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Environmental Fate of Sulfometuron Methyl in Aerobic Soils

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The sulfonylurea herbicide sulfometuron methyl (methyl 2-[[[[(4,6-dimethylpyrimidin-2-yl)amino]-carbonyl]amino]sulfonyl]benzoate) is the active ingredient in Oust Herbicide and is a potent broad spectrum weed control agent that is effective against many broad-leafed weed species and grasses. Environmental fate data for [^{14}C]sulfometuron methyl in aerobic soils were obtained under laboratory and field conditions. Sulfometuron methyl readily decomposed in soil at a rate primarily dependent upon soil pH and moisture content. Saccharin was the major degradation product under sterile conditions, but in the presence of a viable soil microbial population, metabolism of the phenyl ring of [*phenyl*-^{14}C]sulfometuron methyl to $^{14}CO_2$ was observed.

INTRODUCTION

The sulfonylurea herbicide, sulfometuron methyl (methyl 2-[[[[(4,6-dimethyl-2-pyrimidin-2-yl)amino]-carbonyl]amino]sulfonyl]benzoate, Figure 1) is the active ingredient of Oust Herbicide. Oust is an effective weed control agent and a few ounces per acre controls over 60 weed species (Oust Herbicide Non-Crop Information Bulletin). Oust is registered for the control of unwanted vegetation on right-of-ways, industrial sites, and for other non-crop usage.

Because of the general use of Oust Herbicide, it is important to understand the fate of the active ingredient, sulfometuron methyl, in soil under different conditions. A previous publication (Harvey et al., 1985) discussed some of the properties of sulfometuron methyl that could affect the herbicide's environmental fate. The present study describes the fate of sulfometuron methyl in soil under controlled laboratory and approximate field conditions.

MATERIALS

Sulfometuron methyl (methyl 2-[[[[(4,6-dimethyl-2-pyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate), uniformly labeled in the phenyl ring (Harvey et al., 1985) ([^{14}C]sulfometuron methyl, specific activity 12.0 μCi/mg, >99% radiochemical purity, E. I. du Pont de Nemours & Co., Inc., Agricultural Chemicals Department) was used throughout these studies. At times, radiolabeled sulfometuron methyl was mixed with unlabeled sulfometuron methyl to reduce the specific activity. Analytical standard grade sulfometuron methyl and postulated metabolites (Figure 1) were synthesized in the Agricultural Chemicals Department of E. I. du Pont de Nemours and Co., Inc. All solvents used for high-performance liquid chromatography (HPLC) were glass distilled (Burdick and Jackson); all other solvents and common chemicals were reagent grade or better.

EXPERIMENTAL METHODS

Soils Characterization. Soils were characterized by the College of Agricultural Sciences, University of Delaware, Newark, DE (see Table I).

Laboratory Biometer Study. Laboratory biometer flasks (Bartha and Pramer, 1965) containing soil equivalent to 50 g oven-dried weight of fresh Keyport silt loam (Silt Loam, Newark, DE, Table I) were adjusted to 20, 50, 70, or 90% of their normal moisture holding capacity (NMHC). After adjustment of their water content, the soils were treated with [^{14}C]sulfometuron methyl. Flasks received either 0.063 mg (specific activity 0.59 μCi/mg) or 0.007 mg (specific activity 5.9 μCi/mg); these application rates correspond to concentrations of [^{14}C]sulfometuron methyl in the soil of 1.3 ppm and 0.14 ppm, respectively, based on a dry soil basis.

Radiolabeled sulfometuron methyl added to the soil in the biometer flasks was dissolved in acetone (0.5 mL or less) prior to addition to the flasks. This acetone solution was applied uniformly dropwise to the surface of the soil.

The biometer flask CO_2 traps were filled with 10 mL of 0.1 N NaOH before the flasks were flushed with oxygen, sealed with rubber stoppers, and placed in a dark incubator at 25 °C for the duration of the study.

Sterile biometer flasks were prepared by autoclaving biometer flasks containing soil for 1 h at 120 °C, 15 psi on three consecutive days. The water content of the soil in sterile flasks was adjusted with sterile distilled water. These sterile flasks were equipped with cotton plugs placed in the tubing connection between the soil and the CO_2 trap. In addition, a cotton filter was placed in the air inlet of each flask to preserve sterile conditions during oxygenation. Sterile flasks were treated as described above with sulfometuron methyl after autoclaving. All sterilized and

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Table I. Analyses of Soils Used in Laboratory and Field Studies with Sulfometuron Methyl

	Newark,[a] DE	Raleigh, NC	Pendleton, OR	Rosetown, SK	Fort Collins, CO
soil type	silt loam	sand	sandy loam	silty clay loam	loam
sand, %	21	91	34	0	27
silt, %	62	8	61	71	48
clay, %	17	1	5	29	25
organic matter	2.75	0.3	1.9	2.3	2.4
nitrogen	0.97	*b*	*b*	0.12	*b*
pH	6.4	4.9	5.3	7.3	7.4
cation exchange capacity, mequiv/100 g	8.2	6.3	16.7	8.7	22.6
normal moisture holding capacity, %	28.4	*b*	*b*	*b*	*b*

[a] Keyport silt loam. [b] Not determined.

