Fluometuron Interactions in Crop Residue-Managed Soils

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Abstract

This paper reviews a series of studies concerning fluometuron (N,N-dimethyl-N'-[3-(trifluoromethyl)-phenyl]urea) interactions in soil and herbicide-desiccated crop residues. The objective of these studies was to evaluate effects of tillage and cover crop management on fluometuron sorption and degradation. Length of equilibration time and organic C level appeared to be the dominant factors influencing fluometuron sorption quantity and kinetics. Related to these factors, resident time and plant surface accumulation of organic residues may influence the potential for subsequent movement in soil. Fall-seeded ryegrass (*Lolium multiforum*) cover in a cotton (*Gossypium hirsutum* L.) cropping system enhanced biological soil quality and the potential for fluometuron degradation. Fluometuron was more rapidly degraded in annual ryegrass residues and conventional tillage (CT) or no-tillage (NT) soils under a fall-seeded annual ryegrass cover crop than in soils without residue.

Introduction

Fluometuron is widely used to controlbroadleaf and grass weeds in cotton. The adoption of residue management practices may influence the effectiveness of fluometuron as an herbicide and its persistence in soil. Higher organic matter levels in no-tillage soils can enhance sorption (Locke, 1992; Brown et al., 1994) and unextractability (Locke and Harper, 1991) of herbicides in soil. Tillage effects on herbicide degradation are mixed, but metabolism of herbicides may differ between no-tillage and conventional-tillage soils (Locke and Harper, 1991).

Promotion of management practices that enhance plant residue accumulation on the soil surface necessitates research addressing potential environmental impacts of these systems. Plant residues have the potential to intercept and retain surface applied herbicides. Subsequent mobility of the herbicide in runoff water or in leachate may be influenced by herbicide retention at the soil surface. This paper reviews results from a series of studies concerning fluometuron interactions in soil and cover crop residue. The objective of these studies was to evaluate the effects of tillage and cover crop management on fluometuron sorption and degradation.

Materials and Methods Effects of Tillage on Sorption to Soil

Batch sorption techniques were used to characterize fluometuron sorption kinetics in surface (0-5 cm) **Dundee**

silt loam soil (fine-silty, mixed, thermic Aeric Ochraqualf) from conventional tillage and no-tillage soybean (*Glycine* max) plots (Table 1). Fluometuron dissolved in 0.01 *M* CaCl, solution was added to soil (18 mL solution to 3 g air-dry soil). Initial fluometuron concentrations in the sample solutions were 0.286, 1.41, and 7.03 mol L-¹. The fluometuron solutions added contained 134 Bq mL-' of uniformly ring labelled ¹⁴C fluometuron (specific activity 356 MBq mmol⁻¹).

Samples were prepared by weighing 3.0 g air-dry soil into 25-mL glass centrifuge tubes, and adding 15 mL of 0.01 *M* CaCl, solution. After 30 minutes, 3-mL herbicide solution (0.01 *M* CaCl₂) was carefully added to minimize disturbance of the soil settled at the bottom of the tube. The tubes were then sealed with teflon-lined caps and shaken (1, 2, 5, 15, or 30 min; or 1, 3, 24, 48, 72, or 96 hours) at room temperature (25 °C). After shaking, samples were centrifuged, and two 1-mL aliquots of supernatant were counted for ¹⁴C radioactivity. Each shaking time was run in triplicate, and the experiment was repeated.

The difference between initial (C_0 as pmol L⁻¹) and final (Cs) herbicide concentration was attributed to sorption (xm as μ mol kg⁻¹). Fluometuron sorption kinetics were described using a three-site, reversible model (Gaston and Locke, 1994), and sorption at selected shaking times (1, 24, and 96 hours) was evaluated using the Freundlich equation (xm = K_fC_s^{1/n}). Nonlinear regression was used to calculate Kf and n-1 coefficients in the Freundlich equation.

Table 1. Characteristics of Dundee silt loam (0 - 5 cm) in conventional tillage (CT) and no-tillage (NT).

