Effect of Concentration, Sorption, and Microbial Biomass on Degradation of the Herbicide Fluometuron in Surface and Subsurface Soils

Thomas C. Mueller,* Thomas B. Moorman,† and Charles E. Snipes‡

Southern Weed Science Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Stoneville, Mississippi 38776

The variation in adsorption and degradation of fluometuron was determined in soil collected from different depths (0–120 cm) of a Beulah silt loam soil profile. Microbial demethylation was the initial degradation step in both surface and subsurface soils, resulting in accumulations of demethylfluometuron (DMFM). After addition of 1500 ng/g of soil of fluometuron, degradation was adequately described by first-order kinetics. However, these kinetics did not describe degradation after addition of 85 ng/g of soil of [^{14}C-*trifluoromethyl*]fluometuron. At this lower concentration, degradation followed a lag period in the subsurface soil. Degradation rates decreased as depth increased, but rates were not correlated with adsorption coefficients (K_d). Declines in microbial biomass and respiration with depth in the profile contributed to the reduced degradation rates in subsurface zones. Adsorption was primarily a first-order process, with K_d values positively correlating with soil organic matter content. Approximately 56% of adsorbed fluometuron was desorbed in a single equilibration step, suggesting that a large fraction of adsorbed fluometuron was available for degradation. If fluometuron moves into subsurface soils, the decreased adsorption and degradation rates observed would increase potential leaching for fluometuron and its metabolites.

INTRODUCTION

Fluometuron [*N*,*N*-dimethyl-*N*′-[3-(trifluoromethyl)-phenyl]urea] is a widely used herbicide for control of annual and perennial broadleaf weeds in cotton (Darding et al., 1968; Snipes et al., 1984). Recent concerns over the contamination of groundwater supplies by agricultural pesticides has led to renewed interest in the sorption and degradation of herbicides. This interest reflects fluometuron's weak sorption and moderate persistence in surface soils combined with the high rainfall and low soil organic matter content characteristic of the regions in the southeastern United States where cotton is grown. This combination suggests that fluometuron could be a potential problem in these soils. Fluometuron has been detected as deep as 60 cm in field soils (Rogers et al., 1986), although other experiments show considerably less downward movement (Hance et al., 1981; Nicholls et al., 1982).

Sorption of fluometuron in surface soils correlates primarily with organic matter content (Savage and Wauchope, 1974). Fluometuron has an average K_{oc} of 96 ± 49 calculated from published sorption data (Hance et al., 1981; Hornsby and Davidson, 1973; Savage and Wauchope, 1974). This K_{oc} value is less than those reported for atrazine (K_{oc} = 160) and alachlor (K_{oc} = 120) by Jury et al. (1987).

Previous studies of fluometuron dissipation in soil have yielded widely divergent results. In laboratory degradation studies, the half-life of fluometuron ranged from 26 to 73 days in three different soils (Rogers et al., 1985). Fluometuron carry-over following cotton has been shown to reduce growth of sensitive plants (Rogers et al., 1986). Fluometuron is degraded by soil microorganisms, with the metabolites demethylfluometuron (DMFM) and (trifluoromethyl)phenylurea (TFMPU) formed by stepwise demethylation reactions (Bozarth and Funderburk, 1971; Rickard and Camper, 1978; Ross and Tweedy, 1973; Walnöfer et al., 1973).

While the potential mobility of pesticides is often estimated from K_{oc} values and first-order degradation rate constants, such as in the groundwater-ubiquity score system of Gustafson (1989) or the screening model described by Jury et al. (1987), the variability in K_{oc} and degradation rate constants may make such extensions tenuous. In addition, the variability in sorption and degradation parameters found with soil depth is generally unknown for fluometuron and other pesticides. Bouchard et al. (1982) noted that both sorption and degradation rates decreased in the soil taken from a 40–50-cm depth compared to those from a 10–20-cm depth. The breakdown of other herbicides has been reported to be slower in subsurface zones than in surface soils (Hurle and Walker, 1980; Moorman, 1990; Moorman and Harper, 1989; Pothuluri et al., 1990).

The objectives of this research were to determine how sorption and degradation processes varied within a soil profile representing the cotton-producing soils of the Mississippi River delta region. These processes are important to the bioavailability and potential leaching of fluometuron. The relationships between sorption, degradation, and the chemical and biological properties of the soil were also determined.

MATERIALS AND METHODS

Soil. The study was conducted with a Beulah silt loam soil (coarse loamy, mixed, thermic, typic dystrochept) from Stoneville, MS (Table I). The percentage of sand, silt, clay, organic matter, cation-exchange capacity, and pH were determined according to

* Author to whom correspondence should be addressed. Present address: Department of Plant and Soil Science, University of Tennessee, P.O. Box 1071, Knoxville, TN 37901.

† Present address: USDA-ARS, National Soil Tilth Lab, Ames, IA.

‡ Delta Branch Research and Extension Center, Stoneville, MS.

