Products and Kinetics of Cloransulam-methyl Aerobic Soil Metabolism

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Cloransulam-methyl aerobic soil metabolism was investigated to ascertain rates and products of environmental dissipation. Cecil loamy sand and Hanford loam fortified with 66 ng of [^{14}C]-cloransulam-methyl g^{-1} of soil were incubated in the dark at 25 °C and 100 kPa of moisture potential under positive O_2 pressure for up to 357 days. Cloransulam-methyl exhibited a biphasic pattern of degradation. Aerobic soil half-lives were 9 and 13 days, respectively, on Cecil and Hanford soils for data fit to a two-compartment model and 16 and 21 days, respectively, for data fit to a first-order initial rate model. Degradation rates decreased ≈10-fold when soils were incubated at 5 °C or when sterilized by γ-irradiation. Evolved $^{14}CO_2$ accounted for up to 10% of applied ^{14}C. Metabolites (cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam) occurred in acetone/acetic acid extracts at maximum concentrations of 25, 9, and 8 ng g^{-1}, respectively, and were significantly less phytotoxic than the parent molecule. Bound residues accumulated up to 76% of applied ^{14}C. Degradation rate and sorptivity were further investigated on 16 soils fortified with 189 ng g^{-1} of [^{14}C]cloransulam-methyl and incubated for up to 55 days. Apparent first-order half-lives ranged from 13 to 28 days (mean ± SE = 18 ± 4 days). Apparent K_d values, produced using a two-step extraction, ranged from 0.19 to 4.89 L kg^{-1} for cloransulam-methyl. Cloransulam-methyl metabolites, when present, tended to exhibit lower K_d values than the parent molecule. Apparent K_d increased with time.

Keywords: *DE-565; triazolopyrimidine sulfonanalide; soil degradation*

INTRODUCTION

Cloransulam-methyl [*N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide] is a triazolopyrimidine sulfonanilide herbicide effective in control of broadleaf weeds in soybean through acetolactate synthase (ALS) inhibition (DowElanco, 1994; Jachetta et al., 1994; Hunter et al., 1994). Proposed application methods for the molecule include preplant incorporation and preemergent treatment at maximum label rates of 17.5 and 44 g ha^{-1}, respectively.

Cloransulam-methyl [CAS Registry No. (provided by the author) 147150-35-4] has a molecular mass of 429.81 g mol^{-1}. It is stable as a solid at room temperature for >3 months. Water solubility at 20 °C is approximately 3 or 184 mg L^{-1} in pH 5 or 7 buffers, respectively. Solubility in deionized water is approximately 16 mg L^{-1} (DowElanco, 1994). Solubilities in acetone and acetonitrile are 4360 and 5500 mg L^{-1}, respectively (DowElanco, 1994). Cloransulam-methyl dissolved in acetonitrile, water, and acetic acid has an absorption maximum at 248 nm. Vapor pressure is negligible (4×10^{-14} Pa at 25 °C), and the pK_a is 4.81 at 20 °C (DowElanco, 1994).

This investigation was conducted to determine the rate and products of aerobic soil metabolism of cloransulam-methyl and to characterize the distribution of degradation rates and sorptivities across a suite of soils. An initial study examined aerobic soil metabolism of cloransulam-methyl using two differently radiolabeled test substances and two different soils. A subsequent multisoil kinetic study was conducted to develop distributions of degradation rates and apparent sorptivities for 16 soils representative of the midwestern and southern United States.

MATERIALS AND METHODS

Metabolism Study. *Chemicals.* The test substances were [*Pyr*-7,9-^{14}C]cloransulam-methyl (specific activity 27.79 mCi mmol^{-1}; labeled in the 7- and 9-positions of the pyrimidine ring; 99+% radiochemically pure at the time of preparation) and [*Ph*-UL-^{14}C]cloransulam (specific activity 29.9 mCi mmol^{-1}; uniformly labeled in the phenyl ring; 99+% radiochemically pure at the time of preparation). Chromatographic standards (Figure 1) were cloransulam-methyl [purity >98%], 5-hydroxycloransulam-methyl [*N*-(2-carbomethoxy-6-chlorophenyl)-5-hydroxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide; purity >95%;], cloransulam [*N*-(2-carboxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide; purity ≥97%], 5-hydroxycloransulam [*N*-(2-carboxy-6-chlorophenyl)-5-hydroxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide; purity >97%], and *N*-methylcloransulam-methyl (purity 96%). All other solvents or reagents used were of reagent grade or better and were typically obtained from Fisher Scientific (Pittsburgh, PA).

