



DEGRADATION OF 2,4-D AND FLUOMETURON IN COVER CROP RESIDUES

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ABSTRACT

Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) was studied in hairy vetch (*Vicia villosa* Roth) and rye (*Secale cereale* L.) residues. Transformation of fluometuron (1,1-dimethyl-3-(α,α,α -trifluoro-m-tolyl)urea) was also evaluated in annual ryegrass (*Lolium multiflorum* Lam.) residues. Microflora associated with herbicide-desiccated hairy vetch and rye residues were 100-fold or greater than soils. Microbial activity (fluorescein diacetate hydrolysis and respiration) were 6-fold or greater in hairy vetch and rye residues than soil. In 14-d studies, 78 to 82% versus 28 to 40% of ^{14}C -carboxyl-labelled 2,4-D and 48 to 60% versus 5 to 17% of ^{14}C -ring-labelled 2,4-D were mineralized in soil and crop residues, respectively. Fluometuron can be degraded by *N*-demethylation in ryegrass residues at rates similar to soil, however, high moisture content was required. Degradation of herbicides in cover crop residues was most likely due to limited bioavailability rather than biological activity. ©1998 Elsevier Science Ltd. All rights reserved

KEYWORDS - 2,4-D, Fluometuron, Plant Residues, Biodegradation

INTRODUCTION

Conservation management strategies such as reduced-till are being implemented by growers to minimize soil erosion and conserve soil moisture. Direct seeding of soybeans (*Glycine max* (L.) Merr.) into herbicide-desiccated rye residues remaining on the soil surface can reduce erosion and aid in conserving water (1). Cover crop residues remaining on the soil surface can also provide varying degrees of weed control (1, 2, 3). Use of herbicide-desiccated cover crops in a crop production system may impact soil biological and chemical processes, affecting the subsequent fate of agrochemicals. Crop rotations may alter soil chemical/physical properties (4), soil microbial populations (5) and soil enzyme activities (6). Herbicide-desiccated cover crops can have stimulating effects on various soil microbial populations and soil enzyme activities (7).

The effects of residue management techniques such as no-till on the fate of herbicides has been studied for many herbicides, i.e., alachlor (8), atrazine (9), bentazon (10), chlorimuron-ethyl (11), metolachlor (9), and metribuzin (12). Depending on the herbicide, soil characteristics and herbicide history, differential patterns of herbicide degradation in soil were observed in no-till compared to conventional till soils. Little is known on the transformations of herbicides in crop residues. Interception of herbicides by crop residues, may impede their movement into the underlying soil (13, 14). Chlorimuron-ethyl (15) and fluometuron (16) have a greater sorption to cover crop residues compared to soil. Studies on fluometuron degradation (16), indicated it is rapidly degraded in soils previously planted in ryegrass as well as in ryegrass residues compared to soils that were fallow the previous fall.

We studied microbial populations and fluorescein diacetate hydrolysis (FDA) associated with soils and the cover crop residues to ascertain microbial characteristics relative to herbicide degradation. Laboratory studies evaluated the degradation of 2,4-D and fluometuron by cover crop residues relative to soil. 2,4-D can undergo complete metabolism (mineralization) to CO₂ (17-19), while fluometuron is metabolized via sequential demethylation and incorporation into bound soil residues with little mineralization (16, 20). These assays may reflect the potential for biodegradation of these herbicides in crop residues compared to soil under field conditions.

EXPERIMENTAL

Soils and Plant Residues

Soil (Dundee silt loam) and hairy vetch and rye cover crop residues were obtained from soybean plots, while annual ryegrass residues were collected from cotton field plots, near Stoneville, MS. Rye and hairy vetch were sown in the fall. Cover crops and bare ground (winter fallow) treatments in the soybean experiment were sprayed with 1.05 kg a.i. ha⁻¹ paraquat [1,1'-dimethyl-4,4'-bipyridinium ion] in early May. Soil and herbicide-desiccated cover crop residues were collected from bare ground, hairy vetch and rye plots one week later at soybean planting and 6 weeks after planting. Each soil sample was a composite of three 0 to 10 cm cores (5 cm dia.) collected from each of six replicate plots. Plant residues were collected from a 10 by 10 cm region around each core. Soils and ryegrass residues from the cotton study were collected from a five-year field study investigating tillage and cover crop interactions. Annual ryegrass (hereafter referred to as ryegrass) was seeded in November of the preceding year, and all plots were sprayed with 1.1 kg ha⁻¹ of glyphosate in early April. In the cotton study, soil (0-2 cm) was sampled from no-till bare ground (winter fallow) and no-till plots from fall seeded ryegrass plots one month after herbicide application. Soil and ryegrass used in this study was a composite of samples taken from four replicate blocks. Soil and residues were stored at field moisture conditions at 5 °C, and used in the degradation studies within three months of collection.