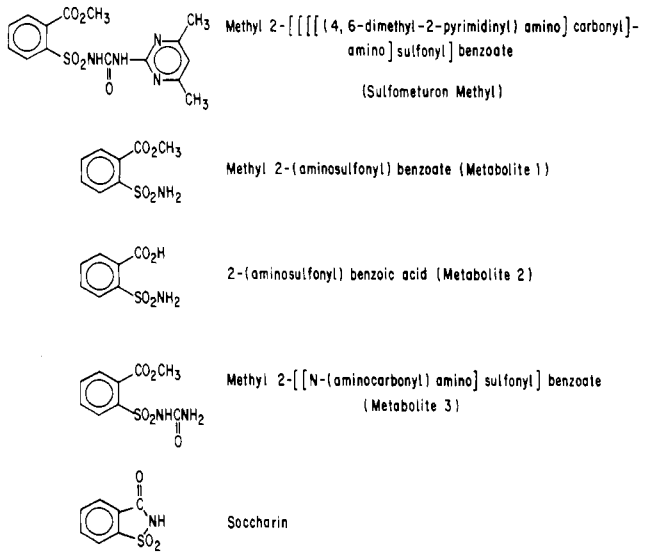

Figure 1. Sulfometuron methyl and suggested metabolites.

unsterilized biometer flasks were prepared in duplicate.

The weights of both sterile and nonsterile flasks were recorded after all additions had been made; this enabled adjustment of the water content of the flasks during the experiment, if needed. Caustic solutions in the CO_2 traps of all flasks were removed weekly, and replaced with fresh solution. At these times, flasks were flushed with oxygen to maintain aerobicity. Aliquots (1 mL) of the CO_2 trap contents were removed in duplicate, and their radioactivity measured by liquid scintillation counting (LSC) in Atomlight Scintillation Cocktail (New England Nuclear) by using a Model 6881 Mark III Liquid Scintillation Counter (Tracor Analytic).

The presence of $^{14}CO_2$ in the biometer flask trap solutions was confirmed by precipitation with saturated barium chloride. Duplicate 0.5-mL aliquots of the caustic solution from the CO_2 traps were removed and placed in 1.5-mL Eppendorf micro test tubes (Bio-Rad Laboratories); to each test tube was added 0.5 mL of a saturated $BaCl_2$ solution. After thorough mixing, 0.1 mL of 2M K_2CO_3 was added and the test tube contents were again thoroughly mixed. After centrifugation for 3 min in an Eppendorf centrifuge (Brinkmann), 0.75 mL of the supernatant solutions in the tubes was removed for LSC in Atomlight.

At the time of application, and after 1, 2, 4, 8, 16, and 24 weeks of incubation with [^{14}C]sulfometuron methyl, duplicate flasks from each treatment level (soils adjusted to 70% of NMHC) were removed from the incubator, and the treated soil was analyzed for radioactive residues. Duplicate sterile flasks at each treatment level were analyzed after 25 weeks only.

The soil in flasks adjusted to 20, 50, or 90% of the soil NMHC were analyzed only after 2, 4, or 8 weeks of incubation. Sufficient sterile flasks were prepared so that soil in sterile flasks as well as in nonsterile flasks could be analyzed at these times.

Field Dissipation Study. Field dissipation studies were performed with [^{14}C]sulfometuron methyl at five locations. These sites were in Delaware, North Carolina, Colorado, Oregon, and Saskatchewan, Canada. The procedure was developed in the Du Pont Agricultural Chemicals Department (Harvey, Jr., 1982).

On July 3rd (Newark, DE), July 18th (Raleigh, NC), July 29th (Rosetown, SK, Canada), September 8th (Pendleton, OR), and November 14th (Fort Collins, CO) of 1980, stainless steel cylinders (10 cm i.d. × 38 cm in length) were driven into undisturbed ground (CO, OR, NC, DE) to isolate a column of soil from the surrounding environment. Approximately 1 to 2 cm of each cylinder protruded from the ground to minimize splashing and runoff. Soil in these tubes experience the same conditions as the soil surrounding the cylinder, and provide a convenient means of removing only treated soil and the soil immediately underneath.

At the Rosetown, SK, site, the soil was of such a nature to preclude driving of the cylinders into the ground. Instead, holes were prepared into which the cylinders were placed in an upright position. The soil removed in digging the holes was repacked into the cylinders as firmly and evenly as possible. Subsurface soil was placed in the tubes first, followed by the top soil. As with the other 4 sites, 1 to 2 cm of the cylinder protruded from the ground after the soil had been replaced.

[^{14}C]Sulfometuron methyl (specific activity 12.0 μCi/mg) dissolved in 5 mL of acetone was applied to the exposed soil within each cylinder at rates of 1.1 kg/ha (DE), 0.91 kg/ha (NC), 0.44 kg/ha (OR), 0.15 kg/ha (CO), and 0.11 kg/ha (SK); the difference in the application rates reflected the differences between the expected use rates at the different sites. Following application, 50–100 mL of water was added to each cylinder to settle the soil surface. One cylinder containing its soil plug was removed immediately, the remaining cylinders (7 at Oregon and Colorado, 6 at Saskatchewan, Delaware and North Carolina) were removed at intervals over the next 1 to 2 years. Once a cylinder containing the soil plug was removed from the ground, it was immediately frozen and kept frozen (−20 °C) until analysis.

