Acifluorfen Sorption, Degradation, and Mobility in a Mississippi Delta Soil

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ABSTRACT

Potential surface water and groundwater contaminants include herbicides that are applied postemergence. Although applied to the plant canopy, a portion of any application reaches the soil either directly or via subsequent foliar washoff. This study examined sorption, degradation, and mobility of the postemergence herbicide acifluorfen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid) in Dundee silty clay loam (fine-silty, mixed, thermic, Aeric Ochraqualf) taken from conventional till (CT) and no-till (NT) field plots. Homogeneous surface and subsurface samples were used in the sorption and degradation studies; intact soil columns (30 cm long and 10 cm diam.) were used in the mobility study. Batch sorption isotherms were nonlinear (Freundlich model) and sorption paralleled organic C (OC) content. All tillage by depth combinations of soil exhibited a time-dependent approach to sorption equilibrium that was well described by a two-site equilibrium–kinetic model. Acifluorfen degradation followed first-order kinetics. No more than about 6% of applied ^{14}C-acifluorfen was mineralized by 49-d incubation. Extracts of incubated soil gave little indication of degradation products; however, ^{14}C did accumulate in an unextractable fraction. Degradation was faster in the surface soils compared to subsurface soils and faster in CT surface soil compared to NT surface soil. Tillage did not affect acifluorfen degradation in subsurface samples. Elution of Br pulses from the intact soil columns under steady-state, unsaturated flow indicated preferential water flow. Nonequilibrium transport of Br was well described using a two-region, mobile–immobile water model. Inclusion of sorption kinetics in the transport model rather than assuming equilibrium sorption led to improved predictions of acifluorfen retardation. Column effluent contained negligible concentrations of acifluorfen degradation products and, as in the incubation study, an unextractable residue developed in the soil columns. However, unlike results from the incubation study, a greater fraction of applied acifluorfen was apparently bound and there was also evidence of extractable degradation products. Furthermore, first-order rate constants obtained from the batch study underestimated acifluorfen degradation during transport. Faster acifluorfen degradation in the soil columns may have been due to poorer aeration compared to the batch systems.

The fate and transport of postemergence herbicides in the soil environment have received little attention. Yet these compounds come in contact with the soil, directly or as foliar washoff (Reddy et al., 1994), and are subject to leaching and runoff. Acifluorfen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid) is a nitrodiphenyl ether postemergence herbicide (applied as the Na salt) that is widely used for the control of certain broadleaf weeds in soybean and peanut crops.

It exhibits a low pK_a of 3.5 (Roy et al., 1983) and is highly dissociated at typical soil pHs. Despite charge repulsion effects, acifluorfen is sorbed by soil or soil constituents (Pusino et al., 1991; Ruggiero et al., 1992; Pusino et al., 1993; Gennari et al., 1994b; Nègre et al., 1995; Locke et al., 1997). Although the extent of sorption in soil is generally proportional to OC content (Gennari et al., 1994b; Nègre et al., 1995; Locke et al., 1997), sorption likely involves processes other than partitioning between aqueous and organic matter phases. In particular, acifluorfen forms complexes with divalent and trivalent cations (Pusino et al., 1991; Pusino et al., 1993) that may be sorbed or precipitated. Complex formation and subsequent sorption may partially account for increased acifluorfen sorption with decreasing soil pH or increasing cation exchange capacity (Pusino et al., 1993; Gennari et al., 1994b; Locke et al., 1997). Also, acifluorfen sorption is a nonequilibrium, time-dependent process (Locke et al., 1997). Thus, the mobility of acifluorfen in soil is affected by the rate as well as the maximum extent of sorption.

Photodegradation of nitrodiphenyl ethers may involve several different reactions including nitroreduction and hydrolysis of the ether linkage (Ruzo et al., 1980). Depending on ring substituents, dechlorination, decarboxymethylation (Ruzo et al., 1980), or, in the case of acifluorfen, decarboxylation may occur (Pusino and Gessa, 1991). Aside from photodegradation, chemical degradation of nitrodiphenyl ethers may be possible. In particular, Ohyama and Kuwatsuka (1983) found that bifenox (methyl 5-[2,4-dichlorophenoxy]-2-nitrobenzoate) underwent nitroreduction in sterilized soil. In sterile microbial culture media (Andreoni et al., 1994), however, acifluorfen does not undergo degradation. Similar to degradation data for bifenox (Ohyama and Kuwatsuka, 1983), Andreoni et al. (1994) found that acifluorfen biodegradation in microbial cultures was more rapid under anaerobic rather than aerobic conditions. Although acifluorfen biodegradation may largely be a cometabolic process (Andreoni et al., 1994), certain bacterial strains are capable of metabolizing the herbicide (Fortina et al., 1996). Degradation products of acifluorfen isolated from microbial cultures include aminoacifluorfen, 5-([2-chloro-4-(trifluoromethyl)phenyl]oxy)-2-aminobenzamide, and 5-([2-chloro-4-(trifluoromethyl)phenyl]oxy)-2-(acetylamino)benzoic acid (Gennari et al., 1994a). Aminoacifluorfen has been recovered from soil treated with acifluorfen that was incubated for 6 d (Locke et al., 1997).

The primary objective of the present study was to quantify the degradation and sorption of acifluorfen in a Mississippi Delta soil and determine whether acifluorfen fate and mobility in this soil may be accurately described on the basis of these underlying processes.

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Published in Soil Sci. Soc. Am. J. 64:112–121 (2000).

Abbreviations: CT, conventional till; HPLC, high pressure liquid chromatography; NT, no-till; OC, organic carbon; TLC, thin-layer chromatography.

Sorption (isotherm and kinetics) and degradation were examined using batch systems. Intact, water-unsaturated soil columns were used to generate data on acifluorfen mobility. Because microenvironmental conditions within such soil columns may more closely match those in field soil than do conditions in batch (aerobic or anaerobic) degradation systems, data for acifluorfen mobility were also used to estimate degradation rates. A secondary objective was to assess the effects of 4 yr of no tillage (NT), compared to conventional tillage (CT), on acifluorfen degradation, sorption, and mobility.

MATERIALS AND METHODS

Soil

Dundee silty clay loam soil (fine-silty, mixed, thermic, Aeric Ochraqualf) was taken from CT and NT plots (subject to cotton [*Gossypium hirsutum*] cropping management) following spring cultivation (tillage operations are listed in Gaston et al. [1996]). No acifluorfen had been applied to this site for four or more years and the soils contained no detectable acifluorfen (extraction and analysis described later).

Samples included intact columns of soil (PVC pipe 10.2 cm i.d. and 30.0 cm long) and bulk soil. Collection of intact soil cores is described in Gaston and Locke (1996). Bulk samples were collected from the 0- to 10-, 10- to 20-, and 20- to 30-cm depths. Bulk soil used in the sorption experiments was air-dried, ground, mixed, and sieved (<2 mm), whereas soil for the degradation experiment was mixed and stored at 4°C until used. Chemical data for the 0- to 10-, 10- to 20-, and 20- to 30-cm depths of the CT and NT soils are given in Table 1.

Table 1. Selected chemical properties of Dundee convention till (CT) and no-till (NT) soil at three depths.