Table I. Soil Characteristics for the Beulah Soil Profile[a]

depth, cm	S, %	Si, %	C, %	OM, %	pH	CEC, mequiv/ 100 g of soil	resp, mg of C (kg of soil)$^{-1}$ day^{-1}	biomass, mg of C/ kg of soil	resp/biomass ratio (× 100)
0–7.5	38	50	12	0.72	6.8	9.9	1.89	262	0.72
7.5–15	35	52	13	0.50	6.9	10.3	1.65	212	0.78
15–30	34	51	15	0.38	7.0	14.9	1.93	163	1.18
30–45	30	55	15	0.38	7.1	16.0	1.57	190	0.83
45–60	35	52	13	0.33	7.2	16.6	1.42	198	0.72
60–90	43	46	11	0.28	7.3	16.8	1.31	140	0.94
90–120	39	47	14	0.31	7.5	16.4	0.96	113	0.85

[a] Abbreviations: S, sand; Si, silt; C, clay; OM, organic matter; CEC, cation-exchange capacity; resp, respiration rate.

Table II. Fluometuron Adsorption and Desorption from Soil Collected at Different Depths[a]

soil depth, cm	k_{oc}	K_d, mL/g	desorbed, % of adsorbed
0–7.5	143	0.599 ± 0.073	52.8 ± 3.7
7.5–15	179	0.519 ± 0.042	54.4 ± 1.2
15–30	221	0.488 ± 0.001	55.2 ± 0.4
30–45	214	0.473 ± 0.057	52.3 ± 4.1
45–60	234	0.448 ± 0.044	52.3 ± 3.9
60–90	217	0.354 ± 0.038	62.9 ± 8.3
90–120	302	0.544 ± 0.051	55.6 ± 5.1

[a] ± standard errors.

the methods of Weber (1977). The soil water content at −50 kPa was determined using a pressure plate apparatus.

Soil Preparation and Treatment. Beulah silt loam soil was collected during the growing season from a cotton field from plots that had received no fluometuron application in the previous 16 months. Analysis of samples prior to fortification indicated no residual fluometuron or its initial soil metabolites. The soil was collected using a hydraulic probe which extracted a soil core 120 cm in depth by 10 cm in width. The soil core was processed in the field by removing the exterior soil and dividing into seven segments corresponding to 0–7.5-, 7.5–15-, 15–30-, 30–45-, 45–60-, 60–90-, and 90–120-cm depths. All materials that came into contact with the soil were sterilized using alcohol solutions. The soil was passed through a 2-mm screen and stored moist at 4 °C until experiment initiation (<4 weeks). Samples of the same composited, screened soil were used for soil characterization and studies on sorption and degradation under controlled conditions.

Soil Biomass Determination. Total microbial biomass was determined according to the chloroform fumigation–incubation method (Parkinson and Paul, 1982) with the following modifications. Samples consisted of 50 g of moist soil contained in 100-mL beakers. Following fumigation, soil incubations were conducted in 0.95-L sealed glass jars for two 10-day increments. The CO_2 was trapped in 10 mL of 1.0 M NaOH. Carbon trapped in the NaOH solution was quantitated using a Dohrmann DC-80 carbon analyzer. Respiration from the 0–10-day incubation of fumigated samples and the 10–20-day period incubation of nonfumigated samples was used in the biomass calculations. Respiration was expressed as an average daily rate [mg of C (kg of soil)$^{-1}$ day^{-1}] of the nonfumigated samples.

Sorption Studies. Fluometuron adsorption kinetics and the adsorption/desorption ratio were examined using a batch equilibration method. A solution/soil ratio of 2:1 with an initial solution concentration of 1 μg/mL fluometuron in 0.01 M $CaCl_2$ was used. Fluometuron (and metabolites if formed) was quantitated as previously described (Mueller and Moorman, 1991). The kinetics study examined the rate of fluometuron adsorption over time and established an equilibration period for later K_d determinations. In the kinetics experiment, fluometuron adsorption was measured in soil samples from the 0–7.5- and 60–90-cm zones at 0, 2, 4, 8, 24, 48, and 96 h after herbicide addition. The kinetics data were adjusted for fluometuron degradation, which was <4% at 96 h. An equilibration period of 24 h was used in subsequent experiments examining fluometuron adsorption in soils from different depths within the Beulah soil profile (Table II). Fluometuron desorption was determined by centrifuging for 15 min at 12000*g* and adding 15 mL of 0.01 M $CaCl_2$ solution which contained no fluometuron and measuring the herbicide concentration after 24 h. Corrections were made for the fluometuron remaining in solution from the adsorption equilibration period.

Degradation Studies. Fluometuron and the metabolites were determined in triplicate soil samples from each soil depth at nine sampling times (0, 7, 14, 28, 50, 70, 93, 114, and 133 days after treatment). Each sample consisted of moist soil (40 g dry wt basis) contained in a 250-mL screw-cap high-density-polyethylene bottle. Additional soil samples from the 0–7.5- and 60–90-cm depths were sterilized by autoclaving two times for 15 min at 120 °C. Samples were treated with an aqueous solution of fluometuron (Chemservices, West Chester, PA; 95% purity) at a rate of 1500 ng/g of soil. After herbicide addition, water was added to bring the soils to −50-kPa water potential. Samples were shaken to mix the herbicide and soil. The bottles were opened at 8, 29, 50, and 72 days after treatment to allow gas exchange. All operations with the sterilized soil samples were conducted in a laminar-flow hood using aseptic technique.

