Properties of Sulfometuron Methyl Affecting Its Environmental Fate: Aqueous Hydrolysis and Photolysis, Mobility and Adsorption on Soils, and Bioaccumulation Potential

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[*phenyl*-^{14}C]Sulfometuron methyl is stable in water at pH 7 or 9, but hydrolyzes readily (half-life 2 weeks) to [^{14}C]methyl 2-(aminosulfonyl)benzoate and [^{14}C]1,2-benzisothiazol-3-one, 2,3-dihydro 1,1-dioxide (saccharin), at pH 5.0. [^{14}C]Sulfometuron methyl was completely photolyzed to $^{14}CO_2$ under aquatic photolysis conditions. [^{14}C]Methyl benzoate was identified as an intermediate in this photolytic degradation. [^{14}C]Sulfometuron methyl was mobile on soils when tested using soil thin-layer plates and soil columns; this mobility agreed reasonably well with Freundlich soil isotherm constants. [^{14}C]-Sulfometuron methyl has a low partition ratio (0.31) between *n*-octanol and 0.01 M phosphate buffer, pH 7.0. It does not accumulate in fish tissue when fish are exposed to 0.01 ppm or 1.0 ppm [^{14}C]-sulfometuron methyl in their environment.

INTRODUCTION

Sulfometuron methyl (methyl 2-[[[[(4,6-dimethylpyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate) (Figure 1) is the active ingredient of Oust Herbicide. Oust is a potent broad spectrum weed control agent that is effective against many broad-leafed weed species and grasses Oust Herbicide Non Crop Information Bulletin) and can be applied either pre- or postemergence.

The studies reported herein investigated the potential environmental impact of sulfometuron methyl when used as a weed control agent. The stability of sulfometuron methyl under both aqueous photolytic and hydrolytic conditions will be discussed, as well as interactions between sulfometuron methyl and animate (fish) and inaminate (soil) segments of the environment.

MATERIALS

[(U)phenyl-^{14}C]Sulfometuron methyl (specific activity 12.0 μCi/mg) was used in all the studies. Unlabeled sulfometuron methyl was added, if needed, to reduce the specific activity of the herbicide for some studies. Radiolabeled sulfometuron methyl was prepared as follows: (I) 1.79 g of [*phenyl*-^{14}C]saccharin (sp. act. 4.37 mCi/mmol, New England Nuclear, custom synthesis) was combined with 15 mL of CH_3OH in a 50-mL round-bottom flask. Rexin 101 (0.65 g) was added to this solution and the mixture heated at reflux for 16 h. After reflux, the reaction mixture was cooled under N_2 purge and the crystals filtered and dried. The yield of methyl 2-(aminosulfonyl)benzoate was 1.3 g. (IIa) The dried methyl 2-(aminosulfonyl)-benzoate was placed in a three-neck flask with 10 mL of thionyl chloride and heated at reflux for 16 h. Most of the excess thionyl chloride was removed by heating accompanied by a N_2 purge. The remainder of the thionyl chloride was removed by addition of 15 mL of toluene, followed by distillation and collection in a Dean-Stark tube. (IIb) Three drops of dry pyridine was added to the sulfonamide sulfoxide and the mixture heated to reflux. While at reflux, 0.5 mL of phosgene in 2 mL of dry toluene was added, and the mixture allowed to reflux for 1 h. After reflux, the excess phosgene was removed with a N_2 sparge. (III) This mixture was filtered into a dry flask under a N_2 blanket and cooled to room temperature. 2-Amino-4,6-dimethylpyrimidine (0.65 mg) was added to this mixture, and stirred for 16 h. The reaction mixture was cooled to −5 °C and filtered, and the crystals were washed with cold acetonitrile and hexane. The yield of [*phenyl*-^{14}C]sulfometuron methyl was 1.2 g (33% yield from saccharin). This radiolabeled sulfometuron methyl was mixed with unlabeled sulfometuron methyl to yield final products with specific activities of 5.9 and 12.0 μCi/mg (99% radiochemical purity).

Analytical standard sulfometuron methyl, and hydrolysis products of sulfometuron methyl (Figure 1) were all synthesized in the Agricultural Chemicals Department of E. I. du Pont de Nemours and Company, Inc. All solvents used for high-pressure liquid chromatography were Glass Distilled (Burdick and Jackson Laboratories). Solvents for other uses, and common chemicals, were reagent grade or better.

EXPERIMENTAL METHODS

Chromatography. Extracts and liquid samples were routinely analyzed by either thin-layer chromatography (TLC) or by high-performance liquid chromatography (HPLC). Identification of radiolabeled species was through cochromatography with standards followed by autoradiography (TLC) or peak trapping and liquid scintillation counting (LSC).

Thin-layer chromatography was accomplished on silica gel thin layers (Silica Gel 60 F254, E. M. Science Division of E. Merck, Darmstadt) containing fluorescent indicator. The solvent system used was *n*-butanol/acetic acid/water, 3/1/1, v/v/v, (TLC solvent 1).

