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Degradation and Sorption of Fluometuron and Metabolites in Conservation Tillage Soils

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Soil sorption and dissipation of fluometuron (FLM) and three metabolites, desmethyl fluometuron (DMF), trifluoromethyl phenyl urea (TFMPU), and trifluoromethyl aniline (TFMA), were assessed in conservation tillage soils. In study I, surface Dundee silt loam soils from no-tillage (NT) and reduced-tillage (RT) areas were treated with ^{14}C ring-labeled FLM or TFMA or unlabeled DMF, incubated for 34−42 days, extracted, and analyzed. Mineralization and volatilization of ^{14}C-labeled FLM or TFMA were monitored. In study II, batch sorption assays (solute concentrations 2−50 μmol L^{-1}; 2:1 solution: soil; 18 h) were conducted using various soils from reduced- (RT) and conventional-tillage (CT) areas to determine the relative affinity of FLM and metabolites for soils with differing characteristics. Mineralization of FLM (3%, day 42) or TFMA (4%, day 34) and FLM volatilization (∼2%) were low for both soils. FLM and DMF dissipated more rapidly in RT soil than in NT soil. In FLM-treated RT soil, DMF and TFMPU accumulated more rapidly than in NT as FLM degraded. TFMA dissipated rapidly, primarily as nonextractable residues (∼70%, day 42) and volatilization (∼16%). For all respective soils in study II, sorption of all four compounds was higher for organic C-enriched RT soils than for CT soils, indicating strong relationships between organic C and FLM and metabolite sorption. For either tillage treatment, the percentage sorption was greater for metabolites (e.g., at lowest initial dosing concentration, TFMPU range, 45−91%; DMF range, 45−90%; and TFMA range, 45−98%) than for FLM (RT soils range, 19−65%). Nonsubstituted amino groups likely facilitated sorption to organic C, with nonsubstituted aniline in TFMA having the greatest affinity. NMR spectra of humic acid extracts from NT and CT Dundee soils indicated similar patterns of humic acid functional groups, but the potential capacity for sorption was greater in NT than in CT. The greater capacity for FLM and metabolite sorption in NT soil helps explain their longer persistence.

KEYWORDS: Tillage; herbicide; sorption; dissipation; fluometuron; metabolite

INTRODUCTION

Fluometuron (FLM) is a soil-applied herbicide used on cotton (*Gossypium hirsutum* L.) produced in the Midsouth region of the United States with a total application of 2.2 million kg in 1997 and usage in 2003 of 0.35 million kg (*1*). It is therefore important to determine factors influencing its dissipation in the environment and to evaluate whether new management practices alter risk to the environment. FLM is a phenylurea herbicide that undergoes a series of oxidative and hydrolytic transformations during microbial metabolism in soil or aquatic environments. FLM sequentially degrades to two metabolites, desmethyl fluometuron (DMF) and trifluoromethyl phenylurea (TFMPU), by demethylation and then to trifluoro-methylaniline (TFMA) by hydrolysis via arylacylmidases (**Figure 1**) (*2*). Other phenylurea herbicides, e.g., diuron, degrade via similar pathways with similar classes of metabolites such as monodemethyl derivatives, dimethylated phenylurea, and dichloroaniline accumulating in soil (*3*). There are reports of FLM metabolites in water (*4*−*7*). DMF has been detected in soil (*8*−*12*). Zablotowicz et al. (*10*, *11*) observed very low quantities of TFMPU in laboratory radiological studies, but we were unable to find published reports of TFMA or TFMPU detected in extracts of soils from field locations where FLM was known to have been applied. In a U.S. EPA risk assessment summarizing unpublished soil environmental fate studies by Ciba Geigy Corp. (Greensboro, NC), it was reported that TFMPU and TFMA were detected in only small amounts (<10% of applied) in all metabolism studies (*12*).

Previous studies have addressed management and other factors influencing the fate of FLM in the environment (*2*, *8*,

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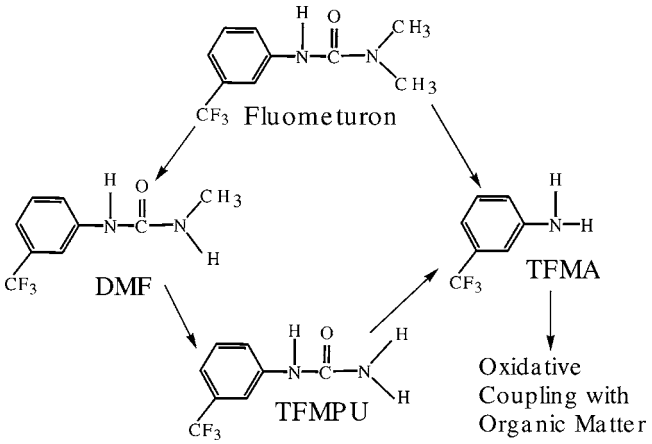

Figure 1. Pathway for the degradation of FLM in soil.

13−*15*), and several have considered the impact of conservation management on FLM fate (*6*, *9*−*11*, *16*−*22*). Very few, however, have considered characteristics or the fate of FLM metabolites in the environment, particularly with regard to conservation management. There are limited data available on the fate or impact of FLM metabolites in terrestrial or aquatic environments, but in an EPA assessment (*12*), one metabolite considered to be of most importance, CGA-41686 or DMF, was assumed to be equipotent to parent FLM. Under in vitro conditions, DMF was found to be more toxic to algae than the parent compound (*23*).

Conservation management practices are promoted to improve and sustain soil production, and an increasing number of farmers are using conservation management practices in cotton production systems. Many of these practices result in accumulation of organic carbon (C) within soil surface layers (*24*). Increased organic C in these soils can enhance FLM sorption to soil but has inconsistent effects on herbicide dissipation (*8*, *9*). It is therefore of interest to evaluate management, soil characteristics, and pesticide characteristics in relation to the behavior of herbicides and metabolites as part of an overall assessment of pesticide fate in the environment. The present studies were conducted because there is relatively little information concerning the effects of conservation management on the fate of pesticide metabolites in soil. This paper reports on two laboratory studies that evaluated the sorption and degradation of FLM and metabolites in conservation tillage soils.

