

# Adsorption of the Herbicide Acifluorfen on Soil Humic Acids

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The amount of acifluorfen adsorbed on eight soil humic acids has been determined in a pH range from 1.6 to 6 at the initial concentration of 40 mg L<sup>-1</sup> using a batch equilibrium method. Most of the adsorption took place between pH 2.5 and 3.5. More than 70% acifluorfen was adsorbed at pH <2.5 and less than 10% at pH >4.5, indicating that adsorption was promoted by the protonation of both acifluorfen and humic acids. Adsorption isotherms were determined on six out of the eight humic acids at pH 3.4 in a concentration range from 4 to 100 mg L<sup>-1</sup> and described by the Freundlich equation.  $1/n$  values were close to 1 indicating a linear ripartition between the liquid and solid phases. Four humic acids had about the same  $K_f$  (84.1–94.1), while the other two exhibited respectively a higher (126.8) and a lower (51.3)  $K_f$ . These results indicate that, beside pH, the nature of humic acid influences the adsorption of acifluorfen, but no correlation was observed between  $K_f$  values and the concentration of acidic functional groups of humic acids.

**Keywords:** *Acifluorfen; humic acids; adsorption; pH*

## INTRODUCTION

Acifluorfen (AC), 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, is a highly effective postemergence herbicide used in selective control of broad-leaf weeds in soybeans, peanuts, and rice (Johnson et al., 1978; Wills and McWhorter, 1981). AC is moderately soluble in water (120 mg L<sup>-1</sup> at 25 °C) and contains a carboxyl group whose  $pK_a$  is 3.5 (Roy et al., 1983).

Several laboratory studies have been performed in order to predict its fate in the environment giving the following information. AC dissipation in soil is highly dependent on the soil type: Half-life time varied from about 20 to more than 100 days (Gennari and Nègre, 1990). Perucci and Scarponi (1993) observed that amendment of a soil with glucose caused a decrease in the half-life time of AC from 40 to 28 days, indicating the involvement of soil microorganisms in the degradation.

The capability of different microbial populations to degrade AC was tested by Gennari et al. (1994a) and Andreoni et al. (1994) in anaerobic and aerobic conditions. The reduction of the nitro group of AC to an amino group occurred, followed in some cases by further transformation of amino-AC to conjugation products. Successive cleavage of the molecule was never observed, suggesting that it is highly resistant to microbial degradation. Photodegradation of AC in aqueous solution occurred to produce decarboxylated AC (Pusino and Gessa, 1991).

Adsorption isotherms on soils with various physicochemical characteristics have been determined by Pusino et al. (1993) and Gennari et al. (1994b). In both studies, the adsorption isotherms were well described by the Freundlich equation and the adsorption capacity expressed as the  $K_f$  coefficient was highly dependent on the soil type with variations of the  $K_f$  value of more than 70 times. The  $K_f$  value was found to be positively correlated with the organic carbon content (Pusino et al., 1993; Gennari et al., 1994b) and with the hydrogen ion concentration of soil solution (Gennari et al., 1994b), while no significant correlation was found with the clay content. The role of organic matter in the adsorption

**Table 1. Characteristics of the Soils**

soil	soil type	clay content (%)	organic carbon content (%)	pH (H <sub>2</sub> O)
A	loam	23.9	0.86	8.0
B	clay loam	33.2	0.91	8.2
C	silty clay	43.0	1.39	8.3
D	loamy sand	3.0	2.26	4.6
E	sandy loam	2.6	2.75	7.5
F	sandy loam	4.1	3.46	6.1
G	clay loam	39.4	9.64	5.0
H	loamy sand	1.5	18.50	6.7

was also pointed out by the decrease of the  $K_f$  value when part of the organic matter was removed by H<sub>2</sub>O<sub>2</sub> oxidation (Gennari et al., 1994b). The dependence of AC adsorption on pH was investigated by Pusino et al. (1993): The herbicide adsorption increased strongly as the pH of the soil solution decreased. The role of organic matter and the influence of pH on the adsorption of AC were pointed out by Ruggiero et al. (1992) in a study of the adsorption of AC on humic acids (HAs) obtained from soil and on standard HAs at pH 3.2, 5, and 7. The adsorption isotherms fitted the Freundlich and Langmuir equations; the amount adsorbed was considerably higher at a pH close to the  $pK$  of the herbicide (3.5). This study pointed out also that at the same pH the adsorption was dependent on the type of HAs.