HPLC analyses were performed with a variety of column packings and mobile phases. HPLC conditions were as follows: 4.6 mm × 25 cm Zorbax SIL (Du Pont Instruments Division, Photo Products Department) column: mobile phase methylene chloride/acetic acid/water, 1500/25/2.8, v/v/v; flow rate 2 mL/min; column temperature 30 °C (HPLC system 1); 6.2 mm by 25 cm Zorbax PSM 60 column: mobile phase deionized distilled filtered water: flow rate 1 mL/min; column temperature 40 °C (HPLC system 2); 4.6 mm × 25 cm Zorbax SIL column: mobile phase CH_2Cl_2: flow rate 2 mL/min; column temperature 30 °C (HPLC system 3); 4.6 mm × 25 cm Zorbax C8 column; mobile phase CH_3CN/pH 2.2 H_3PO_4 adjusted H_2O (3/7, v/v); flow rate 2 mL/min; column temperature 45 °C (HPLC system 4).

Hydrolysis. Three 300-mL samples, each containing 5 ppm of [^{14}C]sulfometuron methyl (1.5 mg, 18.0 μCi) in aqueous solution, were buffered to pH 5.0, pH 7.0, or pH 9.0 by the addition of the appropriate pHydrion Buffer

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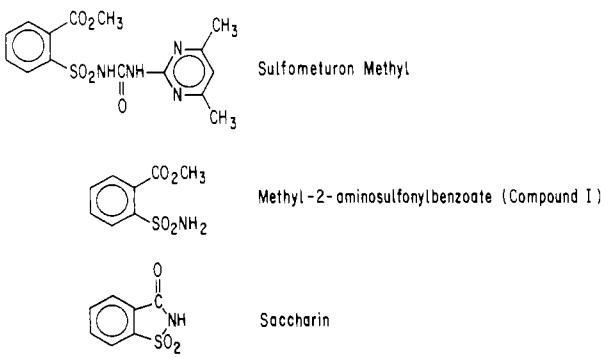

Figure 1. Sulfometuron methyl and suggested degradation products.

Metrepak (Micro Essential Laboratories). The test solutions were maintained in the dark at 25 °C in closed, wide mouth glass bottles. One 20-mL aliquot was taken from each buffer solution after 6 h and 1, 2, 3, 7, 14, 21, and 30 days.

Total radioactivity in each sample was determined by liquid scintillation counting (LSC) on a Tracor Mark III liquid scintillation counter. Each sample was adjusted to pH 7 by addition of dilute sodium hydroxide or nitric acid solution as appropriate, and extracted three times with 20-mL portions of methylene chloride. The extracts were combined, dried over anhydrous $MgSO_4$, and concentrated to 3.5 mL in a stream of N_2. Radioactivity in the extracts, the concentrates, and the aqueous phases after extraction was determined by LSC. Aqueous phases were counted in Formula 947 liquid scintillation cocktail (New England Nuclear) and methylene chloride solutions in Atomlight liquid scintillation cocktail (New England Nuclear).

Methylene chloride concentrates were analyzed in HPLC system 1. Quantitation of each chromatogram was achieved by LSC of aliquots of column effluent which were collected to represent sulfometuron methyl and methyl 2-(aminosulfonyl)benzoate (16 min and 5.2 min, respectively) as well as the intervals before, between, and after them to a maximum of 22 min. Recoveries of injected radioactivity in the total effluent were quantitative.

In order to obtain enough polar decomposition product for identification, the pH 5 solution remaining at the end of the experiment (114 mL) was extracted four times with 114-mL portions of methylene chloride to remove sulfometuron methyl and other methylene chloride soluble compounds and three times with ethyl acetate. No radioactivity was removed by the ethyl acetate. The aqueous phase after the extractions was evaporated under reduced pressure on a rotary evaporator to 20 mL.

A portion of the aqueous concentrate was purified by chromatography in HPLC system 2. A single ^{14}C peak was observed and collected 5.2–5.8 min after injection. The pooled radioactive fraction from 10 injections was evaporated to dryness on the water bath in a stream of N_2. The presence of a considerable quantity of white crystals indicated incomplete separation of buffer, therefore the radioactivity was extracted quantitatively with approximately 2 mL of distilled-in-glass acetonitrile (Burdick and Jackson). The extract was evaporated to dryness in a stream of nitrogen, and the buffer-free residue dissolved in 250 μL of water. Final purification was achieved by reinjecting the entire sample in two portions on the Zorbax PSM 60 column (HPLC system 2). The radioactive peak was collected, concentrated, and analyzed by mass spectrometry. An additional portion of the aqueous concentrate was evaporated to dryness, and resuspended in a mixture of methylene chloride/acetic acid/water (1500/25/2.8, v/v/v). An aliquot of this solution was mixed with analytical standard saccharin and chromatographed in HPLC system 1.