A parallel experiment using soil from the 0–7.5- and 60–90-cm depths was conducted to examine the effect of concentration on the degradation and fate of fluometuron. Soil samples were prepared as described above, except that [^{14}C-*trifluoromethyl*]-fluometuron (Ciba-Geigy Agricultural Chemicals Division; 99% purity) was added at 85 ng/g of soil. At this rate, each sample received 310 000 dpm, as determined by liquid scintillation counting of aliquots from the treatment solution.

Each sample was extracted with 80 mL of methanol (plus the water present in the sample) for 16 h. Concentrations of fluometuron and metabolites (DMFM and TFMPU) were determined according to a previously reported HPLC procedure (Mueller and Moorman, 1991). Concentrations of the radiolabeled herbicides were determined using an in-line radioactive detector after calibration using [^{14}C]fluometuron standards. Soil samples fortified with [^{14}C]fluometuron were extracted three times with 80 mL of methanol. The amount of ^{14}C not extracted from the soil was determined by combustion. Soil was air-dried, thoroughly homogenized, mixed with cellulose powder, and combusted in a Packard oxidizer (data corrected for combustion efficiency and quenching), and ^{14}C present was quantified by liquid scintillation spectroscopy.

Data Analysis. In the adsorption kinetics study, the data were fit to the empirical model

$$k_d = S(1 - e^{-r_1 t}) + r_2 t \quad (1)$$

where k_d is the micrograms of herbicide adsorbed per gram of soil per hour, S is an estimate of k_d at the asymptotic limit to the first-order process, r_1 is the first-order rate constant (h^{-1}), r_2 is the zero-order rate constant (micrograms of herbicide per gram soil per hour), and t is time in hours. The term $S(1-e^{-r_1 t})$ describes fluometuron adsorption as a first-order process (rapid adsorption), and $r_2 t$ represents the longer-term adsorption processes which may be taking place.

Residual fluometuron concentrations were fit to several models, including power-rate (Hamaker and Goring, 1976), two-compartment (Hill and Schaalje, 1985), multicompartment (Gustafson and Holden, 1990), and first-order using nonlinear least-squares regression procedures. A first-order equation had the best empirical fit to the fluometuron degradation added at 1500 ng/g. The model used was

$$C_{FLMT} = C_{0FLMT} e^{-k_1 t} \quad (2)$$

where C_{FLMT} is the fluometuron concentration as a function of time in days (t), C_{0FLMT} is the fluometuron concentration at time 0, and k_1 is the degradation rate constant. Concentrations of DMFM were modeled using

$$C_{DMFM} = C_t e^{-k_2 t} \quad (3)$$

$$\text{where} \quad C_t = C_{0FLMT}(1 - e^{-k_1 t}) \quad (4)$$

and where k_2 is the first-order degradation rate constant for DMFM. The measured concentrations of fluometuron at $t = 0$ were used for C_{0FLMT} values, and k_1 was estimated as described above. C_t (maximum DMFM at some time, t) is approximated as the maximum amount of DMFM produced ($C_{0FLMT} - C_{FLMT}$), assuming that all fluometuron degrades to DMFM. The standard errors of k_2 do not reflect variability in k_1, since k_1 is assumed to be a single value. Additionally, a specific rate constant (k_B) was determined by dividing the first-order rate constant by the biomass.

RESULTS AND DISCUSSION

Adsorption. The sorption of herbicides to subsurface soils may have a significant influence on the fate of herbicides leaching below the soil surface. Fluometuron adsorption kinetics in the surface soil was described by an empirical equation, $K_d = 0.5144(1 - e^{-0.9679t}) + (0.000356t)$, and in the subsurface (60–90 cm) soil zone by $K_d = 0.4012(1 - e^{-1.0068t}) + (0.000618t)$. Fluometuron adsorption followed a biphasic pattern with a rapid adsorption phase in which the partition coefficient increases according to first-order kinetics, followed by a slower, linear phase (Figure 1). Greater quantities of fluometuron were adsorbed in surface than in subsurface soils, as indicated by the parameter S (0.5144 vs 0.4012 mL/g), although the first-order adsorption rate constants (r_1) were similar (0.9679 vs 1.0068 h^{-1}).

The longer-term, zero-order phase was greater in subsurface than in surface soils, as indicated by r_2 values of 0.000618 in the subsurface vs 0.000356 in the surface soil. This indicates that over the long term, the fraction of adsorbed herbicide slowly increases. This may decrease fluometuron movement once it is resident in subsurface soil zones.