Soil	Depth	Organic C¶	pH†
	cm	%	
CT	0–10	0.87b‡	5.79a
	10–20	0.64c	5.77a
	20–30	0.49de	5.80a
NT	0–10	1.02a	5.60a
	10–20	0.56d	5.26b
	20–30	0.44e	5.71a

¶ Modified Mebius method (Nelson and Summers, 1982); average of three replicates.
† 1:1 soil:0.01 *M* $CaCl_2$; average of three replicates.
‡ Within a column, means followed by the same letter are not significantly different (Fisher's LSD, $\alpha = 0.05$).

Sorption Isotherms

Five-g (oven-dry equivalent) samples of air-dry 0- to 10-, 10- to 20-, and 20- to 30-cm depth CT or NT soil were placed in 25-mL glass centrifuge tubes and 15 mL of Na acifluorfen added. The Na salt was prepared from 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid (Chem Service, West Chester, PA), as described by Roy et al. (1983). It contained 33 Bq mL^{-1} ^{14}C-ring uniformly labeled compound (99% purity, BASF, Parsippany, NJ) in 0.01 *M* $CaCl_2$ (consistent with methodology used in the mobility study, discussed below). Suspensions were shaken for 24 h. Concentrations of herbicide applied were 1, 4, 20, 100, and 500 μ*M* (verified by high pressure liquid chromatography [HPLC] using standards of the acid dissolved in methanol), each in triplicate. Soil solution was separated from the suspension by centrifuging (10 min at 12 000 *g*). Sorption was calculated from change in solution concentration of ^{14}C (Tri-Carb 4000, Packard Instruments, Downers Grove, IL). Air-dry soil was used in the equilibrium and kinetic sorption studies to minimize biological activity during the course of these short-term experiments.

Sorption Kinetics

Triplicate 5-g (oven-dry equivalent) samples of 0- to 10-, 10- to 20-, and 20- to 30-cm depth CT or NT soil were shaken with 15 mL of 10.0 μ*M* Na acifluorfen (containing 33 Bq mL^{-1} ^{14}C-acifluorfen) in 0.01 *M* $CaCl_2$ for periods of time up to 32 h. Soil solution was separated from the suspension as above and sorption calculated by change in solution radioactivity.

Degradation

Twenty-five g (oven-dry equivalent) of the 0- to 10-cm CT, 0- to 10-cm NT, 20- to 30-cm CT, or 20- to 30-cm NT soils were transferred to biometer flasks (Bartha and Pramer, 1965) or 200-mL centrifuge bottles. Sufficient Na acifluorfen solution was added to each field-moist sample to supply 0.875 μmol acifluorfen (containing 5100 Bq ^{14}C-acifluorfen) and elevate soil moisture content to 35% by weight. Ten milliliters of 1 *M* NaOH was added to the side arm of each biometer flask and the flasks closed to the atmosphere. Samples in the centrifuge bottles were extracted (procedure discussed below) within 30 min after application. Soil samples were incubated at 25°C in the dark. After 7, 14, 21, 28, 35, and 49 d, soil was quantitatively transferred to 200-mL centrifuge bottles and extracted for acifluorfen and metabolites. Each soil by sampling time combination was replicated three times. The NaOH solutions were removed from all remaining biometer flasks semiweekly and fresh NaOH added. Aliquots were analyzed for $^{14}CO_2$ by liquid scintillation counting.

Soil was extracted using 50 mL of a 60:40 methanol:water solution that was shaken for 24 h. Suspensions were centrifuged (12 min at 8000 *g*), then supernatants decanted. A 1-mL aliquot was withdrawn for ^{14}C analysis and the remainder saved. The soil was extracted a second time for 3 h and then centrifuged. Supernatants were analyzed for ^{14}C and combined with the prior samples. The entrained extractant was allowed to evaporate before the air-dry soil was removed, ground, and duplicate 0.3-g samples combusted (Packard Oxidizer 306, Packard Instruments) to determine unextractable ^{14}C (corrected for contribution from the entrained solution).

Methanol in supernatants was evaporated under vacuum at 45°C (Savant Speedvac SS3, Savant Instruments, Farmingdale, NY). The resulting aqueous concentrates were acidified to pH 2 with 1 *M* HCl and passed through C_{18} solid-phase extraction columns (J.T. Baker, Phillipsburg, NJ). Polar metabolites in the aqueous effluent were measured as ^{14}C. Sorbed acifluorfen and any moderately polar metabolites were eluted from the C_{18} columns with 3 mL methanol; these concentrated samples were then analyzed using an HPLC system (Waters, Milford, MA) consisting of a Maxima controler, 510 pump, 710B autosampler, and 490 UV detector. An Alltima column (Alltech, Deerfield, IL) and 60:40 acetonitrile:water (pH 3.2) eluant were used. Further details on the HPLC method are given in Locke et al. (1997). The system also included an in-line liquid scintillation counter ("-Ram detector, INUS Systems, Tampa, FL). Detection limit for acifluorfen was <0.1 μ*M* (50-μL injection volume).

Concentrated samples were also analyzed by thin-layer chromatography (TLC). Fifty-microliter aliquots were spotted on preadsorbent silica gel plates (20 × 20 cm, 250-μm gel, Whatman, Clifton, NJ), and developed to 10 cm using toluene:ethyl acetate:acetic acid:water (100:100:2:1, volume). The distribution of ^{14}C was revealed using a Bioscan System 200 imaging scanner (Bioscan, Washington, DC).

Mobility Study

The system and procedure used to establish steady-state unsaturated flow through the intact soil columns have been previously described (Gaston and Locke, 1996). Briefly, the bottom of each soil column was covered with a porous glass membrane (11.0 cm diam., Whatman) and sealed with a PVC end-plate assembly that drained into a vacuum flask. A headspace extension attached to the top of the 30-cm PVC pipe opened to a CO_2 trap and supported a sprinkler head. A layer of acid-washed gravel protected the soil surface from the impact of sprinkler drops.

Calcium chloride solution (0.01 *M*) was applied at constant intensity by using a metering pump (model G6 RH1, FMI, Oyster Bay, NY) and constant suction head (60 cm water) was maintained at the bottom. The application rate (1.56 cm d^{-1}, average for all columns) was less than the saturated conductivity of the least conductive soil columns (low end of range as determined in a preliminary study). Steady-state conditions were assumed to exist when the time-averaged change in mass of a soil column reached approximately zero.

Once apparent steady-state flow existed, the gravel was removed and 10.0-mL pulses of 1.0 *M* KBr, followed by 529 μ*M* Na acifluorfen (containing 4475 Bq mL^{-1}, ^{14}C-acifluorfen), were uniformly applied to the soil surface (pulse and sprinkler infiltration rates equal) using glass pipets. Gravel was then replaced and sprinkler infiltration continued.

Column effluent was sampled twice daily through about two cumulative pore volumes and one daily thereafter. Aliquots were saved for Br and ^{14}C analyses. The remainder was pooled into a series of 10 samples, each including effluent for about a 4-d flow period. Bromide was determined using ion chromatography (DX-100, DIONEX, Sunnyvale, CA). The NaOH solutions were replaced weekly and activity of trapped $^{14}CO_2$ measured.

Pooled samples were concentrated before HPLC analysis. Two hundred mL of each aqueous fraction were acidified and passed through a C_{18} solid-phase extraction column as described earlier. Aqueous effluent from extraction columns was checked for polar ^{14}C metabolites. Acifluorfen and moderately polar metabolites were then eluted with 3 mL of methanol.