Soils. The soils used were Hanford loam [coarse-loamy, mixed, nonacid thermic Typic Xerothents: pH 7.0, organic carbon (OC) 0.48%, sampled from Fresno, CA] and Cecil loamy sand (clayey, kaolinitic, thermic Typic Kanhapludults: pH 6.3, OC 0.37%, sampled from Oconee, GA) (Table 1).

Analytical Methods. 1. Chromatography. Reversed phase HPLC was used for isolation of the parent cloransulam-methyl and metabolites. The methodology typically employed a Waters (Marlborough, MA) μBondapak C_{18} 8 mm × 100 mm column and a mobile phase consisting of water, acetonitrile, and acetic acid. A selected subset of samples was analyzed

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0021-8561/96/1444-0324$12.00/0

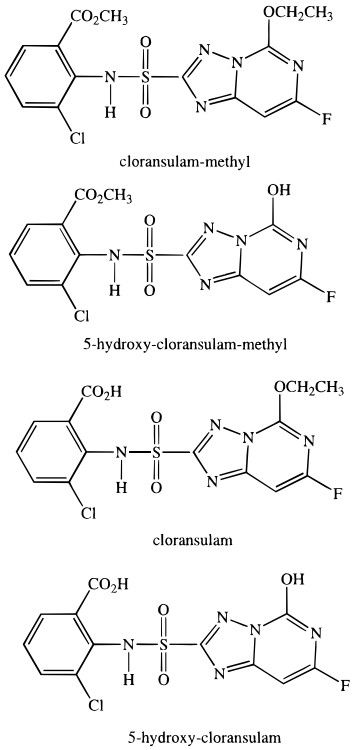


Figure 1. Structure of cloransulam-methyl and aerobic soil metabolites.

using a Hewlett-Packard (Palo Alto, CA) Hypersil ODS 5 μm C_{18} 4.6 mm × 200 mm steel column.

Radiolabeled samples were co-injected with an internal standard comprised of 1000 mg L^{-1} each of nonlableled 5-hydroxycloransulam, 5-hydroxycloransulam-methyl, cloransulam, cloransulam-methyl, and *N*-methylcloransulam-methyl. Nonlabeled standards were detected by UV at 264 nm. Typical retention times were 11, 15, 24, 29, and 34 min for 5-hydroxycloransulam, 5-hydroxycloransulam-methyl, cloransulam, cloransulam-methyl, and *N*-methylcloransulam-methyl, respectively. Fractions were collected from the HPLC and assayed for radioactivity by liquid scintillation counting (LSC); these data were used to construct radiochromatograms.

Confirmatory chromatography was conducted for selected samples by normal phase TLC using a mobile phase of 55:45 v/v acetone/hexane with 3% acetic acid and Whatman (Clifton, NJ) silica gel 60A LK6F plates. Developed plates were scanned for radioactivity using an Ambis Radioanalytic Imaging System (Scanalytics, San Diego, CA).

2. Radioanalysis. Total radioactivity measurements were performed using microprocessor-controlled Packard (Downers Grove, IL) liquid scintillation counters. The minimum quantification amount for a "well-known" blank (=20 dpm) (Currie, 1968) averaged 0.42, 0.035, and 0.42% of applied radiocarbon for NaOH trapping solutions, soil extracts, and combusted soil residues, respectively. The minimum quantifiable limit for extracted soil residues was 9 ng g^{-1}, and the minimum detectable limit (MDL) was 2 ng g^{-1}.