In order to extend the information concerning the adsorption of AC on soil HAs, we examined in this study the adsorption of AC on HAs extracted from eight different soils, over a pH range from 1.6 to 6.

## MATERIALS AND METHODS

**Humic Acids.** HAs originating from the A horizon (0–15 cm) of eight Italian soils with different physicochemical characteristics (Table 1) were used. HAs were prepared according to the Schnitzer procedure (1982). Briefly, HAs were extracted with a mixture of 0.1 M NaOH and 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, precipitated with 6 N HCl, washed with 0.1 N HCl and then with distilled water, and freeze-dried. HA characteristics are reported in Table 2. The total acidity and the amount of carboxyl groups were determined following the methods described by Schnitzer and Gupta (1965). The amount of phenolic OH groups was calculated by difference between the total acidity and the amount of carboxyl groups.  $E_4/E_6$  ratios

**Table 2. Characteristics of the Humic Acids**

humic acid	ash (%)	C (%)	H (%)	N (%)	O (%)	$E_4/E_6$	total acidity (mequiv/g)	COOH groups (mequiv/g)	phenolic OH groups (mequiv/g)
A	4.0	54.5	5.3	5.8	34.4	5.59	5.00	3.19	1.81
B	9.2	55.2	5.1	6.0	33.8	5.28	4.96	2.84	2.12
C	3.0	58.4	5.4	6.1	30.0	6.01	5.40	3.22	2.18
D	2.7	53.9	5.9	5.7	34.5	5.09	3.61	2.74	0.87
E	3.2	55.6	4.8	6.0	33.6	4.37	6.03	3.39	2.64
F	2.2	54.8	6.1	5.6	33.4	5.76	3.15	2.28	0.87
G	3.6	58.2	5.2	4.6	31.9	3.05	7.14	3.37	3.77
H	2.4	56.4	4.5	4.0	35.1	8.71	4.15	3.95	0.20

were determined by the method described by Chen et al. (1977). Elemental composition of HAs was determined with a C, H, N analyzer (LECO C-H-N Analyzer Model 600); the content of oxygen was calculated by difference.

**Chemicals.** AC (97% pure) was supplied by Dr. Ehrenstorfer (Augsburg, Germany). All reagents were analytical or HPLC grade.

**Adsorption Studies.** Suspensions of HAs in AC solutions were prepared in 10 mL glass flasks by adding to 25 mg of HAs 4 mL of water solutions of AC and 1 mL of HCl or NaOH solutions at different concentrations in order to obtain the desired pH value. For the study of the influence of pH on the adsorption, suspensions of HAs in AC solutions at a single concentration (40 mg L<sup>-1</sup>) over a pH range from 1.6 to 6 were used. For the determination of the adsorption isotherms, the suspensions of HAs were prepared at a single pH value (3.4) at initial concentrations of 4, 12, 20, 40, 50, 70, 80, and 100 mg L<sup>-1</sup> AC.

Adsorption studies were performed by shaking the suspensions for 16 h, at 25 °C, in the dark. Preliminary studies showed equilibration to be complete within 16 h, with no degradation of AC occurring in this period. The supernatant was separated by centrifugation and analyzed by HPLC. The different sets of shaking and centrifugation conditions used were as follows: mechanical stirring on a reciprocating mechanical shaker (120 rpm), magnetic stirring, centrifugation at 3000 rpm for 30 min at 25 °C, and centrifugation at 11 000 rpm for 30 min at 4 °C.

The concentration of AC in the supernatant diluted with methanol (1:5, v/v) was determined by HPLC using a Perkin Elmer 250 liquid chromatograph equipped with a Perkin Elmer LC235 diode array detector operating at 295 nm, a SupelcoSil LC 18 column (250 × 4 mm, 10 μm), and a Rheodyne injection valve (6 μL loop). The mobile phase was 80:20 (v/v) acetonitrile:water acidified to pH 3 with orthophosphoric acid flowing at 1 mL/min. The amount of adsorbed AC was calculated from the difference between initial and final solution concentrations.