Mass spectroscopy was performed on a Du Pont 21-492 double focusing magnetic instrument (Du Pont Instruments) with electron impact ionization. For direct probe experiments, the source temperature was 200 °C, ionizing energy 70 eV, and ion resolution set at 1000. The temperature of the probe was raised from 0 to 400 °C over a period of 2 min.

Aqueous Photolysis. Photolysis was carried out in continuously stirred beakers with quartz lids under lamps which provided light (in the 300–400-nm region) equivalent to half the intensity of typical summer sunshine at noon (Harvey and Han, 1978). Aliquots of test water (300 mL) were placed in each beaker. Two beakers received distilled water; one of these was completely wrapped with heavy-duty aluminum foil and acted as a dark control. A third beaker received standard reference water (Freeman, 1953). Clear water freshly obtained from the Brandywine River, a pastoral stream in northern Delware, was added to a fourth beaker. The fifth beaker contained Brandywine River water slightly cloudy with suspended sediment obtained from the Brandywine River bottom. [^{14}C]Sulfometuron methyl (1.7 mg, in 0.7 mL of acetone) was added to each of the test waters to create aqueous solutions containing 5 ppm [^{14}C]sulfometuron methyl. The pH of the sulfometuron methyl solutions was pH 8.6 for distilled water, pH 7.5 for standard reference water, and pH 7.4 for river water. The solutions were stirred with a magnetic stirrer for the duration of the study.

One 20-mL sample was taken from each solution immediately (0 h) and after exposure intervals of 3, 18, 24 and 72 h and 1 and 2 weeks. After the analyses of the 2-week samples had been completed, the experiment was terminated on the 18th day. The volume of the solutions remaining was measured as well as the total radioactivity. The walls of the beakers were rinsed thoroughly with water, acetone, and finally methanol, and the radioactivity in the wash measured by LSC.

Total radioactivity in each sample was determined by LSC. Each sample was adjusted to pH 5 by addition of a few drops of glacial acetic acid and extracted three times with 20-mL portions of methylene chloride. The extracts were combined, dried over anhydrous $MgSO_4$, and concentrated to 2.5 mL in a stream of N_2. Radioactivity in the extracts, the concentrates, and the aqueous phases after extraction was quantitated by LSC. Aqueous phases were counted in Formula 947 and methylene chloride solutions in Atomlight.

Methylene chloride concentrates were analyzed in duplicate in HPLC system 1. Quantitation of each chromatogram was achieved by LSC of aliquots of column effluent which were collected to represent sulfometuron methyl (retention time 16.0 min) and methyl 2-(aminosulfonyl)benzoate (retention time 5.2 min) as well as the intervals before, between, and after them to a maximum of 22 min. Recoveries of injected radioactivity in the total effluent were quantitative.

At the end of the experiment, the remaining solutions from distilled water, standard reference water, and river water were combined, adjusted to pH 5 by addition of a few drops of glacial acetic acid and extracted three times with 400-mL portions of methylene chloride. The aqueous phase after extraction was adjusted to pH 7.5 with dilute ammonium hydroxide and concentrated by rotary evaporation to 20 mL. Portions of this concentrate were fractionated by chromatography in HPLC system 2. A Model

Table I. Soil Characteristics

component	soil type[a] Fallsington[b] sandy loam	Flanagan[c] silt loam	Keyport[d] silt loam	Myakka[e] sand
% organic matter	1.40	4.02	2.75	2.43
% sand (2.0–0.05 mm)	56	5	21	97
% silt (0.05–0.002 mm)	29	64	62	2
% clay (<0.002 mm)	15	31	17	1
pH	5.6	6.5	6.4	6.3
cation exchange, mequiv/100 g (1 N, pH 7.0, NH_4AcO)	4.8	23.4	8.2	3.9

[a] Soil analyses were performed by the College of Agricultural Sciences, University of Delaware, Newark, DE. [b] Glasgow, DE. [c] Rochelle, IL. [d] Newark, DE. [e] Bradenton, FL.

3021 Radioactivity Detector (Packard Instrument Company) was used immediately after the ultraviolet absorbance detector of the chromatograph to locate radioactive peaks in the effluent.

An additional photolysis experiment was carried out in order to collect and characterize the volatile materials lost in the standard photolysis experiment. A 13-ppm solution of [^{14}C]sulfometuron methyl (15 mL) was placed in a quartz test tube (15 mm i.d. × 15 cm long) which was then stoppered with a rubber serum cap. The tube was laid nearly horizontally in an aluminum reflective tray and placed about 5 in. below the light bank described earlier. There was no cooling water, and the temperature of the solution reached 37 °C. The tube was irradiated continuously for 1 week.