MATERIALS AND METHODS

Study I. Soil samples (0−5 cm depth) from a Dundee silt loam (fine-silty, mixed, thermic, Aeric Ochraqualf) were collected in early spring following 3 years of no-tillage (NT) or reduced-tillage (RT) cotton management at the Agricultural Research Service, U.S. Department of Agriculture, Southern Weed Science Research Unit farm near Stoneville, MS. Samples were collected at random within respective tillage management areas, bulked as a composite, and stored moist at 4 °C until use. Soil was characterized for various physical, chemical, and biological parameters (**Table 1**).

The soil pH was measured in water (1:2, soil:water). Total C and N were determined in air-dried, ground soil using a Flash EA 1112 NC Elemental Analyzer (CE Elantech, Lakewood, NJ). The soil texture was determined following methods described by Gee and Bauder (*25*).

Estimates of culturable soil microbial propagules (total and Gram-negative bacteria and total fungi) were determined by serial dilutions and spiral plating (Spiral System Instruments, Bethesda, MD) on selective and semiselective growth media, as described elsewhere (*26*). Fluorescein diacetate (FDA, a substrate for esterase and lipase) hydrolytic activity was used as a general estimate of soil microbial activity (*27*).

Table 1. Chemical, Physical, Enzymatic, and Microbiological Characteristics of Dundee Soil in Study I

	tillage	
soil characteristic	NT	RT
organic C (%)	1.46 (0.03)[a]	1.54 (0.07)
organic N (%)	0.18 (<0.01)	0.19 (0.06)
pH	5.74 (0.03)	6.10 (0.03)
sand (%)	19	21
silt (%)	56	58
clay (%)	25	21
FDA activity	1510[b]	1855
Log (10) GN bacteria	6.06[c] (0.08)	5.72 (0.10)
Log (10) fungi	5.73[c] (0.02)	5.52 (0.01)
Log (10) total bacteria	8.61[c] (0.01)	8.22 (0.05)

[a] For parameters where replicates were separated, the number in parentheses following the mean is the standard error. [b] nmol fluorescein formed g^{-1} h^{-1}. [c] Log CFU.

Technical grade FLM (Chem Service, Lancaster, PA) or TFMA (Sigma Aldrich, St. Louis, MO) working solutions were prepared from technical grade (98% purity) and ^{14}C-labeled chemicals (Syngenta Crop Protection, Inc., Wilmington, DE). The ^{14}C-labeled FLM stock was ring-UL-^{14}C labeled, 99% purity (specific activity, 357.97 MBq $mmol^{-1}$). ^{14}C-labeled TFMA was synthesized by refluxing the ^{14}C-labeled FLM in 4 N NaOH (ratio 0.6 FLM stock solution to 1.0 mL of NaOH) in glass Hungate tubes with a polypropylene-lined septum, at 90 °C for 24 h in a water bath. The reaction was terminated by acidifying with 6 N HCL and adding MeOH to dissolve the product. Synthesized TFMA solutions were verified for greater than 95% purity using high-performance liquid chromatography (HPLC). A DMF solution was prepared from technical grade chemical (98% purity) (Syngenta Crop Protection, Inc.). Chemicals were dissolved in a minimum of methanol and brought to volume with deionized water (final 13% methanol) to yield working stocks of 53 μg mL^{-1} and, if ^{14}C-labeled, 2.62 (FLM) or 2.22 MBq L^{-1} (TFMA) for use in extractability and mineralization/volatilization studies.

To characterize sorption for the soils used for study I, ^{14}C-labeled FLM and TFMA (synthesized, see previously) working solutions of 5 μg mL^{-1} and 0.25 MBq L^{-1} and nonlabeled working solutions of 5 μg mL^{-1} DMF were prepared in deionized water. Air-dried soil samples were placed in 25 mL Corex (Corning, Inc., Corning, NY) centrifuge tubes with PTFE-lined (DuPont, Inc., Wilmington, DE) screw caps (1:2 soil:solution, 5 g:10 mL), shaken for 17 h at 25 °C, centrifuged (12000*g*, 15 min, JA-20 rotor, Beckman Coulter, Inc., Fullerton, CA), and supernatant filtered (42 filter paper, Whatman, Inc., Clifton, NJ). Solutions containing nonlabeled DMF were diluted 1:1 v/v with methanol prior to HPLC analysis. Solutions containing ^{14}C-labeled FLM and TFMA were counted for radioactivity after mixing with Eco-Lite scintillation cocktail (ICN, Costa Mesa, CA) using a Tri-Carb 4000 liquid scintillation counter (LSC) (Packard Instrument Co., Meriden, CT). Samples were run with four replications of each tillage treatment.

Degradation. To evaluate changes in extractable FLM and metabolites during incubation in soil, 6 g of moist RT or NT soil (5 g oven dry equivalent) were weighed into 25 mL Pyrex centrifuge tubes and treated with 0.2 mL of FLM, DMF, or TFMA working solution (described previously) to yield final soil concentrations of 2.1 μg g^{-1} (FLM, DMF, or TFMA) and 105 (FLM) or 89 Bq g^{-1} (TFMA) with 33% soil moisture. Samples were incubated (25 °C) for 42 (FLM or DMF) or 35 days (TFMA). Three replicate tubes from each treatment combination were removed periodically, the soils were extracted twice with MeOH, and extracts were assayed by LSC for total radioactivity recovered (FLM, TFMA), analyzed by HPLC (DMF), or RAD-thin-layer chromatography (TLC) (FLM). Preliminary investigations indicated that in the TFMA-treated soil, TFMA was the only extractable analyte, so it was assumed that all of the extractable ^{14}C was TFMA. This was not the case, however, for FLM-treated soils, so they were further analyzed by RAD-TLC. For ^{14}C FLM- or ^{14}C TFMA-treated soils, extracted soil was air-dried and ground with a mortar and pestle,