3. Metabolite Confirmation. Cloransulam-methyl and metabolites were prepared for confirmation by GC/MS using solvent extraction, solid phase extraction, and derivatization. Derivatization of cloransulam-methyl and metabolites used triethyloxonium tetrafluoroborate (TEOTFB), resulting in the ethylation of the acidic sulfonamide nitrogen group of each, the carboxylic acid group of cloransulam and 5-hydroxycloransulam, and the hydroxyl group of each 5-hydroxy metabolite (Table 2). Metabolites containing the 5-hydroxy group yield two products due to keto−enol tautomerization; this results from O-ethylation of the enol tautomer and N-ethylation of the keto tautomer. It was necessary to separate cloransulam-methyl and cloransulam from the 5-hydroxy metabolites prior to derivatization because identical derivatization products are realized (Table 2).

The scheme for extraction, derivatization, and identification of metabolites (Figure 2) involved extraction of triplicate 10-g subsamples twice with 9:1 acetone/0.1 N HCl. A subsample of the combined liquid phases was reduced in volume using a Zymark (Hopkin, MA) Turbo Vap unit, brought to 20 mL with 0.1 M HCl and then drawn through a preconditioned C_{18} solid phase extraction (SPE) column. The 5-hydroxy metabolites were eluted off the column with 16 mL of a solution containing 20% acetonitrile and 3% acetic acid in 0.1 M HCl. The 5-hydroxy metabolites were partitioned twice into ethyl acetate in the presence of excess NaCl, and the ethyl acetate extracts were composited. The SPE column was dried under vacuum for about 20 min. Next, cloransulam-methyl and cloransulam were eluted from the column with 3 mL of acetonitrile. Both extract fractions were dried using the Turbo Vap.

Samples brought up in 1 mL of acetone were derivatized using 10 μL of triethylamine and 200 μL of 1.0 M TEOTFB in dichloromethane and allowed to react at ambient temperature for about 20 min. Derivatives were partitioned into methyl *tert*-butyl ether in the presence of 5% NaCl solution. The methyl *tert*-butyl ether layer was recovered, dried, and subsequently dissolved in toluene for GC/MS analysis.

Analysis was performed with a Hewlett-Packard Model 5890 gas chromatograph and Model 5971A mass spectrometer. The column used was a J&W Scientific (Folsom, CA) DB-5, 30 m × 0.25 mm i.d. × 0.25 μm film thickness. Helium was the carrier gas (60 cm s^{-1} linear velocity). The detector was maintained at 310 °C and the injector at 280 °C. The oven temperature was varied from 120 to 325 °C at a rate of 20 °C min^{-1}. Selected ion monitoring (SIM) was performed for the major fragments of *m/z* 180, 196, 212, and 226 in electron impact ionization mode. The prominent fragment ions observed in the electron impact mass spectra of all derivatives result from loss of the sulfonyl triazolopyrimidine radical, giving an M − 245 ion or *m/z* 212 and 226 ion for products containing the methyl and ethyl ester groups, respectively. The M − 245 ions undergo further fragmentation through loss of the methanol or ethanol to *m/z* 180 and through loss of methane or ethane to *m/z* 196. As such, the cloransulam-methyl derivative is distinguished from the cloransulam derivative, *N*-ethylcloransulam, by retention time and the characteristic M − 245 ion intensity. Since the prominent ions monitored fingerprint the aniline portion of the molecule, both derivatization products will characterize the 5-hydroxy metabolite SIM fragment patterns as well. The isomeric products are distinguished chromatographically as the 5-oxo isomers exhibit a much longer retention time.

Experimental Methods. 1. Preparation of ^{14}C Dosing Solutions. Dosing solutions of the test materials prepared in acetonitrile were delivered to 50 g of oven-dry equivalent (od) moist soil. Six replicate aliquots of the dosing solutions were taken during the time course of application. On the basis of these amounts, the rates of dosing achieved were 60 ± 3 and 69 ± 1 ng g^{-1} for [*Pyr*-7,9-^{14}C]cloransulam-methyl and [*Ph*-UL-^{14}C]cloransulam-methyl, respectively. These dosing rates are equivalent to nominal field application rates of 30 and 35 g ha^{-1} for an average soil bulk density of 1.33 g cm^{-3} and a 15-cm depth of incorporation.