Tillage	pH (1:l) 0.01 <i>M</i> CaCl,	Organic C e ke-'	
СТ	5.16	10.2	
NT	5.54	16.7	

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Sorption to Cover Crop Material and Soil

Fluometuron sorption was evaluated in Dundee silt loam soil, and rye (*Secale cereale*), hairy vetch (*Vicia villosa*), sampled from the study area described by Wagner et al. (1995). The cover crop material was collected 4 weeks following desiccation with paraquat. The samples were stored at 5 "C until use. Samples were prepared by weighing 1 g moist soil or moist plant residue into 25-mL glass centrifuge tubes. Fluometuron dissolved in 0.01 M CaCl₂ solution was added to the material (12 mL solution to 1 g, fresh weight). Initial fluometuron concentrations in the solutions were 6.50, 13.8, 23.1, 97.3, and 189.9 pmol L^{-1.} Radioactivity in the fluometuron solutions was 353 Bq mL^{-?} The tubes were then sealed with teflon-lined caps and shaken for 48 hours at 5 °C. The low temperature was used to minimize potential degradation during the 48-hour equilibration.

At the end of 48 hours, samples were filtered and centrifuged, and two 1-mL aliquots of supernatant were counted for radioactivity. Separate aliquots were analyzed by HPLC to determine if degradation occurred during equilibration. Parameters of the HPL C analysis included fluorescence (Ex 294 nm, Em 329 nm) and ¹⁴C detection; Econosil reversephase column; flow rate 1 mL min-'; gradient mobile phase acetonitrile:water. The HPLC analysis did not indicate the presence of fluometuron metabolites.

Effects of Tillage and Cover Crop on Degradation

Fluometuron degradation in surface (0-2 cm) soils and ryegrass residues was assessed in the laboratory using ¹⁴C-labeled fluometuron. Five g of soil and 2 g of cover crop residue were placed in 50-mL polypropylene tubes and treated with an aqueous solution of fluometuron to attain 9.7 μ mol kg⁻¹ fluometuron (5.89 x 10⁵ Bq kg⁻¹). Soils were adjusted to 32% (w/w) moisture and ryegrass residues were adjusted to 100% moisture (w/w), and all samples were incubated at 28 °C. Fluometuron and metabolites were extracted with methanol in samples taken 0, 4, 11, and 17 days after treatment. Analysis of processed extracts was by thin-layer chromatography/linear imaging scanning (chloroform:ethanol, 955 v/v) (Ross and Tweedy, 1973), and unextractable ¹⁴C was quantified by oxidation of extracted samples and liquid scintillation counting.

Results and Discussion *Effects of Tillage on Sorption to Soil*

Sorption kinetics between surface soils from two tillage systems were compared using the 1.43 pmol L⁻¹ initial fluometuron concentration (Figure 1). The sorption process was almost completed by 24 hours, although some sorption continued through 96 hours for both soils. Sorption was more rapid in the NT soil. The Freundlich sorption coefficient (K_f) was calculated for 1-, 24-, and 96-hour shaking times (Table 2). Fluometuron sorption was higher in NT than CT, as in-



Figure 1. Sorption kinetics of fluometuron in Dundee conventional tillage and no-tillage soil during a 96-hour equilibration. Symbols are means of observed values, and curves represent values predicted by a three-site, reversible model.

dicated by higher K_f values for all three shaking times. The K_f values for soils from both tillage systems also increased with shaking time, supporting the previous kinetic data. Sorption was nonlinear (n⁻¹ <1), and the exponent parameter was similar for both soils and all shaking times (Table 2). Non-linear characteristics indicate that sorption decreased as initial herbicide concentration increased.

Sorption to Cover Crop Material and Soil

Herbicide sorption was greatest in the rye and lowest in soil (Table 3). The surface area and number of sorption sites of the plant residues were likely greater than that of the soil, but little is known about the reactivity of herbicides with functional groups in decayed plant material. However, the plant materials were heavily colonized by fungi and bacteria (Wagner et al., 1995), and structural components of microbes may have strong sorptive capabilities.