The leaching experiment was terminated 40 d after application of acifluorfen and the change in mass of each column measured. The leaching apparatus was disassembled, soil carefully pushed (from bottom up) out of the PVC casing, and sectioned into 5.0-cm increments. There was no apparent soil compaction during removal. About 50-g subsamples from each section were transferred to 250-mL centrifuge bottles for extraction of acifluorfen and degradation products. Volumetric water content and bulk density with depth were calculated using the remaining soil from each section, corrected for the subsample removed. Soil subsamples were extracted as in the degradation experiment, however, with 100 mL of extractant. Aliquots of supernatant were measured for ^{14}C activity. The entrained extracting solution was allowed to evaporate and unextractable ^{14}C determined from duplicate 0.3-g, air-dry, ground samples upon combustion. Methanol in supernatants was evaporated and aqueous solutions concentrated and analyzed by HPLC as described above.

Models

Batch Systems

Sorption kinetics were described by the two-site equilibrium–kinetic model that assumes instantaneous sorption at a fraction of sites (type 1) as

$$S_1 = k_e C^N \quad [1a]$$

where S_1 is sorbed concentration (μmol kg^{-1}), C is solution concentration (μM), and k_e (L kg^{-1}) and N are empirical constants. Sorption at remaining sites (type 2) was described by Nth-order kinetics as

$$dS_2/dt = k_f C^N - k_r S_2 \quad [1b]$$

where k_f (L kg^{-1} d^{-1}) and k_r (d^{-1}) are forward and reverse rate constants, respectively. Since $S = S_1 + S_2$ and $k_e + k_f/k_r = K_F$ (L kg^{-1}), Eq. 1a and 1b reduce to the Freundlich model, $S = K_F C^N$ at equilibrium.

The first-order kinetic model was used to describe acifluorfen degradation as

$$dM/dt = k_d M \quad [2]$$

where M is substrate mass (μmol) and k_d (d^{-1}) is the degradation rate constant.

Transport Systems

The mobility of acifluorfen under steady-state flow through the intact soil columns was described using the two-region model presented by van Genuchten and Wagenet (1989), which was adapted to account for variability in soil properties with depth (Gaston and Locke, 1996) and sorption kinetics:

$$\theta_{M,j}\partial C_{M,j}/\partial t + \rho_j \partial S_{M,1,j}/\partial t + \rho_j \partial S_{M,2,j}/\partial t + \theta_{IM,j}\partial C_{IM,j}/\partial t + \rho_j \partial S_{IM,1,j}/\partial t + \rho_j \partial S_{IM,2,j}/\partial t = \theta_{M,j} D_j \partial^2 C_{M,j}/\partial z^2 - \theta_{M,j} v_j \partial C_{M,j}/\partial z - F(_{M,j},S_{M,j}) \quad [3a]$$

$$\theta_{IM,j}\partial C_{IM,j}/\partial t + \rho_j \partial S_{IM,1,j}/\partial t + \rho_j \partial S_{IM,2,j}\partial t = \alpha_j (C_{M,j} - C_{IM,j}) - G(C_{IM,j},S_{IM,j}) \quad [3b]$$

where subscripts M and IM refer to mobile and immobile water regions, respectively; subscripts 1 and 2 refer to equilibrium- and kinetic-type sorption sites, respectively; subscript j denotes the j^{th} of N depth increments; θ is volumetric water content; ρ is bulk density (Mg m^{-3}); D is the dispersion coefficient (cm^2 d^{-1}); v is pore water velocity (cm d^{-1}); α is the mass transfer coefficient for diffusion between mobile and immobile water regions (d^{-1}); t is time (d); and z is depth (cm). The functions F and G describe acifluorfen degradation in the mobile and immobile water regions, respectively.

Boundary and initial conditions were

$$-D_1 \partial C_{M,1}/\partial_z + v_1 C_{M,1} = v_1 C_0$$
$$0 < t \le t_p,\ z = 0 \quad [3c]$$

$$-D_1 \partial C_{M,1}/\partial z + v_1 C_{M,1} = 0$$
$$t > t_p,\ z = 0 \quad [3d]$$

$$\theta_{M,j} D_j \partial C_{M,j}/\partial z = \theta_{M,j+1} D_{j+1} \partial C_{M,j+1}/\partial z$$
$$t > 0,\ z = jL/N \quad [3e]$$

$$\partial C_{M,N}/\partial t = 0$$
$$t > 0,\ z = L \quad [3f]$$

$$C_{M,j} = 0$$
$$t = 0,\ 0 \le z \le L \quad [3g]$$

$$C_{IM,j} = 0$$
$$t = 0,\ 0 \le z \le L \quad [3h]$$

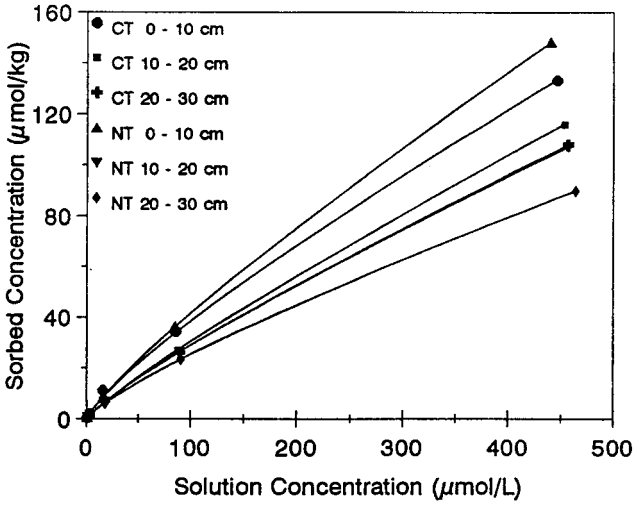

Fig. 1. Acifluorfen sorption isotherms for three depth increments in Dundee conventional till (CT) and no-till (NT) soil. Curves show best-fits of the Freundlich model to each experimental isotherm.

where C_0 is concentration of the input pulse (μmol L^{-1}), L is column length (cm), and t_p is pulse duration (d).

The two-site sorption model for mobile and immobile water regions was

$$S_{M,1,j} = f_j k_{e,j} (C_{M,j})^{Nj} \quad [4a]$$

$$\partial S_{M,2,j}/\partial t = f_j k_{f,j} (C_{M,j})^{Nj} - k_{T,j} S_{M,2,j} \quad [4b]$$

$$S_{IM,1,j} = (1 - f_j) k_{e,j} (C_{IM,j})^{Nj} \quad [4c]$$

$$\partial S_{IM,2,j}/\partial t = (1 - f_j) k_{f,j} (C_{IM,j})^{Nj} - k_{r,j} S_{IM,2,j} \quad [4d]$$

where f_j is the fraction of sorption sites in the mobile water region of depth increment j. This fraction was assumed proportional to the fraction of mobile water, $f_j = \theta_{M,j}/\theta_j$.

If sorption kinetics are ignored, Eq. 4a–4d reduce to corresponding Freundlich models for mobile and immobile water regions written as

$$S_{M,1,j} = f_j K_j (C_{M,j})^{Nj} \quad [4e]$$

$$S_{IM,1,j} = (1 - f_j) K_j (C_{IM,j})^{Nj} \quad [4f]$$

No attempt was made to distinguish between degradation occurring in solution and possibly in the sorbed phase; rather, these processes were lumped, so that

$$F(C_{M,j}, S_{M,j}) = k_{M,j}(\theta_{M,j} C_{M,j} + \rho_j [S_{M,1,j} + S_{M,2,j}]) \quad [5a]$$

$$G(C_{IM,j}, S_{IM,j}) = k_{IM,j}(\theta_{IM,j} C_{IM,j} + \rho_j [S_{IM,1,j} + S_{IM,2,j}]) \quad [5b]$$

where $k_{M,j}$ and $k_{IM,j}$ (d^{-1}) are first-order degradation rate constants for the two regions in depth increment j.