Microbiological Techniques

Moist soils were sieved through a 2.36 mm sieve prior to processing. Cover crop residues were chopped to less than 2 cm length. For estimation of microbial populations, cover crop residues were homogenized in a Sorvall Omni Mixer (Sorvall Instruments, Newton, CT) in phosphate buffer (0.05 M, pH 6.8), at high speed for 2 min. Homogenates were sonicated for 2 min prior to preparing serial dilutions in phosphate buffer. Total bacteria, Gram-negative bacteria, and fluorescent and total fungi were enumerated by serial dilution plating as described elsewhere (8, 11). Colony forming units were calculated on a dry-weight basis of soil or residue transformed to log (10). Fluorescein diacetate hydrolysis was used to estimate microbial activities of soils and residues (21).

Degradation of 2,4-D in Residues and Soil

Two studies assessed the potential for mineralization of 2,4-D to CO₂ by no-residue soil and by hairy vetch and rye cover crop residues. Soil and residue samples used in this study were a composite from all replicate plots collected during the July sample. Solutions of 2,4-D were prepared from ring ¹⁴C-labelled or carboxyl ¹⁴C-labelled compound (>98% radiochemical purity) (Sigma Chemical Co., St. Louis, MO), each diluted with technical grade 2,4-D (Chem Service, Chester, PA). Biometer flasks (250 ml, Belco, Vineland, NJ,) were used to assess mineralization (22). In the first study, these flasks contained either 40 g oven-dry equivalents of soil collected from no-residue control plots or 8-g equivalents of oven-dry vetch or rye residues. Samples were treated to achieve 3.0 µg 2,4-D g⁻¹ and 1640 Bq g⁻¹. Moisture contents were adjusted to 33% (w/w) for the soil and 66% (w/w) for the residues and flasks were incubated at 28 °C. In the second study, the amounts of soil and cover crop residues were halved, but 2,4-D concentration and moisture content were identical. Six replicates were used in both experiments. Side-arms of the biometer flasks contained 10.0 mL of 1.0 N NaOH to trap evolved CO₂. The NaOH solutions were removed typically every 2 days and replaced with fresh solution. Aliquots of NaOH were added to Hi-Ionic-Fluor (Packard, Meriden, CT) scintillation cocktail and the absorbed ¹⁴CO₂ was determined using a liquid scintillation counter (LSC) (Packard TriCarb 4000 series, Packard Instrument, Meriden, CT).

After 14 d incubation, soils and residues treated with ring-labelled 2,4-D were extracted three times with 60 mL methanol. Radioactivity in the extracts was determined by LSC using Ecolume (ICN, Costa Mesa, CA) scintillation cocktail. In the second study, the initial two methanol extracts were reduced to 10 mL in a centrifugal evaporator and distilled water was added to 50 mL. The aqueous solution was acidified to pH 3.0 with 1.0 N HCl and eluted through a C-18 solid phase extraction column (Baker, Phillipsburg, PA). The residual 2,4-D was removed from the C-18 column with 3.0 mL of methanol. Methanol extracts were spotted on silica gel TLC plates (250 µm thick with 3.3 cm pre-adsorbent layer) and developed for 10 cm with Benzene:Acetic acid 50:4 (v:v). The distribution of radioactivity in the chromatogram was analyzed with a Bioscan System 200 Imaging Scanner (Bioscan, Washington D.C.). The R_f values of 2,4-D and 2,4-dichlorophenol were 0.16 and 0.40 respectively. Residual radioactivity in extracted soils and residues were determined by oxidation (Packard

306 Oxidizer) and LSC. In the second study, total CO₂ evolved (respiration) was determined by titration of the NaOH solution following BaCl₂ precipitation (23). Radioactivity remaining in the NaOH solution following titration was determined to assess trapping of volatiles.

