expressing the slope of the adsorption-desorption isotherm.

RESULTS AND DISCUSSION

The adsorption and desorption isotherms of thiazafluron in soils are shown in Figure 1 for some selected soil samples. Most of the adsorption isotherms showed L-type (as soil 2 and 16), although some of them displayed certain C (as soils 9 and 15) or S (as soils 3 and 12) character at higher concentrations. The diverse shape of the adsorption isotherms is indicative that not an unique mechanism is operating on thiazafluron adsorption, due to the heterogeneous nature of the soil surfaces[15]. According to Giles *et al.*[24] L-isotherms correspond to a decrease of site availability as the solution concentration increases and that adsorbing molecules do not suffer competition from the solvent molecules. Examples of systems showing this type of isotherms are those of high polar solutes and substrates[4] and this agrees with the high water solubility of thiazafluron (2.1 g/l) and with the high clay content and low organic matter content of our soils (Table 1).

Adsorption isotherms were fitted to the Freundlich equation and Kf and nf adsorption parameters were calculated for all soil samples. These parameters and the correlation coefficients for the application of the linear Freundlich equation are summarized in Table 2. From this equation, the amounts adsorbed (Cs) for a very low concentration, 1 µg/ml (0.004

Table 2 Thiazafluron adsorption parameters (Kf nd nf) obtained from Freundlich equation and correlation coefficients (r). Amount adsorbed (Cs) for 1 µg/ml thiazafluron solution concentration.

soil sample	*Kf (mmol/Kg)*	*nf*	*Cs (µmol/Kg))*	*r*
1	4.64	0.61	164.7	1.00
2	2.45	0.81	29.1	1.00
3	2.38	0.83	25.3	0.99
4	1.35	0.88	10.9	1.00
5	1.00	0.76	15.6	1.00
6	0.75	0.89	5.8	0.99
7	0.47	0.94	2.7	0.99
8	0.41	0.73	7.5	0.97
9	0.99	0.92	6.4	0.99
10	0.50	0.85	4.8	1.00
11	0.28	0.65	8.0	0.97
12	0.66	0.89	5.1	0.99
13	0.45	1.30	0.4	0.93
14	1.06	0.91	7.3	0.99
15	1.33	0.80	16.7	1.00
16	1.14	0.66	30.8	1.00
17	1.20	0.90	7.3	0.99
18	1.76	0.99	7.8	0.98
19	0.13	0.65	3.7	0.83
20	0.45	0.89	3.5	1.00

mM) was calculated and are also summarized in Table 2. The adsorption capacity values, Kf, indicate that thiazafluron is adsorbed in moderate amounts, as compared with other pesticide adsorption studies performed in our laboratory with these soils and under similar conditions[12,14,15]. This medium soil adsorptivity of thiazafluron agrees with previous reported studies of other urea herbicides[6,18,19].

Regression analysis was used to evaluate the influence of soil properties on the adsorption of thiazafluron by soils. Correlation between Cs at 1 µg/ml concentration and soil properties were used to study the influence of soil properties at low concentration level and correlation between Kf and soil properties to study the influence of soil properties at higher concentrations. Simple (r) and multiple (R) correlation coefficients were calculated and are given in Table 3. Figure 2 shows the regression lines between Kf values and clay, organic matter (OM), illite and cation exchange capacity (CEC). Soil clay and illite contents appeared to be the most important single properties affecting the retention of thiazafluron by soils at low (Cs at 1 µg/ml) and high (Kf) concentrations, although the last simple correlation coefficients were significantly much higher. Significant correlation was also found between Kf and CEC. Low correlation coefficients were found with organic matter and montmorillonite contents.

