Fate of Rimsulfuron in the Environment

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The fate of ^{14}C-labeled rimsulfuron in aqueous and soil environments was examined. Hydrolysis was first-order, pH-dependent, and accelerated at higher temperatures. Rimsulfuron degraded rapidly in pH 5, 7, and 9 buffer solutions (25 °C) with half-lives of 4.7, 7.2, and 0.4 days, respectively, primarily through contraction of the sulfonylurea bridge. Soil metabolism studies also showed rapid decomposition by bridge contraction with half-lives of 24.5 (laboratory) and 5.7 (field) days. The degradation rate and metabolic pathway did not change when aqueous solutions (pH 7 or 9) or soil was kept in the dark or exposed to light. A faster degradation rate in light-exposed pH 5 aqueous solution was observed. Rimsulfuron was moderately adsorbed on soils with high levels of clay or organic matter. Although soil TLC suggested rimsulfuron could be mobile, minimal mobility was observed under field conditions. Rimsulfuron residues (>0.01 ppm) were not observed in rotational crops grown in rimsulfuron-treated soil.

INTRODUCTION

Rimsulfuron [*N*-((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide], the active ingredient in Titus herbicide, is a new highly active sulfonylurea herbicide for over-the-top postemergent use on corn and potatoes to control a wide variety of perennial and annual grasses and some broadleaf weeds at rates of 8–35 g of ai/ha ($^1/_8$–$^1/_2$ oz/acre). The mode of action of sulfonylurea herbicides is inhibition of acetolactate synthase (ALS), a key enzyme in the biosynthetic pathway of branched-chain amino acids (isoleucine, valine) in the plant (Ray, 1984; Chaleff and Mauvais, 1984). Sulfonylureas, in general, have little or no toxicological effects on mammals with oral LD_{50}s usually >5000 mg/kg in rats (Beyer et al., 1988). The environmental fate of several sulfonylureas has been reported (Anderson et al., 1985; Beyer et al., 1988; Blair et al., 1988; Harvey et al., 1985).

This paper provides the first detailed report on the environmental fate of rimsulfuron, including its hydrolytic, photolytic, soil mobility, and soil degradation properties, and the accumulation potential in rotational crops.

EXPERIMENTAL PROCEDURES

Materials. The radiolabeled test substances, [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron, were synthesized at DuPont New England Nuclear Products (Boston, MA). [*pyridine*-2-^{14}C]Rimsulfuron had a radiochemical purity of 99% and a specific activity of 45.1 μCi/mg. [*pyrimidine*-2-^{14}C]Rimsulfuron had a radiochemical purity of 98% and a specific activity of 51.7 μCi/mg. Nonradiolabeled authentic standards of rimsulfuron and potential metabolites (names and structures are listed in Figure 1) were synthesized at DuPont Agricultural Products (Wilmington, DE). All solvents used were of HPLC grade.

The water solubility of rimsulfuron at 25 °C is 135 ppm at pH 5, 7300 ppm at pH 7, and 5560 ppm at pH 9. Its vapor pressure is 1.1×10^{-8} Torr (25 °C).

Test Soils. Cecil sandy loam, Fargo clay loam, Sassafras sandy loam, and Flanagan silt loam soils were obtained from Raleigh, NC, Horace, ND, Penns Grove, NJ, and Rochelle, IL, respectively, and stored moist at 4 °C (for no longer than 1 year) to maintain viability until use. The test soils were collected from a 0–15-cm depth. Each test soil was air-dried at room temperature for at least 24 h and screened to remove any particles larger than 2 mm prior to being analyzed for soil characteristics (Table I).

Radioassay. Total radioactivity of solutions was quantitated in 10–15 mL of scintillation cocktail (i.e., Atomlight, DuPont NEN Products) with a Tracor Analytical Mark III liquid scintillation system (TM Analytic, Inc., Elk Grove, IL). Radioactivity in plant tissue or soil was quantitated by combustion in a Packard Model 306 sample oxidizer (Packard Instrument Co., Downers Grove, IL) or a Model OX300 Oximat sample oxidizer (R. J. Harvey Instrument Co., Hillsdale, NJ), respectively, followed by liquid scintillation counting (LSC) of the trapped $^{14}CO_2$ in either Carbo-Sorb E or Permafluor E (Packard) or carbon-14 cocktail (Harvey).

HPLC and TLC Analysis. Extracts and aqueous samples were routinely analyzed by both high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC). All HPLC analyses were performed on Zorbax ODS or C-8 columns (Mac-MOD Analytical, Inc., Chadds Ford, PA); all TLC analyses were performed on silica gel thin-layer plates (Si 250F, 0.25 mm, J. T. Baker Chemical Co., or Kieselgel 60F254, E. M. Scientific). Table II lists typical HPLC retention times using a DuPont or HP 1090 HPLC system and TLC R_f values for rimsulfuron and potential metabolites in the various HPLC (methods 1 and 2) and TLC systems used for sample analysis.

For HPLC samples containing low levels of radioactivity (<5000 dpm) a fraction collector was used to collect column effluent (1-min fractions) for 50 min followed by analysis by LSC. For samples containing higher levels of radioactivity a Ramona radioactive detector containing a calcium fluoride solid cell (250–500 μL, Raytest USA, Pittsburgh, PA) was used. Identification of radiolabeled species was by means of cochromatography with authentic standards. Radiolabeled species on TLC plates were located by autoradiography with X-ray films. Identification was through cochromatography with authentic standards that were detected under ultraviolet (UV) light.