Table 2. Chemical and Physical Characteristics of Soils Used in Study II

	Dundee		Norfolk		Tunica		Weswood	
soil characteristic	CT[a]	RT[a]	CT[a]	RT[a]	CT[a]	RT[a]	CT[a]	RT[a]
organic C (%)	1.13 (0.05)	2.43 (0.09)	0.46 (0.03)	1.10 (<0.01)	1.12 (0.02)	1.34 (<0.01)	0.99 (0.02)	1.16 (0.11)
organic N (%)	0.08 (<0.01)	0.20 (<0.01)	0.03 (<0.01)	0.08 (<0.01)	0.09 (<0.01)	0.10 (<0.01)	0.06 (<0.01)	0.12 (<0.01)
pH	5.5	5.5	5.8	6.2	5.5	5.4	7.4	7.3
sand (%)	30	33	81	81	5	7	11	10
silt (%)	42	38	6	7	29	30	46	50
clay (%)	28	29	13	12	66	63	43	40

[a] For parameters where replicates were separated, the number in parentheses below the mean is the standard error.

and 0.3 g subsamples were mixed with cellulose and oxidized to determine the nonextractable ^{14}C (Oxidizer 306, Packard Instrument Co.).

In the experiment described above, the experimental variables for FLM-, DMF-, or TFMA-treated soil included tillage (RT, NT) and sampling time (seven times for FLM and TFMA from 0 to 42 days and nine times for DMF from 0 to 35 days), with three replications of each tillage−sampling time combination. Additionally, a preliminary degradation study was run in triplicate with comparable results but is not reported here.

To evaluate mineralization and volatilization of ^{14}C-labeled FLM and TFMA, a separate parallel experiment was conducted using the same treatment conditions as described previously except that the incubation containers were 250 mL biometer flasks. In this experiment, 65 g of moist RT or NT soil (50 g o.d. basis; soil was 33% moisture) was weighed into the biometer flasks and treated with 2.0 mL of FLM or TFMA working solution described previously to achieve a final concentration of 2.1 μg g^{-1} and 105 (FLM) or 89 Bq g^{-1} (TFMA). Each treatment (RT, NT) was replicated six times for FLM or TFMA. Samples were incubated at 25 °C for 42 (FLM-treated soil) or 35 days (TFMA-treated soil). It was not possible to evaluate DMF mineralization in this manner because ^{14}C-labeled DMF was not available.

Mineralization of ^{14}C-labeled FLM or TFMA as $^{14}CO_2$−C was monitored by periodically sampling 1 M NaOH from the biometer sidearm trap, for a total of 10 samplings. At each sampling, all NaOH was removed and replenished with fresh NaOH. One milliliter aliquots of the sampled NaOH were assayed for radioactivity using LSC after mixing sample with Hionic−Fluor scintillation cocktail (Packard Instrument Co.).

Volatilization was measured by periodically (nine times for FLM and 10 times for TFMA during the incubation period) removing a foam core plug, extracting the foam core plug with MeOH, and assaying the extracts for radioactivity. At each sampling, a new foam core plug was put in place.

At the termination of the incubation periods evaluating FLM and TFMA mineralization or volatilization, soil was removed from the biometer flasks and processed for extractable and nonextractable components as described previously.

Study II. Composite soil samples were collected from the surface (0−5 cm) of several soil series and management systems. Dundee (CT or NT soybeans [*Glycine max*. L. Merr.] for 11 years) silt loam and Tunica (RT-stale seed-bed or CT soybeans) clay (clayey over loamy, montmorillonitic, nonacid, thermic Vertic Haplaquept) were alluvial soils from the Mississippi Delta near Stoneville, MS. Weswood silt loam (fine-silty, mixed, thermic Fluventic Ustochrept) is a calcareous alluvial soil from the Brazos River bottom near College Station, TX, and the area was in NT or CT sorghum [*Sorghum bicolor* L. Moench] and cotton production for 10 years. Norfolk loamy sand (fine-loamy, siliceous, thermic Aquic Kandiudult) from Florence, SC, is a kaolinitic soil and was managed as CT or RT tillage cotton. All conservation management soils in study II, whether stale seedbed, some form of RT, or strictly NT, will be referred to as RT in this paper.

To minimize microbial metabolism during sorption (*28*), soils were γ-irradiated (U.S. Department of Agriculture-APHIS, Otis AFB), air-dried under laminar flow hood, and ground with a sterilized mortar and pestle. Aseptic techniques were used in all protocols to minimize transformation of analytes during the sorption equilibration procedure. Soils were characterized for physical and chemical properties (**Table 2**). The soil pH and texture were determined as described previously in this paper. Total C and N in ground samples were analyzed using a Leco CN 2000 analyzer (St. Joseph, MI).

Sorption solutions were prepared in 0.01 M $CaCl_2$ with ^{14}C-labeled FLM (Novartis, Inc., now Syngenta, Inc.) adjusted with appropriate levels of technical grade FLM (see previously) to achieve solute concentrations from 2.2 to 43.0 μM and 0.05 MBq L^{-1}. Nonlabeled technical grade (98% purity) DMF, TFMA, and TFMPU (Novartis, Inc., now Syngenta, Inc.) were prepared at four solute concentrations ranging from 2.3 to 45.9, 2.5 to 49.0, and 3.1 to 61.7 μM, respectively.

FLM or metabolite solution was added to soil (1:2 soil:solution, 5 g:10 mL), and samples were shaken in 25 mL Pyrex centrifuge tubes for 17 h at 25 °C and centrifuged (10000*g*, 15 min), and the supernatant was filtered (Whatman 42 filter paper). Supernatant aliquots of nonlabeled samples (DMF, TFMA, and TFMPU) were diluted 1:1 v/v with methanol to minimize further transformations, and samples were refrigerated until HPLC analysis. ^{14}C-labeled FLM was counted for radioactivity using LSC after mixing 1 mL aliquots of supernatant with Eco-Lite scintillation cocktail (ICN). Nonlabeled samples (DMF, TFMA, and TFMPU) were analyzed using HPLC. For the four compounds of interest, all treatment combinations (four soils, two tillage, and four solute concentrations) were replicated four times, and the entire sorption study was repeated.