Soil in each cylinder was extruded and the entire soil plug divided into four, approximately 8-cm sections; soil compaction during removal of the plug accounted for the difference between cylinder height and the total thickness of the soil sections. Each section was air-dried and mechanically ground to a fine consistency with a hammer mill. The total ^{14}C residue in aliquots of each soil section was measured by combustion analysis with a tube furnace at 700 °C containing a CuO catalyst. Released $^{14}CO_2$ was trapped in Oxisorb 2 (New England Nuclear) followed by

LSC in Oxyprep 2 Liquid Scintillation Cocktail (New England Nuclear).

Analysis of Soils from Both Laboratory Biometer and Field Studies. Extraction of Soil Residues. Single aliquots (100–150 g) of the soil sections from the soil tubes (routinely, sections containing less than 10% of the applied dose were not analyzed) or the entire soil sample from biometer flasks were extracted. The soil samples were combined with 200–300 mL of a solvent mixture containing filtered methylene chloride/methanol/2 M $(NH_4)_2CO_3$ (3/4/1) and mechanically stirred for 1 h. After 1 h, solids were removed from the extract by vacuum filtration, and the solids washed with additional (50–100 mL) extraction solvent. The extract was reduced to a volume of 75 mL on the rotary evaporator (45 °C), the pH adjusted to 5 with glacial acetic acid, and the resultant solution extracted (3X) with CH_2Cl_2. The CH_2Cl_2 extract and the extracted aqueous phase were both reduced to dryness by rotary evaporation.

Although the above procedure quantitatively removed sulfometuron methyl from soil when freshly applied, the total amount of radioactivity that could be extracted from the soil by using the above procedure decreased as the incubation time increased. Consequently, tightly adsorbed residues were subjected to a more rigorous extraction procedure. For soils incubated with sulfometuron methyl for 1 month or longer, samples extracted by the first procedure were in addition extracted with filtered acetone/1 M $(NH_4)_2CO_3$ (3/1, v/v) under reflux conditions for an hour. The mixture was then filtered to remove soil particles, and the extract combined with the previous extract before reduction of volume and CH_2Cl_2 partitioning.

All extracts were assayed for total radioactivity by LSC with either Atomlight Scintillation Cocktail for alkaline samples or Formula-947™ Scintillation Cocktail for neutral and acidic samples. Residual radioactivity left in soil after extraction was quantitated by combustion analysis as previously described.

The methylene chloride extracts were reduced to dryness by rotary evaporation, and the radioactivity quantitatively transferred to a 10-mL graduated centrifuge tube with methylene chloride. Aqueous fractions after methylene chloride extraction were reduced in volume by rotary evaporation, and redissolved in a small volume of methanol. Both the concentrated methylene chloride extract or the concentrated aqueous fraction were then analyzed.

HPLC and TLC Analyses of Soil Extracts. Analysis of extracts of soil treated with [^{14}C]sulfometuron methyl utilized both high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC). All HPLC analyses were performed on Zorbax chromatographic columns (Du Pont Instruments); all TLC analyses were performed on silica gel thin-layer plates (Silica gel 60 F254, E. M. Science Division of E. Merck, Darmstadt). Table II lists the TLC R_f values and the HPLC retention times for sulfometuron methyl and suggested metabolites in the various TLC and HPLC systems used for analysis of soil extracts.

Radiolabeled species on TLC plates were located by autoradiography on X-Omat AR-5 X-ray film (Kodak). Identification of radiolabeled species was through cochromatography with authentic standards. These standards were included on the TLC plates with the chromatographed samples. When analyses were performed by HPLC, a fraction collector was used to collect column effluent. The collected fractions were mixed with Formula 947 Liquid Scintillation Cocktail and analyzed by LSC for radioactivity. Identification of radiolabeled species was by means of cochromatography with standards.

Table II. Chromatographic Behavior of Sulfometuron Methyl and Metabolites

compound	TLC R_f Values: solvent 1[a]	solvent 2[b]	solvent 3[c]
sulfometuron methyl	0.63	0.47	0.71
saccharin	0.49	0.36	0.34
metabolite 1	0.77	0.80	0.86
metabolite 2	0.42	0.20	0.55
metabolite 3	0.36	0.17	0.46

compound	HPLC retention times for system: 1[d]	2[e]	3[f]	4[g]
sulfometuron methyl		7.2		16.0
metabolite 1	6.2	3.2		5.2
metabolite 2	2.9			
metabolite 3	4.5			
saccharin	2.0		9.2	29.0

[a] Acetone/2 M $(NH_4)_2CO_3$ (9/1, v/v). [b] $CH_2Cl_2/CH_3OH/NH_4OH$ (144/50/6, v/v/v). [c] CH_3CN/ethyl acetate/formic acid (150/50/1.5, v/v/v). [d] 25 cm × 4.6 mm Zorbax C8. Mobile phase CH_3CN/pH 2.2 H_2O (phosphoric acid) (1/4, v/v). Flow rate 2 mL/min. Column temperature 23 °C. [e] 25 cm × 4.66 mm Zorbax C8. Mobile phase CH_3CN/pH 2.2 H_2O (phosphoric acid) (36/64, v/v). Flow rate 2 mL/min. Column temperature 23 °C. [f] 25 Cm × 4.66 mm Zorbax NH_2. Mobile phase CH_3CN/0.1 M H_3PO_4 (15//85, v/v). Flow rate 2 ML/min. Column temperature 45 °C. [g] 25 cm × 4.66 mm Zorbax Sil column. Mobile phase methylene chloride/acetic acid/water (1500/25/2.8, v/v/v). Flow rate 2 mL/min. Column temperature 30 °C.

