Effect of Metal-Binding Ability on the Adsorption of Acifluorfen on Soil

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The adsorption of acifluorfen, the sodium salt of 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, on six soils of various physical and chemical properties as well as its dependence on the exchangeable cation (Ca^{2+} and Na^+) and on soil pH was studied. Adsorption isotherms conformed to the Freundlich equation. Soil saturation by Na^+ ions produced a strong decrease in acifluorfen adsorption, whereas the opposite finding was observed for Ca-saturated soils. Adsorption was found to be correlated with cation-exchange capacity (CEC) much better than with other soil properties and decreased with increasing pH. At comparable pH, variations of k_f values after Ca saturation of soils indicated that complex formation reactions, leading to precipitation of insoluble complexes, contribute to simulate high adsorption.

INTRODUCTION

Previous studies on interaction of metal ions with pesticides having metal binding sites have shown stable complexed species can be formed, and they may have relevance to metal ion distribution in soil (Decock et al., 1985; Lerivrey et al., 1986; Pusino et al., 1988). Metal ions forming neutral complexed species may be desorbed from clays and replaced by protons or protonated molecules as the saturating cations (Micera et al., 1988; Pusino et al., 1989). On the other hand, complex formation may affect remarkably the fate of pesticides, e.g., catalyze their decomposition (Pusino et al., 1988; Pusino and Gessa, 1990) or inactivate them (Hensley et al., 1978). For instance, immobilization and mutual inactivation of both metal ions and pesticides are expected upon formation of insoluble complexes.

Sodium acifluorfen, the sodium salt of 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, is a herbicide widely used for selective postemergence control of broadleaf weeds in large-seed legume crops and is provided with a carboxylate group as a potential binding site for metal ions. Our previous studies on the interaction of acifluorfen with Cu^{2+}, Al^{3+}, Fe^{3+}, and Ca^{2+} montmorillonites indicate that the herbicide can extract the exchangeable ions from the clay interlayer and precipitate them on external surfaces (Kozlowski et al., 1990; Pusino et al., 1991). The process, leading to the adsorption of sodium as the saturating ion, can be explained by the formation of insoluble complexes between the herbicide and polyvalent metal ions.

Here the acifluorfen adsorption on six soils of varying physical and chemical properties as well as its dependence on the exchangeable cation (Ca^{2+} and Na^+) and soil pH was investigated. The results indicate that the extent and mechanism of acifluorfen adsorption can be affected by the content and kind of metal ions.

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**Table I. Selected Physical and Chemical Properties of Soils Investigated**

property	Cadriano	Vercelli	Carpi	Monte Acuto	Macomer	Torba
OM, %	1.43	1.45	1.70	2.40	16.00	25.60
clay, %	23.63	10.77	46.58	9.10	14.60	30.68
sand, %	32.56	48.56	16.44	70.10	32.90	5.09
silt, %	38.73	36.83	29.92	16.80	26.20	24.86
water, %	3.25	2.22	4.50	1.40	9.50	12.48
pH[a]	7.40	6.28	7.72	5.24	6.05	4.43
CEC[b]	17.92	7.68	23.73	4.03	17.62	53.32

[a] Soil:water = 1:1. [b] mequiv/100 g.

MATERIALS AND METHODS

Materials. Sodium acifluorfen ($C_{14}H_6ClF_3NNaO_5$), aqueous solubility 500 g L^{-1}, was supplied by Rhône-Poulenc AG Co. as a yellow hygroscopic solid (99.7% purity). Six Italian soils, a clay loam Histosol from Torba (Emilia-Romagna), a clay loam Andosol from Macomer (Sardinia), a silt clay Entisol from Carpi (Emilia-Romagna), a loamy sand Cambisol from Monte Acuto (Sardinia), a sandy loam Alfisol from Vercelli (Piemonte), and a clay loam Entisol from Cadriano (Emilia-Romagna), were examined in this study. The samples were air-dried and sieved to <2 mm. Particle size distributions were performed by the Purdue University Soil Testing Laboratory using the pipet method (Day, 1965), and organic carbon contents were determined according to the modified Walkley–Black (Jackson, 1958) method. Cation-exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (1986). Soil pH was determined on slurries with a soil:water ratio of 1:1. The clay minerals present in the Carpi soil were identified by X-ray diffraction, which showed a mixed mineralogy consisting of illite, kaolinite, and smectite. Selected physicochemical properties of the soils are given in Table I. Ca^{2+}-, and Na^+-exchanged soils were obtained by shaking a suitable weight of soil with 1 N solutions of metal chlorides, followed by centrifugation of the suspension at 5000 rpm for 20 min. The saturation process was repeated three times, and the excess of chloride was then washed out by distilled water. Control soils were obtained under the same experimental conditions of the saturation and washing process used for exchanged soils without salts. No degradation of acifluorfen was observed in the absence of soil, since a constant concentration of the herbicide was monitored throughout the experiment and no other peak appeared in the chromatograms.