Analyses. All HPLC samples were analyzed under the same conditions using a Waters, Inc. (Milford, MA) 2690 HPLC System. Conditions included Waters, Inc. Photodiode Array UV Detector at 235 nm wavelength; Waters, Inc. Scanning Fluorescence Detector 470 at Ex. 294 and Em. 329 nm wavelengths; C_{18} Econosil column, 250 mm × 4.6 mm, 5 μm (Alltech Associates, Inc., Deerfield, IL); isocratic with 55% HPLC grade water/45% acetonitrile at 1 mL min^{-1} flow; 50 μL injection volume; and retention times (min): FLM, 9.5; DMF, 7.3; TFMA, 14.0; and TFMPU, 5.6.

For RAD-TLC analysis of FLM-treated soil, 100 μL aliquots of concentrated methanol extracts were spotted onto silica gel plates (20 cm × 20 cm, 250 μm thickness) (#LKF Whatman) and developed to 10 cm in a chloroform:ethanol (95:5 v:v) solvent system. R_f values for standards were FLM, 0.58; DMF, 0.30; TFMPU, 0.13; and TFMA, 0.76. Developed TLC plates were scanned using Bioscan System 200 Imaging Scanner (Bioscan, Washington, DC) to determine ^{14}C spots.

For NMR characterizations of soil, humic substances were extracted from NT or CT Dundee soil with an aqueous solution of 0.1 M NaOH + 0.1 M $Na_4P_2O_7$ following procedures similar to Clapp et al. (*29*) and Holzclaw et al. (*30*). Extracts were acidified to pH 2 with 1 M HCl, and the supernatant fulvic acid fraction was removed. The precipitated humic acid was resuspended in 0.5 M NaOH, and a 2.5 mL aliquot was combined with 0.5 mL of D_2O for NMR spectroscopic analysis. The samples were referenced to the external standard di-isopropylsiloxane. Humic acids were analyzed by ^{13}C liquid-state NMR on a General Electric Omega 400, 400 MHz wide-bore spectrometer. Spectra were obtained at an absolute frequency of 100.6236799 MHz with a delay of 2.0 s, a 45° pulse width, and a sweep width of 35087.72 Hz. Proton decoupling utilized waltz 16 sequence, which was on only during acquisition. The decoupler was set at 4.00 ppm and a frequency of 400.132980 MHz. The number of data points was 8000, and the number of scans was 45000−65000 depending on the sample. Data were processed with the first point in each freed

induction decay signal manually set to zero followed by exponential multiplication with a line broadening of 80 Hz followed by Fourier transform. Also see Kingery et al. (*31*) for information on NMR procedures and interpretation.

Characterization of FLM and Metabolites. Water solubility of FLM, DMF, TFMA, or TFMPU was determined by adding an excess of appropriate solute to 20 mL of autoclaved HPLC grade water, shaking for 120 h in an incubator at 25 °C, centrifuging, and analyzing the supernatant by HPLC. Samples were run in triplicate.

To determine coefficients for the partitioning of FLM, DMF, TFMA, or TFMPU between *n*-octanol and water (K_{ow}), procedures according to the U.S. EPA shake flask method were followed (*32*). Briefly, 5 μg mL^{-1} stock solutions were prepared using technical grade FLM, DMF, TFMA, or TFMPU dissolved in HPLC grade water. Experiments were conducted using *n*-octanol to water ratios of 1:1, 2.75:1, and 1:2.75, with three replication of each ratio. Solutions at the appropriate ratios were added to 30 mL Corex centrifuge tubes and equilibrated at controlled temperature (25 °C) for 1 h. After equilibration, samples were centrifuged (10000*g*) for 10 min and then allowed to stand for 1 h. Aliquots of the *n*-octanol and water layers were removed and analyzed by HPLC.

Statistics and Computations. SAS Version 9.1 (SAS Institute, Cary, NC) was used to evaluate the statistical significance of treatments. The standard error was calculated for all treatment means. Sorption studies were repeated, and all sorption data were used to evaluate statistical significance using analysis of variance (PROC GLM) general linear model procedures with Fisher's LSD to separate means. Analysis of variance procedures also were used to assess statistical significance in the degradation study. The sorption distribution coefficient K_d, Freundlich sorption parameter K_f, and K_{oc} were calculated from the batch sorption data. The degradation study was partially repeated (parallel studies were run, see previous), and where the same measurements were made, data from the two studies were combined. Also, a preliminary degradation study of comparable length yielded similar results (data not reported here). FLM dissipation was evaluated with first-order kinetics, and nonlinear regression techniques (SAS PROC NLIN) were used to calculate parameters (*k*, half-life).

RESULTS AND DISCUSSION

Degradation: Study I. Most study I soil physical and chemical characteristics were similar for both tillage systems, although organic C and pH were slightly higher in RT than in NT (**Table 1**). Only limited tillage was used in either system (none for NT and only once each year for RT) since establishment of the experimental area in 2000. Slightly more mixing of the RT soil due to the one tillage event each fall after harvest, however, may have resulted in more aeration and an even distribution of organic residues, although microbial populations were higher in the NT soil (**Table 1**). Initial moisture was virtually the same in both soils (NT, 12.5%; RT, 12.2%). FDA hydrolysis, an indicator of the hydrolytic enzymes (esterases, lipases, and proteases), was higher in the RT soil (**Table 1**), perhaps a result of better aeration and more available labile carbon residues from incorporation of crop residues.

Mineralization measured as trapped $^{14}CO_2$−C was a minor route of dissipation for both FLM (approximately 3%, day 42) and TFMA (approximately 4%, day 34), regardless of tillage system (**Figure 2**). FLM mineralization in RT (cumulative 4.1%) was greater than in NT (cumulative RT 4.1% vs NT 2.9%, LSD $P < 0.05$) (**Figure 2a**), and the enhanced FLM mineralization in RT might be attributed to greater aeration and higher enzyme activities (FDA), indicative of more active microbial populations. TFMA mineralization did not differ much between RT and NT (cumulative RT 4.0% vs NT 3.7%, LSD $P < 0.05$) (**Figure 2b**). One might expect TFMA and FLM mineralization to be low considering that mineralization requires hydroxylation and formation of a catechol prior to ring cleavage and subsequent oxidation to CO_2. Also, substitution of halogenated groups in the meta position may retard mineralization of TFMA and FLM. For example, TFMA (with halogenated alkyl group in meta position, **Figure 1**) mineralization in the present study was much less than that of the 4-isopropyl aniline metabolite of isoproturon (with large nonhalogenated alkyl group in meta position) in another study (*33*).