Extraction and Purification of [^{14}C]Saccharin from Soil for Mass Spectral Identification. Sieved (4 mm) Keyport silt loam (300 g) was placed in a 500-mL Erlenmeyer flask and treated with 50 mg of [^{14}C]sulfometuron methyl (specific activity 0.056 μCi/mg) in acetone solution (5 mL). After evaporation of the acetone, the flask was flushed with oxygen and placed in an incubator at 25 °C; the flask was flushed with oxygen weekly to maintain aerobic conditions. After 6 weeks the soil was extracted as previously described; volumes of solvents were scaled up to extract 300 g of soil. The water fraction containing polar metabolites (including saccharin) was acidified to pH 1 with hydrochloric acid and extracted three times with methylene chloride. The methylene chloride extract containing [^{14}C]saccharin was concentrated to dryness by rotary evaporation, resuspended in a small volume of methylene chloride, applied to a silica gel thin-layer plate, and developed in TLC system 2. The single radiolabeled band (R_f 0.40) was scraped, eluted with methanol, dried, and dissolved in acetonitrile/0.1 M H_3PO_4 (15/85, v/v). This fraction was then further purified by chromatography with HPLC system 3. The radioactive peak eluting at 9.2 min was trapped; mobile phase containing the radioactive peak was adjusted to pH 1 and extracted with methylene chloride. This methylene chloride extract was concentrated with a nitrogen evaporator before it was chromatographed in HPLC system 4. Radioactivity eluting at 7.1 min was trapped, the solvent evaporated, and submitted for mass spectral analysis. Mass spectral analysis was performed by using a Du Pont Model 21-492 electron impact mass spectrometer equipped with a Vespel probe.

RESULTS AND DISCUSSION

Laboratory Biometer Study. [^{14}C]Sulfometuron methyl was applied to Keyport silt loam adjusted to 70% of its NMHC and incubated in the dark at 25 °C. Under these conditions, the ultimate fate of sulfometuron methyl was degradation of the [^{14}C]phenyl portion of the molecule to carbon dioxide.

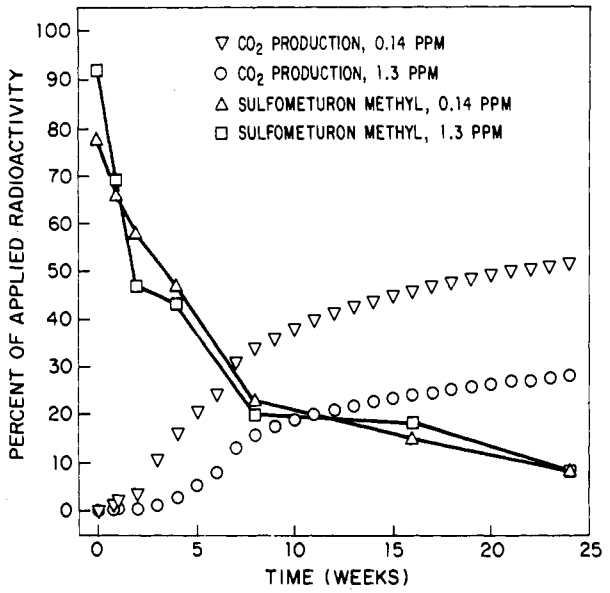

Figure 2. Residues of sulfometuron remaining and carbon dioxide produced in biometer flasks as a function of time (calculated as the percent of applied material).

Table III. Residue of Sulfometuron Methyl Remaining and CO_2 Released after Incubation[a] on Keyport Silt Loam

application rate, kg/ha	soil condition[b]	sulfometuron methyl, as % of applied	CO_2 released, % of applied
0.14	sterile	12	<1
	nonsterile	8	51
1.3	sterile	8	<1
	nonsterile	9	28

[a] 25 weeks incubation for sterilized soils; 24 weeks incubation for nonsterile soil. [b] Soil was at 70% of its moisture holding capacity.

At the low application rate (0.14 ppm), 50% of the applied radiolabel was recovered in the biometer flask caustic traps after 21 weeks of incubation (Figure 2). The radioactivity that was present in the caustic traps was identified as $^{14}CO_2$ by precipitation of $Ba^{14}CO_3$ coupled with analysis by LSC. During this same time period (21 weeks), 27% of the applied radiolabel was recovered from Keyport silt loam treated with [^{14}C]sulfometuron methyl at a 9-fold higher rate (concentration of 1.3 ppm in the soil). There was no detectable $^{14}CO_2$ evolution (<1% of applied radiolabel) from flasks containing sterilized soils.