Soil Extraction Method. Fifty milliliters of acetonitrile/water (2:1 v/v) was added to the soil (50 g) in a 250-mL plastic bottle and shaken with a wrist-action shaker for 20 min. The mixture was centrifuged at approximately 2500 rpm for 5–10 min and the supernatant decanted. The soil was re-extracted two additional times as described above. All extracts were combined and measured, and triplicate aliquots (0.1–1 mL) were analyzed by LSC to determine the total extractable radioactivity. If 85% of the applied radioactivity was not extracted by the above procedure, an additional extraction with 50 mL of water was included and combined with the other extracts. Acetonitrile in the combined extracts was removed using a rotary evaporator (40 °C), and water was removed by freeze-drying. The ^{14}C residue was redissolved in 2 mL of water/acetonitrile (80:20 v/v), filtered through a 0.2-μm filter to remove any soil particles, and analyzed for rimsulfuron and its metabolites by HPLC. Triplicate aliquots

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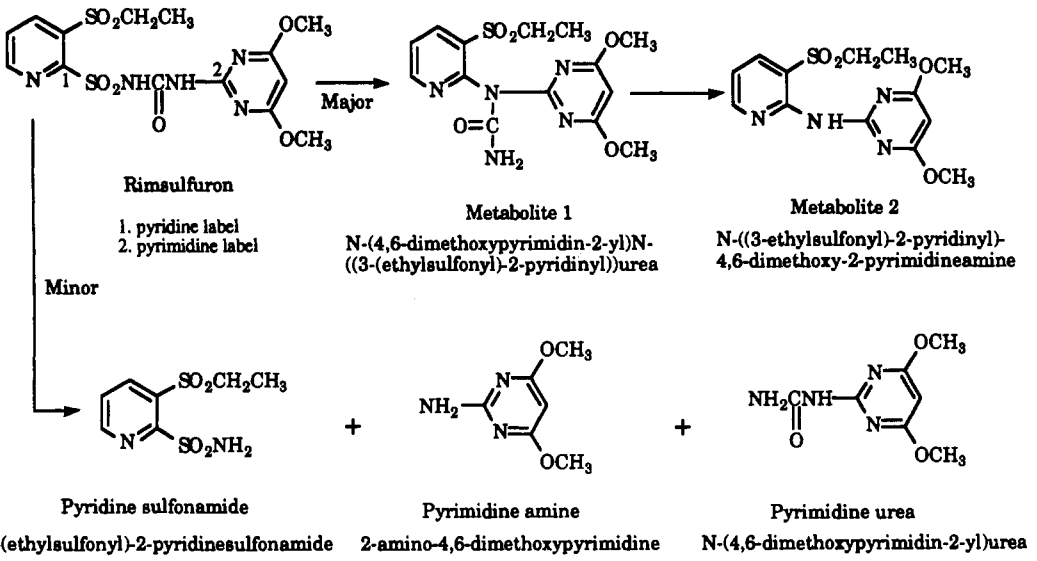


Figure 1. Degradation pathway(s) of rimsulfuron in soil and hydrolytic solutions.

Table I. Soil Characterization[a]

	Cecil sandy loam	Fargo clay loam	Sassafras sandy loam	Flanagan silt loam	Fullsington[b] silt loam
origin	Raleigh, NC	Horace, ND	Penns Grove, NJ	Rochelle, IL	Newark, DE
% sand (0.05–2.0 mm)	61	22	74	2	13
% silt (0.002–0.05 mm)	21	44	16	81	65
% clay (<0.002 mm)	18	34	9	17	22
% organic matter	2.1	4.3	1.0	4.3	1.4
pH	6.5	7.7	6.3	5.4	6.0
CEC (mequiv/100 g)	6.6	29.7	3.5	21.2	4.9

[a] Soil analyses were performed at the Soil Testing Laboratory, College of Agricultural Sciences, University of Delaware, Newark, DE, or at A&L Eastern Agricultural Laboratories, Inc., Richmond, VA. [b] Field dissipation study.

Table II. Typical HPLC Retention Times and TLC Values of Rimsulfuron and Metabolite Reference Standards

	HPLC retention times R_t (min)		TLC R_f values[c]
	method 1[a]	method 2[b]	
rimsulfuron	30.6	14.4	0.24
pyridine sulfonamide	5.7	4.0	0.21
pyrimidine amine	6.8		0.46
pyrimidine urea	13.4		0.25
metabolite 1	19.8	6.7	0.29
metabolite 2	28.8	17.7	0.59

[a] Method 1: DuPont HPLC System with 8800 gradient controller and 850 UV detector: 25 cm × 4.6 mm Zorbax ODS (C-18) column. Mobile phase linear gradient: t = 0 min 20% A, 80% B; t = 10 min 20% A, 80% B; t = 45 min, 75% A, 25% B; t = 50 min 20% A, 80% B; A = CH_3CN, B = H_2O, both containing 0.1% formic acid and 0.1% triethylamine, flow rate 1 mL/min. Column temperature 35 °C. UV detector 254 nm. [b] Method 2: Hewlett-Packard 1090 HPLC: 25 cm × 4.6 mm Zorbax C-8 column. Mobile phase: 35% CH_3CN/65% pH 2.5 H_2O (phosphoric acid), flow rate 1 mL/min. Column temperature 45 °C. UV detector 250 nm. [c] Chloroform/methanol/acetic acid (190:10:2 v/v/v).

(200 mg) of the unextractable ^{14}C soil residues were quantitated by combustion and LSC. Unextractable ^{14}C residues were further fractionated using a method described by Stevenson (1965) into humic acid, fulvic acid, and humic fractions. This extraction method gave greater than 90% extraction efficiency for rimsulfuron in unaged soils.

Hydrolysis Rate Determination. The hydrolysis rate was determined by monitoring the rate of disappearance of [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron in 0.01 M aqueous buffer solutions (pH 5 acetate buffer, pH 7 phosphate buffer, and pH 9 borate buffer). To ensure that the observed hydrolytic degradation was not affected by microorganisms, buffer solutions and all glass apparatus were heat-sterilized by autoclaving (Venitron Verna-clave) for 60 min at 121 °C and 15 psi before use. Aseptic techniques were used throughout the study to maintain sterility.

Two stock solutions containing 25 ppm of either [*pyridine*-2-^{14}C]rimsulfuron or [*pyrimidine*-2-^{14}C]rimsulfuron in acetonitrile were prepared. A 750-μL aliquot was added aseptically to 75 mL of each heat-sterilized buffer solution. Duplicate solutions (one for each label) were prepared at each pH. The treated buffer solutions were maintained in darkness at approximately 25 °C. Five-milliliter aliquots were removed from each flask using sterilized pipets 0, 0.5, 1, 1.5, 2, 3, 8, 14, 21, and 30 days after the pH 5 test solution was prepared; 0, 1, 2, 3, 7, 14, 21, and 30 days after the pH 7 test solution was prepared; and 0, 1, 2, 3, 5, 7, and 23 h after the pH 9 test solution was prepared. Each test solution was analyzed directly by LSC (3 × 100 μL), TLC (10 μL), and HPLC (20 μL, method 1) to determine the total amount and distribution of [^{14}C]rimsulfuron and its hydrolysis products. Structures were confirmed by LC/MS analysis using the method recently reported by Shalaby et al. (1992).