Adsorption Measurements. The adsorption of acifluorfen was determined at 25 ± 2 °C. In general, triplicate samples of 5 g of air-dried soil sieved through a 2-mm mesh screen were equilibrated in centrifuge tubes with 5 or 10 mL of acifluorfen

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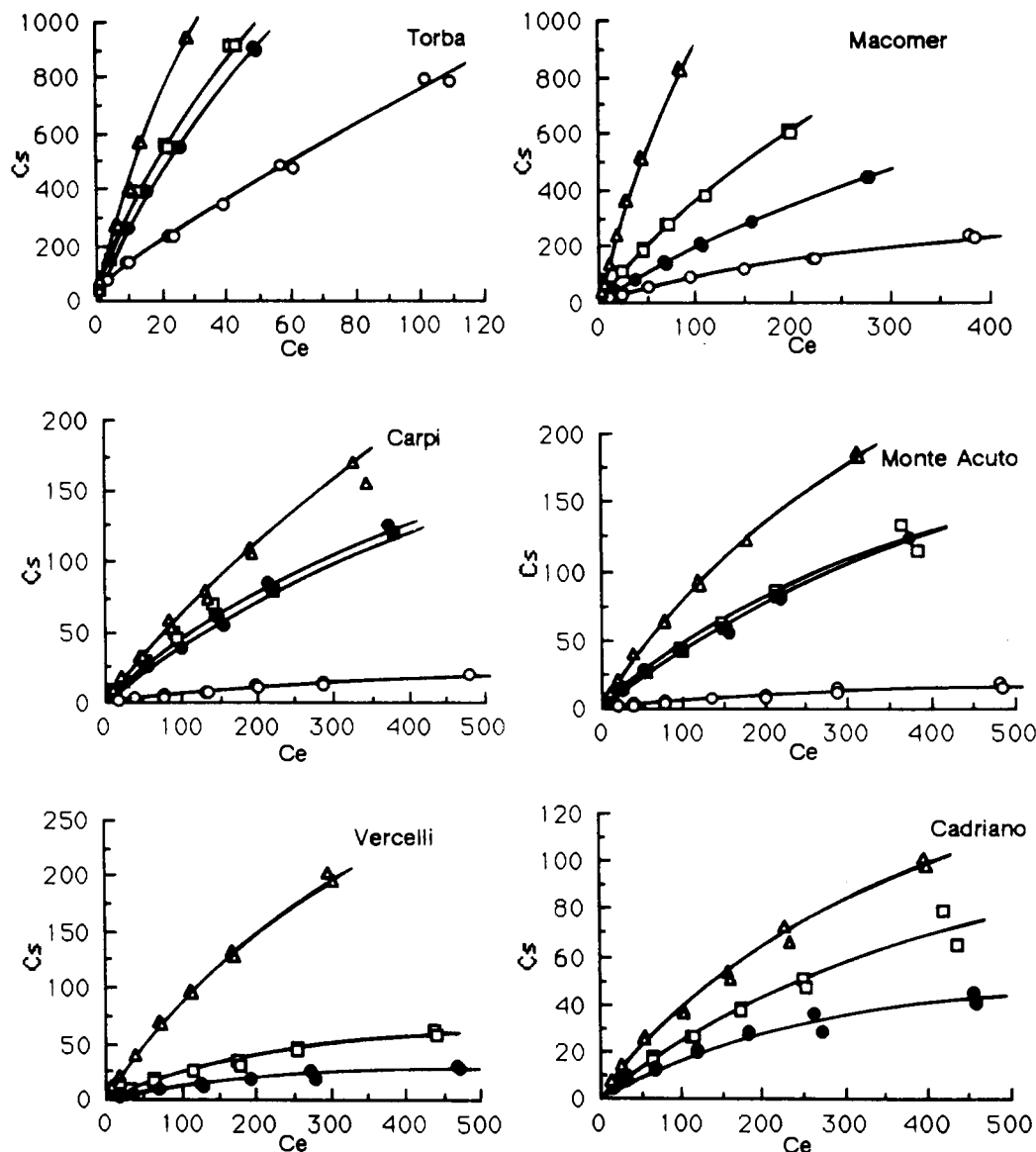
Figure 1. Adsorption isotherms of acifluorfen on six soils: (□) natural soil; (●) washed soil; (○) Na soil, (▲) Ca soil. C_e (μmol/L); C_s (μmol/kg).