Fluometuron Degradation in Ryegrass Residues and Amended Soils

Laboratory studies evaluated the interactions of moisture content of ryegrass residues and inoculation with soil on the degradation of fluometuron. Technical grade fluometuron was obtained from Chem Service, Chester, PA, and ¹⁴C-ring labelled fluometuron (>98% radiochemical purity) and metabolite standards were contributed by Ciba (now Novartis), Greensboro, NC. An aqueous soil suspension (1:10 w:w) of Dundee soil was prepared by shaking vigorously for 2 h. Ryegrass residues, 1.18 g (1.00 g oven dry weight), were placed in centrifuge tubes (25 mL glass, screw cap). The residues were treated in one of three ways: 300 μL of water, 300 μL of soil suspension, or left untreated. The tubes were capped with polyurethane plugs, and samples were incubated for 48 h at 28 °C. Residues were then treated with either 300 μL of 32.3 μM fluometuron solution (16.7 KBq mL⁻¹ of ¹⁴C-ring labelled fluometuron), or 700 μL of 13.85 μM fluometuron solution (7.1 KBq mL⁻¹ of ring labelled fluometuron). These treatments resulted in three final moisture contents (48, 78 and 118% water w/w basis) and a fluometuron concentration of 9.7 μmol kg⁻¹ ryegrass. Residues were incubated at 28 °C with triplicate tubes of the five treatments (three moisture contents in addition to the two highest moisture contents inoculated with soil extract) sampled at 4, 7, and 11 d after treatment.

The effects of incorporation of ryegrass residues in soil on fluometuron degradation were compared to nonamended soil from no cover crop (fallow) plots or soil collected from ryegrass plots. Dundee soil (0 to 2 cm sample) and residues were collected 1 month after application of glyphosate from no-tillage plots. Soil (5.0 g air dried equivalent) was added to centrifuge tubes (25-mL screw cap). Finely-chopped ryegrass residues (100 mg of 1 to 2 mm pieces) were added to one set of tubes containing the soil from fallow plots and mixed well. Fluometuron solution (730 μL containing 4167 Bq ¹⁴C-ring labelled fluometuron), was added to attain 9.7 μmole kg⁻¹ soil. Four tubes of each treatment were sampled after incubating for 4, 7, and 11 d at 28 °C.

Fluometuron and metabolites were removed from residues and soils with four 15-mL methanol extractions (extraction efficiency = 99%). Radioactivity recovered in each extract was determined by LSC, and the first two extracts were combined and reduced to 3 mL under N₂ gas. Fluometuron and metabolites were determined by TLC and linear image scanning, using chloroform:ethanol (95:5, v:v) as solvent and silica gel plates as described elsewhere (16, 20). R_f values for standards were: fluometuron = 0.58, desmethyl fluometuron (DMF) = 0.30, trifluoromethyl phenylurea (TFMPU) = 0.13, and trifluoromethyl aniline (TFMA) = 0.76. Nonextractable radioactivity was determined in soils by oxidation as previously described in the 2,4-D study.

RESULTS AND DISCUSSION

Microbial populations and activity

Microbial propagules recovered from soil were significantly influenced by hairy vetch and rye cover crops (Table 1). Overall, soils from hairy vetch plots had a greater stimulation of certain microbial groups, i.e. Gram-negative bacteria and fluorescent pseudomonads (May sample) compared to soil from rye plots. Similar effects were observed in other studies (10). Although a significant enhancement of certain soil microbial populations was observed due to cover crops, the magnitude of effects may have minimal effects on herbicide transformation and other microbial activity in soil. Cover crop residues maintained approximately 100- to 1000- fold greater propagule densities compared to the underlying surface soils; the magnitude of differences depended upon residue type, microbial group and date of sampling (Table 1). Similar levels of FDA hydrolytic activity were observed in soil regardless of cover crop (Table 2). Increased microbial populations, therefore, had little effect on this enzymatic

Table 1. Microbial propagules associated with soils and cover crop residues at two samplings.

