Effect of Soil Properties on Adsorption and Desorption of Acifluorfen

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The adsorption and subsequent desorption of acifluorfen were investigated in five soils of various physical and chemical properties. The adsorption and desorption of acifluorfen were essentially dependent upon pH, organic carbon content, and ammonium oxalate extractable iron content of the soil but not on clay content. The data for the adsorption experiments fit the Freundlich equation and, depending on the soil, the adsorption constant K_f ranged from 0.57 to 43.10, while n varied from 0.84 to 1.04. Removal of organic matter from soil with H_2O_2 caused loss of the capacity to adsorb acifluorfen. Desorption of acifluorfen showed a hysteresis effect.

INTRODUCTION

Acifluorfen, 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, is a highly effective postemergence herbicide used in the selective control of broad-leaf weeds in soybeans (Johnson et al., 1978; Wills and McWhorter, 1981). Acifluorfen contains a carboxylic acid group whose pK_a is 3.5 (Roy et al., 1983). It is expected that acifluorfen exists as the dissociated anion in most agricultural soils since the pH of these soils usually exceeds the pK_a of the acid. Negatively charged adsorption sites were therefore not expected to contribute to the adsorption process. Recent studies on the interaction of sodium acifluorfen with montmorillonite saturated with Cu(II), Ca(II), Al(III), and Fe(III) showed that the herbicide was not adsorbed on the clays but formed carboxylate complexes with the exchangeable cations which precipitate on the outer surfaces of the clays (Pusino et al., 1991). The literature indicates that adsorption of acidic pesticides is positively related to the organic carbon content and pH of the soils (O'Connor and Anderson, 1974; Farmer and Aochi, 1974; Murray and Hall, 1989). Ruggiero et al. (1992) reported that acifluorfen was adsorbed on a humic acid extracted and purified from an Andosol soil and that adsorption was partially reversible. Since information on the behavior of acifluorfen in soil is essential in predicting its leaching potential and contamination of groundwater, we conducted a study on the adsorption and desorption of this herbicide in five soils of various physical and chemical properties.

MATERIALS AND METHODS

Adsorption. Five soils differing widely in their physicochemical characteristics (Table 1) were used in this study. Soils were collected at 0−15 cm depth, air-dried, and passed through a 2 mm sieve. Herbicide solutions were made in 0.01 N $CaCl_2$ and contained 1, 2, 4, 8, 12, 16, or 20 mg L^{-1} acifluorfen. Precipitation of acifluorfen in the presence of calcium is excluded as the ionic product of the two species in solution was below the solubility product (1.5×10^{-9}) of the complex $Ca(acifluorfen)_2$ (A. Pusino, personal communication). Adsorption of acifluorfen was studied using a batch equilibrium method. Duplicate samples of 5 g of air-dried soil and 25 mL of the herbicide solution were placed in 50 mL of polyethylene bottles (PE). Additionally, two samples for each concentration without soil were carried through the procedure to account

Table 1. Selected Properties of the Soils

| soil[a] | particle size distribution, % | | | | |
	coarse sand, 2−0.2	fine sand, 0.2−0.05	coarse silt, 0.05−0.02	fine silt, 0.02−0.002	clay, <0.002
A	0.9	9.5	9.8	36.4	43.4
B	2.7	31.6	18.1	22.7	24.9
C	34.4	38.2	15.4	9.8	2.2
D	54.1	13.4	15.2	11.5	2.9
E	28.4	16.4	7.5	22.1	25.7

| soil | oxalate extractable, g/100 g of soil | | CEC, mequiv/100 g | OC, % | pH 1:2.5 soil:water |
	Fe	Al			
A	0.3	0.1	20.9	0.98	8.0
B	0.3	0.1	13.9	0.83	7.9
C	0.2	0.2	11.6	2.35	5.6
D	0.6	1.2	54.2	11.31	5.6
E	1.5	0.5	56.1	14.80	4.6

[a] A and B, Entisol; C, Inceptisol; D, Andosol; E, Istosol.