solution. Acifluorfen concentrations before equilibration ranged from 20 to 500 μM. The tubes were shaken (end-over-end) for 24 h. Generally, 95% of the adsorption was found to occur in the first 5 h. After equilibration, the suspension was centrifuged at 20 000 rpm for 15 min, and the supernatant was pipetted off and analyzed immediately. The amount adsorbed by a soil was calculated from the difference between the initial and final concentrations of acifluorfen in solution. To evaluate the role of the different soil-saturating cations on acifluorfen adsorption, the isotherms were carried out on the same soils after saturation with Ca^{2+} and Na^+, respectively, and, for comparison purposes, on control soils. The effect of varying pH was examined by the addition of HCl or NaOH and equilibration overnight.

Acifluorfen Analyses. Acifluorfen concentrations were determined by high-performance liquid chromatographic (HPLC) analyses. A Waters 501 liquid chromatograph equipped with a 300 × 4 mm i.d. Waters μBondapak C_{18} (10 μm) analytical column, a multiwavelength Waters 490 programmable detector operating at 296 nm, and a Waters Baseline 810 chromatography workstation was used. The mobile phase (1 mL min^{-1}) was composed of acetonitrile plus water (70 + 30 by volume, pH 3). In these conditions the retention time of acifluorfen was 4.7 min.

RESULTS AND DISCUSSION

The adsorption of acifluorfen by all of the samples studied may be described by Freundlich's adsorption equation (r = 0.99) (Figure 1). In the linear form this relation can be expressed as

$$\log C_s = \log k_f + 1/n \log C_e$$

where C_s (μmol kg^{-1}) is the amount of herbicide adsorbed by soil, C_e (μM) is the equilibrium concentration in solution, and k_f and $1/n$ represent the intercept and the slope of the isotherm, respectively. The Freundlich constants k_f and $1/n$ determined on our system are given in Table II. The values of $1/n$ for acifluorfen adsorption on all soil samples were less than one, indicating a convex or L-type of isotherm (Giles et al., 1960) and suggesting a minor competition between solute and solvent molecules for the adsorbing sites of the surface. Isotherms (Figure 1) and k_f values (Table II) indicate that the adsorption capacity follows the sequence Torba > Macomer > Carpi > Monte Acuto > Vercelli ≥ Cadriano, with a rather high value for Torba soil. Simple linear regressions of k_f with various soil properties indicated that acifluorfen adsorption correlates well with cation-exchange capacity (CEC) (r = 0.92, significant at the 0.009 probability level) and much less with organic matter content (OM) (r = 0.89, p = 0.02). No significant correlation (p < 0.05) was observed between k_f and other soil properties. Soil rinsing did not