| Sample, Date | Log (10) colony forming units g ⁻¹ † | | | |
|-----------------------|---|------------------------|--------------------------|-------------|
| | Total Bacteria | Gram-negative Bacteria | Fluorescent Pseudomonads | Total Fungi |
| <u>Soils, May</u> | | | | |
| Hairy vetch soil | 8.13 a | 7.26 a | 6.30 a | 5.17 a |
| Rye soil | 8.12 a | 6.89 b | 5.87 b | 5.21 a |
| No cover soil | 7.95 b | 6.44 c | 5.36 c | 5.22 a |
| <u>Residues, May</u> | | | | |
| Hairy vetch | 10.40 a | 9.66 a | 9.00 a | 8.09 a |
| Rye | 10.16 b | 9.86 a | 9.15 a | 7.67 b |
| <u>Soils, July</u> | | | | |
| Hairy vetch soil | 7.62 a | 6.20 a | 4.95 a | 5.17 a |
| Rye soil | 7.25 b | 5.89 ab | 5.02 a | 4.72 ab |
| No cover soil | 7.20 b | 5.92 ab | 4.76 a | 4.63 b |
| <u>Residues, July</u> | | | | |
| Hairy vetch | 10.48 a | 9.21 a | 8.08 a | 6.54 a |
| Rye | 10.05 a | 9.12 a | 7.99 a | 6.45 a |

†Values are the mean of six samples; means within a column for a given type of sample and date followed by the same letter do not differ significantly at the 95 % level by Fishers LSD.

activity in soil. FDA-hydrolytic activity was also similar between hairy vetch and rye residues. However, cover crop residues had 7- to 12-fold greater FDA hydrolytic activity than their respective soils. FDA hydrolysis is a generic indicator of microbial activity (21). It is a broad substrate for esterases, lipases and certain proteases and is correlated with microbial respiration. Schnurer and Rosswall (21) found that FDA-hydrolysis was more rapid in straw than soil, similar to what we observed in the cover crop residues. The FDA hydrolytic activities observed in the cover crop residues may reflect both the greater microbial density as well as greater availability of suitable substrates to support microbial activity.

Table 2. Fluorescein diacetate-hydrolysis (esterase) activity of soils and cover crop residues.

| Sample Date | $\mu\text{mol Fluorescein Formed g}^{-1} \text{h}^{-1} \dagger$ | | |
|-------------|---|-------|--------------------|
| | Cover Crop | Soil | Cover Crop Residue |
| May | Hairy Vetch | 200ns | 1970ns |
| | Rye | 206 | 1640 |
| | None | 196 | - |
| July | Hairy Vetch | 181ns | 2075ns |
| | Rye | 190 | 2215 |
| | None | 163 | - |

[†]Means within a column for a given sample date were not significantly different at the 95 % level as determined by Fisher's LSD. ns = not significant.

2,4-D Degradation

Two laboratory studies assessed the potential for degradation of 2,4-D by rye and vetch residues relative to soil. Summaries of cumulative $^{14}\text{CO}_2$ evolution from these studies are presented in Figures 1 and 2. In Study 1, 77% of the carboxyl-labelled 2,4-D was metabolized to CO_2 by soil compared to less than 30% by residues of the two cover crops, and 60% of ring-labelled 2,4-D was mineralized to CO_2 by soil compared to less than 10% by the crop residues during the 14-d incubation. In the second study, 82, 37, and 40% of carboxyl-labelled 2,4-D was evolved as CO_2 by soil, rye, and vetch, respectively. Mineralization of ring-labelled 2,4-D by soil was 47.9% compared to 12.9 and 17.2% by the rye and vetch residues, respectively. The parent compound and metabolites (dichlorophenol and volatile organic acids) could have been trapped in the NaOH solutions. Minimum radioactivity (typically less than 5% of initial from both ring- and carboxyl-label) was recovered in solutions following BaCl_2 precipitation, indicating that our assessment of mineralization was representative of CO_2 evolved. Higher rates of both ring and carboxyl-labelled 2,4-D degradation were observed by reducing the amount of cover crop residues by 50% in the biometer flasks. Lower 2,4-D mineralization in the first study may be due to