Soils from biometer flasks were extracted and analyzed by TLC systems 1 and 2 (see Table II for chromatographic behavior of sulfometuron methyl and degradation products). Soils were removed for analysis of residues of [^{14}C]sulfometuron methyl and any radiolabeled degradation products at selected times, ranging from 0 to 25 weeks of incubation. Comparison of sulfometuron methyl decomposition in sterilized (Table III) and microbially active (Table III and Figure 2) soil demonstrated that sulfometuron methyl was chemically decomposed at a much faster rate than the rate at which it is converted to $^{14}CO_2$. Whereas 50% conversion of the applied radiolabel to CO_2 occurred after 21 weeks at the low application rate, 90% of the active ingredient had decomposed by this time.

The rate of breakdown of sulfometuron methyl was not concentration dependent at the application rates studied which indicates that degradation follows first-order kinetics. The half-life of sulfometuron methyl, under the conditions studied, was about 1 month at either application rate. Although no $^{14}CO_2$ was produced from flasks containing sterilized soil, sulfometuron methyl did decompose readily. After 24 weeks (25 weeks for sterilized flasks),

Table IV. Maximum and Final Concentrations of Saccharin in Laboratory Soil Treated with Sulfometuron Methyl

application rate, kg/ha	condition	maximum concn, as % of applied	final[a] concn, as % of applied
0.14	sterile		54
	nonsterile	26 (2 weeks)	3
1.3	sterile		58
	nonsterile	33 (4 weeks)	17

[a] 25 weeks incubation on sterile soils; 24 weeks incubation on nonsterile soil.

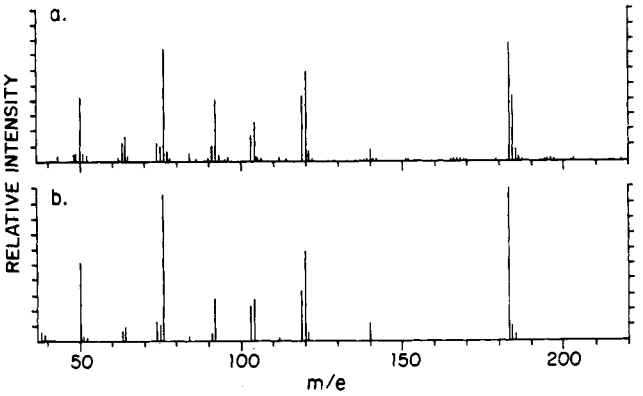

Figure 3. Comparison of the mass spectra of (a) the major soil metabolite of sulfometuron methyl and (b) saccharin.

sulfometuron methyl had decomposed to an equivalent extent in both the sterilized and microbially active soils (Table III).

Identification of Metabolites in Biometer Flask Soil Extracts. Biometer soils analyzed for residual levels of [^{14}C]sulfometuron methyl were also analyzed for any degradation products of the herbicide intermediate to the formation of $^{14}CO_2$. The principle nonvolatile degradation product of [^{14}C]sulfometuron methyl was [^{14}C]1,2-benzisothiozol-3-one, 2,3-dihydro 1,1-dioxide ([^{14}C]saccharin, Figure 1, Table IV). [^{14}C]Saccharin was previously identified as a hydrolysis product of sulfometuron methyl (at pH 5, Harvey et al., 1985). Presumably this is the mechanism through which it arose in these biometer flasks. [^{14}C]Saccharin was isolated from extracts of a Keyport soil treated at a high level (167 ppm) with [^{14}C]sulfometuron methyl. [^{14}C]Saccharin isolated from the soil extracts had an identical mass spectrum to an authentic sample of saccharin (Figure 3). In nonsterile soils adjusted to 70% of the soils' moisture holding capacity, [^{14}C]saccharin never exceeded, at any sampling time, a concentration higher than 33% of the radiolabeled material originally applied to the soil. At the end of 24 weeks of incubation, the level of saccharin had decreased (Table IV). Although the amount of saccharin remaining on nonsterile soils was no higher than 17% of the label originally applied to soil (more at 1.3 ppm than at 0.14 ppm), the level in sterile flasks was much higher; saccharin was present at a level equivalent to 58% of the label originally applied to these sterile soils. Little difference was observed between application rates.

Saccharin was not the only radiolabeled metabolite present in extracts of soil treated with [^{14}C]sulfometuron methyl. Other metabolites that have been identified were methyl 2-(aminosulfonyl)benzoate (metabolite 1, Figure 1), 2-(aminosulfonyl)benzoic acid (metabolite 2), and 2-[[(aminocarbonyl)amino]sulfonyl]benzoate (metabolite 3). Metabolite 1 was also detected in the previously mentioned hydrolysis study. Metabolite 2 is the ring opened form of saccharin. Metabolite 3 is a conceivable hydrolysis product

Table V. Effect of Soil Moisture Content on the Degradation of Sulfometuron Methyl on Soil

incubation time, weeks	soil moisture content, % of NMHC[a]	CO_2, as % of applied	sulfometuron methyl remaining, as % of applied	
			nonsterile	sterile
2	20	<1	64	71
	50	<	74	66
	90	1	57	55
4	20	<1	54	52
	50	1	50	45
	90	5	36	27
8	20	<1	35	38
	50	4	33	25
	90	9	28	21

[a] NMHC = normal moisture holding capacity.

of sulfometuron methyl but was not detected in the hydrolysis study (Harvey et al., 1985). None of these radiolabeled compounds accounted for, at any of the sampling periods, a level greater than 10% of the radiolabel originally applied to the soil. All these metabolites were identified strictly by their chromatographic behavior in TLC Systems 1 and 2. When the original soil extract was partitioned with methylene chloride, sulfometuron methyl and metabolite 1 were the principle radiolabeled components of the methylene chloride phase. Metabolites 2 and 3 and saccharin remained in the aqueous phase.