Additionally, $\theta_{M,j}$ was assumed to be directly proportional to total volumetric water content, θ_j ($\theta_{M,j}/\theta_j = \theta_M/[\theta_{M,j} + \theta_{IM,j}] = \varepsilon$), and D_j and α_j directly proportional to pore water velocity, v_j ($D_j/v_j = D_j\theta_j/q = \Psi$ [cm]; $\alpha_j/v_j = \alpha_j\theta_j/q = \phi$ [cm^{-1}]). Justifications for these assumptions have been discussed in Gaston and Locke (1996). The parameters ε, ϕ, and ψ were determined from tracer elution curves. Bulk density ρ_j and total volumetric water content θ_j were determined from masses of column sections before and after drying.

Approximate solutions were generated using an implicit finite difference method. A least-squares procedure (van Genuchten, 1981), coupled with either the transport model (Eq. [3]–[5]) or batch sorption kinetics model (Eq. [2a] and [2b]), was used for parameter estimation.

Table 2. Sorption isotherm and two-site equilibrium–kinetic model parameters for Dundee conventional till (CT) and no-till (NT) soil at three depths.

Soil	Depth	Sorption parameter				
		K_F	N	k_e	k_f	k_r
	cm	L kg^{-1}		L kg^{-1}	L kg^{-1} d^{-1}	d^{-1}
CT	0–10	0.83 ± 0.04¶	0.82 ± 0.01	0.57 ± 0.02	0.82 ± 0.34	3.0 ± 1.4
	10–20	0.52 ± 0.05	0.87 ± 0.02	0.44 ± 0.01	0.11 ± 0.09	0.7 ± 1.5
	20–30	0.54 ± 0.02	0.85 ± 0.01	0.40 ± 0.02	0.36 ± 0.30	2.4 ± 2.4
NT	0–10	0.80 ± 0.01	0.85 ± 0.01	0.58 ± 0.02	0.43 ± 0.21	1.6 ± 1.1
	10–20	0.54 ± 0.02	0.85 ± 0.01	0.41 ± 0.02	0.22 ± 0.18	1.1 ± 1.6
	20–30	0.56 ± 0.01	0.81 ± 0.01	0.37 ± 0.02	0.71 ± 0.37	3.6 ± 2.0

¶ Standard error.

RESULTS AND DISCUSSION

Sorption Isotherms

Freundlich models for acifluorfen sorption (Fig. 1) indicated greater sorption in the Dundee NT compared with the CT surface soil. This is consistent with the slightly greater OC content of the NT soil (Table 1). In general, the extent of acifluorfen sorption paralleled OC content, decreasing with increasing depth below the soil surface. Also, greater sorption in the CT subsurface, compared with the NT subsurface (10 to 20 cm and 20 to 30 cm), was consistent with slightly higher OC content in the CT soil samples. However, differences due to tillage at the three depths were sufficiently small and uncertainty in Freundlich parameters (Table 2) sufficiently high that models for sorption in CT and NT soil at any depth were not significantly different (Taylor series approximation method of Hinds and Milliken [1987]; data not shown). On the other hand, comparison of sorption at each initial acifluorfen concentration (Table 3) shows that sorption was generally greater in the NT surface soil than in the corresponding CT soil and that sorption was generally greater in the subsurface CT soils than in corresponding NT soils.

Sorption Kinetics

Sorption of acifluorfen in all depths of the CT and NT Dundee soils was time-dependent and well described by the two-site kinetic–equilibrium model. Figures 2a–2c show effect of tillage on extent of sorption (fraction of maximum based on K_F calculated from fitted parameters $K_F = k_e + k_f/k_r$) as a function of reaction time in the 0- to 10-, 10- to 20-, and 20- to 30-cm depths (parameter values given in Table 2). Also shown are best-fits of the

Table 3. Acifluorfen sorption in Dundee conventional till (CT) and no-till (NT) soil at three depths and five initial acifluorfen concentrations.

Soil	Depth	Initial acifluorfen concentration (μM)				
		1	4	20	100	500
	cm	μmol/kg				
CT	0–10	0.57a¶	1.8b	7.8b	32.9a	125.7b
	10–20	0.46c	1.6c	7.2b	25.1b	105.7c
	20–30	0.49b	1.6c	6.5c	24.1bc	96.9c
NT	0–10	0.48bc	2.0a	8.6a	35.1a	141.2a
	10–20	0.41d	1.5cd	6.4c	24.6b	98.9c
	20–30	0.39d	1.4d	5.6d	21.6c	80.5d

¶ Within a column, means followed by the same letter are not significantly different (Fisher's LSD, α = 0.05).

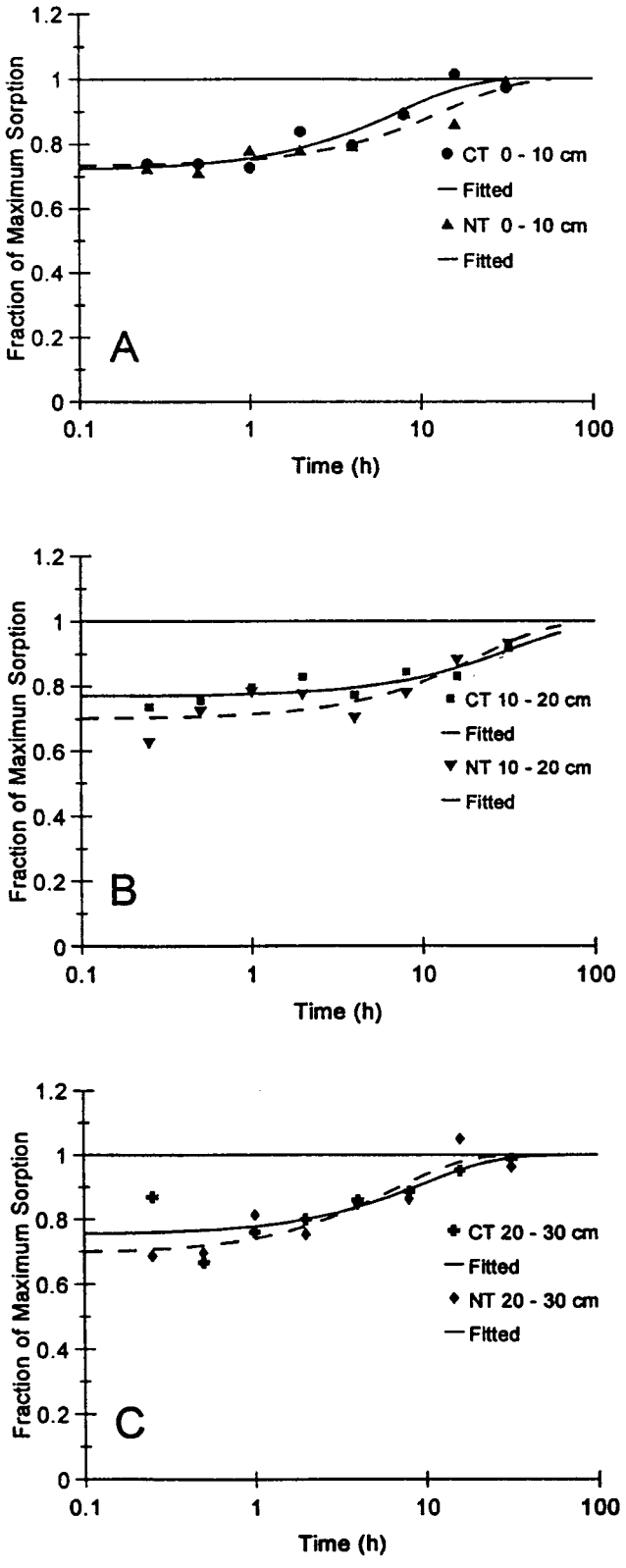

Fig. 2. Acifluorfen sorption kinetics for: (A) 0–10 cm, (B) 10–20 cm, and (C) 20–30 cm depth increments in Dundee conventional till (CT) and no-till (NT) soil. Curves show best-fits of the two-site equilibrium–kinetic model to each time-course data set. All data are relative to equilibrium sorption.