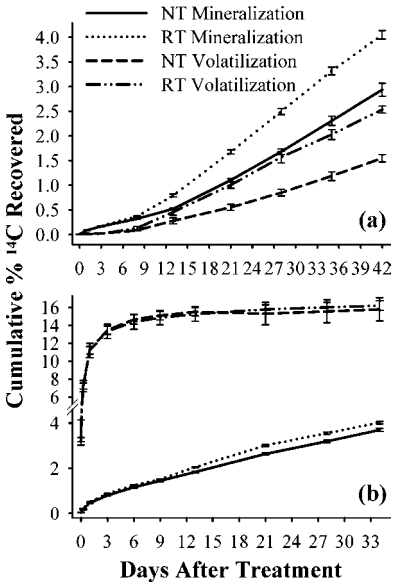

Figure 2. Cumulative recovery of ^{14}C applied as (**a**) FLM or (**b**) TFMA in study I: Mineralized as $^{14}CO_2$ for NT (—) and RT (• • •) or volatilized and captured in foam plug material for NT (- - -) and RT (- • -). Error bars represent standard errors for each mean.

FLM volatilization was low, and kinetics followed a pattern similar to mineralization (**Figure 2a**), with total volatilization loss slightly higher in RT than in NT (cumulative RT 2.5% vs NT 1.5, LSD $P < 0.05$). Volatilization of TFMA did not differ between NT and RT (LSD $P < 0.05$ not significant), although it was a major pathway of loss (cumulative 16%) (**Figure 2b**). TFMA (bp 187 °C; vapor pressure, 1.0 mmHg; 20 °C) has a higher disposition toward volatilization than FLM (9.38×10^{-7} mmHg; 20 °C), which helps to explain the higher volatilization measured for TFMA. TFMA volatilization followed a hyperbolic loss pattern with the greatest volatility shortly after application as compared to a rather linear volatilization pattern observed for FLM. Contributions to dissipation arising from differences between RT and NT (e.g., higher soil organic C in RT) apparently were overshadowed by the rapid volatilization, i.e., TFMA volatilization occurred so rapidly that there was not sufficient time for soil characteristics to prevail, thus similar results for both soils.

The kinetics of ^{14}C-labeled FLM dissipation based on total ^{14}C recovered by MeOH extraction is shown in **Figure 3a**. The half-life for total ^{14}C in FLM-treated RT soil was 23 days as compared to 38 days for NT (dissipation *k* parameter: RT, 0.030 SE 0.001; NT, 0.018 SE <0.001). The dissipation of FLM alone in FLM-treated soil (**Table 3**) shown in **Figure 4a** parallels the total ^{14}C dissipation, with FLM degrading more rapidly in RT (half-life: RT, 11 days; NT, 16 days). This more rapid dissipation corresponds to trends of slightly greater mineralization in RT (**Figure 2a**) and higher nonextractable ^{14}C in RT after day 28 (**Figure 3a**). As discussed previously, more aeration and labile organic C likely enhanced the activity of herbicide-degrading soil microorganisms, allowing more rapid FLM dissipation in RT. The more rapid accumulation of both DMF and TFMPU as FLM degraded in the FLM-treated RT soil was

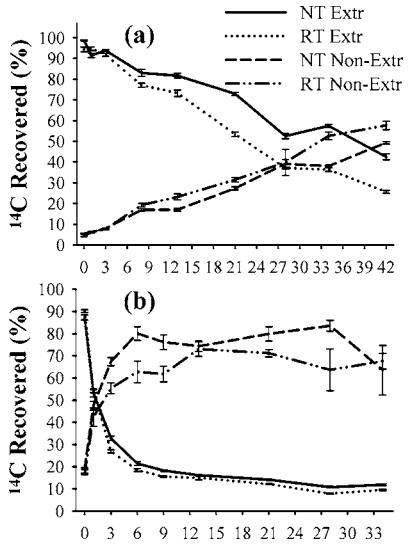

Figure 3. Percent recovery of analytes from soils treated with (**a**) ^{14}C-labeled FLM or (**b**) ^{14}C-labeled TFMA in study I. The total extractable ^{14}C is represented by NT (—) and RT (• • •), and the nonextractable ^{14}C is represented by NT (- - -) and RT (- • -). Error bars represent standard errors for each mean.

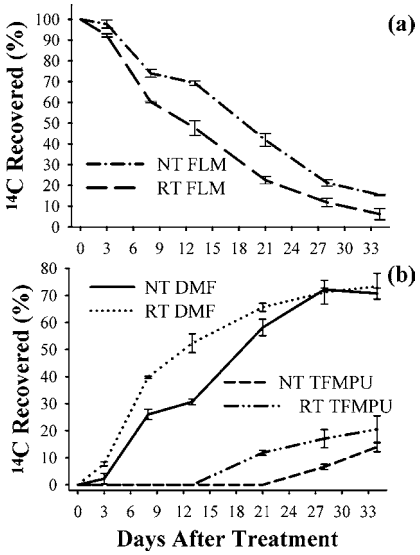

Figure 4. Components of extracts from NT and RT soils treated with ^{14}C FLM in study I. Percent ^{14}C recovered as (**a**) FLM in NT (- • -) and in RT (– – –) and as (**b**) DMF in NT (—) and in RT (• • •), and TFMPU in NT (- - -) and in RT (- • -). Error bars represent standard errors for each mean.

Table 3. First-Order Kinetics Constant (k) and Calculated Half-Life for the Dissipation of Extractable FLM, DMF, and TFMA, Respectively, in FLM-, DMF-, and TFMA-Treated Soils, Study I

	tillage					
parameter	NT[a]	RT	NT	RT	NT	RT
analyte	FLM		DMF		TFMA	
k (days^{-1})	0.043	0.065	0.030	0.069	0.271	0.363
	(0.003)	(0.003)	(0.003)	(0.004)	(0.004)	(0.005)
half-life (days)	16	11	21	10	3	2

[a] The standard error of k parameter is in parentheses.

indicative of increased oxidative metabolism (**Figure 4b**) and corresponded inversely to the dissipation of FLM (**Figure 4a**). No TFMA was observed during the incubation period in either RT or NT soil, similar to another study (*10*).