Table II. Parameters of the Freundlich Equation for Natural, Washing, and Na- and Ca-Saturated Soils

soil	pH	k_f	$1/n$	r
Torba (Tb)	4.43	53.86[a]	0.77	0.999
Wash-Tb	4.65	53.70[a]	0.72	0.998
Na-Tb	5.10	36.94[a]	0.63	0.996
Ca-Tb	4.42	66.20[a]	0.80	0.998
Macomer (Mc)	6.05	7.55[a]	0.84	0.990
Wash-Mc	6.14	5.54[a]	0.77	0.998
Na-Mc	6.74	3.20[a]	0.71	0.999
Ca-Mc	5.36	15.41[a]	0.91	0.998
Carpi (Cp)	7.72	1.34[b]	0.77	0.996
Wash-Cp	7.71	1.11[b]	0.79	0.998
Na-Cp	8.80	0.17[b]	0.78	0.994
Ca-Cp	7.35	1.50[b]	0.81	0.998
Monte Acuto (MA)	5.24	0.98[b]	0.82	0.998
Wash-MA	5.30	1.08[b]	0.80	0.998
Na-MA	6.24	0.24[b]	0.69	0.993
Ca-MA	5.10	2.18[b]	0.78	0.999
Vercelli (Vc)	6.28	0.74[b]	0.73	0.997
Wash-Vc	6.34	0.51[b]	0.67	0.998
Na-Vc	6.73			
Ca-Vc	5.26	2.14[b]	0.80	0.998
Cadriano (Cd)	7.40	0.73[b]	0.76	0.998
Wash-Cd	7.36	0.65[b]	0.70	0.991
Na-Cd	8.54			
Ca-Cd	6.97	1.27[b]	0.73	0.997

[a] Soil:solution = 1:2. [b] Soil:solution = 1:1.

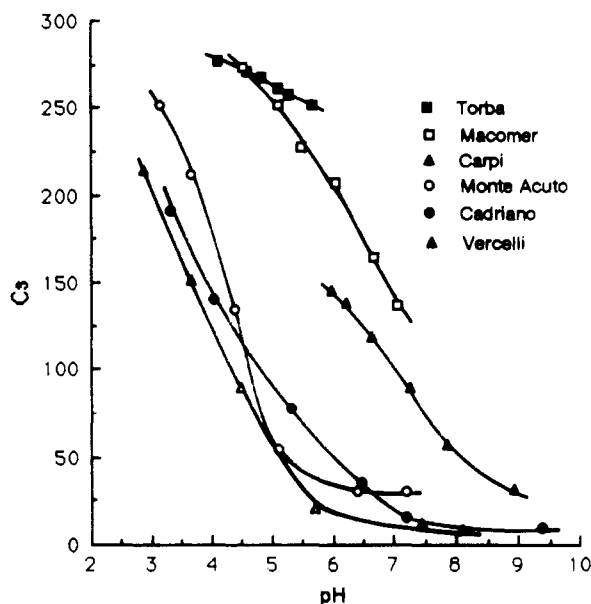**Figure 2.** Effect of pH on the adsorption of acifluorfen on six soils. C_s (μmol/kg).

modify substantially the adsorption trend, though the k_f values were smaller than those found on the natural soil. Instead, soil saturation by Na^+ ions resulted in a strong decrease in acifluorfen adsorption, whereas the opposite finding was observed for Ca-saturated soils (Table II).

Since the pH of soil suspensions depends also on the saturating ion, being higher for Na than for Ca soils, the different extent of the adsorption could be somewhat affected by this pH variation. To check this hypothesis, the dependence of acifluorfen adsorption on pH was investigated for the different soil samples (Figure 2). It was found that the herbicide adsorption increased as the pH of the soil solution decreased, according to the general trend for the interaction of ionizable molecules with organic matter (Nicholls and Evans, 1991). Actually, at lower pH

Table III. Parameters of the Freundlich Equation for Natural Soils at pH Values Adjusted about to That of the Corresponding Ca-Saturated Soils

soil	pH	k_f	$1/n$	r
Torba	4.50	55.17	0.74	0.999
Macomer	4.10	9.37	0.86	0.998
Carpi	7.08	1.60	0.84	0.998
Monte Acuto	4.83	1.61	0.93	0.997
Vercelli	5.40	1.03	0.86	0.997
Cadriano	6.76	0.80	0.86	0.996

levels, several adsorption mechanisms, involving weak physical forces or hydrogen bonding through the undissociated carboxylic group, are possible. As pH increases, anionic molecules are desorbed because of the repulsion with the predominantly negatively charged soil surfaces. According to these trends, Na saturation, which led to an increase of pH with respect to the natural soil, lowered k_f values. Instead, in spite of the minor changes in pH values, Ca saturation induced a strong increase of k_f values (Table II).