two-site model. Comparison of these scaled data reveals little or no differences among the soils in extent of instantaneous sorption (average $k_e/K_F \sim 0.7$). Because of fairly large uncertainty in estimations of k_f and k_r (Table 2), the effect (if any) of tillage on acifluorfen sorption kinetics is unclear. It is apparent from Fig. 2a–2c, however, that equilibrium was generally not achieved by 24-h contact time.

Degradation

Despite up to 40% degradation of acifluorfen during the 49-d experiment (Table 4), chromatograms of the concentrated ^{14}C extracts gave no evidence of metabolites; corrected for background, ^{14}C-acifluorfen accounted for essentially all (average $>$ 99%) radioactivity in the HPLC and TLC chromatograms. In particular, no extractable aminoacifluorfen was found. Furthermore, the solid-phase extraction procedure recovered >99% of initially extracted ^{14}C. Thus, any polar metabolites (unrecovered in this step), along with any less-polar metabolites retained by the C_{18} extraction columns, constituted a very minor fraction of extracted ^{14}C.

Degradation of acifluorfen was accompanied by development of an unextractable fraction of ^{14}C (Table 4). Recent work by Locke et al. (1997) showed that aminoacifluorfen exhibited high sorption affinity ($K_F >$ 40 L kg^{-1}) in a Dundee soil, especially at low concentrations (highly nonlinear, with $N = 0.41$), and that less than 10% of the applied aminoacifluorfen was extractable after 24-h contact. Similar reactivity of aminoacifluorfen in the Dundee CT and NT soils may account for absence of this metabolite and, in part, contribute to accretion of the unextractable fraction of ^{14}C. Based on previous work (Locke et al., 1997), binding of acifluorfen to soil colloids seems unlikely. Although short-term sorption kinetics were well-described by the two-site equilibrium–kinetic model, continued sorption of ^{14}C beyond about 48 h could not be accounted for by assuming irreversible sorption of acifluorfen. However, the time-dependent increase in ^{14}C could be described by assuming irreversible sorption of acifluorfen degradation products (Locke et al., 1997).

Slow mineralization of acifluorfen was consistent with negligible concentration of extractable degradation intermediates. Despite the generally slow rate of evolution of ring-^{14}C as radio-labeled CO_2, the data revealed differences among the four soils due to tillage and depth below the soil surface (Table 4). Mineralization was generally faster in the surface soils than in the corresponding subsurface soils and faster in the 0- to 10-cm CT soil than in the corresponding NT surface soil. Relative mineralization among the four soils was consistent with extent of acifluorfen degradation and accumulation of unextractable ^{14}C (Table 4).

Acifluorfen degradation was generally greater in the surface soils for incubation times beyond 14 d (Table 4). By Day 21, degradation was generally greater in the surface CT than in the respective NT soil. There was no effect due to tillage in the subsurface soils. Acifluorfen degradation was described by first-order kinetics (Eq.

Table 4. Recovery of acifluorfen and ^{14}C applied in the acifluorfen degradation study.

Data set	Soil	Depth	Incubation time (d) 7	14	21	28	35	49
		cm	% of applied					
Acifluorfen	CT†	0–10	93.0a¶	83.7b	78.5c	78.6c	77.8c	61.0b
	NT‡	0–10	94.2a	87.8b	88.4b	87.4b	80.0bc	72.0ab
	CT	20–30	93.8a	95.6a	91.6a	92.6a	85.3ab	80.9a
	NT	20–30	93.7a	86.9b	91.6a	93.9a	87.7a	80.4a
Mineralized	CT	0–10	1.8a	3.2a	4.0a	4.4a	5.6a	6.2a
	NT	0–10	1.5b	2.7b	3.3b	4.0b	4.3b	5.2b
	CT	20–30	1.4c	2.4c	3.0c	3.5c	4.2b	4.7b
	NT	20–30	1.3c	2.1d	2.7d	3.2d	3.7c	4.1c
Unextractable	CT	0–10	5.9a	7.6a	11.0a	10.9a	12.2a	12.1a
	NT	0–10	3.8b	5.9b	7.2b	8.8a	9.7a	9.4b
	CT	20–30	1.6c	1.3c	2.7c	3.2b	3.0b	3.4c
	NT	20–30	1.7c	2.5c	3.5c	4.6b	5.0b	4.7c
Total ^{14}C	CT	0–10	99.7	94.5	93.5	93.9	95.6	79.3
	NT	0–10	99.5	96.4	94.9	100.2	94.0	86.6
	CT	20–30	96.8	99.3	97.3	99.3	92.5	89.0
	NT	20–30	96.7	91.5	97.8	100.7	96.5	89.2

¶ In data set, within a column, means followed by the same letter are not significantly different (Fisher LSD, $\alpha = 0.05$).
† CT, conventional till.
‡ NT, no-till.

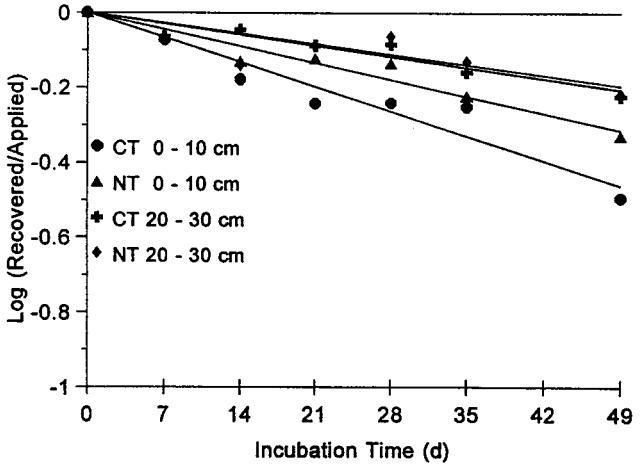

Fig. 3. Degradation kinetics of acifluorfen in surface and subsurface Dundee conventional till (CT) and no-till (NT) soil. Lines show best-fits of the first-order model to each experimental data set.

[2]), as shown in Fig. 3. The modeled data indicate faster degradation in the CT surface soil than in corresponding NT soil, faster degradation in the surface soils than in subsurface soils, but no difference due to tillage in the subsurface soils. Rate constants are given in Table 5.