After the irradiation period, the content of the tube was made basic by addition of 1.0 mL of 0.1 N sodium hydroxide by injection, and the tube shaken by hand. The contents were removed and counted by LSC. The alkaline solution was placed in the first of two small gas washing bottles connected in series. The second bottle contained 20 mL of 0.1 N sodium hydroxide. Air was drawn through the two solutions so that any volatiles in the sample would be scrubbed in the alkali solution. The sample was then acidified with 10% sulfuric acid, and air drawn through the apparatus for 45 min. Radioactivity in the trap contents was determined by LSC. To 2.0 mL of the trap contents was added 5 mg of sodium carbonate, and the total carbonate ion content precipitated by addition of 2 mL of 20% barium chloride. After filtration, the radioactivity remaining in the clarified solution was determined by LSC.

Soil Characterization. One-kilogram aliquots of screened (2 mm), homogenized soils were characterized by the College of Agricultural Sciences, University of Delaware (Table I). Organic matter, pH, and CEC were determined on the integral samples. Mechanical analysis, establishing the sand, silt, and clay content, was conducted on the mineral base after the organic matter had been removed by wet oxidation.

Soil TLC Values (R_f). Aliquots of screened soil were hammer milled with a final 400-μm screen. Inspection by microscopy showed the particles to be <10 μm. The hammer milled soils were applied as a water slurry to 20 cm × 20 cm glass plates at a thickness of 400 μm. After drying, duplicate plates were spotted with [^{14}C]sulfometuron methyl (specific activity = 5.9 μCi/mg) and developed for a distance of 10 cm in water. The radiolabeled herbicides were located on the soil TLC plates by autoradiography with Kodak SB-5 X-ray film.

***K* Values (Freundlich Isotherm Constants).** Freundlich Isotherm Constants were determined in duplicate by using the method suggested by the EPA (Environmental Protection Agency) (Hitch, 1982). Five grams of soil (dry weight) were placed in 4-oz polypropylene bottles equipped with polypropylene lined screw caps. To these soils were added 20 mL of a 0.01 N $CaSO_4$ solution containing either 0.2, 0.5, 1.0, 2.5, or 5.0 ppm of radiolabeled sulfometuron methyl. Blanks consisting of only the soil plus 20 mL of 0.01 N $CaSO_4$ were also run. The soil slurries were allowed to equilibrate at 25 °C with agitation in a constant temperature water bath for 24 h after which the slurries were centrifuged and triplicate 1.0-mL aliquots of the clear phase were taken for liquid scintillation counting. LSC was performed with Formula 947 Scintillation Cocktail.

The Freundlich K value(s) were determined from the Y intercept(s) plots of log C_s vs, log C_2. This relationship was obtained after rearrangement of the Freundlich equation (Bailey and White, 1970). The concentration of materials in the soil (C_s) was established by determining the difference between the quantity of radiolabeled material in the starting solution (C_1) and that in solution after equilibration with the soil (C_2). The coefficient of adsorption per unit organic matter (K_{om}) was calculated from:

$$k_{om} = \frac{K \times 100}{\%\ \text{organic matter}}$$

Leaching Studies on Unaged Treated Soils. Screened soil was added to a glass column (2 in. i.d.) and distilled, deionized water was percolated through for settling. Sufficient soil was added until an 18-in. depth had been established.

The chloride breakthrough volume (V_{Cl^-}) (Dannals and Kucharzyk, 1974) was determined for each column by applying a standard solution of Na^{36}Cl (0.22 mg, specific activity 3.11 μCi/mg, radiochemical purity 99%) to the soil surface. Afterwards, 0.22 mg of [^{14}C]sulfometuron methyl (specific activity, 5.9 μCi/mg) was added to correspond to a field application rate of 1 kg/ha. Distilled deionized water (20 in.) was percolated through the column over a 24-h period, the leachate was collected in 10-mL increments, and 1-mL aliquots were removed for LSC in Formula 947. A single value of the chloride breakthrough volume and of the sulfometuron methyl breakthrough volume was obtained simultaneously for each soil column.

To establish the distribution of radiolabeled material retained in the soil after leaching, the soil was extruded from the column, was divided into 2-in. increments, air-dried, homogenized, and analyzed by combustion analysis (Packard Model 306 Tri-Carb Sample Oxidizer) followed by LSC.

Leaching Studies on Aged Treated Soils. A single leaching test was performed on a soil sample treated with [^{14}C]sulfometron methyl and aged in the greenhouse for 30 days. This soil which was treated at a rate of 1 kg/ha corresponded to the uppermost 2-in. layer of the soil column. This aged soil was added, in toto, to the top of a 10-in. column of untreated soil and leached with 20 in. of distilled, deionized water over a 45-day period. The chloride breakthrough volume of the 12-in. column as well as the distribution of radiolabeled materials in the soil and

leachate were determined as previously described.

Octanol/Water Partition Coefficient (K_{ow}). A 2-ppm solution of [^{14}C]sulfometuron methyl in 0.01 M K_2HPO_4, adjusted to pH 7.0, was partitioned against purified (Karickhoff and Brown, 1979) *n*-octanol.