All experiments were duplicated. Blanks (without HAs) were run for each experiment to assess that no adsorption on the vials and/or degradation of AC occurred.

## RESULTS AND DISCUSSION

**Experimental Conditions.** Preliminary experiments were conducted in order to choose an experimental method suitable for the adsorption study of a poorly soluble molecule over a large pH range. Despite the large amount of research on the adsorption of xenobiotics on soils and HAs, no standardized method of study has been defined. The slurry method including shaking of the suspensions to equilibrium and separation of the liquid phase by centrifugation is generally used. However, the literature reports large discrepancies between the operating conditions. In some cases, no indication is given about the shaking system and the rate of centrifugation (Nearpass, 1976; Maqueda et al., 1983, 1990). The shaking is generally performed using a mechanical shaker (Carringer et al., 1975; Che et al., 1992) or a magnetic stirrer (Senesi et al., 1994). The rates and times of centrifugation cover a large range of conditions, for example, 2287g for 15 min (Che et al.,

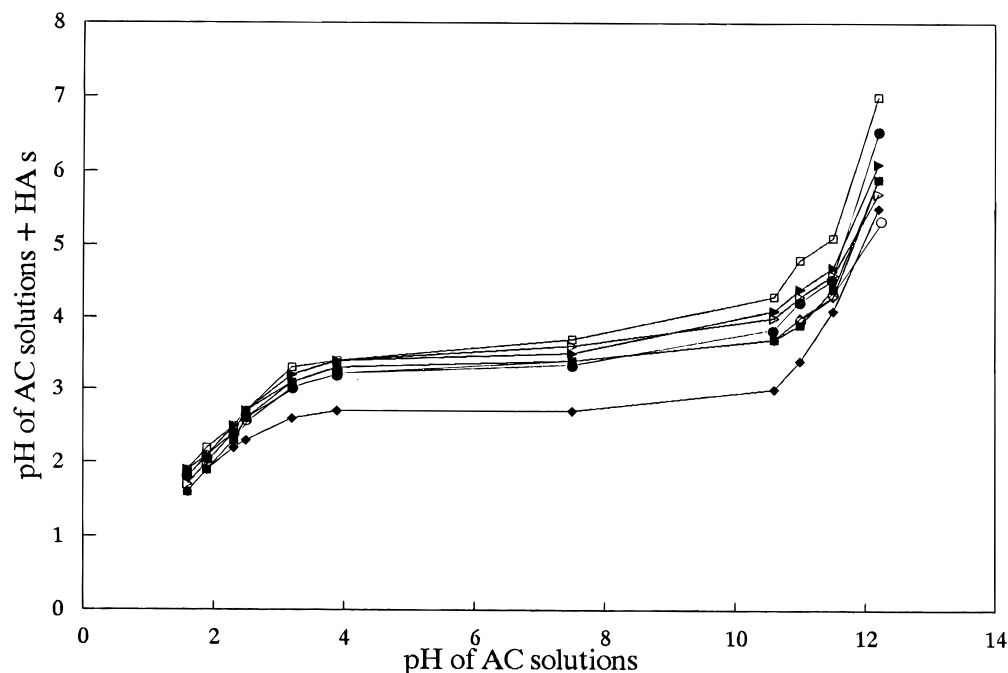
1992), 11 000 rpm for 30 min (Senesi et al., 1994), and 20 000 rpm for 2 min (Carringer et al., 1975). In our experiment we compared the amount of AC adsorbed by D HA from a solution at 40 mg L<sup>-1</sup>, in various shaking–centrifugation conditions in a pH range from 1 to 6.

**Mechanical versus Magnetic Shaking.** Performing blank controls (without HAs), we observed that the magnetic stirrer caused the precipitation of AC at pH values below 1.6, while no precipitation was observed when using the mechanical shaker over the entire pH range. An explanation for this behavior is that at low pH the water solubility of AC decreases because of the prevalence of its undissociated form. Its precipitation is probably promoted by the energetical motion of the magnetic stirrer and indicates that it is nearly insoluble at pH < 1.6. The lack of precipitation when using the mechanical shaker should correspond to a metastable equilibrium which is undisturbed in these shaking conditions. We chose to limit our study at pH values > 1.6 in order to avoid the condition of metastable equilibrium which could be broken by uncontrolled factors leading to erroneous results. In the 1.6–6 pH range, the same amount of adsorbed AC was obtained with both stirring systems, but we preferred the mechanical shaker to the magnetic stirrer because it allowed a better control and standardization of the shaking rate.