Additional [*Ph*-UL-^{14}C]cloransulam-methyl dosing solution, for use in low-temperature incubation and sterile soil studies, was prepared by dilution of the solution described above. The rates of dosing achieved for these treatments was 73 and 69 ng g^{-1} of od soil for Hanford loam and Cecil loamy sand, respectively.

2. Preparation, Dosing, and Sampling. a. Core Study. Moist soil (nominally 50-g od equivalant) was weighed into aerobic soil incubation flasks (biometers) (Laskowski et al., 1983). Appropriate aliquots of the [^{14}C]cloransulam-methyl spiking solutions were delivered to the soil, soils were mixed with a spatula, and sufficient deionized water was added to adjust the final moisture to 100 kPa. After mixing a second time, 100 mL of 0.2 M NaOH was added to side chambers (CO_2 traps) of each biometer. Flasks were placed under positive O_2 pressure in the dark at 25 °C.

Duplicate flasks of treated soils were sampled and analyzed for each ring label at each sampling interval. At each time of

Table 1. Selected Properties of Test Soils

soil	series	taxonomic family	pH	OC, %	CEC, cmol kg^{-1}	100-kPa moisture %	viability,[a] % mineralized
		Soil Metabolism Study					
M396	Cecil loamy sand	clayey, kaolinitic, thermic Typic Kanhapludults	6.3	0.37	1.9	5	
M388	Hanford laom	coarse-loamy, mixed, nonacid thermic Typic Xerothents	7.0	0.48	11.5	12	
		Multisoil Kinetics Study					
M345	Hoytville clay	fine, illitic, mesic Mollic Ochraqualfs	7.0	1.23	14.4	28	24
M354	Barnes clay loam	fine-loamy, mixed Udic Haploborolls	7.8	2.52	20.1	20	32
M355	Cecil sandy loam	clayey, kaolinitic, thermic Typic Kanhapludults	7.1	0.31	2.8	6	34
M356	Appling coarse sandy clay loam	clayey, kaolinitic, thermic Typic Kanhapludults	6.6	0.60	3.0	7	29
M369	MN clay loam		7.4	1.94	17.3	21	29
M373	Sharkey silty clay	very-fine, montmorillonitic, thermic Vertic Haplaquepts	7.4	1.06	19.9	26	28
M378	MN loam		5.7	2.96	18.1	21	29
M388	Hanford loam	coarse-loamy, mixed, non-acid thermic Typic Xerothents	7.0	0.48	11.5	12	30
M393	Catlin silt loam	fine-silty, mixed, mesic Typic Agriudoll	6.5	1.96	13.5	14	30
M395	Tama silt loam	fine-silty, mesic Typic Agriudoll	6.8	2.52	11.4	17	32
M396	Cecil loamy sand	clayey, kaolinitic, thermic Typic Kanhapludults	6.3	0.37	1.9	5	27
M398	Mhoon clay loam	fine-silty, mixed, nonacid, thermic Typic Fluvaquents	7.2	1.02	19.0	17	31
M400	Barnes loam	fine-loamy, mixed Udic Haploborolls	7.9	2.70	22.2	20	29
M403	Hanford sandy loam	coarse-loamy, mixed, nonacid thermic typic Xerothents	7.5	0.56	6.9	7	26
M404	Catlin silt loam	fine-silty, mixed, mesic Typic Agriudolls	6.9	2.08	12.3	17	30
M405	Commerce silt loam	fine-silty, mixed, nonacid, thermic Aeric Fluvaquents	7.7	0.94	9.7	13	33

[a] Percent of applied [^{14}C]glucose detected as ^{14}CO, after 192 h of incubation.