Fifty milliliters of the aqueous [^{14}C]sulfometuron methyl solution was added to each of three 250-mL centrifuge bottles containing 50-mL of *n*-octanol. The centrifuge bottles were tightly capped and after vigorous hand agitation were transferred to a reciprocating shaker–water bath (25 °C) where they were shaken for 15 min. After this equilibration time, these octanol–water mixtures were phase separated by centrifugation at 2500 RPM for 5 min.

After phase separation, duplicate 0.5-mL aliquots were removed from each phase, and the level of ^{14}C in each phase was determined by LSC in Formula 947 Scintillation Cocktail (New England Nuclear). When the aliquots were removed from the water phase, care was taken to insure that no *n*-octanol contaminated the syringe needle.

When the aliquots had been removed for analysis of ^{14}C levels, 100 μL of each water phase were removed and combined. To this combined water phase sample was added 50–100 μg of nonradiolabeled sulfometuron methyl. An aliquot (100 μL) of this mixture was analyzed for levels of [^{14}C]sulfometuron methyl in HPLC system 4. The column eluate corresponding to the elution of sulfometuron methyl was trapped and ^{14}C level determined by LSC. A similar procedure was followed for analysis of the octanol phase.

Following the removal of the water and octanol aliquots for analysis, the entire octanol phase was removed from each of the centrifuge bottles and replaced with fresh octanol. This entire partitioning and analysis procedure was then repeated for a total of three consecutive partitionings.

Fish Accumulation Study. In this dynamic bioaccumulation study, bluegill sunfish (*Lepomis macrochirus*) were selected from a population acquired from Southern Fish Culturists, Inc. in Leesburg, Florida, and acclimated to laboratory conditions for 10 weeks. The means of standard deviations for wet body weights and standard lengths of the experimental fish were 1.43 ± 0.47 g and 3.8 ± 0.4 cm, respectively.

The exposure system was a 4-cell proportional diluter (Mount and Brungs, 1967) modified to allow independent control of test substance addition via metering pumps. This system produced an average turnover of 6 water volumes per chamber per 24 h. Exposure tanks were 57-L all-glass aquaria fitted with an overflow drain to maintain 30-L exposure volumes.

After the system had been in operation for 25 h, 71 fish were placed in each tank. Concentrations of [^{14}C]sulfometuron methyl were maintained at nominal levels of 0.01 ppm and 1.0 ppm in the treatment tanks. Both a carrier solvent (acetone) and dilution water control were used. The concentration of acetone in the solvent control was equivalent to the amount of acetone in the high exposure concentration. Water samples (1.0 mL) were collected daily on normal working days from each exposure chamber and the level of radioactivity determined by LSC.

Exposure to [^{14}C]sulfometuron methyl was continued for 28 days, at which time the fish were transferred to "clean" tanks continuously supplied with fresh water free of test material for the 14 day depuration phase. A 20-mL water sample and 4 fish were collected from each experimental tank on days 0, 1, 3, 7, 10, 14, 21, and 28 of the uptake phase, and on days 1, 3, 7, 10, and 14 of the depuration phase.

Table II. Hydrolysis of Sulfometuron Methyl

incubation time, days	sulfometuron methyl, %		
	pH 5	pH 7	pH 9
0	96	[a]	[a]
0.25	98	97	98
1	94	95	98
2	90	96	97
3	84	98	95
7	70	93	93
14	49	93	95
21	34	88	92
30	22	87	91

[a] Analysis not performed.

Each sample fish was rinsed with water, decerebrated, and blotted dry. The liver, viscera, and portions of muscle were excised, individually weighed, and packaged in combustion cups inside glass vials. All samples were frozen until analyzed for total ^{14}C level by combustion in a Model 306 Sample Oxidizer (Packard Instrument Co.).

Each 20-mL water sample was adjusted to pH 4 with acetic acid and extracted three time with 20-mL portions of methylene chloride. The extracts were combined, dried over anhydrous magnesium sulfate, and concentrated in a stream of nitrogen to 1.0 mL. A 500-μL aliquot of each concentrate was analyzed in HPLC system 1. For each injection, the effluent corresponding to methyl 2-(aminosulfonyl)benzoate (t_{max} 4.7 min) and sulfometuron methyl (t_{max} 11.1 min) was collected and counted (LSC).