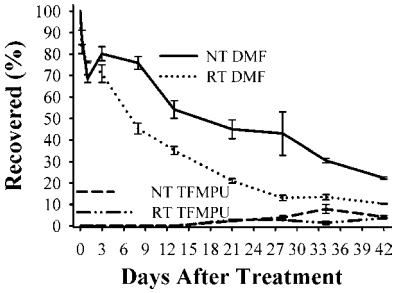

Figure 5. Percent recovery of analytes from soils treated with unlabeled DMF in study I. Extractable DMF is represented by NT (—) and RT (• • •), and extractable TFMPU (as a percentage equivalent of DMF applied) is represented by NT (- - -) and RT (- • -). Error bars represent standard errors for each mean.

Dissipation of total MeOH-extractable ^{14}C in soil treated with ^{14}C-labeled TFMA was rapid for both RT and NT soils (half-life of 2−3 days) (**Figure 3b** and **Table 3**). Although volatilization accounted for a significant portion of the dissipation (**Figure 2b**), the formation of nonextractable ^{14}C was the greatest sink for TFMA during the incubation period, accounting for 60−80% of added ^{14}C by day 7 (**Figure 3b**). While a decline in MeOH-extractable ^{14}C did not differ between NT and RT, nonextractable ^{14}C appeared to increase slightly more rapidly for NT in the first few days. This may be due to differences in humic material (*34*) for NT as compared to RT soil; however, there was little discernible difference in nonextractable ^{14}C between the two soils by the end of the incubation period.

As indicated previously, nonextractable ^{14}C was a major sink for both FLM- and TFMA-treated soil. A mechanism for oxidative incorporation of isoproturon into humic and fulvic acids was proposed by Reuter et al. (*35*). In their study, the 4-isopropylaniline (4-IPA) moiety was readily incorporated into polymers in the presence of the humic monomer catechol. Polymerized 4-IPA was more recalcitrant to degradation as compared with either 4-IPA or isoproturon.

For evaluating DMF dissipation in DMF-treated soil (**Figure 5**), HPLC analysis was used because there was no ^{14}C-labeled DMF compound available. Similar to FLM, DMF dissipated more rapidly in RT soil than in NT soil, with a half-life of 10 days for RT vs 23 days for NT (**Table 3**). TFMPU was the only metabolite recovered in extracts from DMF-treated soil (**Figure 5**) but was not detectable until day 21, as also observed in the FLM-treated soil. In contrast to FLM-treated soil, the highest percentage recovery of TFMPU (as an equivalent of DMF applied) was 7.9% (SE 2.1) for NT 34 days after application as compared to 3.6% (SE 0.26) for RT on day 42.

Sorption: Studies I and II. FLM sorption in Dundee NT and RT soils for study I was comparable (FLM NT K_d 1.48, SE 0.009; RT K_d 1.47, SE 0.012), but sorption of DMF and TFMA was higher in RT soil as compared to NT (LSD $P <$ 0.05) (DMF NT K_d 1.86, SE 0.006; RT K_d 2.21, SE 0.012; TFMA NT K_d 2.63, SE 0.009; RT K_d 2.77, SE 0.011). Given the similarity in organic C for the two soils (**Table 1**), very few conclusions can be drawn related to tillage management and sorption of FLM and metabolites in study I.

All soils in study II that were managed under various degrees of conservation management (RT) had higher organic C than respective conventionally managed soils (**Table 2**), indicative of accumulated surface plant residue and complex humic constituents. Freundlich sorption parameters (K_f, N) and K_{oc} values for FLM and metabolites were calculated for FLM and metabolites in study II to evaluate the influence of elevated soil

Table 4. Freundlich Sorption Coefficients Describing Interactions of FLM and Metabolites with Various Soils in Study II[a]

soil		FLM	DMF	TFMPU	TFMA
Dundee CT	K_f	1.44 (0.07)	3.03 (0.35)	4.47 (1.64)	7.10 (0.73)
	N	0.89 (0.02)	0.77 (0.04)	0.67 (0.12)	0.80 (0.04)
	K_{oc}[b]	118	240	285	703
Dundee RT	K_f	3.66 (0.39)	9.49 (3.63)	11.9 (2.99)	21.2 (3.22)
	N	0.88 (0.04)	0.66 (0.15)	0.62 (0.10)	0.73 (0.08)
	K_{oc}[b]	143	454	896	1066
Norfolk CT	K_f	0.42 (0.10)	1.40 (0.15)	2.48 (1.39)	3.26 (0.88)
	N	0.96 (0.07)	0.74 (0.03)	0.62 (0.17)	0.80 (0.08)
	K_{oc}[b]	79	174	222	400
Norfolk RT	K_f	0.96 (0.16)	2.75 (0.43)	4.38 (1.85)	7.63 ()1.17
	N	0.97 (0.05)	0.80 (0.05)	0.68 (0.14)	0.71 (0.05)
	K_{oc}[b]	84	212	245	463
Tunica CT	K_f	1.56 (0.10)	3.74 (0.50)	5.70 (1.57)	6.17 (1.21)
	N	0.95 (0.02)	0.76 (0.04)	0.63 (0.09)	0.80 (0.07)
	K_{oc}[b]	162	318	477	550
Tunica RT	K_f	2.16 (0.12)	5.33 (0.54)	7.03 (1.81)	12.9 (1.99)
	N	0.91 (0.02)	0.72 (0.04)	0.64 (0.09)	0.71 (0.06)
	K_{oc}[b]	169	448	557	2073
Weswood CT	K_f	0.54 (0.07)	1.51 (0.20)	2.65 (1.30)	1.10 (0.30)
	N	0.89 (0.04)	0.72 (0.04)	0.63 (0.15)	1.02 (0.08)
	K_{oc}[b]	45	110	137	119
Weswood RT	K_f	0.88 (0.07)	2.43 (0.46)	3.65 (1.36)	4.41 (0.93)
	N	0.97 (0.02)	0.79 (0.06)	0.73 (0.12)	0.89 (0.07)
	K_{oc}[b]	74	170	218	356

[a] The number in parentheses following K_f and N parameters is the standard error of the nonlinear regression. [b] K_{oc} calculated using the equation K_d/organic C, where K_d was calculated using nonlinear regression across all initial concentrations, while holding N constant at 1.