Results obtained at only one concentration of herbicide should be interpreted carefully because relatively small shifts in isotherm slope can result in large changes in relative adsorption (Bowman and Sans, 1985). Therefore, for a better understanding of the pH effect in the Ca-saturated soils, entire adsorption isotherms were performed on natural soils after adjustment of pH approximately to the value of the respective Ca-saturated soils. In all cases, the measured k_f values were decidedly lower than those observed on Ca soil (Table III). This behavior suggests that, besides pH, other factors affect acifluorfen adsorption in the presence of calcium ions.

In our previous studies it was found that very insoluble complexes are formed by acifluorfen yields with metal ions such as iron(III) and aluminum(III) ($K_{sp} < 3 \times 10^{-24}$) and that the solubility product of the Ca^{2+} complex, about 1.5×10^{-9}, is of the same order of magnitude as that of calcium carbonate. This rather low solubility promotes the desorption of exchangeable ions from the interlayer of phyllosilicates and their precipitation on the outer surfaces (Pusino et al., 1991). It is conceivable that precipitation of acifluorfen, in addition to adsorption by organic matter, can occur in soil solution. This hypothesis is in accord with the observation that adsorption of acifluorfen increases with increasing CEC, indicating a positive correlation with metal ion content, to the greatest extent when Ca^{2+} is the exchange cation. The mechanism of the complex reaction involves the replacement of sodium as the positive saturating ion. A limited adsorption of herbicide is observed on Na-saturated soils because precipitation of this cation does not take place due to the solubility of sodium acifluorfen.

The formation of Ca bridges between the clay layers and the carboxyl ligands of the herbicide is not consistent with our previous finding that, upon treatment of homoionic clays with acifluorfen, sodium becomes the saturating ion in the interlayer (Pusino et al., 1991). On the other hand, due to the lower stability expected for Ca^{2+} complexes of acifluorfen, as compared with those formed by the polymeric organic matter, it is also unlikely that the herbicide is able to compete with the binding groups of organic matter for the metal ion unless insoluble metal–herbicide complexes are formed.

A support to the role of metal ion in the adsorption mechanism derives also from examination of the pH dependence of the process. The adsorption of acifluorfen on Monte Acuto, Cadriano, and Vercelli soils was strongly reduced when soil pH was increased to 5.5–6.5 (Figure 1),

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most likely because of the electrostatic repulsion between the negatively charged carboxylate groups of organic matter [pK_a values around 5 according to Stevenson (1972)] and that of acifluorfen ($pK_a = 3.38$) and, more generally, due to the negative pH dependence of anion adsorption onto variable charge soil surfaces. On the other hand, in the same pH range as above, soils with greater CEC (Torba, Macomer, and Carpi) still exhibited a rather high extent of acifluorfen adsorption, indicating that metal complex formation is a competitive process. Thus, while the adsorption of free herbicide molecules plays a major role at low pH values because of the participation of undissociated molecules in the bonds, the complexing behavior becomes more important as carboxylic groups deprotonate.

CONCLUSIONS

This study indicates that the adsorption of acifluorfen is a process controlled by many factors, some of which are related to each other. At low pH, in the presence of neutral surfaces, the adsorption mechanisms are likely regulated by physical forces like hydrophobic effects and hydrogen bonding even if, under the slurry conditions of this study, the potential H-bonding sites could be likely occupied by water molecules. As pH increases, further mechanisms must be effective and, in the present state of knowledge, complex formation reactions leading to precipitation of insoluble complexes most likely are the competitive processes. Since the relative importance of these mechanisms can be affected to some extent by soil features, attempts to classify this herbicide on the basis of this adsorption behavior can only be approximate. In fact, depending on the conditions (pH, herbicide concentration, amount and kind of metal ions present in the soil) precipitation can simulate adsorption. These findings are significant for the soil chemistry of acifluorfen inasmuch as the inactivation following complex formation can be responsible for the loss of herbicidal activity.

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