RESULTS AND DISCUSSION

Hydrolysis. The stability of sulfometuron methyl in aqueous solution was markedly influenced by pH (Table II). At pH 5, hydrolysis of [^{14}C]sulfometuron methyl was extensive (Table II) with an estimated half-life of 2 weeks. The only other radiolabeled product found in the methylene chloride extracts was methyl 2-(aminosulfonyl)-benzoate (compound I, Figure 1) (60% after 30 days) which was identified by its HPLC retention time. However, further degradation to more polar materials was indicated by the fact that the percentage of the original radiolabel not extracted into methylene chloride rose from an initial value of 1% to 25% at the end of 30 days. When the polar, water soluble material was chromatographed in HPLC system 2, only a single radiolabeled compound was recovered. This radioactive polar material cochromatographed with saccharin in TLC solvent 1 (R_f 0.50) and HPLC system 1 (retention time of 21.8 min). Direct probe mass spectal analysis confirmed the structure of this polar material as saccharin with a base peak (parent ion) of 183 m/z, and major fragments at 76, 92, and 120 mass units.

At pH 7 and pH 9, [^{14}C]sulfometuron methyl was much more stable throughout the course of the 30-day experiments than at pH 5.0 (Table II); only unchanged sulfometuron methyl was detected by HPLC in the methylene chloride concentrates. However, the percentage of total radioactivity not extracted by methylene chloride under the conditions of the analysis rose gradually from about 1% at the start to 12% at the conclusion of the exposure period for both solutions. The nature of this material was not investigated further, but was most likely hydrolysis products.

Aqueous Photolysis. The recovery of total radioactivity in the test solutions decreased with time (Figure 2), and the loss in radioactivity varied from 37 to 56% after 2 weeks. The material balance obtained when the experiment was termined (18th day) showed that although there was very little evaporation of water (<5%) from the irradiated samples, there was extensive loss of volatile

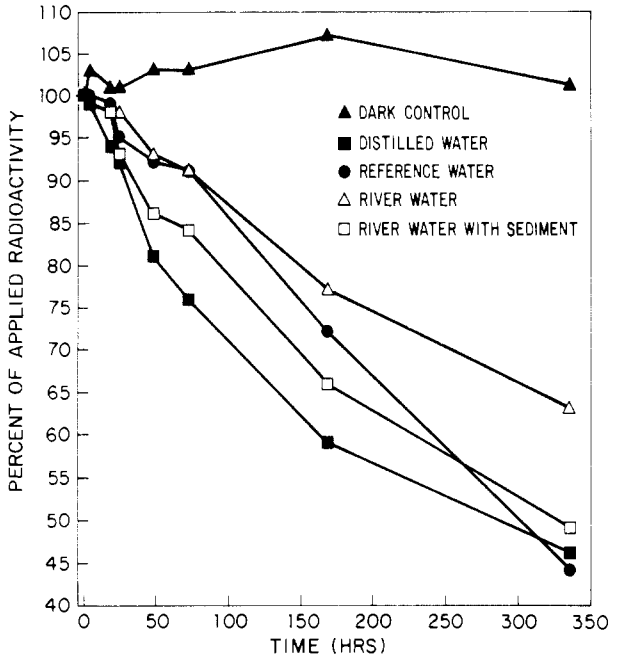

Figure 2. Recovery of radiolabel for photolysis reaction vessels as a function of time.

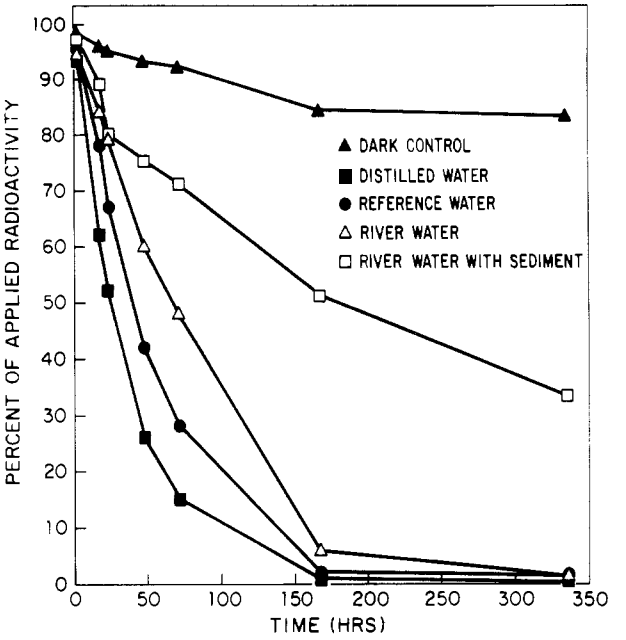

Figure 3. Percentage of intact sulfometuron meethyl remaining in photolysis vessles as a function of time.

radioactive material. The rinses of the covers and beaker walls showed that no residue (<1%) absorbed or condensed on the glassware. On the other hand, little radioactive material was lost from the dark control (3%), although evaporation here had been considerable (26%) over the 18-day period. Evaporation of this solution took place because the beaker was covered only with foil (no glass cover).

During the course of the experiment the nonvolatile, irradiated–radioactive materials became increasingly more polar. At the end of 2 weeks exposure, 80–90% of the radioactivity remaining in solution in the clear photolyzed water was no longer extractable with methylene chloride (intact sulfometuron methyl will partition into methylene chloride). In contrast, the radioactivity in the dark control remained almost all extractable (91%).