**Separation of the Liquid Phase.** The separation of the liquid phase is a critical point since it must ensure a complete sedimentation of HAs. HAs not sedimented could complex AC; in this case the amount of AC measured in the liquid phase would be higher than the amount actually present in solution, inducing erroneous results.

We tested two centrifugation conditions: (a) 11 000 rpm for 30 min at 4 °C as proposed by Senesi et al. (1994) for a similar study concerning adsorption of alachlor on HAs; the high rate of centrifugation has been seen to ensure a good sedimentation of HAs; and (b) 3000 rpm for 30 min at 25 °C as used in our previous work on the adsorption of AC in soils (Gennari et al., 1994).

The same percentages of AC were adsorbed on D HA in the two centrifugation conditions over the entire pH range, indicating that in the case of AC, reliable results are obtained also at 3000 rpm. We chose to work at the centrifugation rate of 3000 rpm to maintain the same conditions as in our previous study on adsorption of AC on soil and also because the drastic decrease of temperature required by the high-speed centrifugation caused the precipitation of AC from the most concentrated solutions used to determine adsorption isotherms. In the conditions “mechanical shaking and centrifugation at 3000 rpm at 25 °C for 30 min”, the recovery of AC from blank samples (without HAs) was 100% over the entire pH range, indicating that no artifacts such

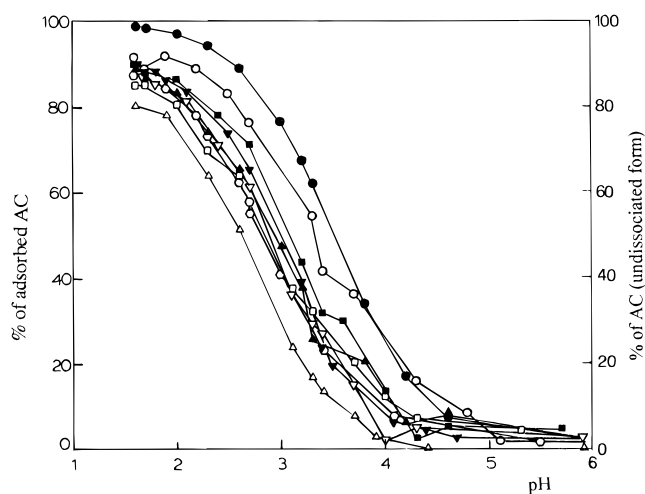


**Figure 1.** Variation of pH due to the addition of HAs (A,  $\blacklozenge$ ; B,  $\blacktriangle$ ; C,  $\diamond$ ; D,  $\bullet$ ; E,  $\blacksquare$ ; F,  $\square$ ; G,  $\triangle$ ; H,  $\circ$ ) to aqueous solutions of acifluorfen ( $40 \text{ mg L}^{-1}$ ) at various pH values.

as adsorption on container surfaces, volatilization, or degradation occurred.

**Influence of pH.** The variation of the ambient pH induces protonation or deprotonation of both HAs and AC. HAs are considered as "weak acid polyelectrolytes" whose acidic character is mainly due to carboxyl and phenolic hydroxyl groups. The carboxyl groups are known to be completely undissociated at  $\text{pH} < 3$  and mostly ionized at  $\text{pH} > 7$ , while the dissociation of the hydroxyl phenolic groups occurs at higher pH values. HAs exhibit buffer capacity over a large pH range. This effect is evident in Figure 1 which reports the pH of the supernatant of the HA suspensions in AC solutions versus the pH of the corresponding AC solutions without HAs, added with the same amount of HCl or NaOH. These curves point out the large buffer capacity of HAs since variations of 7 pH units (3–10) of the AC solutions correspond to a variation of less than 1 pH unit (about 3–4) of the AC solutions + HAs. At  $\text{pH} < 3$ , the pH of the suspensions is about the same as the pH of the solutions indicating that the added hydrogen ions remained as cations, indicating that all the carboxyl groups are also undissociated. The pH influences also both the shape and the size of HA particles. This effect has been reported by Schnitzer (1991): At low pH, HAs tend to aggregate, forming elongated fibers and bundles of fibers. The aggregation appears to be a consequence of hydrogen bonding, van der Waals forces, and interaction between electrons of adjacent aromatic rings as well as between free radicals. As the pH increases, these forces become weaker, and because of increasing ionization of carboxyl and phenolic hydroxyl groups, particles separate and begin to repel each other so that HAs behave like flexible linear polyelectrolytes.