Table 2. Products of Cloransulam-methyl and Metabolite Derivatization with Triethyloxonium Tetrafluoroborate (TEOTFB)

analyte	product(s) of derivatization
cloransulam-methyl	*N*-ethylcloransulam-methyl
cloransulam	*N*-ethylcloransulam-ethyl
5-hydroxycloransulam-methyl	*N*-ethylcloransulam-methyl, *N*-ethyl-5-oxo-6-(*N*-ethyl)cloransulam-methyl
5-hydroxycloransulam	*N*-ethylcoransulam-ethyl, *N*-ethyl-5-oxo-6-(*N*-ethyl)cloransulam-ethyl

sampling NaOH trapping solution was recovered from the side chambers and 1-mL aliquots were assayed for ^{14}C by LSC. For the final time of sampling, aliquots of trapping solution were reacted with an excess of $BaCl_2$ to confirm the presence of dissolved CO_2 and carbonates. Sampling times were 0, 3 , 7, 14, 21, 28, 56, 129, 224, and 357 days after treatment (DAT).

b. Supplementary Studies with Sterile Soils and Low-Temperature Incubation. Moist Hanford loam (5 g) was weighed into borosilicate glass tubes for use in studies of soils incubated at low temperature (5 °C) or sterilized by γ-irradiation.

For the sterile treatments, soils in capped tubes were submitted to the Nuclear Reactor Laboratory of the University of Michigan, Ann Arbor, where they were exposed to a ^{60}Co source for a gamma dose of 5×10^6 rad. Duplicate tubes were sampled prior to fortification with [^{14}C]cloransulam-methyl to verify that sterility had been achieved by culturing an aliquot of the soil in tryptase soy broth.

The remaining sterile treatments and those samples designated for low-temperature incubation were dosed with [*Pyr*-^{14}C]cloransulam-methyl. Soils received no additional moisture; the moisture potential on incubation was approximately 60% of 33 kPa. Low-temperature treatments were incubated in the dark at 5 °C, and sterile treatments were incubated in the dark at 25 °C. Low-temperature and sterile treatments were sampled at 0, 7, 14, 28, 58, 110, and 397 DAT.

3. Soil Extraction. At each time of sampling, soils were extracted with acidified acetone extractant (79:20:1 acetone/water/glacial acetic acid). Approximately 5 g of moist soil was weighed into 25-mL screw-capped centrifuge tubes along with 15 mL of extracting solution. The soil plus extractant was shaken for 1 h and centrifuged at about 1600 rpm for 10 min, and the supernatant was decanted to 50-mL volumetric flasks. The extractions were repeated an additional two times, supernatants were composited, and the total volume was brought to 50-mL with extracting solution. The extracts were mixed by inversion and transferred to brown glass bottles and refrigerated when not in use.

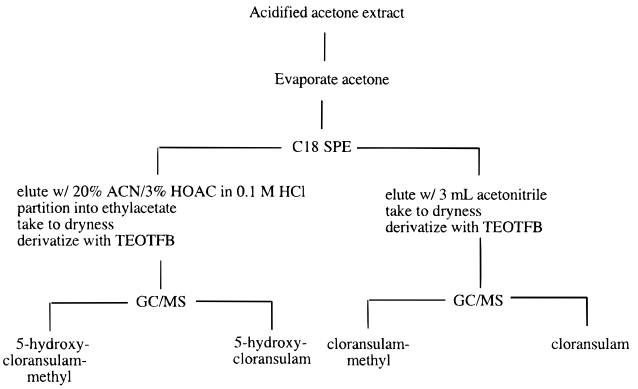


Figure 2. Scheme for isolation and identification of chloransulam-methyl and aerobic soil metabolites.

Aliquots of soil extracts (typically 1 mL) were assayed for total ^{14}C by LSC. Extracts were prepared for HPLC by evaporating an aliquot (typically 10 mL in a Reactivial) to ≈1 mL under a stream of N_2. This was then brought to 2 mL volume with acetonitrile and was filtered through an 0.2-μm Gelman (Ann Arbor, MI) PTFE Acrodisc; 500 μL of the filtered solution was analyzed by HPLC co-injected with 25 μL of the mixed chromatographic internal standard (see Chromatography).