Hydrolysis Rate Dependent on Temperature. The effect of temperature and pH on the rate of hydrolysis of [*pyridine*-2-^{14}C]rimsulfuron was determined in sterile 0.01 M aqueous buffer solutions (pH 4–9) at 10, 20, and 30 °C. The buffers used were acetate (pH 4, 5), 2-(*N*-morpholino)ethanesulfonic acid (pH 6), 2-(*N*-morpholino)propanesulfonic acid (pH 7), and borate (pH 8, 9). A total of 12 solutions were used as follows: pH 4 at 20 °C, pH 5 at 10, 20, and 30 °C, pH 6 at 20 °C, pH 7 at 10, 20, and 30 °C, pH 8 at 10, 20, and 30 °C, and pH 9 at 20 °C. Six hundred microliters of acetonitrile containing 1.5 mg of [*pyridine*-2-^{14}C]-rimsulfuron was added aseptically to 75 mL of each heat-sterilized buffer solution. The final concentration of rimsulfuron in each solution was 20–25 ppm as determined by LSC analysis of two 10-μL aliquots. One milliliter aliquots were removed from each solution at time 0 and at appropriate sampling intervals up to 49 days, dependent on the rate of hydrolysis. A minimum of 12 samples were taken at each temperature and pH to determine the hydrolysis rate of the herbicide. An example of sample times for pH 5 at 20 °C is as follows: 0, 4, 7, 10, 12, 23, 29, 48, 72, 96, 120, and 144 h. Each sample was analyzed by HPLC (10-μL injection, method 2). The pH of each sample was also measured and did not vary by more than 0.1 pH unit for all buffer solutions.

Aqueous Photolysis Rate Determination. The rate of photolysis, determined by monitoring the disappearance of [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron in 0.01 M aqueous buffer solutions (pH 5 acetate buffer, pH 7

phosphate buffer, and pH 9 borate buffer), was examined for approximately 30 days (August–September 1988) under natural sunlight. All experiments were conducted under sterile conditions. The hydrolysis study served as the dark controls.

The photolysis vessels consisted of 250-mL water-jacketed beakers covered with quartz lids to prevent evaporation and permit ultraviolet light transmission. Samples of the buffer solutions were withdrawn via a Teflon stopcock fitted to the side of each vessel. Two stock solutions containing 25 ppm of either [*pyridine*-2-^{14}C]rimsulfuron or [*pyrimidine*-2-^{14}C]rimsulfuron in acetonitrile were prepared, and a 1.5-mL aliquot was added aseptically to 150 mL of heat-sterilized buffer solution in each photolysis vessel. Duplicate vessels (one for each label) were prepared for each pH buffer solution. The photolysis vessels were maintained at approximately 25 °C by circulating water from a thermostatically controlled water bath. Five-milliliter aliquots of each pH 5 and 7 irradiated solution were removed for analysis on days 0, 0.5, 1, 1.5, 2, 3, 8, 14, and 21. pH 5 also had a day 30 sampling. Five-milliliter aliquots of the pH 9 solutions were removed for analysis at 0, 1, 2, 3, 4, 5, 7, and 23 h and at 1, 2, 3, 7, 14, 21, and 30 days. The total amount of radioactivity in each test solution was quantitated directly by LSC (3 × 100 μL) and analyzed immediately by one-dimensional TLC (10 μL) and HPLC (20 μL, method 1) to determine the distribution of [^{14}C]rimsulfuron and its photolysis products.

Soil Surface Photolysis. The photolytic degradation of [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron on Sassafras sandy loam soil was examined for approximately 30 days (June–July 1988) under natural sunlight. A thin layer (approximately 1 mm thick) of a Sassafras sandy loam slurry (2 g of soil/1 mL of water) was spread on microscope slides (1 × 3 in.) using a TLC spreader. One hundred microliters of acetonitrile containing 10 μg (~0.5 μCi) of [^{14}C]rimsulfuron was applied to each soil plate. Thirteen soil plates (seven dark control and six irradiated) were prepared for each radiolabel. Soil plates were placed on stainless steel heat exchangers contained within custom-made, watertight Lucite chambers fitted with quartz windows. The nonirradiated samples were shielded from light by covering with aluminum foil. The heat exchangers were connected to a circulating water bath that maintained the soil plates at approximately 25 °C. The soil photolysis chambers were equipped with vents that allowed a slow stream of air to be drawn through each chamber and into a gas washing bottle containing 1 N sodium hydroxide to collect any evolved $^{14}CO_2$ and volatile degradates.

Soil samples were taken at 1, 2, 3, 6, 9, and 27 days after treatment for the irradiated soils and at 0, 1, 2, 3, 6, 9, and 34 days for the nonirradiated soils. At each sampling point, two soil-coated slides were removed and the soil was scraped into centrifuge tubes (50 mL). The soil was extracted two or three times with 30 mL of acetonitrile/water (2/1 v/v) by first agitating in an ultrasonic bath for 5 min and then shaking on a wrist-action shaker for 30 min followed by centrifuging at 2500 rpm. Supernatants were decanted and triplicate aliquots of the pooled extracts analyzed quantitatively by LSC (100 μL) and qualitatively by HPLC (method 1, 100 μL) and TLC (100 μL). Triplicate aliquots (200 mg) of the unextractable ^{14}C soil residues were quantitated by combustion and LSC as previously described. Triplicate 2-mL aliquots of the sodium hydroxide solution from the volatile traps were analyzed for total radioactivity by LSC. Greater than 90% of the radioactivity could be extracted by this method.

Aerobic and Anaerobic Soil Metabolism. The degradation/metabolism of rimsulfuron in sandy loam soil under laboratory aerobic and anaerobic conditions was investigated in the dark at approximately 25 °C. Twenty-six flasks (for aerobic conditions) and 10 flasks (for anaerobic conditions), each containing Sassafras sandy loam soil (equivalent to 50 g of oven-dried soil) were treated with either 4.97 μg of [*pyridine*-2-^{14}C]rimsulfuron in 1 mL of acetonitrile or 4.82 μg of [*pyrimidine*-2-^{14}C]rimsulfuron in 1 mL of acetonitrile. This application rate is equivalent to a field application rate of 110 g of ai/ha (3.2× maximum use rate). The soil moisture was adjusted to approximately 75% of the field moisture holding capacity. The flasks were fitted with air inlets and outlets and connected to a vacuum manifold system. The outlet of each flask was connected to traps containing 1 N sodium hydroxide solution to collect $^{14}CO_2$ and volatile degradates. Soils held under aerobic conditions were purged continuously with a slow stream of humidified air. Soils held under anaerobic conditions were initially incubated aerobically for 10 days (observed aerobic soil half-life) and then converted to anaerobic conditions by addition of 100 mL of water to saturate the soil and by purging N_2 through these flasks. The soil was incubated under anaerobic conditions for an additional 60 days.