The influence of pH on the percentage of adsorbed AC is shown in Figure 2. The adsorption of AC is highly dependent on the pH of the suspensions. Less than 10% of AC is adsorbed at  $\text{pH} > 4.5$  for the eight HAs. A large increase of the adsorption takes place between pH 2.5 and 3.5, and variations of a few tenths of a pH unit in this range provoke a very large variation of adsorption. The adsorption curves are very similar to the protona-



**Figure 2.** Adsorption of acifluorfen on HAs (A,  $\circ$ ; B,  $\blacktriangledown$ ; C,  $\nabla$ ; D,  $\blacktriangle$ ; E,  $\triangle$ ; F,  $\circ$ ; G,  $\blacksquare$ ; H,  $\square$ ) and protonation curve of acifluorfen ( $\alpha$ ,  $\bullet$ ).

tion curve of AC (% of undissociated form versus pH), also reported in Figure 2, suggesting that AC is adsorbed in its undissociated form. The low adsorption at  $\text{pH} > 4.5$  can be explained by the prevalence (>90%) of the anionic form of AC which has a higher affinity for the aqueous phase than the undissociated form and which could be repelled by the partial negative charges of the HA carboxyl groups. At decreasing pH, this repulsion is eliminated by the progressive protonation of the carboxyl groups of both HAs and AC. In the pH range from 4.5 to 3, the percentage of undissociated AC increases from 9% to 76% and a drastic change of the protonation level of HA carboxyl groups occurs—from largely dissociated to completely undissociated. Adsorption increases in this pH range, as the consequence of the decreasing polarity of both AC and HAs, but at pH 3, the amount of adsorbed AC corresponds to only a part of the amount of its undissociated form (about 37–86% depending on the HAs). A large increase of adsorption takes place at lower pH values (80–90% of the molecular form at pH 1.6). These results suggest

**Table 3. Freundlich Coefficients of Adsorption of Acifluorfen on Humic Acids at pH 3.4**

humic acid	$K_f$	$1/n$	$R^2$
B	84.1	0.95	0.995
C	94.4	0.93	0.998
E	51.4	0.99	0.997
F	126.8	0.98	0.993
G	87.2	0.99	0.998
H	89.6	0.95	0.998

**Table 4. Freundlich Coefficients of Adsorption of AC on Two Humic Acids at Two pH Values**

humic acid	pH	$K_f$	$1/n$	$R^2$
A	3.1	148.7	0.93	0.995
A	2.7	346.0	0.91	0.996
D	3.2	87.3	1.02	0.997
D	3.0	107.0	1.00	0.996

that, beside the complete protonation of HAs, the increase of their lipophilic character at low pH values due to the formation of coiled structures enhances AC adsorption.

**Influence of the Humic Acids.** The percentage of AC adsorbed at each pH (Figure 2) is about the same for six out of the eight HAs. Two HAs (E and F) exhibit respectively a higher and a lower capacity than the others indicating that, beside pH, the nature of HAs influences the adsorption. Since the amount adsorbed at a single concentration is not representative of the phenomenon, we determined the adsorption isotherms on six HAs at pH 3.4 over a concentration range from 4 to 100 mg L<sup>-1</sup> limited by the solubility of AC (120 mg L<sup>-1</sup>). The isotherms fitted the Freundlich equation (1):