for possible losses due to adsorption on PE bottles, volatilization, or degradation. The samples were equilibrated by shaking on a reciprocating mechanical shaker for 16 h at 25 °C. A previous study (Gennari and Nègre, 1990) indicated no significant change in acifluorfen adsorption between 2 and 48 h of shaking at 25 °C for soils A−D and between 16 and 48 h of shaking for soil E. Following equilibration, the suspensions were centrifuged for 15 min at 1200g and the supernatant was filtered on a Whatman No. 42 paper filter. The amount of acifluorfen in supernatant was determined by HPLC using a Varian 5020 instrument equipped with a UV−vis detector operating at 296 nm and a 250 × 4 mm LiChrospher RP 18 analytical column. The mobile phase (1 mL min^{-1}) was composed of water acidified to pH 3 with orthophosphoric acid plus acetonitrile (30:70 v:v) (Gennari et al., 1990). The method limit of detection was 6 ppb. The amounts of acifluorfen retained by the soils were calculated by the formula

$$x/m = (C_0 - C)v/w$$

where x/m is the concentration in soil (mg kg^{-1}), C_0 is the initial concentration in solution (mg L^{-1}), C is the final concentration in solution (mg L^{-1}), v is the solution volume (25 mL), and w is the weight of soil (5 g).

Desorption. The same sample bottles used for the adsorption studies were used for determining successive desorption of acifluorfen from the soils. Once the adsorption equilibrium had been reached, the suspension was centrifuged for 15 min at 1200g, and then 15 mL of supernatant was replaced with

Table 2. Freundlich Constants and Coefficient of Determination (r^2) for Acifluorfen Adsorption and Desorption

soil	isotherm	initial concn, $\mu g/mL$	K_f	n	$r^{2\,a}$	K^b	$K_{OC}{}^c$	n_{ads}/n_{des}
A	adsorption		0.64	1.05	0.964***		65.3	
	desorption	20.0	7.38	0.03	0.997*	1053.1		35.1
	desorption	8.0	0.92	0.45	0.999*	43.8		2.3
B	adsorption		0.57	1.01	0.965**		68.7	
	desorption	20.0	6.94	0.09	0.892*	1117.5		11.1
	desorption	8.0	2.23	0.16	0.981*	291.2		6.3
C	adsorption		5.48	1.04	0.985***		233.2	
	desorption	20.0	19.06	0.45	0.991***	247.3		2.3
	desorption	8.0	13.51	0.46	0.983***	146.4		2.2
D	adsorption		16.22	0.84	0.996***		143.5	
	desorption	20.0	25.17	0.56	0.998***	55.4		1.5
	desorption	8.0	21.07	0.52	0.996***	30.1		1.6
E	adsorption		43.11	0.86	0.997***		291.3	
	desorption	20.0	62.34	0.42	0.983***	44.6		2.2
	desorption	8.0	37.06	0.35	0.956***	-0.1		2.5
Eoss[d]	adsorption		21.75	0.88	0.999***		560.6	
	desorption	20.0	18.89	0.92	0.954***	-0.1		0.9
	desorption	8.0	18.54	0.96	0.941***	-0.1		0.9

[a] ***, $P < 0.001$; **, $0.001 < P < 0.01$; *, $0.01 < P < 0.05$. [b] $K = (K_{fdes} - k_{fads}/K_{fads} \times 100$. [c] $K_{OC} = (K_f \times 100)/\%$ OC. [d] Eoss, soil E treated with 400 mL of H_2O_2.