These results suggest the hypothesis that in acid soils, microorganisms do not play a major role in the initial degradation of sulfometuron methyl; instead, a nonbiological hydrolysis predominates, resulting in among other products, saccharin. Soil microbes then act on these [^{14}C]phenyl containing hydrolysis products to eventually convert them to CO_2.

Measurement of Bound Residues in Soils from Biometer Flasks. The radioactivity remaining on the soil in biometer flasks could not be completely extracted with the methods employed. As the incubation time increased, the level of unextracted residues increased, and these were quantitatively analyzed by combustion techniques following extraction of the soil. Radiolabeled unextractable residues were present at a level equivalent to 4 and 5% of the applied dose at zero day (low and high dose, respectively), and they increased to 21% and 17% at the end of 24 weeks of incubation. Unextractable radiolabeled residues were 10% and 9% (low and high rates, respectively) in sterile flasks incubated for 25 weeks. These observations are not unexpected. Whenever microorganisms utilize a carbon source for their growth and maintenance, not all the carbon is oxidized to CO_2; some of the carbon source is incorporated into cellular materials (Clifton and Logan, 1939). A similar process likely occurred in these biometer flasks. Cellular materials such as proteins, carbohydrates, etc. would not be soluble in the extraction solvents used in this study. Other contributing mechanisms for these soil bound residues could be adsorption by organic matter in the soil, adsorption by clay particles, or other microbial or soil mediated processes (Kaufman et al., 1976).

Effect of Soil Moisture Content on the Metabolism of [^{14}C]Sulfometuron Methyl. In order to assess the effect of soil moisture content on the degradation rate of sulfometuron methyl, separate sets of biometer flasks were prepared with the Keyport silt loam adjusted to 20, 50, or 90% of its NMHC. These flasks were analyzed after 2, 4, and 8 weeks. Increasing the soil moisture content increased slightly the extent of degradation of [^{14}C]sulfometuron methyl, and increased the extent of $^{14}CO_2$ production in nonsterile soils (Table V). When the soil moisture content was increased from 20 to 90% of the maximum holding capacity, the level of [^{14}C]sulfometuron methyl remaining after 8 weeks decreased from 31% of applied (20% of NMHC) to 26% of applied (90% of NMHC). Little difference was also observed in the residues of sulfometuron methyl remaining on soil between sterile and nonsterile soils.

Table VI. Residues of Sulfometuron Methyl in Field Soil Tubes as a Function of Time

time, weeks	% of applied [^{14}C]sulfometuron methyl remaining				
	DE	NC	OR	CO	SK
0	64	76	90	90	85
2	59	18	67	*a*	35
4	10	15	61	64	51
8	2	5	66	*a*	31
16	<1	2	45	33	18
20	*a*	*a*	*a*	42	*a*
26	*a*	2	37	*a*	*a*
30	*a*	*a*	*a*	26	*a*
32	4	*a*	*a*	*a*	*a*
38	*a*	*a*	*a*	12	*a*
43	*a*	*a*	*a*	*a*	16
52	1	<1	6	12	*a*
78	*a*	*a*	*a*	9	*a*
104	*a*	*a*	3	*a*	5

[a] No cylinder removed at this time.

Table VII. Residues of Sulfometuron Methyl and Total Radioactivity Remaining on Soil at Each Test Site after 1 Year, Compared with Soil pH, Rainfall, and Local Temperature

	eastern soils		western soils		
	NC	DE	OR	CO	SK
sulfometuron methyl, as % of applied	<1	1	6	18	12[a]
total ^{14}C remaining,[b] as % of applied	19	23	54	56	50
soil pH	4.9	6.4	5.3	7.3	7.4
rainfall, in.	30	32	17	16	10
av temp	59	54	52	50	41

[a] The value of percent sulfometuron methyl remaining on soil after 1 year at the Saskatchewan site was obtained by interpolation of the available data. [b] Includes residues of sulfometuron methyl, as well as metabolites 1, 2, and 3, saccharin, and unextractable residues.

Degradation of [^{14}C]Sulfometuron Methyl under Field Conditions. The five sites chosen for this field dissipation test can be divided, for comparison purposes, into eastern and western soils. The eastern soils include Delaware and North Carolina, and the western soils, Oregon, Colorado, and Saskatchewan. The rate of decomposition of sulfometuron methyl varied from site to site; Table VI lists the residues of sulfometuron methyl remaining on soil in the soil tube as a function of time. Because the soil at these five locations was treated at different times of the year, a direct comparison of the sulfometuron methyl half-life at these different sites would be deceiving. The initial degradation rate of sulfometuron methyl in Colorado soil would be expected to be less than that observed in Delaware. Colorado soils were treated in mid-November and would therefore experience (initially at least) colder temperatures and slower degradation rates of sulfometuron methyl than Delaware soils treated in mid-July. A comparison of the levels of sulfometuron methyl and total radioactivity after 1 year of aging is more useful for comparative purposes. Only 1% or less of the applied sulfometuron methyl remained after 1 year on the