$$x/m = K_f c^{1/n}$$

$c$  (mg L<sup>-1</sup>) and  $x/m$  (mg kg<sup>-1</sup>) are the concentrations of AC at equilibrium in the liquid and solid phases, respectively. The values of the empirical parameters of the Freundlich equation,  $K_f$  and  $1/n$ , are reported in Table 3.  $1/n$  values are close to 1 indicating that a linear partition of AC between the liquid and solid phases takes place over the entire concentration range (Giles et al., 1960). The  $K_f$  values of B, C, G, and H HAs are about the same (84.1–94.1, SD = 6.8), while  $K_f$  values of HAs E and F are respectively 51.3 and 126.8, confirming that these HAs exhibit different affinity for AC. In order to verify if the acidic groups of HAs are involved in the interaction with AC, we tried to correlate their content (Table 2) with  $K_f$  values. No simple correlation has been obtained between  $K_f$  and these parameters. However, F HA, with the highest  $K_f$  value, has the lowest carboxyl group content and total acidity suggesting that these parameters influence negatively the adsorption of AC.

#### Adsorption Isotherms at Different pH Values.

In Table 4 are reported the Freundlich coefficients of the adsorption isotherms of AC on HAs at two pH values. While  $1/n$  values are not affected by pH variation,  $K_f$  values change considerably. The increase of 0.2 pH unit causes a significant decrease of the  $K_f$  value of D HA (from 107.0 to 87.3), and the increase of 0.4 pH unit causes a decrease of the  $K_f$  value of A HA of about 3 times (from 346.0 to 148.7). These results clearly indicate how important it is to perform adsorption studies at a carefully controlled pH value when the interaction between pesticide and HA is pH-dependent.

**Conclusion.** The main factor controlling the adsorption of AC on soil HAs is the ambient pH: Adsorption

is affected by pH variations as small as 0.2 pH unit. AC is adsorbed in its undissociated form, and its adsorption is promoted by the increase of the lipophilic character of HAs. At a determined pH, the different HAs exhibit different adsorption capacities. Though the pH dependence could suggest that HA acid functional groups were involved, no correlation has been found between the amount of these groups and the amount of adsorbed AC.

Though more specific studies are required to obtain information on the adsorption mechanisms, some considerations can be done on the basis of our results. The fact that adsorption is promoted by the protonation of carboxyl groups of both HAs and AC suggests that H-bonding between their carboxyl groups could take place. Such a mechanism has been observed for the adsorption on HAs of organic compounds with a carboxyl group such as (chlorophenoxy)alkanoic acids at pH values below their  $pK_a$  (Khan, 1973; Senesi and Chen, 1989; Senesi, 1992). However, the lack of correlation between adsorption and the amount of carboxyl groups does not support this hypothesis. The fact that adsorption is enhanced by the increase of the lipophilic character of HAs suggests that hydrophobic bonding could take place. This type of interaction is known to occur between the hydrophobic regions of HAs and nonpolar pesticides and has also been observed for molecules having nonpolar regions of significant size in proportion to polar regions (Khan, 1978). The lipophilic character of AC due to the presence of two aromatic rings and the decrease of its polarity at low pH values support the hypothesis of hydrophobic interaction.