15 mL of 0.01 N CaCl$_2$. The bottles were manually shaken to disperse the soil pellets and then mechanically shaken for 2 h and recentrifuged. This process was repeated four times. Preliminary trials showed that the variation in desorption of acifluorfen by the soil between 2, 16, and 24 h of equilibrium period was within the variability of the analytical method (2%). This result allows us to think that desorption equilibrium was reached within 2 h. The concentration of acifluorfen present in the supernatant after each desorption step was assayed by HPLC, and the amount of acifluorfen adsorbed onto the soil after each desorption process was calculated by difference. The adsorption and desorption isotherms were obtained by plotting the concentration of acifluorfen in soil (milligrams per kilogram) versus the concentration of acifluorfen in solution at equilibrium (milligrams per liter). To understand better the role of organic matter on the adsorption–desorption process of acifluorfen, isotherms were also determined with soil E pretreated with H$_2$O$_2$ to oxidize organic matter. A 100 g sample of soil E was treated with about 400 mL of H$_2$O$_2$ to obtain partial oxidation of organic matter. Another 100 g sample was treated with H$_2$O$_2$ until the maximum removal of organic matter which can be obtained with this method was reached. The amounts of organic carbon in soil E after treatments with H$_2$O$_2$ were 3.88% and 0.55%, respectively.

RESULTS AND DISCUSSION

Adsorption. All of the adsorption data were described by the empirical Freundlich equation

$$\log x/m = \log K_f + n \log C$$

where x/m is the concentration of the adsorbate per unit amount of adsorbant (mg kg^{-1}), C is the adsorbate concentration in solution after equilibration (mg L^{-1}), and K_f (mg^{1-n} kg^{-1} L^n) and n are constants relative to the affinity of the adsorbent for the adsorbate and to the degree of curvative of the isotherm, respectively.

Freundlich constants K_f and n and the corresponding coefficient of determination (r^2) for the relationship between $\log n$ and $\log C$ are given in Table 2. In general, the isotherms fit the Freundlich adsorption equation with r^2 values >0.964. The adsorption isotherms of acifluorfen by the soils A–C, with organic carbon content equal to or lower than 2.4%, are of C type according to the classification of Giles et al. (1960). This indicates that the amount of acifluorfen adsorbed

onto the soils was independent of the initial concentration of the acifluorfen solution. The soils with a higher organic carbon content gave isotherms of the L type, which indicates that there is a great affinity of these soils for the pesticide at low pesticide concentrations.

The value of K_f for the five soils varied from 0.57 for soil B to 43.10 for soil E. The K_f values, when subjected to simple correlation analysis with soils properties, yielded significant correlation with [H$^+$] ($r^2 = 0.92$; $P = 0.04$), organic carbon ($r^2 = 0.93$; $P = 0.03$), and ammonium oxalate extractable iron content ($r^2 = 0.97$; $P = 0.01$). No significant correlations were found between K_f values and cation exchange capacity, ammonium oxalate Al content, or percent of sand, clay, or silt.

Since the adsorption of acifluorfen was highly correlated with changes in the organic carbon content, reduction or removal of organic matter was expected to reduce greatly the adsorptive capacity of the soils for the herbicide. Reduction of organic carbon in soil E from 14.8% to 3.8% decreased the adsorptive affinity of soil E for the pesticide. As can be seen in Table 2, the K_f value decreased from 43.10 to 21.75. However, no variation of n value occurred. Referring K_f values to the organic carbon content of the soil, we observed a higher value for oxidized than for untreated soil E (Table 2). One possible explanation is that the treatment with hydrogen peroxide induced a selective disruption of the organic matter. Reduction of organic matter in soil E to 0.55% resulted in a negligible ($x/m < 0.3$ mg kg^{-1}) adsorption, and no significant relationship between adsorption and herbicide concentration was found. The decrease in acifluorfen adsorptive capacity of soil E following oxidation confirms that acifluorfen has a high affinity for the organic adsorptive surfaces. This supports what many workers have reported in the literature about the affinity of anionic pesticides for the organic matter of the soil (O'Connor and Anderson, 1974; Reddy and Gambrell, 1987; Senesi and Chen, 1989).