Fluometuron adsorption was greater in surface than in subsurface soils (Table II), although adsorption in the 90–120-cm soil zone was somewhat higher than in other subsurface zones. This magnitude of fluometuron adsorption is in agreement with previous results using similar soils (Savage and Wauchope, 1974). The S value from our kinetics study would correspond to a K_d value, since the majority of the observed adsorption in our time course was due to rapid adsorption. Additionally, fluometuron adsorption was weakly correlated ($r = 0.566$) with organic matter (Table III). Organic matter also declined with soil depth (Table I). In our work, fluometuron sorption was negatively correlated with soil pH, but we ascribe this to the coincidental increase with pH with soil depth, since fluometuron is not readily altered into a charged species by pH changes.

The k_{oc} of fluometuron in the surface zone was 143, which is comparable to values previously discussed (Table II). In the subsurface soil zones, k_{oc} ranged from 217 to 302 (Table II) with adsorption correlating with organic matter, but a correlation coefficient of 0.556 does not fully explain the observed adsorption (Table III). Fluometuron adsorption to subsurface soils is controlled by a combination of physical and chemical factors, whose mechanism of adsorption is not known.

The amount of fluometuron desorbed during a single equilibration ranged from 52 to 63% of the initially sorbed herbicide (Table II). Fluometuron desorption was not correlated with any soil factor (Table III). This relatively high level of desorption indicated that most of the fluometuron would be available for breakdown by microorganisms, and thus models which imply protection of the sorbed herbicide from degradation would not be applicable.

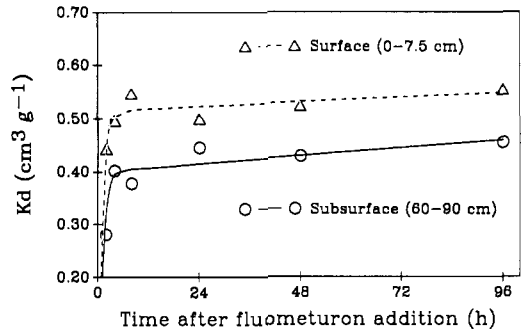

Figure 1. Fluometuron adsorption coefficients over time in Beulah silt loam soil surface and subsurface soil zones. Data points are means of four replicates, and predicted values are shown by dotted or solid lines according to eq 1 defined in the text.

Table III. Correlation Coefficient (R) of Adsorption and Desorption with Soil Properties[a]

parameter	adsorption, K_d	desorption, %
organic matter, %	0.556**	0.265
clay, %	0.001	0.013
cation-exchange capacity	−0.209	−0.013
pH	−0.343*	−0.105

[a] Correlation significance denoted at the 0.01 level (**) and the 0.05 level (*).

Table IV. Pseudo-First-Order Rate Constants and Calculated Half-Lives Describing Degradation of Fluometuron (k_1, k_B)[a] and DMFM (k_2) in Soil

soil depth, cm	k_1,[b] $days^{-1}$	FLMT $t_{1/2}$, days	k_B	k_2,[b] $days^{-1}$	DMFM $t_{1/2}$, days
0–7.5	0.0376 ± 0.0029	18	0.144	0.0677 ± 0.0056	10
0–7.5 (sterile)	0.0022 ± 0.0003	315	ND[c]	ND	ND
7.5–15	0.0336 ± 0.0011	21	0.159	0.0407 ± 0.0020	17
15–30	0.0224 ± 0.0022	31	0.137	0.0230 ± 0.0029	30
30–45	0.0130 ± 0.0005	53	0.068	0.0255 ± 0.0029	27
45–60	0.0101 ± 0.0006	69	0.051	0.0176 ± 0.0025	39
60–90	0.0048 ± 0.0005	144	0.034	0.0144 ± 0.0008	61
90–120	0.0047 ± 0.0005	147	0.042	0.0081 ± 0.0009	86
90–120 (sterile)	0.0017 ± 0.0003	408	ND	ND	ND

[a] Specific rate constant, k_B = (k_1/biomass × 1000). [b] Values ± standard errors. [c] ND, not determined.

Degradation. First-order kinetics are often used to describe herbicide degradation in soil. Degradation over a range of concentrations should be described by a single first-order rate constant. Degradation of fluometuron was more rapid in surface than in subsurface soils, as indicated by larger first-order rate constants (k_1) and the corresponding soil half-lives (Table IV). Fluometuron was degraded biologically at all soil depths, however, with more rapid degradation than in sterilized soil. First-order kinetics provided a good fit to the data (model F statistic significant at $P = 0.01$ level) when fluometuron was added to soil at 1500 ng/g (Figure 2) but did not adequately describe degradation when fluometuron was applied at 85 ng/g soil (Figure 3). Because first-order kinetics (eq 2) did not describe fluometuron degradation after addition of relatively low fluometuron concentrations, the term pseudo-first-order kinetics will be used to describe degradation when fluometuron was added at 1500 ng/g soil, since the analysis (eq 2) provided a good empirical fit to the data (Figure 2).