Soil samples were taken in duplicate (one for each label) at 0, 1, 3, 7, 10, 15 days; at 1, 2, 3, 6, 9, and 12 months after treatment (aerobic conditions); and at 5, 10, 15, 28, and 60 days after establishment of anaerobic conditions. All soil samples were extracted as previously described under Soil Extraction Method and the extracts analyzed quantitatively by LSC (3 × 250 μL) and qualitatively by HPLC (method 1, 250 μL) and TLC (100 μL). Water covering the anaerobic soil was decanted from the soil before extraction, concentrated, and analyzed separately by HPLC (method 1) and LSC. Triplicate 2-mL aliquots of the sodium hydroxide solution from the volatile traps were analyzed for total radioactivity by LSC.

Soil Mobility Potential. The soil mobility of [*pyrimidine*-2-^{14}C]rimsulfuron was evaluated by adsorption/desorption and by soil TLC in Cecil sandy loam, Fargo clay loam, Sassafras sandy loam, and Flanagan silt loam soils. Adsorption/desorption of rimsulfuron on these four soils was assessed using the method described by the Environmental Protection Agency (Hitch, 1982). Adsorption of rimsulfuron on soil was determined by mixing 10 g of each soil type with 40 mL of 0.01 N calcium sulfate containing either 0.1, 0.5, 1.0, or 5.0 ppm of [*pyrimidine*-2-^{14}C]rimsulfuron in 125-mL plastic bottles. Duplicate samples were run for each concentration. The soil slurry was shaken for 4 h in a water bath (25 °C) to equilibrate the soil adsorption of rimsulfuron (previous experiments showed rimsulfuron reached equilibrium between soil and water in 4 h). After equilibration of rimsulfuron soil adsorption, each soil slurry was centrifuged (~2000 rpm) for 10 min and aliquots of the supernatant (2 × 200 μL) were analyzed by LSC.

Desorption of rimsulfuron from each soil type was determined by first removing 20 mL of the supernatant from each adsorption experiment. Twenty milliliters of fresh 0.01 N calcium sulfate solution (untreated) was added to each soil type, equilibrated for 4 h, and centrifuged, and the supernate was analyzed by LSC as described for adsorption. The desorption equilibrium was repeated once more, using fresh 0.01 N calcium sulfate solution.

Freundlich isotherm constants (K) for rimsulfuron were calculated using

$$\log C_s = {}^1/_n \log C_2 + \log K \quad (1)$$

This relationship was obtained after rearrangement of the Freundlich equation (Bailey and White, 1970). The concentration of rimsulfuron in the soil (C_s) was established by determining the difference between the quantity of [^{14}C]rimsulfuron in the starting solution (C_1) and that in the solution after equilibration of rimsulfuron with the soil (C_2).

The soil mobility potentials of [^{14}C]rimsulfuron and its major radiolabeled soil degradates (metabolites 1 and 2, Figure 1) were determined by soil TLC using the four soil types. ^{14}C-Labeled diuron and bromacil were used as reference standards. A slurry of each soil type (sieved to remove particles greater than 250 μm) was applied to two clean 20 × 20 cm glass plates to a soil thickness of 500–750 μm for fine-textured soils and 750–1000 μm for soils containing a high proportion of sand (greater than or equal to 50%) and allowed to air-dry. Each plate was spotted 2 cm above the base with approximately 0.01 μCi (0.2–2.6 μg) of each radiolabeled compound. Each soil plate was placed at an angle in a developing chamber containing distilled deionized water (0.5 cm deep) and allowed to develop at room temperature. Plates were removed when the solvent front had migrated 12 cm up the plate. Soil TLC plates were air-dried for 24 h, the movement of the radiolabeled compounds was determined by autoradiography, and frontal R_f values were calculated.

Field Soil Dissipation. A field soil dissipation study was conducted in stainless steel cylinders at one field location with a procedure developed at DuPont Agricultural Products (Harvey, 1982). Twenty-two stainless steel cylinders (10 cm i.d. × 38 cm) were driven into the ground at Newark, DE (Fullsington silt loam; Table I). Approximately 2.5 cm of the rim of each cylinder was allowed to protrude above ground level to contain rain water