The significant correlation between acifluorfen adsorption coefficient K_f and ammonium oxalate extractable iron indicates the importance of amorphous and less crystalline iron oxides in acifluorfen adsorption in soils. Interaction between oxides and hydrous oxides

Adsorption and Desorption of Acifluorfen in Soils

J. Agric. Food Chem., Vol. 42, No. 10, 1994 **2331**

of iron and anionic organic compounds is well documented (Watson et al., 1973; Huang et al., 1977; McConnel and Hossner, 1985; Thoisy-Dur et al., 1988). The adsorption of carboxylic acids on iron oxide surfaces is essentially attributed to a ligand exchange mechanism involving the OH or OH_2 groups on the iron oxide surface and the carboxylic group of the organic compound (Kung and McBride, 1989). The pH is indicated to be an important factor in adsorption of anionic pesticides on iron oxides, with decreasing pH favoring increased adsorption (Thoisy-Dur et al., 1988). The increase of adsorption with the decrease in pH is generally assumed to be due to the increase in net positive charge at the surface of the iron oxides. The adsorption is characterized by an envelope showing a maximum adsorption at a pH near the pK_a of the pesticide when the increase of the surface positive charge is counterbalanced by a decrease of the anionic form of the adsorbate (Schwertmann et al., 1986).

Pusino et al. (1993) reported a decrease of adsorption of acifluorfen with increasing pH. Also in the present study an inverse relationship was found between soil $[H^+]$ and adsorption of acifluorfen. The pH of the soils varied between 4.8 and 8.5. Since the pK_a of acifluorfen is 3.5, the herbicide can be expected to be always in anionic form. Since the zero point charge of pure amorphous iron oxide occurs at approximately pH 8.5 (Sposito, 1989), it is possible that an interaction takes place between the positively charged amorphous iron surface at pH below 8.5 and the negatively charged acifluorfen.

Desorption. By fitting desorption data to the linearized log-transformed Freundlich equation, we obtained the K_f values (K_{fdes}) and n values listed in Table 2. The desorption isotherms of acifluorfen had n values lower compared to the adsorption isotherms, indicating an hysteretic desorption process. The values for the ratio n_{ads}/n_{des} are reported in Table 2. These values ranged between 1.5 and 2.5 for soils C−E, whereas they were much higher in soils A and B. Values of n_{ads}/n_{des} close to 2.3 were reported in several studies on adsorption and desorption of pesticides (Hornsby and Davidson, 1973; Swanson and Dutt, 1973; Van Genuchten et al., 1977). The foregoing results indicate that soils A and B, with the lowest adsorption capacity, show also the least tendency to desorb acifluorfen. However, the irreversibility of the adsorption process in these soils was lower at low adsorption levels. This is confirmed by the K values (the percent change in the adsorption−desorption K_f value) for soils A and B compared with that for soils C−E (Table 2).

Coincidence of the desorption−adsorption isotherms was found for soil E partially oxidized with hydrogen peroxide, indicating a complete reversibility of the adsorption process in this soil. The reversibility of the adsorption process in the oxidized soil compared with the partial irreversibility in the natural ones suggests that the nature of the organic matter may also play a role in the adsorption process. This statement is supported by several works (Calvet, 1989; Chassin and Calvet, 1984; Gerstl and Kliger, 1990) which reported that the magnitude and the mechanism of adsorption of several pesticides in soil and sediments can be related to the nature of the organic matter. This fact would also offer a key as to why acifluorfen was poorly adsorbed by soils A and B (with low organic matter content) but the process was more irreversible than in the other soils.

Several hypotheses to explain herbicide hysteresis have been proposed, including nonattainment of equilibrium during desorption or loss of pesticide by volatilization and chemical or biological degradation (Koskinen and Cheng, 1983; Koskinen et al., 1979). The possibility that hysteresis in the desorption of acifluorfen was due to nonattainment of equilibrium was investigated by varying the equilibration time. Increasing the equilibration time from 2 to 24 h did not affect the amount of observed hysteresis. These data indicate that hysteresis was not the result of inadequate equilibration. The possibility of loss of pesticide by volatilization or degradation can also be ruled out as increasing times of desorption did not cause hysteresis increase. Moreover, no detectable loss of acifluorfen was shown from analyses of blank samples.

In conclusion, though the cause of observed hysteresis is still unknown, it seems reasonable to assume that it could be the result of irreversible binding of acifluorfen to the soil. Further studies would be necessary to determine the binding mechanisms that might be responsible for irreversible adsorption.

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