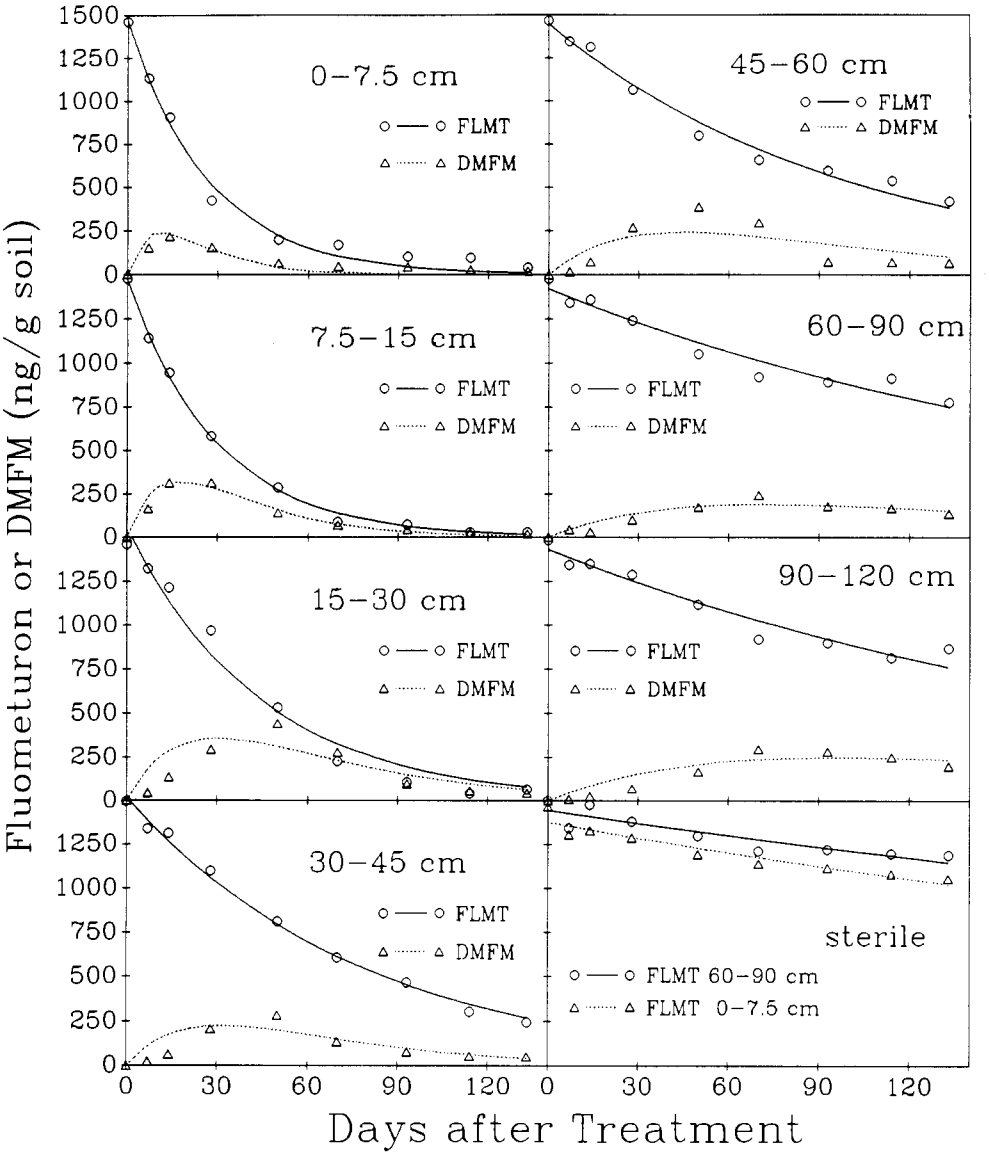

Figure 2. Fluometuron (FLMT) and DMFM concentrations in a Beulah silt loam soil profile. Data points are means of three replicates, and predicted concentrations are shown by dotted or solid lines according to eqs 2 and 3 defined in the text (Table IV).

Other models were also fit to the fluometuron degradation data to further explore the suitability of first-order kinetics and the possibility of sorption–degradation interactions. The power-rate model, the multicompartment model, and the two-compartment model reduced to forms equivalent to first-order kinetics. These models, including the two-compartment model, fit the data well (model F statistic significant at $P = 0.01$ level). However, the fit of the multiparameter models to the data was not better than that of the first-order model, so the use of these more complex models to describe these data was not justified.

The two-compartment model is based on herbicide movement into a restricted pool, where it is protected from degradation, and then movement into an unprotected pool, where it can be degraded or leached. Since the two-compartment model reduced to a first-order model, this supports the hypothesis that there is no protective fluometuron adsorption in this soil.

DMFM degraded more slowly in subsurface than surface soil zones (Table IV). DMFM degraded at rates equal to or greater than that of fluometuron in all soil zones, with half-lives usually about half that of the parent herbicide. The metabolite formed from DMFM breakdown, TFMPU, was occasionally detected, but the concentrations were <25 ng/g of soil (data not shown). The maximum DMFM concentrations occurred earlier in the surface soil zones than in subsurface soils (Figure 2). The regression procedures overestimated DMFM concentrations in the 0–25-day interval for the soil from the 15–30- and 30–45-cm soil zones. This may have been due to some other pathway being operative or some unexplained lag in DMFM production following fluometuron degradation.