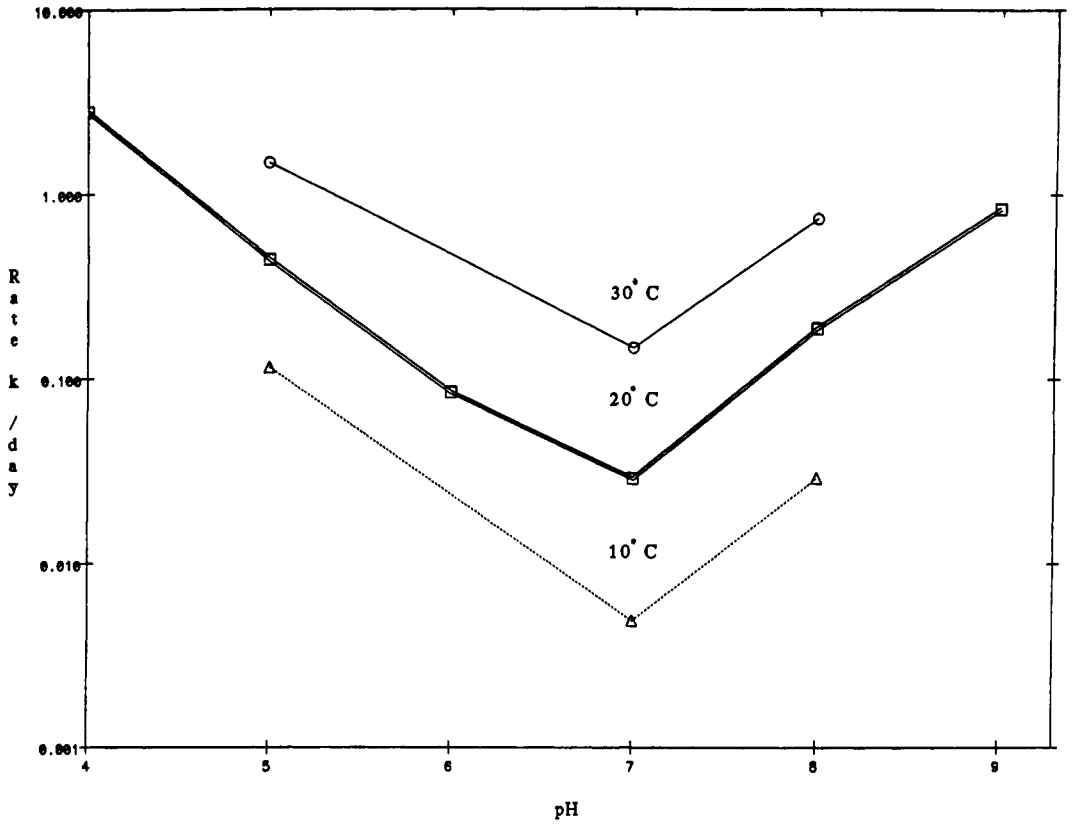


Figure 2. Rate constant (k/day) for hydrolysis of rimsulfuron as affected by temperature and pH.

and minimize the loss of applied radioactivity through runoff and splashing. [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron treatment solutions were prepared by dissolving 0.8 mg of [^{14}C]rimsulfuron in 3 mL of acetonitrile, followed by 0.8 mg of the inert 50 DF (50% dry flowable) formulation ingredients used in Titus herbicide, and 25 mL of distilled water. Two milliliters of each [^{14}C]rimsulfuron treatment solution was applied uniformly by volumetric pipet to the bare soil surface within each stainless steel cylinder (11 cylinders per label), which is equivalent to an application rate of 70 g of ai/ha (2× maximum use rate). The soil cylinders were held under natural environmental conditions, and two cylinders, one from each label, were removed after 0, 1, 3, 7, 14, 30, 60, 120, 240, and 365 days, frozen in dry ice, and transferred to the laboratory for analysis. Each soil sample was thawed, extruded from the cylinder, and divided into four approximately 8-cm segments. Each segment was homogenized in a grinding mill and a portion of each air-dried and analyzed for total ^{14}C residues by combustion (5 × 0.1 g) and LSC as described previously. Soil segments that contained significant ^{14}C residues (>0.01 ppm) were extracted as described under Soil Extraction Method and qualitatively analyzed by HPLC (method 1, 250 μL).

Rotational Crop Residue Study. A rotational crop study was conducted by treating soils with [*pyridine*-2-^{14}C]rimsulfuron and [*pyrimidine*-2-^{14}C]rimsulfuron, aging the soil, and planting rotational crops to monitor plant uptake of aged ^{14}C residues. Sixty plastic pots (38 cm in diameter) were filled to a depth of 30 cm with Sassafras sandy loam soil, watered, and allowed to settle for several weeks. A solution of 0.61 mg of [^{14}C]rimsulfuron (4.5 μCi/mg) in 500 mL of water was evenly poured over the soil surface of each of 48 pots, 24 pots for each radiolabel. This is equivalent to an application rate of 52 g of ai/ha (1.5× maximum use rate). The remaining 12 pots were treated with 500 mL of water per pot and were used as controls. These soils were aged under greenhouse conditions for 1, 4, and 10 months before crops were planted.

Wheat (Anza), soybean (McCall), lettuce (Prizehead), and sugar beet (USH-11) seeds were planted in the 1- and 4-month-aged soils. Wheat and soybean seeds were planted in the 10-month-aged soil. Five pots (two treated pots for each radiolabel and one control) were used for each crop and each aging period. The crops were grown under greenhouse conditions following accepted agricultural practice. Harvesting procedures for each mature crop are described below. (The differences in time to maturity from the different aging periods are due to variations in day length and greenhouse temperatures during the study.)

Soybeans. Mature soybean plants were harvested 91, 106, and 88 days after planting in the 1-, 4-, and 10-month-aged soils, respectively. Whole plants were cut near the soil surface. The beans, pods, and straw were separated prior to analysis.

Lettuce. Mature lettuce leaves were harvested 76 and 64 days after planting for the 1- and 4-month-aged soils, respectively, by cutting the leaves near the soil surface.

Wheat. Mature wheat plants were harvested 91, 106, and 88 days after planting in the 1-, 4-, and 10-month-aged soils, respectively. The straw, grain, and chaff were separated prior to analysis.

Sugar Beets. Mature sugar beets were harvested 196 and 147 days after planting in the 1- and 4-month-aged soils, respectively. The foliage was separated from the roots, and soil adhering to the roots was removed by washing with water prior to analysis.

Fresh crop samples were homogenized (Waring blender) and radioassayed for total ^{14}C residues by combustion (5 × 0.1 g) and LSC, as previously described, immediately after harvest. Crop fractions containing greater than 0.05 ppm of total ^{14}C residues were extracted and analyzed for [^{14}C]rimsulfuron and metabolites. Ten-gram tissue samples (fresh weight) were extracted three times with 100-mL portions of acetonitrile/water (2:1 v/v) using a Tissumizer (Tekmar Co., Cincinnati, OH) for 5 min followed by centrifugation (2500 rpm). Supernatants were decanted, combined, and filtered through Whatman No. 4 filter paper. The combined extracts were concentrated *in vacuo* by rotary evaporation (40 °C) to remove the acetonitrile, and the total extracted radioactivity was determined by LSC (3 × 0.5 mL). The extracts were freeze-dried and redissolved in 2.0 mL of water/acetonitrile (80:20 v/v) for analysis by HPLC (method 1, 250 μL) and TLC (100 μL). Seventy-five to 100% of the total radioactivity could be extracted from the plant matrix using this method.