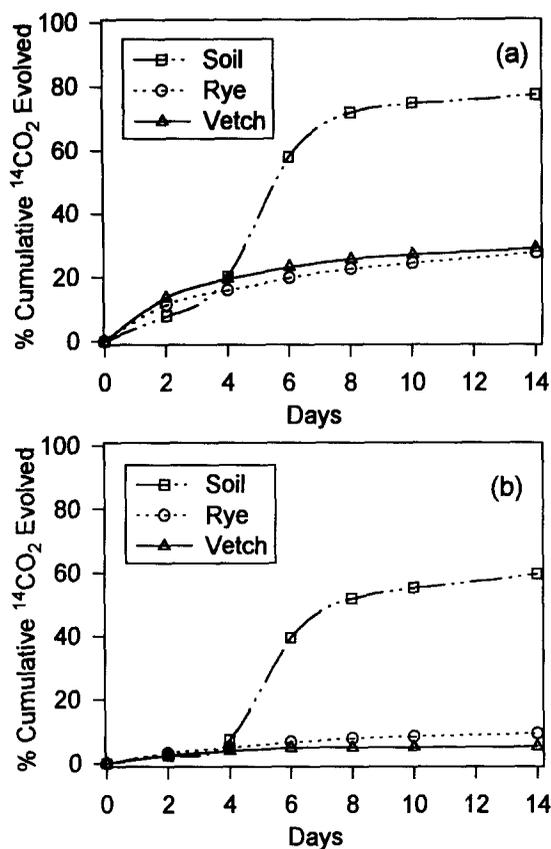


Fig 1. Mineralization of (a) ^{14}C -carboxyl and (b) ring-labelled 2,4-D by soil, rye and hairy vetch residues, 2,4-D Degradation Study 1.

limited O_2 availability caused by the amount of residue and subsequent respiration. However, trends in Study 1 are similar to those in Study 2. In the second study, greater mineralization of ring labelled 2,4-D was observed in vetch compared to rye (Fig. 2). Higher rates of respiration (total CO_2 evolution) were observed for the residues compared to soil. Respiration in rye was significantly greater ($P > 0.01$) than vetch residues (Fig. 3). The respiration studies indicate that microbial activity was about 6- to 7- fold greater in the crop residues compared to soil during the 2,4-D degradation studies. The enhanced microbial activity observed in residues compared to soil (i.e., respiration and FDA hydrolysis), however, did not result in greater 2,4-D mineralization. A summary of the recovery of ^{14}C -ring labelled 2,4-D is presented in Table 3. In both studies, a greater proportion of the radioactivity added was extractable from rye and vetch residues than from soil. TLC analysis of extracts from the second experiment indicated that all radioactivity corresponded to 2,4-D with no accumulation of metabolites (data not shown). A similar distribution of ^{14}C in the nonextractable fraction was observed for soil and residues in both studies. However, the ratio of ^{14}C mineralized compared to nonextractable in soil was 1.83 and 1.04, while

this ratio in the two cover crop residues was 0.23 (rye) and 0.36 (vetch). These results suggest that incorporation of 2,4-D or its metabolites into humic components or microbial biomass was the dominant fate of this herbicide in crop residues. Metabolism of certain herbicides may be restricted or altered under certain high organic matter situations. Locke and Harper (29) noted reduced mineralization of metribuzin when soybean residues were added to a Dundee silt loam compared to nonamended soil. Their data, however, indicate that residue-amended soil exhibited similar dissipation of extractable metribuzin to non-amended soil. In another study, low mineralization (< 2 %) of chlorimuron-ethyl was observed in hairy vetch or rye residues, while greater than 15% was mineralized in soil during a 28-d incubation (30).

The microbial metabolism of 2,4-D proceeds via an initial cleavage of the ether-linked acetic acid side-chain which is readily metabolized to CO₂ prior to metabolism of the dichlorophenol ring (20, 25). Based upon