The calculated fluometuron and DMFM pseudo-first-order rate constants were correlated with several soil parameters (Table V). Fluometuron degradation was positively correlated with microbial biomass and respiration. The rate of degradation of several other herbicides has been found to be correlated with microbial populations or biomass (Allen and Walker, 1987; Anderson, 1984; Moorman and Harper, 1989). Other factors correlating were soil depth (a composite of the other factors), sand, and pH. The correlation of sand and pH was deemed to be coincidental. Fluometuron degradation was not correlated with fluometuron adsorption, which was consistent with the data analysis using the two-compartment model. Correlations of DMFM degradation rate constants with soil and biological properties were similar to those obtained with fluometuron, with DMFM degradation positively correlated with microbial biomass and organic matter. Other correlations were considered to be ancillary.

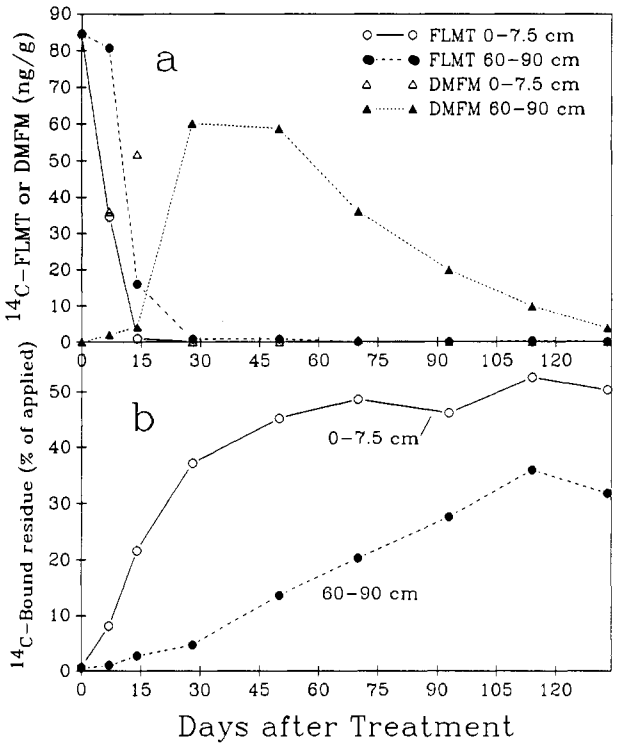

Figure 3. (a) [^{14}C]Fluometuron (FLMT) and [^{14}C]DMFM concentrations in surface and subsurface samples from a Beulah silt loam soil profile. Data points are means of three replicates. (b) Formation of ^{14}C-bound residue in surface and subsurface samples from a Beulah silt loam soil profile.

Table V. Correlation of Rate Constants for Fluometuron (k_1) and DMFM (k_2) Degradation with Soil Properties[a]

parameter	R (k_1)	R (k_2)
soil depth, cm	−0.903**	−0.827*
microbial biomass, (mg of C/kg of soil)	0.808*	0.910**
respiration, mg of C kg^{-1} day^{-1}	0.793*	0.708
adsorption, K_d	0.651	0.663
organic matter, %	0.909**	0.991**
clay, %	−0.123	−0.240
sand, %	0.757*	0.734
pH	−0.934**	−0.860*

[a] Correlation significance denoted at the 0.01 level (**) and the 0.05 level (*).

An effective means of predicting the decrease in degradation rate with increasing soil depth might allow more accurate modeling of pesticide transport in soils. One approach has been the extrapolation of degradation rates determined in surface soils into the subsurface soils. Donigan and Carsel (1987) estimated subsurface rates as a constant fraction of surface degradation rates. Jury et al. (1987) assumed that degradation rates were proportional to biomass and that biomass declined exponentially with depth to a residual value. Our first-order rate constants correlate negatively with soil depth and positively with biomass (Table V). However, an improved relationship was obtained if degradation was considered to decline exponentially as soil depth increased (Figure 4).

The relationship between microbial biomass and fluometuron degradation was further investigated by calculation of k_B, a biomass-specific rate constant. This approach has been utilized to describe bacterial degradation of several pesticides in aquatic systems (Paris and Rogers, 1986). The specific rate constant normalizes the pseudo-first-order rate constant (k_1) for biomass content at each soil depth. If fluometuron degradation follows second-order kinetics (dependent on herbicide concentration and biomass present), then the calculated specific rate constants from each depth would be approximately the same. However, the specific rate constant was higher in surface soil zones than in subsurface zones (Table IV). This lower efficiency of the microbial biomass is probably due to a smaller fractional population of fluometuron degraders in the subsurface biomass than in the biomass of surface soils. The fumigation–incubation method determines total microbial biomass including microorganisms that are incapable of degrading fluometuron. Microbial activity as measured by respiration rates was also lower in the subsurface soils, but the ratio of respiration to biomass is fairly constant at all soil depths (Table I). Despite these uncertainties, values of k_B clearly segregate soils into two groups (Table IV). Those soils above 30-cm depth had a mean k_B of 0.147 ± 0.011, and those deeper than 30-cm had a mean k_B of 0.049 ± 0.015. This grouping would correspond to the depth of tillage in this soil. The variability associated with k_B was less than that associated with k_1, suggesting that biomass-specific rate constants deserve further investigation as a parameter for describing herbicide degradation.