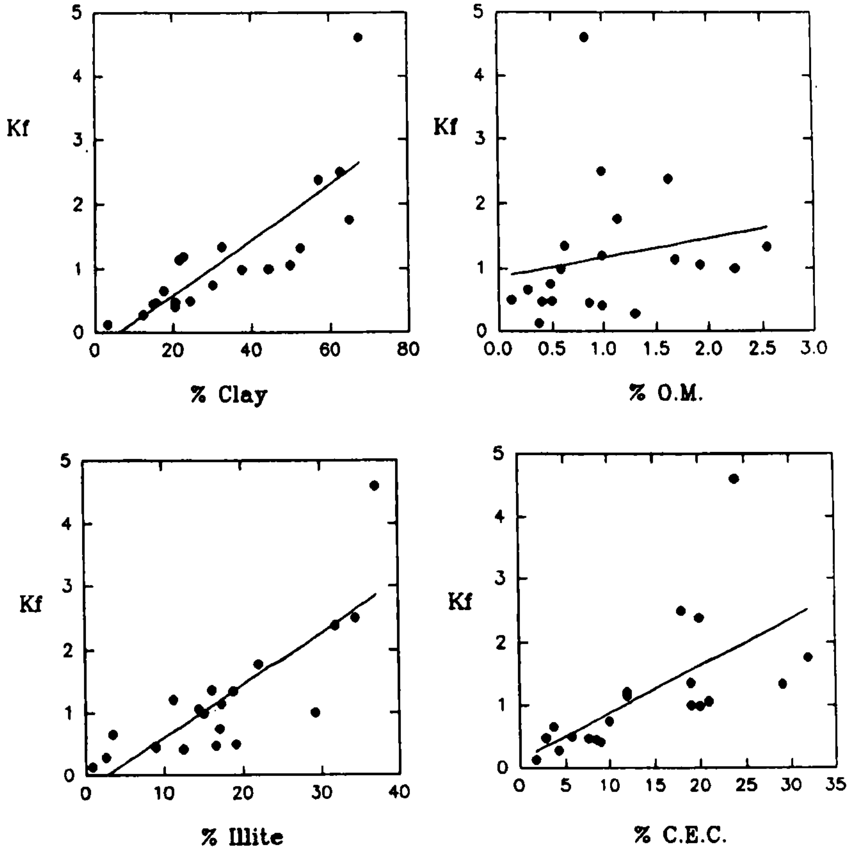


Figure 2. Regression lines between Kf and selected soil properties.

Table 3 Simple correlation coefficients (r) betweeen Cs calculated for 1 µg/ml thiazafluron solution and kf values and soil properties, simple correlation coefficients between clay and selected soil properties and multiple correlation coefficient (R) between clay and organic matter (O.M.) and Kf.

Soil properties	*Kf*	*Cs (1ppm)*	*Clay*
Clay	r= 0.81****	r=0.52**	—
Illite	r=0.81****	r=0.60***	r= 0.85****
Montmorillonite	r= 0.43*	r= 0.11	—
Ortganic matter	r= 0.44**	r= 0.07	r= 0.60***
C.E.C.	r= 0.65***	r= 0.45**	r= 0.87****
PH	r= 0.26	r= 0.28	—
Fe_2O_3	r= 0.18	r= 0.12	—
Clay and O.M.	R= 0.81****	R= 0.60***	—

**** Significant at <0.001 level
*** Significant at 0.01 to 0.001 level
** Significant at 0.05 to 0.01 level
* Significant at 0.1 to 0.05 level

These results do not agree with other studies on adsorption of substituted urea herbicides by soils[6,18,19], although most of these studies considered soils with lower clay contents and higher organic matter content than those of our soils. In relation to this, the high water solubility of thiazafluron should be noticed: organic molecules with high water solubility are more likely to be adsorbed on mineral sorbents than on organic matter[8]. Furthermore, the high clay content and low organic matter content of most of our soils (Table 1) would also contribute to the results obtained, including the high correlation between Kf and CEC as a consequence of the high correlation observed between CEC and clay content[25] (Table 3). A high multiple correlation coefficient (R) was found between Kf and soil organic matter and clay (Table 3), but this correlation does not seem to be significant since organic matter and clay contents of the soils studied are both significantly correlated and, thus, this R value could be a consequence of the correlation between these two soil properties.

Another interesting result obtained by regression analysis is the high correlation between Kf and soil illite content and the low correlation found with montmorillonite content. Montmorillonite has higher surface area and cation exchange capacity than illite and, hence, greater thiazafluron adsorption onto this mineral would be expected. This could be a consequence of the homogeneous composition of the clay fraction of the soils with little as predominant component (r = 0.85 between clay and illite contents). On the other hand, the high correlation observed between Kf values and soil illite content could also indicate that this mineral is present in these soils in a very alterated form giving rise to higher surface area and CEC than the pure mineral normally has. This was concluded by Moreno *et al.* (1980)[26] in their study on the mineralogical composition of clay in marsh soils of SW Spain. Some of the soils considered in our study are marshy soils of the lower zone of the Guadalquivir River (SW Spain) and are affected by a high salt concentration that would contributed to the mineral weathering[27,28] and, thus, to the swelling character observed in some of the illitic soils studied, specially in samples 1 and 2. The increase in significance of the correlation coefficient between Kf values and montmorillonite content (r = 0.61) when these soil samples were neglected seems to confirm this suggestion.

Table 4 Desorption parameters for thiazafluron initial solution concentration 1 and 1.8 mM (Kfd$_1$ and nfd$_1$ and Kfd$_{1.8}$ and nfd$_{1.8}$, respectively) obtained from Freundlich equation, correlation coefficients (r) and desorption percentages (D).