Faster degradation in the surface soils compared with subsurface soils was consistent with greater metabolic activity and high numbers of microorganisms in the surface soils (Table 2, Gaston et al., 1996). However, faster acifluorfen degradation in the CT, compared with NT, surface soil (Fig. 3 and Tables 4 and 5) would not have been expected on the basis of microbiological data that indicated no difference in degradation potential. On the other hand, slightly greater acifluorfen sorption in the NT surface soil might result in slower degradation if degradation were limited to solution phase substrate. However, fits of the two-site model (Eq. [1a] and [1b]), extended to include solution phase first-order degradation of acifluorfen and irreversible sorption of degradation product(s) (Locke et al., 1997) to data for recovered acifluorfen and unextractable ^{14}C, failed to account for the inconsistency between degradation and microbial data. The degradation rate constant estimated for the CT soil remained larger (CT $k_d = 0.025 \pm 0.02$ and NT $k_d = 0.018 \pm 0.01$) due to only slightly greater sorption in the NT surface soil. Apparently, the greater rate of acifluorfen degradation (and mineralization) in the CT surface soil simply reflected a larger population of microorganisms capable of degrading acifluorfen.

Preferential Flow through Intact Soil Columns

All Br elution curves indicate some degree of preferential flow. Examples in Fig. 4 for columns CT 1 and NT 2 show a range of Br peak concentrations from about 0.2 to 0.4 pore volumes earlier, respectively, than expected in the absence of preferential flow. The mobile–immobile water model (Eq. [3], without sorption or degradation) was capable of providing good descriptions of Br elution in all cases. Optimized parameters are given in Table 6. Measured variation in soil bulk density and water content with depth below the surface of each soil column is shown in Table 7. Small ϕ values (Table 6) indicate slow mass transfer between mobile and immobile water regions.

Acifluorfen Mobility

Experimental Results

Chromatograms of soil column effluents revealed no ^{14}C peaks other than for ^{14}C-acifluorfen (corrected for background, radioactivity eluting with acifluorfen accounted for ave. 99% in chromatograms). Less than 2% effluent ^{14}C passed through the C_{18} extraction columns used in HPLC sample preparation, indicating low concentration of polar ^{14}C-compounds. There was loss of <2% of the effluent ^{14}C during solid-phase extraction.

Table 5. First-order rate constants for acifluorfen degradation obtained from batch and transport data.

Soil	Depth	Batch k_d	Transport k_d from soil column CT 1	CT 2	NT 1	NT 2
	cm	d^{-1}				
CT†	0–10	0.0094 ± 0.0007¶	0.045 ± 0.006	0.054 ± 0.011		
	20–30	0.0041 ± 0.0004	0.060 ± 0.009	0.016 ± 0.004		
NT‡	0–10	0.0064 ± 0.0004			0.059 ± 0.006	0.096 ± 0.012
	20–30	0.0042 ± 0.0009			0.011 ± 0.004	0.002 ± 0.001

¶ Standard error.
† CT, conventional till.
‡ NT, no-till.

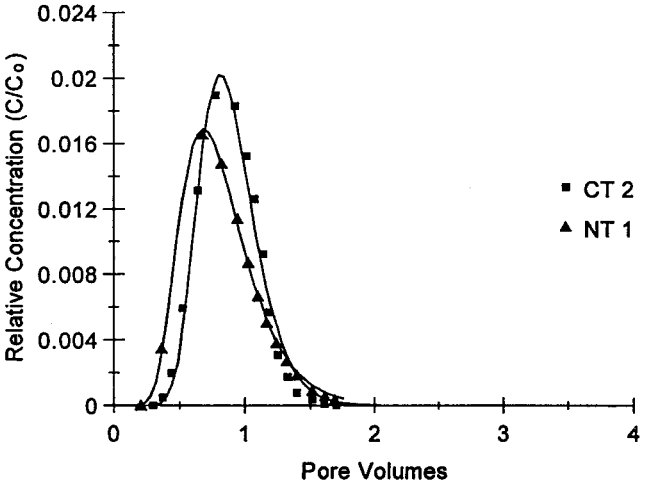

Fig. 4. Example Br elution curves from two intact soil columns showing the effect of preferential water flow. Curves are best-fits of the two-region mobile–immobile water model.

Therefore, ^{14}C-acifluorfen accounted for about 97% of the radioactivity in column effluent and ^{14}C effluent concentrations may be taken as proportional to effluent acifluorfen concentrations. Figure 5 shows average effluent concentrations of ^{14}C-acifluorfen for the CT and NT soil columns. Acifluorfen elution from the NT columns was slightly delayed compared to elution from the CT columns.

Although there was little evidence for acifluorfen degradation products in the soil column effluent, about 39% of the ^{14}C extracted from the soil columns could not be attributed to acifluorfen. Due to low total radioactivity in these extracts, however, the only obvious chromatographic peak was ^{14}C-acifluorfen. Of the total ^{14}C extracted, about 26% was not retained by the C_{18} columns and 13% unrecovered in either HPLC samples or as polar compounds in aqueous effluent from the C_{18} columns. The concentration of degradation products was greatest at the soil surface (0–5 cm depth segment). About 11% of the applied acifluorfen was recovered from the NT soil columns by extraction, whereas 9% was extracted from the CT columns. Slightly greater solute retardation in the NT soil columns (Fig. 5) may account for this small difference in acifluorfen recovery. Table 8 shows ^{14}C recovered as leachate, soil extract, and liberated upon combustion.

Data on sorption affinity (or poor extractability) of acifluorfen degradation products such as aminoacifluorfen (Locke et al., 1997) suggest that development of an unextractable fraction reflects degradation of acifluorfen to more highly sorbed compounds. If this is the case, slightly greater accumulation of unextractable ^{14}C in the CT soil columns (34% of applied compared to 27% in the NT columns) may indicate a somewhat faster rate of acifluorfen transformation in the CT soil, consistent with biometer flask data for the 0- to 10-cm depth soils (Tables 3 and 4). Also, average sum of unextractable ^{14}C plus extractable degradation products was higher in the CT soil (39% compared with 35%). However, lower recovery of degradation products from the NT soil columns may reflect lower average total recovery of ^{14}C (Table 8).

Table 7. Volumetric water content (θ) and bulk density (ρ) at various depths in the Dundee soil columns.

	Column							
	CT† 1		CT 2		NT‡ 1		NT 2	
Depth	θ	ρ	θ	ρ	θ	ρ	θ	ρ
cm		Mg m^{-3}		Mg m^{-3}		Mg m^{-3}		Mg m^{-3}
0–5	0.358	1.11	0.335	1.10	0.398	1.22	0.369	1.07
5–10	0.444	1.51	0.403	1.45	0.390	1.41	0.390	1.44
10–15	0.402	1.49	0.405	1.53	0.392	1.54	0.400	1.52
15–20	0.409	1.47	0.387	1.43	0.384	1.53	0.371	1.57
20–25	0.417	1.48	0.400	1.48	0.390	1.53	0.376	1.59
25–30	0.410	1.44	0.356	1.48	0.396	1.51	0.364	1.58

† CT, conventional till.
‡ NT, no-till.