#### LITERATURE CITED

- Andreoni, V.; Colombo, M.; Gennari, M.; Nègre, M.; Ambrosoli, R. Cometary degradation of acifluorfen by a mixed microbial culture. *J. Environ. Sci. Health* **1994**, *B29* (5), 963–987.
- Carringer, R. G.; Weber, J. B.; Monaco, T. J. Adsorption-desorption of selected pesticides by organic matter and montmorillonite. *J. Agric. Food Chem.* **1975**, *23*, 569–572.
- Che, M.; Loux, M. M.; Traina, S. J.; Logan, T. J. Effect of pH on sorption and desorption of imazaquin and imazethapyr on clays and humic acids. *J. Environ. Qual.* **1992**, *21*, 698–703.
- Chen, Y.; Senesi, N.; Schnitzer, M. Information provided on humic substances by E4/E6 ratios. *Soil Sci. Am. J.* **1977**, *41*, 352–358.
- Gennari, M.; Nègre, M. Acifluorfen behaviour in soil. Proceedings of the International 3rd Workshop on Study and Prediction of Pesticides Behaviour in Soils, Plants and Aquatic Systems, Munich, May 30–June 1, 1990.
- Gennari, M.; Nègre, M.; Ambrosoli, R.; Andreoni, V.; Vincenti, M.; Acquati, A. Anaerobic degradation of acifluorfen by different enrichment cultures. *J. Agric. Food Chem.* **1994a**, *42*, 1232–1236.
- Gennari, M.; Nègre, M.; Raimondo, E. Effect of soil properties on adsorption and desorption of acifluorfen. *J. Agric. Food Chem.* **1994b**, *42*, 2329–2331.
- Giles, C. H.; MacEwan, T. H.; Nakhawa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and measurements of specific surface areas of solids. *J. Chem. Soc.* **1960**, *4*, 3973–3993.
- Johnson, W. O.; Kollman, G. E.; Swithenbank, C.; Yih, R. Y. Rh-6201 (Blazer): a new broad herbicide for postemergence use in soybeans. *J. Agric. Food Chem.* **1978**, *26*, 285–286.
- Khan, S. U. The interaction of organic matter with pesticides. In *Soil Organic Matter*; Schnitzer, Khan, Eds.; Elsevier: New York, 1978.

- Maqueda, C.; Pérez Rodriguez, J. L.; Martin, F.; Hermosin, M. C. A study of the interaction between chlordimeform and humic acid from a chromoxerert soil. *Soil Sci.* **1983**, *136*, 75–81.
- Maqueda, C.; Morillo, E.; Pérez Rodriguez, J. L.; Justo, A. Adsorption of chlordimeform by humic substances from different soils. *Soil Sci.* **1990**, *150*, 431–437.
- Nearpass, D. C. Adsorption of picloram by humic acids and humin. *Soil Sci.* **1976**, *121*, 272–277.
- Perucci, P.; Scarponi, L. Microbial Biomass-Persistence Relationships of acifluorfen in a Clay-loam soil. *Zentrabl. Mikrobiol.* **1993**, *148*, 16–23.
- Pusino, A.; Gessa, C. Photolysis of acifluorfen in aqueous solution. *Pestic. Sci.* **1991**, *32*, 1–5.
- Pusino, A.; Weiping, L.; Zhuo, F.; Gessa, C. Effect of metal-binding ability on the adsorption of acifluorfen on soil. *J. Agric. Food Chem.* **1993**, *41*, 502–505.
- Roy, T. A.; Meeks, J. R.; Mackerer, C. R. Ion pair reverse phase liquid chromatographic determination of sodium acifluorfen in feed. *J. Assoc. Off. Anal. Chem.* **1983**, *66*, 1319–1321.
- Ruggiero, P.; Crecchio, C.; Mininni, R.; Pizzigallo, M. D. R. Adsorption of the herbicide acifluorfen on humic acids. *Sci. Total Environ.* **1992**, *123/124*, 93–100.
- Schnitzer, M. Organic matter characterisation. *Methods of Soil Analysis. Part II. Agronomy 9*; American Society of Agronomy: Madison, WI, 1982.
- Schnitzer, M. Soil organic matter—the next 75 years. *Soil Sci.* **1991**, *151*, 41–58.
- Schnitzer, M.; Gupta, V. C. Determination of acidity in Soil Organic Matter. *Soil Sci. Soc. Proc.* **1965**, *29*, 274–277.
- Senesi, N. Binding mechanisms of pesticides to soil humic substances. *Sci. Total Environ.* **1992**, *123/124*, 63–76.
- Senesi, N.; Chen, Y. Interaction of TOCs with humic substances. In *Toxic Organic Chemicals in Porous Media-3, Ecological Studies*, 73; Gerstl, Z., Chen, Y., Mingelgrin, U., Yaron, B., Eds.; Springer-Verlag: Berlin, 1989.
- Senesi, N.; Brunetti, G.; La Cava, P.; Miano, T. Adsorption of alachlor by humic acids from sewage sludge and amended and non-amended soils. *Soil Sci.* **1994**, *175*, 176–184.
- Wills, G. D.; McWhorter, C. G. Effect of environment on the translocation and toxicity of acifluorfen to showy crotalaria (*Crotalaria spectabilis*). *Weed Sci.* **1981**, *29*, 397–401.

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