Soil cores (2 cm i.d. × 30 cm) were taken at treatment (five pots/label) and at each planting interval (one core/pot) and divided into three segments, and like segments were pooled, homogenized in a roller mill, and analyzed for total ^{14}C residues (5 × 0.5 g) by combustion. Soil segments containing ^{14}C residues

Table III. Rate of Aqueous Hydrolysis and Photolysis

	photolysis (light) av[a] $T_{1/2}$[b] (days)	hydrolysis (dark) av[a] $T_{1/2}$[b] (days)
pH 5	0.9	4.7
pH 7	11.6	7.2
pH 9	0.5	0.4

[a] All time points were used to calculate the half-life. The amount of rimsulfuron remaining at each time point was the average of the amount of [*pyridine*-2-^{14}C]- and [*pyrimidine*-2-^{14}C]rimsulfuron found. The variability of duplicate samples was no more than 5% except at pH 9, where rapid degradation resulted in larger variability. [b] $T_{1/2} = 0.693/K$, where K is the first-order rate constant (slope) determined from linear least-squares best fitting line to first-order rate equation ln[rimsulfuron] = slope(time) + b.

>0.01 ppm were extracted as described under Soil Extraction Method and qualitatively analyzed by HPLC (method 1, 250 μL).

RESULTS AND DISCUSSION

Hydrolytic and Aqueous Photolytic Degradation. The hydrolysis rate of rimsulfuron was pH-dependent, followed first-order kinetics, and was accelerated by both acidic and alkaline conditions. Rimsulfuron degraded rapidly in pH 5, 7, and 9 buffer solutions at 25 °C with average (from both radiolabels) half-lives of 4.7, 7.2, and 0.4 days, respectively (Table III). The hydrolysis rate of rimsulfuron was affected by temperature (Figure 2). The rate of hydrolysis increased 3–6-fold with each 10 °C increase in temperature.

The primary hydrolysis product at pH 5 was metabolite 1, resulting from contraction of the sulfonylurea bridge (Figure 3; see Figure 1 for structure). Minor hydrolysis products, resulting from cleavage of the sulfonylurea bridge, included pyridine sulfonamide, pyrimidine amine, and pyrimidine urea. Metabolite 2 was the major hydrolysis product at pH 7 and 9 (Figure 3). These hydrolysis products were identified on the basis of their HPLC retention times compared to authentic standards, TLC cochromatography with authentic standards, and LC/MS analysis.

Under neutral to alkaline aqueous conditions rimsulfuron did not photolyze since exposure to light did not affect the rate of degradation (Table III) or the nature of the degradation products (data not shown). However, an acceleration in degradation rate was seen in pH 5 aqueous solution (Figure 4), and the degradates degraded further to give minor amounts of polar products.

The sensitivity of the degradation rate of rimsulfuron to small shifts in pH was observed in the pH 7 photolysis and hydrolysis experiment (11.6 vs 7.2 days, respectively). The pH under photolysis stayed close to pH 7 during the experiment, while the pH under dark conditions increased to 7.6 pH units. Rimsulfuron degraded very rapidly under basic conditions ($T_{1/2}$ = 0.4 h, pH 9); therefore, a small shift toward basic pH was enough to increase the rate of degradation of rimsulfuron in the dark vs the light.

Soil Surface Photolysis. Rimsulfuron does not undergo soil photolysis as evidenced by similar half-lives of approximately 11 days under both irradiated and nonirradiated conditions (data not shown). Major degradates under both conditions were metabolites 1 and 2. Further degradation of the primary degradates to several minor polar compounds occurred under irradiated conditions. Generation of $^{14}CO_2$ or volatile components was not observed.

Aerobic and Anaerobic Soil Metabolism. Rimsulfuron degraded rapidly in sandy loam soil under laboratory aerobic and anaerobic condition. The calculated soil half-lives (average of both radiolabels) of rimsulfuron (based on 60 days of data) were 24.5 and 22.2 days (Figure 5) under aerobic and anaerobic conditions, respectively. The variability of duplicate samples was less than 10%.

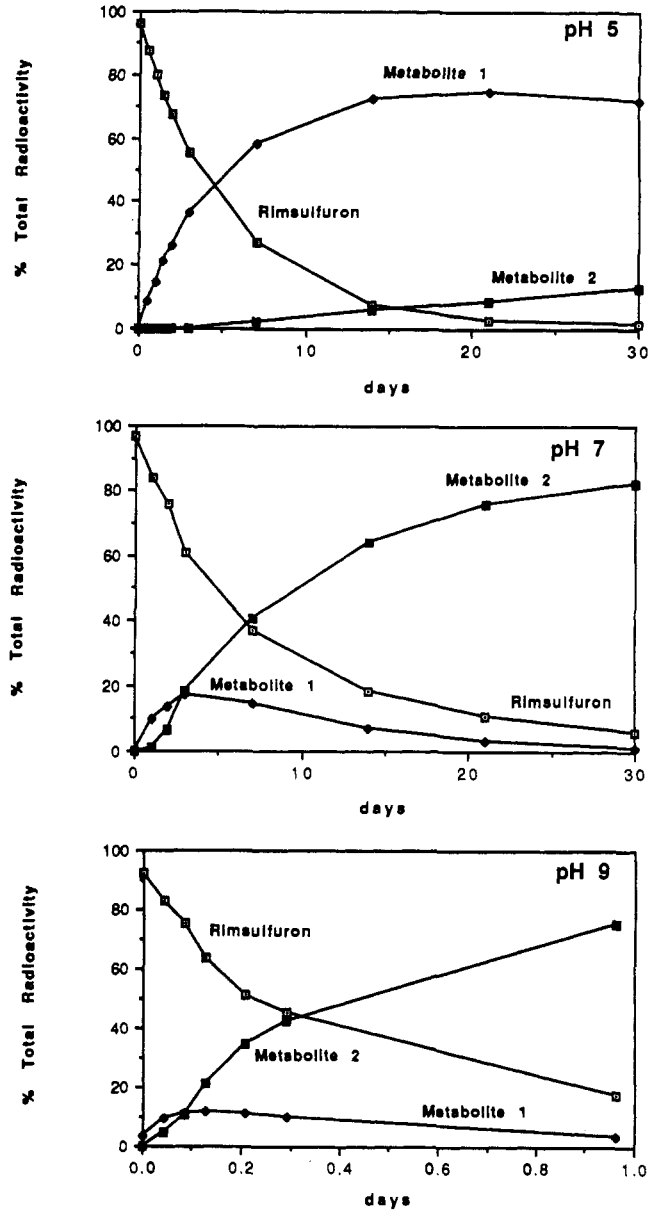


Figure 3. Hydrolysis of [^{14}C]rimsulfuron at pH 5, 7, and 9.