4. Postextraction Combustion. The residue from soil extractions was air-dried and crushed, and subsamples (typically duplicate samples of 0.5−1 g) were analyzed for residual ^{14}C by oxidation and trapping of $^{14}CO_2$. The combustion recoveries were performed robotically using a Harvey (Hillsdale, NJ) OX-400 biological oxidizer coupled to a Zymate II robot. The $^{14}CO_2$ evolved was trapped in a scintillation vial containing 15 mL of Harvey carbon-14 cocktail to which 2.5 mL of Permafluor cocktail was subsequently added; assay of activity was performed by LSC. Occasionally, samples were combusted manually using a Harvey OX-300 biological oxidizer.

5. Characterization of Bound Materials. Pilot studies to determine the extractability of cloransulam-methyl and residues from soil aged for 140 days showed that ^{14}C recalcitrant to three sequential extractions with the acidified acetone extractant was released with continued extraction and/or modification of the acid component of the extraction mixture. Therefore, selected samples were re-extracted with acetone/1 M HCl (90:10 v/v) to ascertain the effect on recoveries of cloransulam-methyl and metabolites.

Following the acetone/mineral acid extraction of selected samples, the residual soil was extracted with a heated citrate/

dithionate mixture (<80 °C). This mixture was characterized for its molecular weight distribution using molecular cutoff filtration. The residual soil was next extracted with 0.1 M NaOH, and aliquots of the extract were assayed for ^{14}C. Finally, the residual soil was combusted to determine what amount of applied radiocarbon was recalcitrant to this series of extractions.

6. Storage Stability. Typically, soils were extracted the day of sampling and chromatography was conducted shortly thereafter. Storage stability was demonstrated for selected samples that were re-extracted and analyzed at a later date as well as for selected extracts that were reanalyzed following a period of storage. Cloransulam-methyl, cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam were shown to be stable in extracts stored for up to 339 days and in soils stored for up to 601 days.

7. Statistical Methods. Statistical analysis was limited to means and standard errors for the summarization of all results. Best-fit apparent kinetics were fit by SimuSolv (The Dow Chemical Co., Midland, MI) nonlinear modeling and optimization software; fit of models was described by the standard deviation for kinetic parameters and the percent variation explained for the overall model (Steiner et al., 1986). Data were also fit to apparent first-order kinetics by regression of natural logarithm transformed recoveries of cloransulam-methyl on time using Cricket (Malvern, PA) software to output the best-fit line and R^2.

Multisoil Kinetics Study. *Chemicals.* Chemicals were the same as described for the metabolism study. [*Ph*-UL-^{14}C]-Cloransulam-methyl was the test material. Reference standards of nonradiolabeled cloransulam-methyl and metabolites were used to establish the TLC R_f.

Soils. The soils were chosen to reflect a variety of common conditions across the southern and midwestern United States. Soils were collected from 1990 through 1991. They were sieved to pass 2-mm diameter openings and stored refrigerated in a moist condition until use. Taxonomic description and selected physicochemical properties of these soils are summarized in Table 1.

Since soils had been sampled and stored for various lengths of time, $^{14}CO_2$ evolution with time was compared among soils treated with [^{14}C]glucose to assure that all soils were microbially active. Moist soil samples (5-g od equivalent weight) were weighed into 50-mL serum vials and adjusted to 33-kPa moisture potential. Samples were preincubated in the dark for 3 days at 25 °C and then fortified with [^{14}C]glucose solution (0.13 nmol g^{-1}). Vials containing 1 mL of 2 N NaOH trapping solution were suspended within the serum vials for trapping of $^{14}CO_2$. Treated soils were incubated in the dark at 25 °C. Trapping solutions were sampled, assayed by LSC, and replenished with NaOH at 24, 48, 96, and 192 h following treatment. After the final sampling of the NaOH trap, the soils were air-dried and then combusted to determine materials balance. Microbial viability was expressed as the percent of total [^{14}C]glucose mineralized (Table 1).

Experimental Methods. 1. Preparation, Spiking, and Sampling. For each soil and sampling interval, 5 g of moist soil was weighed into a 15-mL borosilicate glass centrifuge tube. The soils were brought to 100-kPa moisture potential with glass-distilled water and stored at 25 °C until use.