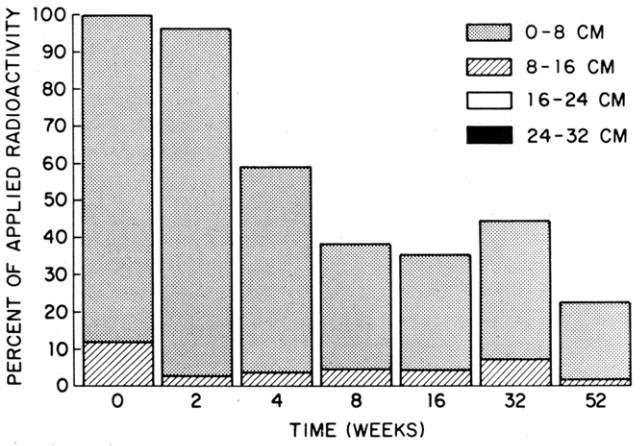

Figure 4. Location of total radioactivity in Delaware soil cylinders as a function of time.

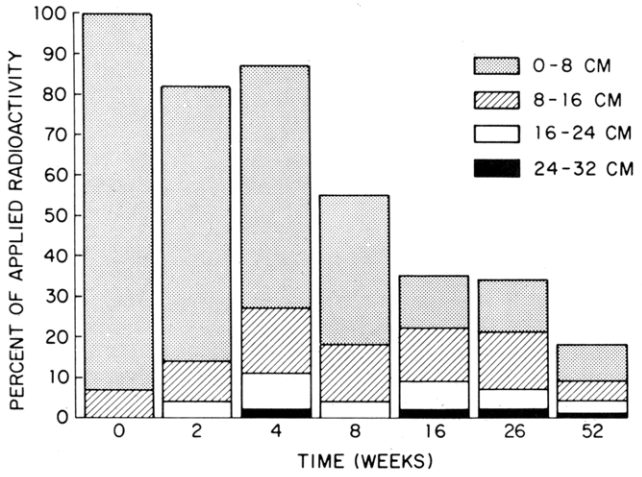

Figure 5. Location of total radioactivity in North Carolina soil cylinders as a function of time.

eastern soils, while 6–18% remained on the Western soils (Table VII). In addition, the total residues remaining in the eastern soils was roughly half that remaining on the Western soils.

The faster degradation rate in the east could possibly be attributed to environmental factors. The eastern soils were generally more acidic than the western soils (Table I and VII). Sulfometuron methyl is stable in aqueous solution at pH 7 and 9, but hydrolyzes at pH 5 (Harvey et al., 1985). Hydrolysis of sulfometuron methyl would be more likely in the Delaware and North Carolina soils than in the western soils.

Low soil pH was not the only factor which increased the rate of breakdown of sulfometuron methyl; the soil moisture content may also have been important. This concept is illustrated by the Oregon soil, which had a similar pH to the eastern soils, but exhibited a much lower rate of breakdown of sulfometuron methyl. In the soil biometer studies, increasing the moisture content of the soil increased breakdown of sulfometuron methyl and increased metabolism to CO_2. The eastern soils, in addition to having a lower average soil pH, also experienced twice as much rainfall as the western sites (and were therefore probably moister). These sites not only exhibited faster degradation of sulfometuron methyl, but had greater loss of the applied label from the soil (presumably as CO_2).

Another factor affecting the degradation rates of sulfometuron methyl in soil was the temperature of the soil throughout the exposure period. The average yearly temperatures experienced at the three western sites were lower

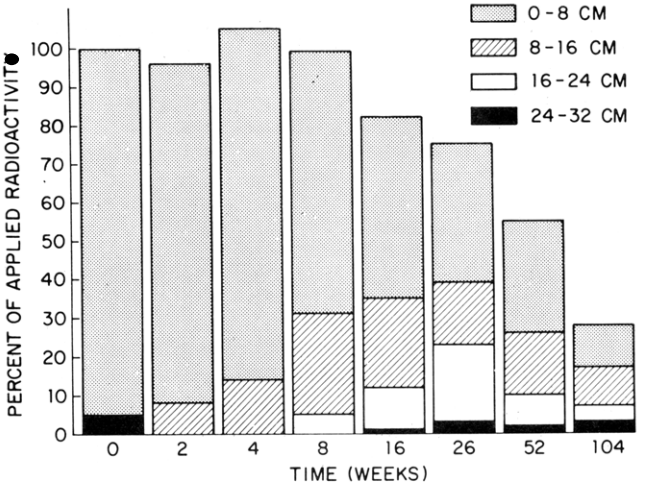

Figure 6. Location of total radioactivity in Oregon soil cylinders as a function of time.

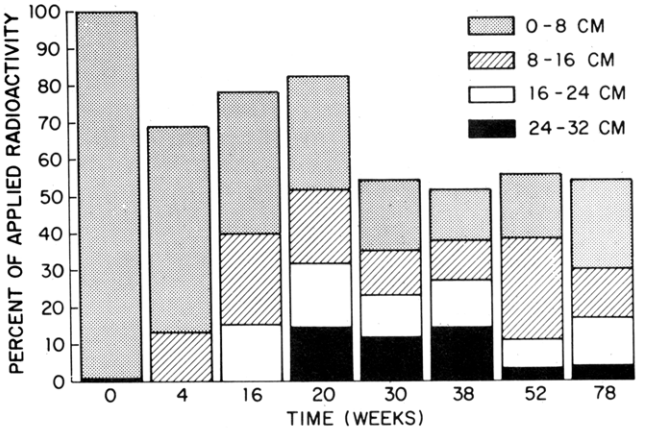

Figure 7. Location of total radioactivity in Colorado soil cylinders as a function of time.