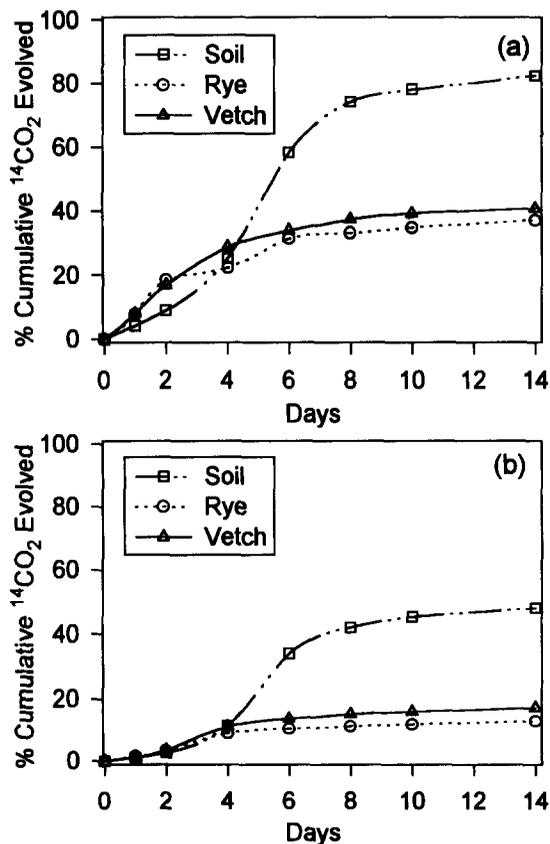


Fig 2. Mineralization of (a) ¹⁴C-carboxyl and (b) ring-labelled 2,4-D by soil, rye and hairy vetch residues, 2,4-D Degradation Study 2.

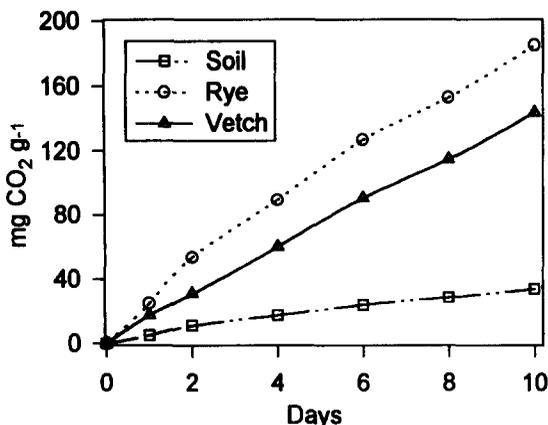


Fig 3. Cumulative respiration in soils and residues, 2,4-D Degradation Study 2.

patterns of $^{14}\text{CO}_2$ evolution, this is the case for both soil and cover crop residues. Initially, mineralization of the side-chain was greater for both cover crops than for soil (day 1 and 2). Following a 2- to 4-d lag period, the carboxyl group was rapidly mineralized to CO_2 in soil, while rates of carboxyl-labelled metabolism were progressively reduced after day 4 in the cover crop residues. Mineralization of the ring-labelled 2,4-D in soil exhibited a 4-d lag; thereafter following rapid mineralization similar to the carboxyl labelled 2,4-D. A lag followed by rapid mineralization of both carboxyl and ring-labelled 2,4-D in soil suggests adaptation of the

Table 3. Fate of ^{14}C -ring labelled 2,4-D, 14 days after application to soil or vetch and rye residues in two experiments.

| Source | ^{14}C recovered, (% of applied) [†] | | |
|---------------------|--|-------------|----------------|
| | CO_2 Mineralized | Extractable | Nonextractable |
| Experiment 1 | | | |
| Soil | 59.6 a | 7.9 b | 32.5 a |
| Hairy vetch | 5.3 b | 71.3 a | 23.4 a |
| Rye | 9.4 b | 63.6 a | 27.0 a |
| Experiment 2 | | | |
| Soil | 47.9 a | 6.2 b | 45.9 a |
| Hairy vetch | 17.2 b | 35.1 a | 47.4 a |
| Rye | 12.9 c | 38.2 a | 48.9 a |

[†]Mean of six replicates, means within a column for a particular study followed by the same letter do not differ at the 95 % probability level as determined by Fishers LSD.

microbial population to degrade 2,4-D. Microbial adaptation to 2,4-D has been reported for several soils (18, 19). Substantial population increases of 2,4-D degraders also occur during exposure to 2,4-D. Although higher microbial populations and activities (e.g., FDA hydrolysis and respiration) were observed in rye and vetch, higher mineralization of the carboxyl-labelled compared to ring-labelled 2,4-D in the residues suggests that degradation of 2,4-D in plant residues was less extensive than in soil. Typically, a greater proportion of carbon from the side-chain of 2,4-D can be incorporated into microbial biomass compared to that from the ring-labelled moiety of 2,4-D (20). The dichlorophenol ring can also be subjected to enzyme-mediated oxidative coupling reactions (26, 27), resulting in polymerization into humic compounds. Oxidoreductive enzymes such as tyrosinases, laccases and peroxidases are present in many fungi and certain bacteria associated with plant residues. Reducing the cover crop residue mass by 50% doubled the incorporation of ring-labelled 2,4-D into nonextractable components, indicating an oxygen-dependent reaction. Nonextractable radioactivity measured in our studies can be explained as amount of initial 2,4-D either incorporated into microbial biomass and/or incorporated into either humic or lignocellulose materials.