These changes were indicative of a rapid breakdown of sulfometuron methyl under photolytic conditions, confirmed by analysis of the methylene chloride extracts for sulfometuron methyl (Figure 3) in HPLC system 1 (retention time of sulfometuron methyl is 16.0 min in this HPLC system). Under the photolytic conditions of this experiment, the half-life of sulfometuron methyl was on the order of 1–3 days. In the dark control, on the other hand, sulfometuron methyl was far more stable with 83% recovered intact after 2 weeks.

HPLC system 1, used in the analysis for sulfometuron methyl, is also capable of determining the normal hydrolysis product (compound I, Figure 1, retention time 5.2 min) and detecting a less polar material which was nearly unretained on this column. (Retention time 1.9–2.5 min.) When the mobile phase was changed to pure CH_2Cl_2, the retention time of this material changed to 4.6 min and cochromatographed with methyl benzoate. The maximum level of methyl benzoate was 6% in the distilled water photolysis vessel, calculated as percent of original total radioactivity. The level dropped to 2% after two weeks.

Compound I is the normal hydrolysis product of sulfometuron methyl, and as such is the only product seen in the dark control. Although compound I appeared as a product in all the samples, methyl benzoate appeared only in the irradiated samples. Methyl benzoate would be expected as an intermediate photolysis product of this sulfonylurea by analogy to the work of Weiss et al. (1980).

Table III. Freundlich Isotherm Constants (K), Soil TLC R_f Values, and Ratios of Soil Column Breakthrough Volumes (V_{sm}) to the Soil Column Void Volume (V_{Cl^-}) for [^{14}C]Sulfometuron Methyl on Four Agricultural Soils

soil	K	R_f	V_{sm}/V_{Cl^-}
Keyport silt loam	0.97	0.53	1.13
Fallsington sandy loam	0.71	0.80	1.51
Myakka sand	1.0	0.85	2.41
Flanagan silt loam	2.85	0.33	2.52

Sediment in the photolyzed river water appears to reduce the rate of breakdown of sulfometuron methyl (Figure 3). However, the conversion of radioactivity to its volatile form was almost as fast in the river water plus sediment as in the other irradiated solutions (Figure 2). The initial breakdown products apparently form at a slower rate in the presence of the sediment and do not accumulate because of further degradation.

The volatile radioactive material lost during the standard photolysis experiment accounted for about half of the original radioactivity after 2 weeks. Evidence that this fraction was truly gaseous was provided by the photolysis experiment conducted in the sealed tube. When the sealed photolysis tube was made alkaline prior to opening, 57% of the initial radioactivity was recovered in the aqueous phase. After acidification, about half of this additional recovery was trapped in an alkali trap and precipitated quanitatively (98%) as barium carbonate.

The identification of $^{14}CO_2$ as a major part of the volatile fraction indicates that the phenyl ring of sulfometuron methyl has been completely destroyed. Attempts to identify intermediate photolysis products met with little success. Chromatography of the aqueous phase of the distilled water photolysis reaction vessel in HPLC system 2 indicated a large number of fragments. None of these fragments was present in quantities sufficient for identification.

Behavior of Sulfometuron Methyl on Soil. The mobility of sulfometuron methyl in soil was dictated by the characteristics of the soil (Table I). On sandy soils (Myakka sand and Fallsington sandy loam) sulfometuron

Table IV. Levels of Radioactivity in Bluegill Sunfish during the Dynamic Bioaccumulation Study[a]

	0.01 ppm level				1.0 ppm level			
exposure time	water	muscle	liver	viscera	water	muscle	liver	viscera
day 1	0.008	<0.001	0.004	0.001	0.619	<0.01	<0.01	0.09
day 3	0.011	0.004	0.015	0.003	1.034	0.03	0.53	0.21
day 7	0.009	<0.001	0.018	0.005	1.009	0.06	1.6	0.40
day 10	0.008	<0.001	0.006	0.001	0.704	0.07	1.4	0.12
day 14	0.011	<0.001	<0.001	0.002	1.062	<0.01	<0.01	0.14
day 21	0.010	0.006	<0.001	0.007	1.020	0.02	<0.01	0.09
day 28	0.010	<0.001	<0.001	0.007	0.881	0.05	1.2	0.10
				Depuration				
day 1	b	<0.001	0.03	0.003	b	<0.01	<0.01	0.20
day 3	b	0.003	0.02	0.010	b	0.04	0.33	0.15
day 7	b	0.001	<0.001	<0.001	b	0.05	1.84	<0.01
day 10	b	<0.001	0.011	<0.001	b	0.06	0.15	<0.01
day 14	b	0.005	0.015	0.002	b	0.16	1.5	0.10

[a] Each number represents the average of four replicates and is calculated as ppm of sulfometuron methyl. [b] Not determined.

methyl was mobile on soil TLC plates (R_f 0.8). On loamy soil (Flanagan) sulfometuron methyl showed low to intermediate mobility (R_f 0.3).