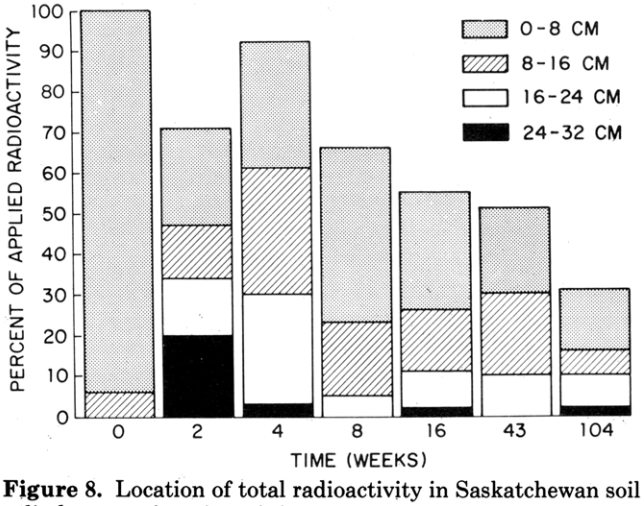

Figure 8. Location of total radioactivity in Saskatchewan soil cylinders as a function of time.

than those experienced at the two eastern sites. This would also contribute to the slower dissipation of the herbicide on these soils based upon kinetic principles.

The higher loss of total radiolabel from the soils in Delaware and North Carolina than from those of Oregon, Colorado, or Saskatchewan (Figures 4–8) could be due to the faster rate of conversion of applied radiolabeled herbicide to CO_2 that had been shown to occur in more moist soils. This assumes that the primary mechanism of loss of label is by metabolism of the herbicide to CO_2. There

is at least one other possibility. Leaching of the radioactivity from the bottom of the soil tube could occur if the compounds were mobile and there was sufficient rainfall. These two mechanisms for loss of radiolabel from the soil are illustrated when the Delaware and Colorado sites (Figures 4 and 7) are compared. Leaching of radiolabel from the cylinders was not a factor in the Delaware soil. In Figure 4 the percent of total applied radioactivity in the Delaware soil cylinders is portrayed as a function of time and depth. Little, if any, of the radioactivity was detected below the second section (16 cm mark). In the Colorado soils, however (Figure 7), migration into the lower sections of the cylinder occurred. Analysis of these migrating materials showed them to be sulfometuron methyl, saccharin, unextractable residues, and small amounts (≤7% of applied radioactivity) of unidentified radiolabeled residues.

There was generally more migration of radiolabel down the soil tube in the western soils than in the eastern soils. The increased mobility of sulfometuron methyl on these western soils, as compared to the eastern soils, can be attributed to differences in soil pH. Sulfometuron methyl has a p*K*a of 5.2. At the soil pH's experienced in the western soils (pH >7 for Colorado and Saskatchewan), sulfometuron methyl is ionized. The sulfometuron methyl anion, being more soluble in water than the unionized species (Oust Herbicide Non-Crop Information Bulletin), would move more readily in the soil column when water was applied to it than would the unionized species. Also, the sample in Colorado was applied in winter when most precipitation occurred and essentially no metabolism occurred.

The other radiolabeled metabolites and degradates isolated in this study were previously observed in the soil biometer studies. The principle intermediate metabolite was again saccharin.

SUMMARY

The phenyl ring of [(U)phenyl-^{14}C]sulfometuron methyl decomposed on soil to CO_2. The initial step in the breakdown of sulfometuron methyl was apparently hydrolysis mediated in acidic soils after which microbial attack occurred on the fragments. No statements can be made concerning the fate of the pyrimidine ring of sulfometuron methyl after hydrolysis since this portion of the molecule was unlabeled. Sulfometuron methyl also decomposed in alkaline soils. In this case, it is believed that microbial action is the rate-limiting step since this compound is hydrolytically stable under neutral and alkaline conditions. Both the initial decomposition of sulfometuron methyl and subsequent conversion to CO_2 by soil microbes, was enhanced by a high soil moisture content. The primary nonvolatile metabolite of sulfometuron methyl was saccharin, which was transient in nature. Under controlled laboratory conditions, sulfometuron methyl had a first half-life of approximately 1 month. The rate of breakdown of sulfometuron methyl in the field under actual use conditions was dependent on the soil pH, the amount of rainfall, and the local temperature.

Sulfometuron methyl (or its degradation products) was more mobile in soils with pH 7 or greater than in soils with pH near or below the sulfometuron methyl p*K*a value of 5.2. This increased mobility was attributed to ionization of sulfometuron methyl and hence increased water solubility.

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Registry No. CO_2, 124-38-9; sulfometuron methyl, 74222-97-2; saccharin, 81-07-2; metabolite 1, 57683-71-3; metabolite 2, 632-24-6; metabolite 3, 95473-30-6.

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