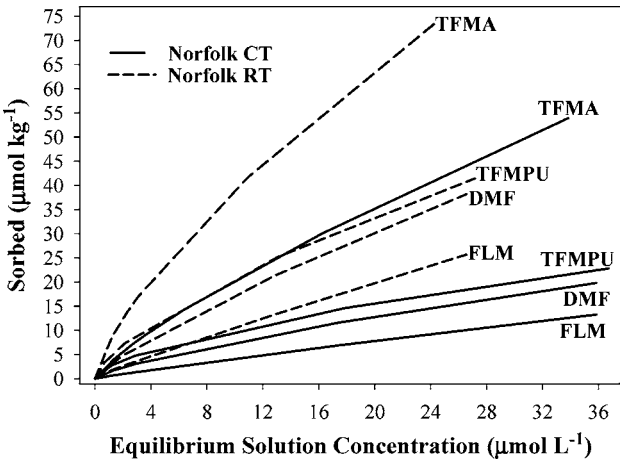

Figure 6. Sorption isotherms for FLM, DMF, TFMA, and TFMPU in CT (—) and RT (– – –) Norwood soils in study II.

organic C on analyte sorption (**Table 4**). Some general comments can be made based on patterns observed for the various analytes and initial dosing concentrations. Sorption was typically curvilinear for all analytes, indicated by N values less than 1 (**Table 4**), with a higher percentage sorption at lower initial concentrations than at higher concentrations. This trend of decreasing percentage sorption with increasing initial dosing concentration, and illustrated with representative isotherms for Norfolk soil in **Figure 6**, was observed over the range of concentrations for all soils (LSD $P < 0.05$ for all analytes).

Another observation was that sorption of FLM and metabolites increased with decreased proportion of amino group substitution, i.e., sorption of FLM < DMF < TFMPU < TFMA (**Figures 1** and **6** and **Table 4**), and this trend was consistent across tillage treatments and soil types. Our experimental determinations of log K_{ow} were FLM 2.23 (SE 0.02), DMF 2.43 (SE 0.01), TFMA 2.16 (SE 0.01), and TFMPU 2.36 (SE 0.01),

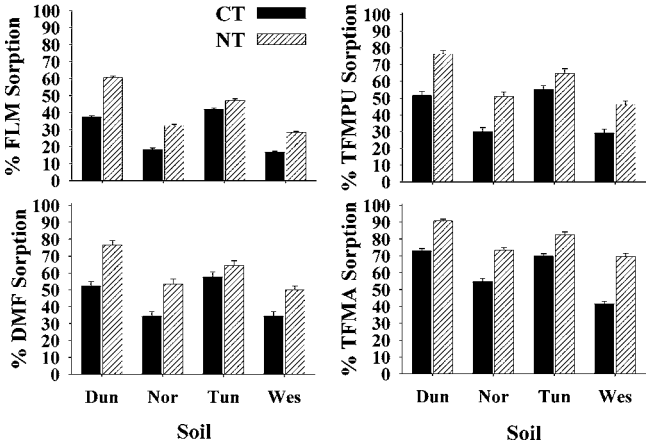

Figure 7. Percentage sorption of FLM, DMF, TFMPU, or TFMA for CT and RT Dundee, Norfolk, Tunica, and Weswood soils in study II. LSD $P < 0.05 = 0.92$, 1.41, 1.99, and 1.91 for FLM, DMF, TFMPU, and TFMA, respectively. Error bars represent standard errors for each mean.

and water solubilities were 89.2 (SE 1.54), 359 (SE 2.04), 4448 (SE 53), and 572 (SE 9.10) mg L^{-1}, respectively. These characterizations agree with other reports (36, Syracuse Research Corp., Oct. 13, 2005 http://www.syrres.com/esc/physdemo.htm) and suggest that the metabolites, particularly TFMPU and TFMA, are more polar than FLM, although they all likely possess both polar and nonpolar characteristics. This is understandable, since TFMPU and TFMA have smaller molecular volumes, fewer methyl substitutions, and more amine functional groups. These characteristics might lead to increased H-bonding, which in turn results in increased sorption to soil organic components. The mechanism for sorption of the TFMPU and TFMA therefore might be more H-bonding than hydrophobic due to increased amino group substitution. This affinity for soil organic functional groups may overcome the higher water solubility and tendency for mobility in soil.

The percentage sorption for all four analytes was higher for RT soils across soil types and initial solute concentrations (DMF: RT, 62%; CT, 43%; LSD $P < 0.05 = 1.2$; TFMA: RT, 79%; CT, 60%; LSD $P < 0.05 = 2.4$; TFMPU: RT, 63%; CT, 46%; LSD $P < 0.05 = 1.8$; FLM: RT, 43%; CT, 29%; LSD $P < 0.05 = 0.7$). The magnitude of difference to which this occurred, however, did vary with soil and analyte, i.e., the interaction of soil type and tillage was significant ($P < 0.05$) (**Figure 7**). The higher organic C in conservation management soils together with larger K_{oc}, K_f, and percentage sorption values suggests a strong relationship between organic C content and sorption of FLM and associated metabolites (**Table 4** and **Figure 7**). Significant and positive correlations between percent solute sorption and organic C level in study II soils support this conclusion (**Table 5**). Additionally, when comparing the correlations of solute sorption and organic C levels at lower and higher concentrations, there was always a stronger correlation (r) at the higher concentration (**Table 5**). At the lower concentrations, sites from both mineral and organic soil components likely contributed to sorption. At higher solute concentrations when more site saturation was taking place, the organic sites may have proportionally contributed more to sorption, resulting in the higher correlation of sorption with organic C (**Table 5**).