The mobility of sulfometuron methyl on soil TLC plates (Table III) was related to the Freundlich isotherm constants measured on these soils (Table III). On soils where sulfometuron methyl had the highest mobilities (R_f values of 0.80, 0.53, and 0.85 respectively on Fallsington, Keyport, and Myakka soils), it also had the smallest K values (0.71, 0.97, and 1.0, respectively). Of the four soils tested, sulfometuron methyl had the greatest affinity for Flanagan silt loam. On this soil, sulfometuron methyl had a K value of 2.85 and a R_f value on soil TLC plates of 0.33.

The difference in affinity of sulfometuron methyl for the different soils appears to be due to differences in soil organic matter content and soil pH. Sulfometuron methyl had the greatest affinity for Flanagan silt loam as measured by K value and soil TLC R_f value; this soil also had the highest organic matter content. Of the other three soils tested, sulfometuron methyl had equivalent affinities for the Keyport and Myakka soils; these two soils had similar levels of organic matter.

The soil pH has an effect on soil herbicide interactions, as demonstrated by the behavior of sulfometuron methyl on Fallsington soil TLC plates. Fallsington soil has the lowest amount of organic matter of the four soils tested, but had the second lowest R_f value. At the pH of this soil (pH 5.6), sulfometuron methyl (a weak acid, pKa 5.2) would be more protonated than on the other soils (average pH 6.4). Sulfometuron methyl becomes much less water soluble as it becomes protonated. (OUST HERBICIDE Non Crop Information Bulletin, solubility 10 ppm at pH 5 and 300 ppm at pH 7), and presumably would have more affinity for the hydrophobic regions of the soil particle.

The leaching behavior of [^{14}C]sulfometuron methyl on soil columns was reasonably consistent with soil K values but less so with soil TLC values. Table III lists the ratios of breakthrough volume of sulfometuron methyl (V_{sm}) to the chloride breakthrough volume (V_{Cl^-}) of the soil columns. Sulfometuron methyl was a mobile compound in all the soils, with mobility decreasing in the order Keyport silt loam > Fallsington sandy loam > Myakka sand > Flanagan silt loam. As with the soil TLC plates, [^{14}C]-sulfometuron methyl was retarded the most on Flanagan silt loam.

In Fallsington sandy loam treated with [^{14}C]sulfometuron methyl and aged in the greenhouse for 30 days, 76% of the applied radiolabel leached from a 12-in. soil column over a 45-day period. The breakthrough volume for these leachable materials was 8.63 in. of water or $1.73V_{Cl^-}$. Therefore, most of the residual materials remaining on the soil after the 1-month incubation period were mobile. Combustion analysis of the leached soil showed that much (11%) of the residual ^{14}C-labeled material remained in the 0–2-in. layer with the remainder of the nonleachable radioactivity distributed evenly in each 2-in. increment throughout the remainder of the column.

Octanol–Water Partition Coefficient. The partition ratio of sulfometuron methyl between octanol and an aqueous phase was determined in order to predict the bioaccumulation potential of this herbicide. The partition ratio obtained was not strictly speaking a rigorous K_{ow}, because the partition of sulfometuron methyl ratio was obtained between 0.01 M phosphate buffer, pH 7.0, and octanol, not between pure distilled water and octanol. A partition ratio between pH 7 phosphate buffer and octanol more nearly mimics expected environmental conditions where aqueous phases will be buffered to some degree, presumably near pH 7.0. Three successive partition ratios were determined and were respectively 0.32, 0.31, and 0.31. These values were not corrected for any radiolabeled species in either the aqueous or octanol phase other than [^{14}C]sulfometuron methyl because the radiochemical purity of [^{14}C]sulfometuron methyl in the aqueous and octanol phases respectively was 96% and 95%. A partition ratio of this magnitude is indicative of a compound with low bioaccumulation potential (Karickhoff and Brown, 1979). This predicted low tendency of sulfometuron methyl to bioaccumulate was substantiated by the fish accumulation study.

Fish Bioaccumulation Sudy. When sulfometuron methyl was tested in a dynamic fish bioaccumulation experiment, we found that no significant bioaccumulation occurred, as predicted by the octanol/H_2O partition. Table IV lists the concentration of radioactivity in the water, and in the fish tissue, during this study. Analysis of the water found [^{14}C]sulfometuron methyl as the only detectable radioactive species. The level of radioactivity measured in tissue represents random variations between normal background and the level of radioactivity in the water.

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Registry No. Sulfometuron methyl, 74222-97-2; methyl 2-(aminosulfonyl)benzoate, 57683-71-3; saccharin, 81-07-2; methyl benzoate, 93-58-3; carbon dioxide, 124-38-9.

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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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