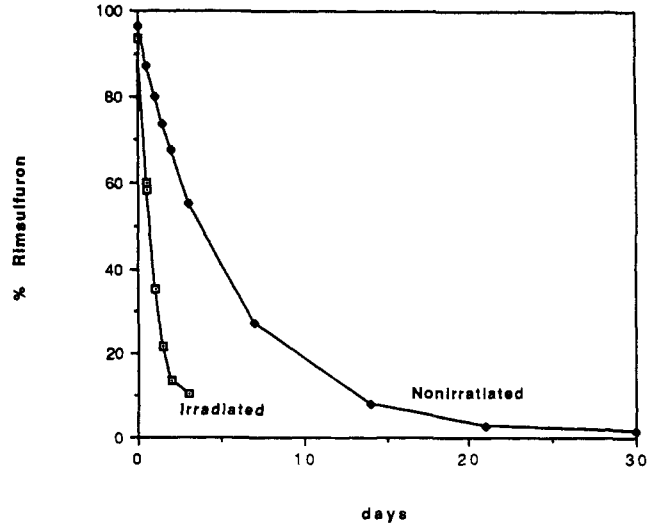


Figure 4. Percent rimsulfuron remaining under irradiated and nonirradiated conditions in pH 5 aqueous solutions.

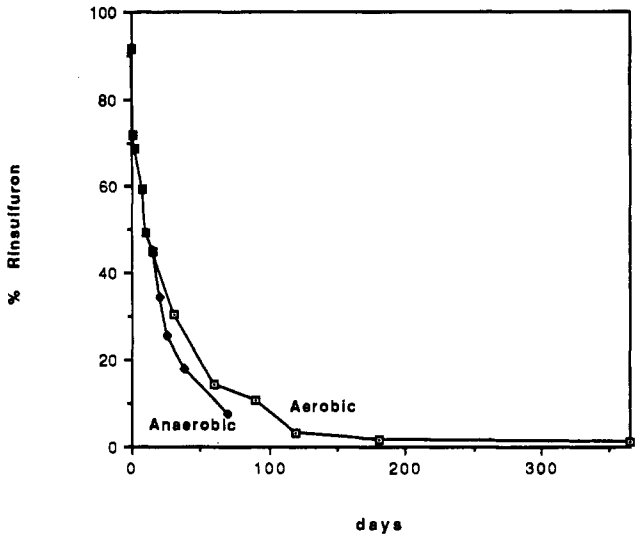


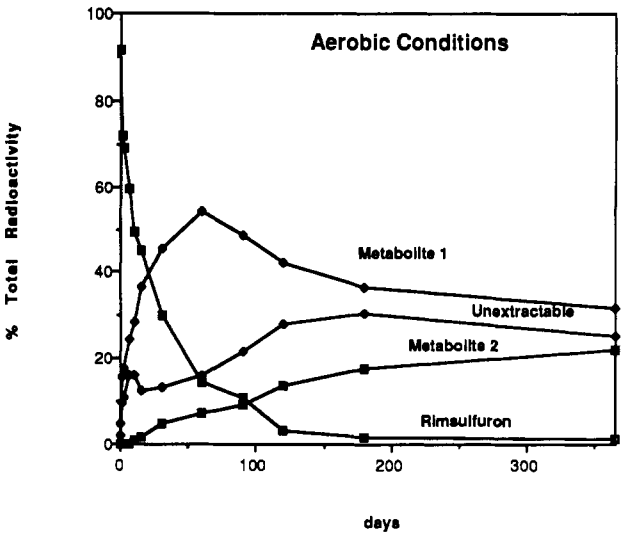
Figure 5. Percent rimsulfuron remaining in aerobic and anaerobic soils over time.

Metabolites 1 and 2 and pyridine sulfonamide were the major degradation products under aerobic conditions. The formation of metabolite 2 from metabolite 1 increased under anaerobic conditions (Figure 6). No significant volatile metabolites were detected under either aerobic or anaerobic conditions. The sum of extracted and unextracted radioactive recoveries ranged from 95 to 100% of the applied radioactivity throughout the study. Under aerobic conditions unextractable ^{14}C residues accounted for up to 25% of the applied radioactivity after 12 months of incubation. Further fractionation of these unextractable ^{14}C residues found approximately 19% of the applied radioactivity was associated with the fulvic acid fraction of soil.

Soil Mobility Potential. The adsorption of rimsulfuron differed among the various soil types. Adsorption of rimsulfuron appeared to increase with increasing amounts of organic matter or clay content. Rimsulfuron was weakly adsorbed (K_a = 0.23 and 0.32) on the two sandy loam soils and moderately adsorbed on the clay loam (K_a = 1.36) and silt loam soils (K_a = 1.57). Adsorbed radioactivity was moderately desorbed from all soil types (Table IV).

On the basis of the soil mobility classifications published by Helling (1971) and the R_f values of rimsulfuron on soil TLC plates relative to those of the bromacil and diuron standards, rimsulfuron is intermediately mobile to very mobile (Helling's R_f classification: intermediate 0.35–0.64, mobile 0.65–0.89, and very mobile 0.90–1.0). It is mobile on Cecil sandy loam soil, intermediate mobile on Fargo clay loam and Flanagan silt loam soils, and very mobile on Sassafras sandy loam soil. Metabolites 1 and 2 are less mobile than rimsulfuron (Table V).

Field Soil Dissipation. The dissipation of rimsulfuron and the formation and decline of major degradation products under field conditions were consistent with data generated under laboratory conditions. Rimsulfuron degrades rapidly with a half-life of 5.6 days (average of both radiolabels) under field conditions (based on first 14 days of data). The major metabolite is metabolite 1; its concentration increased to a maximum of 0.03 ppm at 7 days and then decreased to ≤0.01 ppm at 365 days (Table VI). All other ^{14}C residues were below the detection limit (<0.01 ppm). When formulated rimsulfuron was applied in the field at twice the normal application rate (70 g of ai/ha), no significant ^{14}C residues were detected below 8 cm (>0.01 ppm). One hundred forty-two centimeters of precipitation occurred at the field site during the experiment. Field data suggested low potential for rimsulfuron leaching to groundwater under these conditions. Although soil TLC indicated rimsulfuron would be mobile in the