Cell components (lipids, proteins, soluble sugars, and poly-

Table 2. Freundlich parameter coefficients characterizing the effects of tillage on fluometuron sorption at selected equilibration times.

	Conventional Tillage			No-Tillage				
Time (h)	Kf ^l	s.e. ²	[n ⁻¹] ³	s.e. ²	Kf'	s.e. ²	[n ⁻¹] ³	s.e ^{.2}
1	1.04	0.025	0.83	0.017	1.53	0.025	0.85	0.018
24	1.44	0.033	0.85	0.018	2.02	0.024	0.85	0.007
96	1.81	0.025	0.83	0.014	2.45	0.031	0.85	0.010

'Freundlich sorption coefficient.

²Asymptotic standard error.

³Freundlich exponent.

 Table 3. Freundlich parameters describing fluometuron sorption in rye. hairv vetch. and Dundee soil.

Sorbent	K _f ¹	s.e. ²	[n ⁻¹] ³	s.e. ²
Rye	21.8	1.11	0.96	0.01
Hairy Vetch	28.0	4.25	0.84	0.03
Dundee Soil	2.60	0.26	0.86	0.02

'Freundlich sorption coefficient.

²Asymptotic standard error.

³Freundlich exponent.

saccharides) in the plant residue material were likely consumed by microbes in initial decomposition stages. However, basic plant structural components were intact. Of these constituents, relative abundance in plant material is generally cellulose >lignin>suberin>cutin, and all are resistant to decomposition. Dao (1991) observed that cellulose extracted from wheat straw had low affinity for metribuzin, but that the acid-detergent fiber fraction (cellulose/lignin polymers) had a much higher affinity for metribuzin. Silica may also play a role in the sorption of herbicides to the plant residue. Substantial silica deposits in epicuticular cells have been observed in many grass species.

Effect of Tillage and Cover Crop on Degradation

Soil organic carbon in the surface (0-2 cm) soil was 74% higher in NT compared to CT soils without ryegrass, and 108% higher in NT compared to CT soils from plots with annual ryegrass (Wagner et al., 1995). After 4 years of NT, minimal effects on soil microbial populations were observed in the 0-2 cm surface soil. The annual ryegrass cover crop stimulated all microbial populations evaluated in the surface soil for all sampling periods in both tillage regimes (Wagner et al., 1995). Transient increases in microbial populations due to the ryegrass cover crop were most pronounced in CT plots compared to the NT plots in the 2-10 cm depths. Soil aryl acylamidase and esterase activity and microbial biomass were greatest in NT-ryegrass plots (0-2 cm) with no differences in these parameters attributable to tillage or ryegrass at 2- to 10-cm depth.

Soils from the NT ryegrass plots exhibited the greatest incorporation of fluometuron into unextractable components (data not shown). Fluometuron degradation occurred most rapidly in soils from NT and CT plots with ryegrass (halflife 8 days) (Figure 2). Half-lives of 10.5 days were observed in ryegrass residues and 15 to 16 days for CT and NT soils, respectively, from plots without the ryegrass cover crop.

Microbial populations associated with the ryegrass soils were significantly greater than those of the bare soils (Wagner et al., 1995). All of the soils have received annual applications of fluometuron for at least 4 years. Thus, a microbial communit y capable of rapid fluometuron metabolism most likely enhanced fluometuron degradation under ryegrass.

Trifluoromethyl aniline was infrequently detected, and when observed was less than 2% of recovered ¹⁴C.



Figure 2. Interaction of annual ryegrass cover and tillage on fluometuron persistence and appearance of desmethyl fluometuron and triflouromethylphenylurea 17-day incubation study.

Desmethyl-fluometuron (DMFM) was the primary accumulating metabolite observed in soil. Trifluoromethylphenylurea (TFMPU) was only observed after accumulation of DMFM, and the greatest accumulation of TFMPU was in ryegrass residues.

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