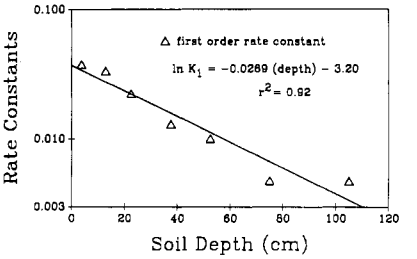

Figure 4. Correlation of fluometuron pseudo-first-order rate constants with sample depth in a Beulah soil loam soil profile.

[^{14}C]Fluometuron added at 85 ng/g of soil degraded rapidly in the soil (Figure 3). The degradation was not described by first-order kinetics but was more accurately described by zero-order kinetics (Figure 3). No detectable [^{14}C]fluometuron was found 14 and 28 days after treatment in surface and subsurface soil zones, respectively. These degradation rates were much greater than those observed when fluometuron was added at 1500 ng/g of soil. There also appeared to be a lag phase in [^{14}C]fluometuron degradation in subsurface soil zones, and this lag phase is inconsistent with true first-order kinetics. The [^{14}C]-fluometuron dissipation rate was slower in sterilized soil (data not shown).

[^{14}C]DMFM production and subsequent degradation were more rapid in surface than in subsurface soil. This slower [^{14}C]DMFM dissipation rate in subsurface zones was presumably due to lower microbial biomass and activity.

The mineralization of [^{14}C-*trifluoromethyl*]fluometuron in previous research was very slow (<5% at 90 days) (data not shown). Slower breakdown in subsurface zones may be due to reduced microbial biomass and activity. It should be pointed out that activity and biomass are not synonymous terms. Microorganisms can increase or decrease activity without changing the biomass. Respiration rate is our surrogate measurement of activity of the total microbial population.

The incorporation of ^{14}C into soil organic matter as bound residue was more rapid in the surface soil (Figure 3b). However, bound residue formation was an important process in that 50 and 30% of the applied ^{14}C was eventually bound in the surface and subsurface soils. These results are similar to those obtained with metribuzin in another delta soil (Moorman and Harper, 1989). Presumably, the smaller amount of bound residue formed in

the subsurface soil was due to the reduced microbial activity and lower organic matter in this zone. The exact form of the bound residue may include herbicide, metabolites, or extensively degraded materials. Studies with triazine herbicide indicate that these residues are highly stable, although tiny fractions of the bound materials can be released (Kahn and Hamilton, 1980; Capriel et al., 1985). However, bound residues would not be expected to contribute significantly to any pool of potentially leachable herbicide or metabolites.

Under actual field conditions, fluometuron is initially loaded into the soil environment via surface applications, so for any subsurface soil effects to be manifested the herbicide must first move from the surface soil zone. In many situations this may not occur, since fluometuron degradation and adsorption were greatest in this surface soil. Within the profile, degradation and adsorption were correlated with organic matter and biological activity. Besides only partially degrading fluometuron to DMFM (and causing a resultant loss in weed control), surface soils were also more adept at incorporating fluometuron into organic matter (as indicated by ^{14}C incorporation into bound residue). However, if fluometuron were to move into subsurface soil zones, the combination of slower degradation and lower adsorption could contribute to greater fluometuron movement.

LITERATURE CITED

Allen, R.; Walker, A. The influence of soil properties on the rates of degradation of metamitron, metazachlor, and metribuzin. *Pestic. Sci.* **1987**, *18*, 95–111.

Anderson, J. P. E. Herbicide degradation in soil: influence of microbial biomass. *Soil Biol. Biochem.* **1984**, *16*, 483–489.

Bouchard, D. C.; Lavy, T. L.; Marx, D. B. Fate of metribuzin, metolachlor, and fluometuron in soil. *Weed Sci.* **1982**, *30*, 629–632.

Bozarth, G. A.; Funderburk, H. H. Degradation of fluometuron in sandy loam soil. *Weed Sci.* **1971**, *19*, 691–695.

Capriel, P.; Haisch, A.; Kahn, S. U. Distribution and nature of bound (nonextractable) residues of atrazine in a mineral soil nine years after the herbicide application. *J. Agric. Food Chem.* **1985**, *33*, 567–569.

Darding, R. L.; Freeman, J. F. Residual phytotoxicity of fluometuron in soils. *Weed Sci.* **1968**, *16*, 226–229.

Donigan, A. S.; Carsel, R. F. Modelling the impact of conservation tillage practices on pesticide concentrations in ground and surface waters. *Environ. Toxicol. Chem.* **1987**, *6*, 241–250.

Gustafson, D. I. Groundwater ubiquity score: A simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **1989**, *8*, 339–357.

Gustafson, D. I.; Holden, L. R. Nonlinear pesticide dissipation in soil. A new model based on spatial variability. *Environ. Sci. Technol.* **1990**, *24*, 1032–1038.