Fluometuron Degradation

Fluometuron degradation in ryegrass residues was significantly affected by moisture content (Fig. 4). Fluometuron was sequentially demethylated to DMF and TFMPU as described elsewhere (16, 20, 27, 28). Minimal fluometuron degradation was observed at the lowest moisture content, as only 11% was transformed to DMF, and no TFMPU was detected. At the highest moisture content, greater than 65% of the radioactivity was recovered as DMF and TFMPU. The greatest accumulation of TFMPU occurred at the highest moisture content and degradation was comparable to soil (Table 4). During this short-term assay, greater than 97% of the radioactivity was methanol-extractable in all treatments (thus nonextractable ^{14}C was not determined) and no formation of TFMA was observed. Pre-treatment of the residues with soil suspensions had no effect on fluometuron degradation at the intermediate moisture content, however inoculation with soil extract enhanced fluometuron degradation at the highest moisture content. This suggests that microflora associated with the ryegrass residues may not have been as effective in fluometuron degradation as soil microflora present in soil with a long-term history of fluometuron exposure. The bioavailability of substrates for microbial degradation in soil can also be limited by interactions between water potential and sorption as was demonstrated for the insecticide carbofuran (28). The high lignocellulose component of plant materials enables a greater water holding capacity compared to mineral soils. The adjusted moisture content of residues used in these studies was greater than that typically observed under field conditions (15 to 30 % moisture, unpublished field observations). This was evident in these studies where minimal fluometuron transformation occurred in ryegrass at 48% moisture, while degradation rates similar to soil (Table 4) were observed at 118% moisture. The degradation of fluometuron was more rapid in soil collected from no-till ryegrass plots than in soils from bare ground no-till plots (Table 4), confirming previous observations (16). Incorporating ryegrass into soil from bare ground no-till plots resulted in the most rapid fluometuron dissipation and accumulation of *N*-dealkylated metabolites (Table 4). Our previous

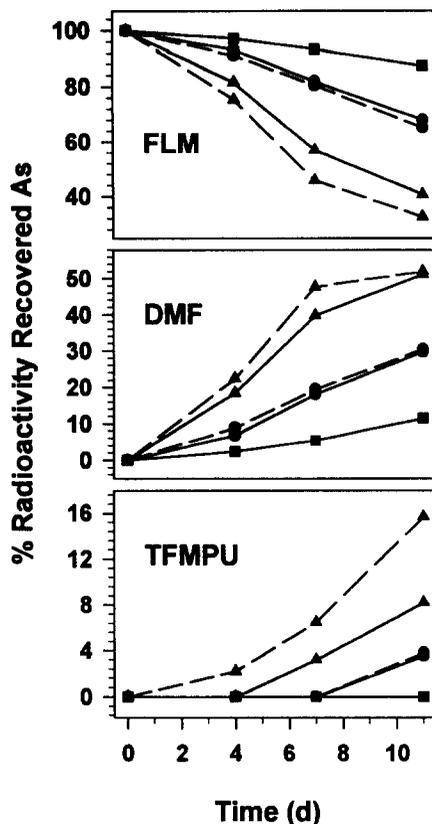


Fig 4. Effect of moisture content and inoculation with soil extract on fluometuron degradation in treated (dashed line) and nontreated (solid line) ryegrass residues; FLM = fluometuron, DMF = desmethyl fluometuron, and TFMPU = treated trifluoromethyl phenylurea. ■ = 48 % moisture, ● = 78 % moisture, ▲ = 118 % moisture.

studies also indicated that fluometuron degradation proceeded more rapidly in surface no-till soils where either the ryegrass residues remained on the soil surface or where the ryegrass was incorporated into the soil by tillage. Compared to ryegrass residues, a rapid incorporation of ^{14}C into methanol-nonextractable soil components was observed (15 to 25% after 11 d). The highest levels of TFMPU accumulation and nonextractable ^{14}C were observed in soil amended with ryegrass. Other studies (24) have shown that ryegrass is an effective biostimulating amendment to enhance the degradation of high concentrations of cyanazine and fluometuron in soils. Amending soil with ryegrass, or perhaps other crop residues, provides carbon substrate to enhance soil microbial activity, resulting in enhanced potential for herbicide degradation. Use of a fall-seeded cover crop such as ryegrass, under either a no-till or conventional tillage system, may decrease the persistence of fluometuron in soil applied the following spring. Plant residues such as herbicide-desiccated cover crops are predominantly