Simulation Results

Bromide elution curves indicated that water flow through the intact soil columns bypassed a portion of the total pore water volume (Fig. 4). Results of the batch sorption study showed that acifluorfen sorption in Dundee CT and NT soils is time-dependent (Fig. 2a–2c). Thus, it seems possible that sorption kinetics as well as preferential water flow might affect acifluorfen transport. Figure 6 shows ^{14}C-acifluorfen effluent concentrations for column CT 1 compared to simulations assuming either instantaneous sorption equilibrium (Eq. [4e]–[4f]) or time-dependent sorption (Eq. [4a]–[4d]). Sorption parameters given in Table 2 were used. Inclusion of sorption kinetics led to a better description of acifluorfen retardation (Fig. 6). However, the fairly slow pore water velocity (Table 5) and long solute residence time favored close approach to sorption equilibrium; ignoring sorption kinetics resulted in <10% error in predicted retardation (Fig. 6).

In general, use of the batch sorption kinetics data in the transport model led to accurate prediction of acifluorfen mobility through the intact soil columns. Fig-

Table 6. Transport model parameters for the Dundee soil columns.

	Column			
Parameter	CT† 1	CT 2	NT‡ 1	NT 2
ε (=θ_m/θ)	0.81 ± 0.01	0.88 ± 0.01	0.82 ± 0.01	0.94 ± 0.01
ϕ (=$\alpha\theta/q$, cm^{-})	0.001 ± 0.001	0.001 ± 0.002	0.001 ± 0.001	0.001 ± 0.001
ψ (=$D\theta/q$, cm)	1.10 ± 0.03	0.96 ± 0.08	1.96 ± 0.05	2.6 ± 0.2
q (cm d^{-1})	1.53	1.53	1.67	1.57
t_p (d)	0.080	0.080	0.076	0.080

† CT, conventional till.
‡ NT, no-till.

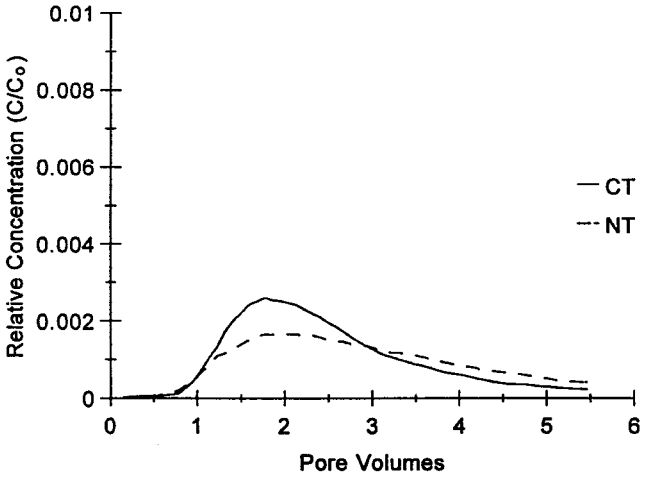

Fig. 5. Effect of tillage on elution of acifluorfen pulses applied to the surface of intact columns of Dundee conventional till (CT) and no-till (NT) soil. Average relative concentrations are shown.

ure 7a presents average measured and predicted acifluorfen effluent concentrations for the four soil columns. Although the batch sorption data were clearly appropriate for predicting volume of water required to displace acifluorfen, the batch degradation data substantially underestimated the rate of acifluorfen degradation in the soil columns. Comparison of measured and predicted distribution of unextractable (apparently bound) ^{14}C reveals a similar discrepancy.

Based on results from the degradation and mobility studies, intermediate products of acifluorfen degradation in the Dundee soils apparently exhibit high affinity for sorption. Thus, to a first approximation, such compounds may be assumed immobile (within the time scale of the transport experiment) and to accumulate in place where formed. Concentrations of acifluorfen degradation products predicted using Eq. [5a] and [5b] may be compared to the sum of extractable degradation products plus unextractable ^{14}C. Figure 7b shows this comparison the for upper, middle, and lower 10-cm soil segments. Concentrations predicted on the basis of batch data were smaller, indicating that acifluorfen degradation proceeded at a faster rate in the soil columns than in the batch systems.

To quantify the magnitude of error in batch degradation rate constants that was responsible for the discrepancies between predicted and measured data (Fig. 7a and 7b), rate constants were adjusted to fit the acifluorfen effluent concentration and residual ^{14}C data. First-order degradation was assumed and rate constants for the top and bottom 10-cm segments were optimized to obtain best-fits to the experimental data. The rate constant for the middle segment was assumed to be the average of these values. Also, based on the results of Gaston and Locke (1996), there was little to be gained by trying to estimate different rate constants for mobile and immobile water regions because mass transfer between these regions was slow (Table 6). Calculated first-order degradation rate constants for the four soil columns are listed in Table 5.

Estimated rate constants were often nearly an order

Table 8. Recovery of ^{14}C applied to the Dundee soil columns.

Column	Fraction			Total
	Effluent	Extractable	Unextractable	
	% of ^{14}C applied			
CT† 1	45.7	16.7	30.0	92.4
CT 2	57.1	10.1	38.4	105.5
NT‡ 1	55.3	14.0	23.4	92.7
NT 2	35.0	23.7	31.0	89.7

† CT, conventional till.
‡ NT, no-till.

of magnitude greater than the corresponding values obtained from the biometer flask study. Consistent with the batch data, however, rate constants for the surface soil were generally greater than those for the 20- to 30-cm depth. Adequacy of fits to the NT 1 column data are shown in Fig. 8a and 8b. The mass of acifluorfen displaced through the soil column was accurately described (Fig. 8a) and distribution of residual ^{14}C better estimated (Fig. 8b) than when batch degradation data were used.

Since acifluorfen degradation is more rapid under anaerobic conditions (Andreoni et al., 1994), greater degradation rates in the soil columns may reflect poorer aeration than in the biometer flasks. In contrast to the batch systems, which each contained a thin layer of 25-g soil and were vented when NaOH was replaced, only the top surface of the soil columns was exposed to the atmosphere (directly, during replacement of NaOH, or indirectly, via sprinkler application of aerated 0.01 *M* $CaCl_2$ solution). Thus, the ratio of external surface area to internal volume was much larger and path length for O_2 diffusion much shorter in the batch systems.

Because intact soil columns are approximate models for undisturbed soil, the distribution of k_d values with depth may be similar to field values under similar moisture conditions (wet, though unsaturated, with an average 0.07 void space, as calculated from the data in Table 7, assuming soil particle density of 2.65 Mg m^{-3}). Therefore, k_ds obtained from the mobility study may tend

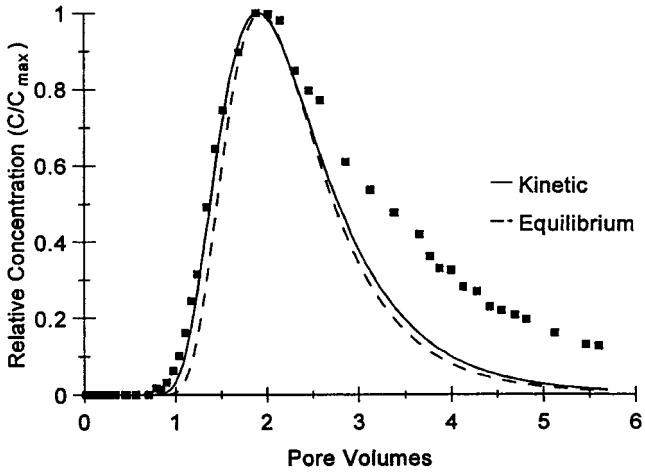

Fig. 6. Predictions of acifluorfen elution from intact conventional till (CT) soil column 1 obtained when allowing for sorption kinetics or assuming sorption equilibrium compared with measured effluent concentrations. All concentrations in a curve are relative to the maximum concentration in that data set.