Hamaker, J. W.; Goring, C. A. I. *Organic chemicals in the soil environment*; Dekker: New York, 1976; Vol. 1, pp 219–243.

Hance, R. J.; Embling, S. J.; Hill, D.; Graham-Bryce, J.; Nicholls, P. Movement of fluometuron, simazine, $^{36}Cl^{1-}$ and $^{144}Ce^{3+}$ in soil under field conditions: qualitative aspects. *Weed Res.* **1981**, *21*, 289–297.

Hill, B. D.; Schaalje, G. B. A two-compartment model for the dissipation of deltamethrin on soil. *J. Agric. Food Chem.* **1985**, *33*, 1001–1006.

Hornsby, A. G.; Davidson, J. M. Solution and adsorbed fluometuron concentration distribution in a water-saturated soil: experimental and predicted evaluation. *Soil Sci. Soc. Am. Proc.* **1973**, *37*, 823–828.

Hurle, K.; Walker, A. Persistence and its prediction. In *Interactions between Herbicides and the Soil*; Hance, R. J., Ed.; Academic: New York, 1980; pp 83–122.

Jury, W. A.; Focht, D. D.; Farmer, W. J. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *J. Environ. Qual.* **1987**, *16*, 422–428.

Kahn, S. U.; Hamilton, H. A. Extractable and bound (nonextractable) residues of prometryne and its metabolites in an organic soil. *J. Agric. Food Chem.* **1980**, *28*, 126–132.

Moorman, T. B. Adaption of microorganisms in subsurface environments. In *Enhanced Biodegradation of Pesticides in the Environment*; Racke, K. D., Coats, J. R., Eds.; American Chemical Society: Washington, DC, 1990; pp 167–180.

Moorman, T. B.; Harper, S. S. Transformation and mineralization of metribuzin in surface and subsurface horizons of a Mississippi delta soil. *J. Environ. Qual.* **1989**, *18*, 302–306.

Mueller, T. C.; Moorman, T. B. Liquid chromatographic determination of fluometuron and metabolites in soil. *J. Assoc. Off. Anal. Chem.* **1991**, *74*, 671–673.

Nicholls, P. H.; Bromilow, R. H.; Addiscott, T. M. Measured and simulated behavior of fluometuron, aldoxycarb and chloride ion in a fallow structured soil. *Pestic. Sci.* **1982**, *13*, 475–483.

Paris, D. F.; Rogers, J. E. Kinetic concepts for measuring microbial rate constants: effects of nutrients on rate constants. *Appl. Environ. Microbiol.* **1986**, *51*, 221–225.

Parkinson, D.; Paul, E. A. Microbial biomass. In *Methods of Soil Analysis, Part 2— Chemical and Microbiological Properties*, 2nd ed.; Page, A. L., Miller, R. H., Keeny, R. D., Eds.; American Society of Agronomy: Madison, WI, 1982; pp 821–830.

Pothuluri, J. V.; Moorman, T. B.; Obenhuber, D. C.; Wauchope, R. D. Aerobic and anaerobic degradation of alachlor in samples from a surface-to-groundwater profile. *J. Environ. Qual.* **1990**, *19*, 525–530.

Rickard, R. W.; Camper, N. D. Degradation of fluometuron by *Rhizoctonia solani*. *Pestic. Biochem. Physiol.* **1978**, *9*, 183–189.

Rogers, C. B.; Talbert, R. E.; Mattice, J. D.; Lavy, T. L.; Frans, R. E. Residual fluometuron levels in three Arkansas soils under continuous cotton (*Gossypium hirsutum*) production. *Weed Sci.* **1985**, *34*, 122–130.

Rogers, C. B.; Talbert, R.; Frans, R. Effect of cotton (*Gossypium hirsutum*) herbicide carryover on subsequent crops. *Weed Sci.* **1986**, *34*, 756–760

Ross, J. A.; Tweedy, B. G. Degradation of four phenylurea herbicides by mixed populations of microorganisms from two soil types. *Soil Biol. Biochem.* **1973**, *5*, 739–746.

Savage, K. E.; Wauchope, R. D. Fluometuron adsorption-desorption equilibria in soil. *Weed Sci.* **1974**, *22*, 106–110.

Snipes, C. E.; Walker, R. H.; Whitwell, T.; Buchanan, G. A.; McGuire, J. A.; Martin, N. R. Efficacy and economics of weed control methods in cotton (*Gossypium hirsutum*). *Weed Sci.* **1984**, *32*, 95–100.

Walnöfer, P. R.; Safe, S.; Hatzinger, O. Microbial demethylation and debutynylation of four phenylurea herbicides. *Pestic. Biochem. Phys.* **1973**, *3*, 253–257.

Weber, J. Soil properties, herbicide sorption, and model soil systems. In *Research Methods in Weed Science*; Truelove, B., Ed.; Auburn Printing: Auburn, AL, 1977; pp 155–189.

Received for review July 1, 1992. Accepted September 24, 1992.

Registry No. Fluometuron, 2164-17-2.