Table 4. Fluometuron degradation in no-till Dundee silt loam soil from winter fallow plots, annual ryegrass plots, and fallow plots amended with 2 % ryegrass residues

| Time (d), Treatment | % ¹⁴ C Initially Applied Recovered as [†] | | | |
|--------------------------------------|---|--------|-------|----------------|
| | Fluometuron | DMF | TFMPU | Nonextractable |
| 4, Fallow soil | 90.7 a | 3.7 b | nd | 3.8 c |
| 4, Ryegrass soil | 85.6 b | 12.8 a | nd | 5.8 b |
| 4, Ryegrass added to fallow soil | 72.9 c | 13.8 a | 2.7 a | 7.1 a |
| 7, Fallow soil | 67.3 a | 26.6 a | 0.6 c | 6.1 c |
| 7, Ryegrass soil | 57.1 b | 29.8 a | 2.9 b | 9.1 b |
| 7, Ryegrass added to fallow soil | 51.9 c | 30.8 a | 4.8 a | 11.0 a |
| 11, Fallow soil | 50.7 a | 32.5 a | 1.8 c | 14.9 c |
| 11, Ryegrass soil | 42.9 b | 30.2 a | 3.7 b | 20.5 b |
| 11, Ryegrass added to fallow soil | 35.1 c | 32.1 a | 3.7 b | 24.2 a |

[†]Values are mean of four replicates; means within a column for a given sample date followed by the same letter do not differ significantly at the 95% level. nd = not detected.

composed of lignin, cellulose and hemicellulose and differences in this composition can be attributed to species and duration of aging in the field (31). A 3-fold greater sorption of 2,4-D, alachlor and acifluorfen was observed in rye and hairy vetch residues compared to soil (32). Freundlich sorption parameters (Kf) for 2,4-D were 3.98, 4.34 and 1.21 for rye, vetch, and soil, respectively. In another study (15), chlorimuron-ethyl had greater potential for sorption to hairy vetch residues compared to rye residues, which were greater than soil. Fluometuron (16) had higher sorption potential to hairy vetch (Kf = 28.0) compared to rye (Kf = 21.8) and sorption by both residues was greater than soil (Kf = 2.6). The greater sorption of herbicides in hairy vetch compared to rye may be due to higher lignin content as postulated by Reddy et al. (15).

Although metribuzin is highly absorbed by wheat straw, there was minimal sorption of metribuzin to cellulose from wheat straw (33), implicating lignin as the component responsible for sorption of this herbicide. The greater potential for sorption in crop residues compared to soil could reduce the amount of 2,4-D or fluometuron in solution, thus restricting the bioavailability for microbial degradation. The role of sorption in limiting 2,4-D degradation in crop residues is supported by the observation that initially rapid rates of carboxyl mineralization were observed in the initial 2 to 4 d of the studies, followed by a rapid decline in mineralization rates. There may also be a difference in microbial populations capable of degrading 2,4-D in crop residues compared to soils, and this would be suitable topic for further study.

SUMMARY AND CONCLUSIONS

Our studies indicate that herbicide-desiccated cover crop residues are biologically more active than their underlying soils, however the degradation of 2,4-D is less extensive in crop residues than in soil. *N*-demethylation of fluometuron in cover crop residues can proceed as rapidly as soil, but only under high moisture conditions. These results suggest that physical-chemical factors such as sorption of the herbicides to lignocellulose components of the plant residues may reduce the effective solution concentration, thus impeding bioavailability and subsequent biodegradation. The potential for biodegradation of other herbicides by crop residues and interactions between sorption and bioavailability needs to be elucidated to understand the impacts of crop residue management systems on herbicide efficacy and environmental fate. Direct seeding into herbicide-desiccated cover crop residues may offer many environmentally desirable benefits such as moisture conservation, erosion and weed control. However, interception of herbicides by surface crop residues may prolong their persistence by rendering them unavailable for biodegradation, especially under low moisture conditions.

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