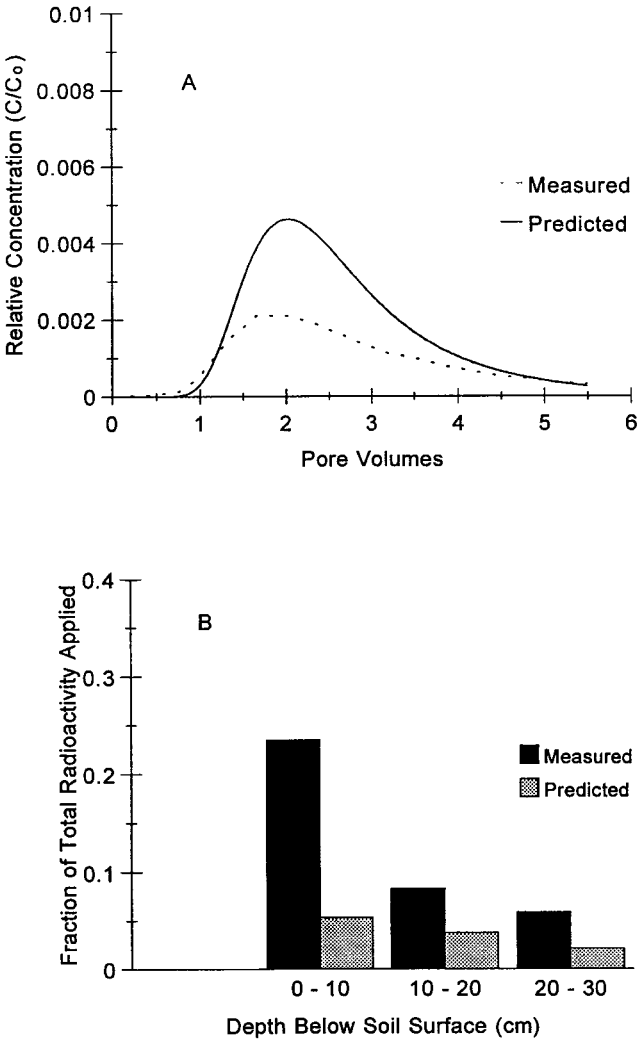

Fig. 7. (A) Average predicted and measured effluent concentrations of acifluorfen from the intact soil columns. (B) Average predicted and measured concentrations of residual ^{14}C (unextractable and extractable, exclusive of acifluorfen) in three depth increments of the soil columns.

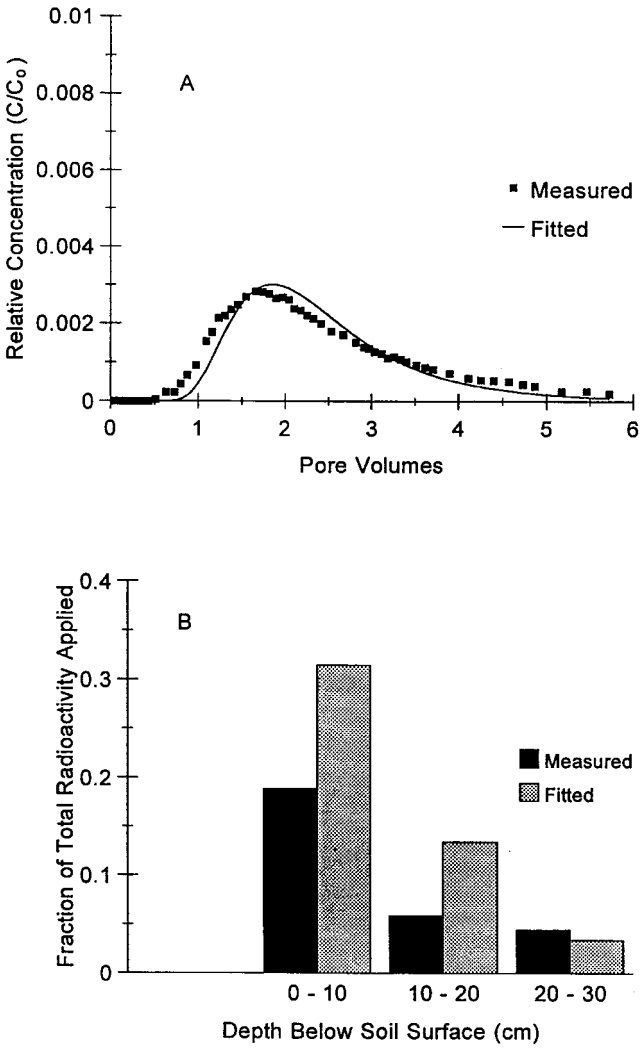

Fig. 8. (A) Simulation of acifluorfen elution from intact and no-till (NT) soil column 1 generated using best-fit values for k_d in the 0–10 and 20–30 cm depths compared with measured effluent concentrations. (B) Distribution of residual ^{14}C (unextractable and extractable, exclusive of acifluorfen) with depth obtained using best-fit values for k_d compared with measured residual ^{14}C.

toward the high end of the possible range in values for the Dundee soils. On the other hand, aeration in the biometer flasks may have been artificially high with respect to field soil at similar water content (particularly below the soil surface). Thus, k_ds from the batch systems, though obtained at 35% moisture, may be more indicative of acifluorfen degradation under drier, more aerated conditions.

SUMMARY

Effects of tillage on acifluorfen sorption isotherms in the Dundee CT and NT soils were related to amount and distribution of OC. Higher content of OC in the 0- to 10-cm NT led to greater acifluorfen sorption than in the surface CT soil, but more OC in the subsurface CT soils resulted in greater sorption than in the corresponding NT soils. Sorption isotherms for all six tillage–depth combinations were nonlinear. Approach to equilibrium was time-dependent and conformed to the two-site equilibrium–kinetic model. Kinetics were rapid (>70% of total sorption occurring almost instantaneously and, typically, more than 90% within 24 h) but revealed no clear trend with respect to tillage or OC content. Nevertheless, inclusion of sorption kinetics in the transport model for acifluorfen mobility gave more accurate predictions of retardation than assumption of instantaneous sorption equilibrium.

Acifluorfen degradation was more rapid in topsoil (0- to 10-cm) than in subsoil (20- to 30-cm). The first-order rate constant was larger for the CT topsoil, but there was no difference between CT and NT subsoils in rate of acifluorfen degradation. The incubation study revealed slow rates of acifluorfen mineralization and transformation to unextractable forms of ^{14}C. There was little evidence for extractable degradation products. Analysis of effluent from the intact soil columns also indicated negligible concentration of degradation products. Thus, intermediate products of acifluorfen are apparently

highly sorbed. However, unlike the incubation study, extracts of soil column segments did contain degradation products, particularly extracts of the soil surface segments. Discrepancy between these results likely reflects greater rates of acifluorfen degradation in the intact soil columns.

Although use of batch degradation rate constants in the transport model underpredicted the extent of degradation, the model was capable of describing effluent concentration of acifluorfen and distribution of residual ^{14}C if degradation rate constants were optimized. Best-fit first-order rate constants were several-fold larger than rate constants calculated from the incubation study. Since acifluorfen degradation is faster under anaerobic conditions, more rapid degradation in the soil columns may have been promoted by poorer aeration than in the batch systems. Thus, degradation rate constants obtained from the mobility study may tend toward the high end of a possible range of values.

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