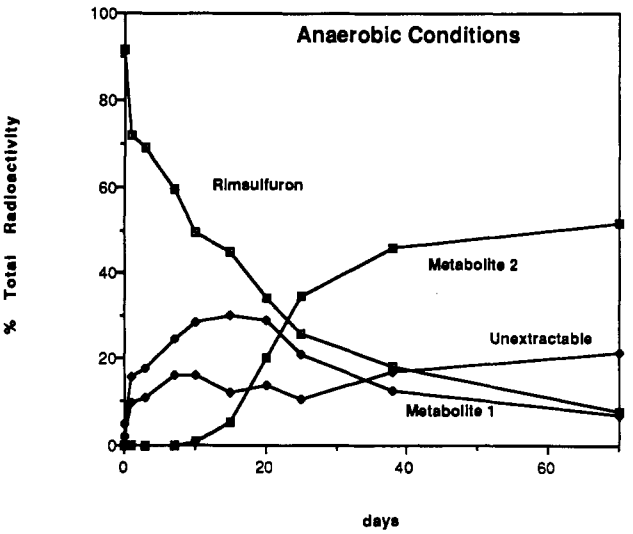


Figure 6. Distribution of ^{14}C residues under aerobic and anaerobic conditions.

Table IV. Freundlich Isotherm Constants (K) of Rimsulfuron on Four Soils

	K^a	k^b first	k^b second
Cecil sandy loam	0.23[c]	0.17	0.27
Fargo clay loam	1.36	0.25	1.12
Sassafras sandy loam	0.32	0.12	0.25
Flannagan silt loam	1.57	0.39	1.03

[a] Adsorption experiment. [b] Desorption experiment. [c] Average of duplicate samples. The variability of duplicate samples was less than 5%.

Table V. Soil Thin-Layer Chromatography Frontal R_f Values of Rimsulfuron, Major Soil Degradates, and Reference Standards on Four Soils

	Cecil sandy loam	Fargo clay loam	Sassafras sandy loam	Flanagan silt loam
rimsulfuron	0.71, 0.52[a]	0.56, 0.30	0.93, 0.74	0.53, 0.27
metabolite 1	0.65, 0.49	0.17, 0.07	0.74, 0.59	0.29, 0.16
metabolite 2	0.41, 0.26	0.18, 0.08	0.56, 0.36	0.07, 0.02
diuron	0.18, 0.07	0.15, 0.05	0.27, 0.14	0.09, 0.02
bromacil	0.58, 0.43	0.38, 0.23	0.79, 0.66	0.51, 0.33

[a] Data from duplicate plates.

Table VI. Average Concentration of Rimsulfuron and Metabolite 1 in the 0–8-cm Field Soil Dissipation Cylinder Segment[a]

	[14C]rimsulfuron equivalent residues (ppm)									
	at day 0	at day 1	at day 3	at day 7	at day 14	at day 30	at day 60	at day 180	at day 240	at day 365
% total radioactivity recovered	98	113	95	93	93	74	77	71	67	51
ppm extracted radioactivity	0.07	0.08	0.06	0.06	0.06	0.05	0.05	0.05	0.04	0.03
rimsulfuron	0.06[b]	0.04	0.04	0.02	0.01	<0.01	<0.01	<0.01	<0.01	c
metabolite 1	<0.01	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.02	≤0.01

[a] No radioactivity >0.01 ppm was detected in soil segments below 8 cm. [b] Average of two cylinders per time point. The variability of duplicate samples was less than 15%. [c] Not detected.

soil, this technique represents a continually saturated soil environment vs normal wet and dry periods in the field. Also, the use of formulated material could affect soil mobility and binding.

Rotational Crop Residue Study. The dissipation of [14C]rimsulfuron in pots was consistent with field dissipation. [14C]Rimsulfuron concentrations declined from 0.03–0.05 ppm, immediately after treatment, to <0.01 ppm 1 month after treatment. Metabolite 1 was the major soil degradate after 1 month, and its concentration was <0.01 ppm 4 months after treatment. [14C]Rimsulfuron and its degradation products showed low soil mobility potential since 14C residues were not detected in the lower soil segments (>8 cm).

The amount of total 14C residues in the various crop species was minimal, and significant accumulation (>0.01 ppm) of rimsulfuron residues in rotational crops under good agricultural practices is not anticipated. Mature lettuce, sugar beet leaves and roots, wheat grain, and soybeans contained no detectable 14C residues (<0.05 ppm); however, 14C residues were detected in the soybean and wheat straw grown in the 1-month-aged soil (0.06–0.46 ppm). 14C residues in soybean and wheat straw grown in 10-month-aged soil were lower (<0.05–0.08 ppm). The major radiolabeled metabolites in the wheat straw extracts consisted of metabolite 1 and two polar 14C metabolites. Pyridine sulfonamide and 2-amino-4,6-dihydroxypyrimidine were tentatively identified as the major polar metabolites. No [14C]rimsulfuron was detected in any extracted fraction.

Conclusion. The fate of [*pyridine*-2-14C]rimsulfuron and [*pyrimidine*-2-14C]rimsulfuron in aqueous and soil environments was investigated. Rimsulfuron degraded rapidly in soil and water primarily by contraction of the sulfonylurea bridge to give metabolite 1 [*N*-(4,6-dimethoxypyrimidin-2-yl)-*N*-((3-ethylsulfonyl)-2-pyridinyl)urea] and metabolite 2 [*N*-((3-ethylsulfonyl)-2-pyridinyl)-4,6-dimethoxy-2-pyrimidineamine]. Cleavage of the sulfonylurea bridge to give 3-(ethylsulfonyl)-2-pyridinesulfonamide and 2-amino-4,6-dimethoxypyrimidine was a minor degradation pathway (Figure 1). Rimsulfuron did not undergo photolysis in soil or neutral and alkaline aqueous solutions. However, an acceleration in degradation rate was seen in light-exposed pH 5 aqueous solution. Although soil TLC data suggested that rimsulfuron could be mobile in soil, the field data discussed here demonstrated that rimsulfuron and its metabolites are not very mobile in a silt loam soil. Rapid degradation of rimsulfuron to less mobile metabolites, as well as field data presented here, indicates low potential for leaching into groundwater. Very little root uptake and translocation of [14C]rimsulfuron residues occurred in rotational crops grown in soils containing aged [14C]rimsulfuron residues. Portions of lettuce, sugar beets, wheat, and soybeans used for human consumption contained no detectable 14C residue. Significant accumulation of rimsulfuron into rotational crops is not anticipated.

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