Figure 8 shows an NMR spectrum for a humic acid extracted from the Dundee CT and NT soils. In comparing structures of humic acids from Dundee NT and CT, differences in the concentration of functionalities on a mass or molar basis were

Table 5. Correlation (r) and Level of Statistical Significance (α) of Soil Organic C and Percent Solute Sorption Evaluated at Two Initial Dosing Concentrations in Study II

FLM concn (μM)	r (α)	DMF concn (μM)	r (α)
2.2	0.76 (0.03)	2.3	0.73 (0.05)
43.0	0.82 (0.02)	45.9	0.88 (0.01)
TFMPU concn (μM)	**r (α)**	**TFMA concn (μM)**	**r (α)**
2.5	0.73 (0.05)	30.9	0.74 (0.04)
49.0	0.88 (0.01)	61.7	0.77 (0.03)

[a] The two highest solute concentrations for TFMA were the only ones where there was a significant correlation with organic C.

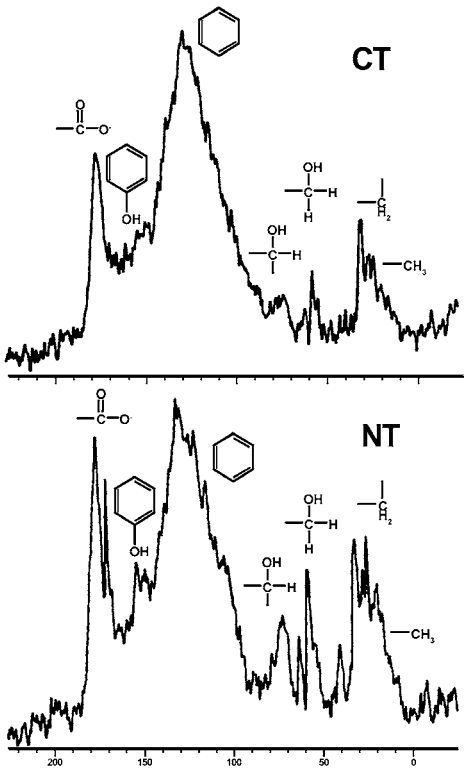

Figure 8. ^{13}C liquid-state NMR spectra of humic acid extracts from Dundee (**a**) CT and (**b**) NT soils.

observed. For example, a greater abundance of functional groups such as carboxyls, aliphatic hydroxyls, and phenolics was measured in the NT humic acids, and these groups have been implicated as potential sorption sites for compounds such as FLM. These sites could also play a greater role in the sorption of the metabolites. The presence of nonsubstituted amino groups likely facilitated sorption to organic C, with a reactive aniline in TFMA having the greatest affinity. However, for the most part, qualitative differences in the organic components between the two spectra were minimal, with the greatest difference as the greater abundance of functional groups in the NT humic acid. This is consistent with other studies (e.g., *37*).

Within a soil type, sorption patterns were generally consistent (with a few exceptions) but, among soils, varied in ways expected based on clay content, clay type, and pH, thus complicating the simple relationship between FLM or metabolite sorption and organic C level. For all four analytes, the percentage sorption increased in the order of Weswood < Norfolk < Tunica < Dundee across all initial solute concentrations and tillage treatments ($P < 0.05$, LSD = 0.65 FLM, 0.99 DMF, 1.41 TFMPU, and 1.35 TFMA). Differences in sorption among the four soils primarily were attributed to the relative proportion of organic C and clay as well as the predominant clay mineral in individual soils. The soil organic C content was comparable for Dundee and Tunica CT soils (**Table 2**), but FLM, DMF, and TFMPU sorption in Tunica CT were slightly higher than in the Dundee soil, indicating that clay content contributed to the difference in sorption for the two CT soils (**Figure 7**). The higher clay content in Tunica likely provided a great capacity for sorption, suggesting that the clay minerals, especially those of 2:1 structure, are an important source of polar sites for sorption. Although smectitic clays also were predominant in the Dundee, the clay content was lower. Thus, given similar organic C levels, the contribution of clay to sorption was not as important in Dundee as in Tunica. Despite relatively high clay contents with smectitic characteristics, Weswood had the lowest sorption of the four soils. The low organic C content was likely a key factor. In addition, Weswood is a calcareous soil, and potential sorption contributed by hydrogen bonding may have been more limited at higher pH. Weswood also has significant levels of free iron oxides, although it is not clear how this factor might have influenced the sorption of FLM and metabolites. Norfolk has kaolinitic clay and a high sand content, thus potentially high AEC and low CEC. These characteristics likely contributed to lower sorption of FLM and metabolites than the two Mississippi soils of comparable pH.

In conclusion, surface soils managed under RT averaged 18−139% higher organic C levels than respective conventionally tilled soils. The RT soils also exhibited higher sorption of FLM and metabolites DMF, TFMA, and TFMPU, indicating strong relationships between organic C and FLM or metabolite sorption (correlation coefficients ranged from 0.73 to 0.88). Higher concentrations of functional groups such as carboxyls and hydroxyls in the RT humic material supported these observations implicating organic C as a major contributor to FLM and metabolite sorption. For either tillage treatment, the percentage sorption increased in the order of FLM < DMF < TFMPU < TFMA, suggesting that nonsubstituted amino groups facilitated sorption to organic C, with nonsubstituted aniline in TFMA having the greatest affinity. Increased affinity of the metabolites relative to FLM for soil components suggests that in RT systems where there is an accumulation of organic matter, mobility of these compounds may be inhibited.

FLM and DMF dissipated more rapidly in RT Dundee soil (half-lives of 11 and 10 days, respectively) than in the NT counterpart (half-lives of 16 and 23 days, respectively). In FLM-treated RT soil, DMF and TFMPU accumulated more rapidly than in NT as FLM degraded. Slightly more mixing of the RT soil may have resulted in more aeration, even distribution of organic residues, and elevated enzyme levels and contributed to the more rapid dissipation of FLM and metabolites. Extractable TFMA dissipated rapidly (half-life of 2−3 days) regardless of tillage, primarily as nonextractable residues (~70%, day 42) and volatilization (~16%). The large proportion of TFMA as nonextractable residues suggested that incorporation into humic polymers may have been a factor.

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