Sample	*Kfd1*	*nf1*	*r*	*% D*	*Kfd1.8*	*nf1.8*	*r*	*% D*
1	2.47	0.11	0.99	9.3	4.01	0.10	1.00	9.2
2	1.70	0.09	0.99	11.6	2.76	0.07	0.97	9.3
3	1.69	0.11	1.00	12.4	2.78	0.14	0.94	9.4
4	1.18	0.08	0.97	12.1	1.78	0.05	0.94	8.2
5	0.98	0.11	0.99	14.7	1.42	0.10	0.98	14.3
6	0.73	0.08	0.98	13.7	1.14	0.03	1.00	5.2
7	0.43	0.09	0.84	17.8	0.88	0.02	0.72	3.3
8	0.37	0.08	0.99	13.7	0.57	0.1	0.92	15.3
9	1.11	0.10	0.97	15.3	1.08	0.10	0.92	9.6
10	0.45	0.09	0.98	15.2	0.93	0.03	0.97	5.2
11	0.22	0.04	0.95	9.1	0.45	0.03	0.91	4.2
12	0.50	0.08	0.92	14.1	0.85	0.09	0.90	15.2
13	0.32	0.06	0.98	9.4	0.36	0.17	0.91	14.6
14	0.80	0.10	0.97	16.4	1.05	0.15	0.99	20.4
15	0.89	0.10	0.97	14.2	1.46	0.10	0.96	6.8
16	0.91	0.09	0.96	12.6	1.29	0.08	0.97	12.3
17	0.83	0.09	0.99	8.7	1.40	0.08	0.99	12.6
18	0.94	0.04	0.90	7.3	3.92	0.01	0.94	3.4
19	0.10	0.04	0.91	10.2	0.24	0.04	0.92	7.5
20	0.43	0.09	0.83	11.4	0.72	0.03	0.95	7.9

The desorption curves are shown in Figure 1 for some selected soils. As the curves shown in Figure 1, the thiazafluron desorption from all soils were found to be hysteretic, showing higher amounts of thiazafluron adsorbed as a function of the equilibrium concentration, when compared with the adsorption isotherms. Desorption isotherms were adjusted to the Freundlich equation and desorption parameters Kf$_d$ and nf$_d$ were calculated for both desorption branches and are summarized in Table 4, besides Freundlich correlation coefficients and the overall desorption percentage after the three successive dilutions. The slope of the desorption isotherms (non-adjusted isotherms, Figure 1) and nf$_d$ values (adjusted isotherms, Table 4) were in all cases much smaller than those for adsorption isotherms and similar for both desorption branches, indicating very low desorption intensity. Desorption

Table 5 Simple correlation coefficients (r) between Kfd$_1$ and Kf$_{1.8}$ and selected soil properties.

Soil properties	*Kfd$_1$*	*Kfd$_{1.8}$*
Clay	0.81****	0.87****
Illite	0.85****	0.78****
Montmorillonite	0.38*	0.63***
Organic Matter	0.41*	0.38*
C.E.C.	0.63***	0.74****
Fe_2O_3	0.19	0.12
pH	0.25	0.14

**** Significant at <0.001 level
*** Significant at 0.01 to 0.001 level
* Significant at 0.1 to 0.05 level

Table 6 Desorption percentages versus desorption equilibration time for soil sample 16.

Desorption time	16	24	32	48	72
% Desorbed	5.28	6.24	3.48	3.68	3.30

percentages also indicate that only a small amount of the herbicide adsorbed was recovered after three desorption cycles with 0.01 M $CaCl_2$ (Table 4). This could indicate that thiazafluron molecules are strongly adsorbed to soil active surfaces, preferentially to soil clay, as discussed above.

Hysteresis observed in non-volatile organic compounds in soils has been attributed mainly to three different processes which may concur[29–31]: (1) irreversible binding of the organic molecules to soil components, (2) non-attainment of the equilibrium during adsorption or desorption and (3) losses by degradation. Measurements of desorption kinetics for soil sample 16 showed that desorption percentage did not increase from 16 to 72 h of desorption equilibration time, by the contrary a small decrease was measured as shown in Table 6 which could be attributed to biodegradation. The desorption kinetic for this sample monitored by HPLC showed not only a decrease in thiazafluron desorption but also a small peak at lower retention time which area increased from 32 to 72 hours of desorption and that could be a degradation product. The lag phase (24 hours of adsorption plus 32 hours of desorption equilibration time) for this degradation product to appear suggests that could be due to biodegradation processes[31]. From these data, the hysteresis of the adsorption process seems to be due to both, irreversibility of adsorption and biodegradation.

Regression analysis between Freundlich Kf_d desorption parameters and soil properties were calculated and summarized in Table 6. This analysis rendered similar correlation coefficients than those obtained for adsorption (Table 3), corroborating that soil clay content and illite content are the most important factors affecting adsorption-desorption of thiazafluron by these soils and it could indicate that most of the hysteresis seems to be due to tightly bound herbicide molecules to clay particle surfaces. It is noticeable the great increase of significance of the correlation coefficient between Kf_d values and montmorillonite content at higher thiazafluron concentration branch, which is probably due to the herbicide interlamellar adsorption in this mineral. This interlamellar adsorption, showed for other polar organic molecules[32], could be contributing to the observed hysteresis.

CONCLUSIONS

Adsorption studies of thiazafluron by 20 soil samples showed that soil clay and illite clay content are the most important single factors affecting the retention. The altered illite of some saline soils seems to be a very active component in thiazafluron adsorption. The hysteresis observed for the desorption seems to be due mostly to the irreversible binding of the herbicide molecules to the clay particles, specially to illite and montmorillonite minerals, although some biodegradation seems to be also contributing. Results of the present work emphasizes the importance of the mineral composition of the clay fraction in pesticide adsorption.

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