Moist soils were spiked with [^{14}C]cloransulam-methyl solution to achieve 189 ng $g^{-1}$of soil. This level of fortification is equivalent to a nominal field application of 95 g ha^{-1} (or 2.2 times the maximum projected field use rate) when distributed to a 15-cm depth in soil with bulk density of 1.33 g cm^{-3}. The exaggerated level was used to facilitate metabolite identification by the TLC procedures employed. Soils were mixed well after spiking.

Fortified soils, in centrifuge tubes, were placed into the sample side of the biometer flasks, and the flasks were sealed with ground glass stoppers. The sidearm flask of the biometer contained 40 mL of 0.2 M NaOH for trapping of evolved $^{14}CO_2$. Each flask was placed in the incubator and attached to an oxygen manifold by an expansion tube. Biometer flasks were incubated in the dark at a setting of 25 °C under a positive O_2 pressure of 35 kPa. Times of sampling were 0, 2, 6, 13, 20, 27, and 55 DAT.

2. Soil Extraction. At each time of sampling, the volatile trapping solutions were removed and triplicate 1-mL aliquots were counted by LSC and averaged. The centrifuge tube with soil was also removed from the incubation flask, and the initial weights of the tube, soil, and moisture were recorded. For each soil, an appropriate volume of 0.01 M $CaCl_2$ was added to achieve a water to soil ratio of 0.6. The weights of the tube, soil, and $CaCl_2$ were recorded. The sample was then placed horizontally on an Eberbach (Ann Arbor, MI) reciprocating shaker and allowed to shake for 30 min on high speed. The sample was centrifuged in a DuPont (Wilmington, DE) Sorvall RC-5 centrifuge at approximately 5000 rpm for 20 min. The supernatant was removed and stored in a refrigerator at a setting of 5 °C until analyzed, and the tube, soil, and remaining water were weighed. The soils were then subjected to three repeated organic solvent (90:10 v/v acetone:water) extractions for which the soil/extract mixture was shaken first for 2 h and then for 30 min on high speed. These subsequent organic extractions were performed with 5 mL of the mixture. After shaking, the samples were centrifuged at approximately 5000 rpm for 20 min and the supernatant was decanted and composited. The supernatant from the three organic solvent extractions was then reduced in volume under N_2 and resuspended in a 2-mL volumetric flask with acetone/water (90:10 v/v). Organic extracts were filtered using Gelman PTFE 0.45-μm pore-size syringe filters and stored in a 5 °C refrigerator until analyzed. The residual soils, following extraction, were air-dried and subsamples (typically duplicate 0.5-g samples) were analyzed for residual ^{14}C by oxidation and trapping of $^{14}CO_2$ as previously described.

3. Analysis. Triplicate 100-μL aliquots of the extraction liquid were counted by LSC as previously described. The extracts from both the $CaCl_2$ and the organic extractions were analyzed by TLC using a normal phase 60 Å TLC plate with a preabsorbent strip fluorescent at 254 nm. Typically, eight lanes per plate were spotted with 100-μL aliquots of sample extracts, and an additional lane was spotted with 100 μL of a stock solution containing 1000 μg L^{-1} each of cloransulam-methyl, cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam. The plates were developed using 55:45 acetone/hexane with 3% acetic acid. The developed plates were radioscanned for 135 min, and the distribution of parent and the degradation products was determined. Approximate R_f values were 0.07, 0.28, 0.43, and 0.92 for 5-hydroxycloransulam, 5-hydroxycloransulam-methyl, cloransulam, and cloransulam-methyl, respectively.

4. Storage Stability. Samples were extracted the day of sacrifice, and analyses by LSC and TLC were performed on the extracts within 2 weeks of extraction. Time zero samples were frozen following fortification and extracted 72 DAT. Frozen storage appeared to decrease extractability of cloransulam-methyl from soil. Therefore, the time zero values were not used in the determination of half-life.

5. Statistical Methods. Statistical analysis was limited to means and standard errors for the summarization of results. Data were fit to apparent first-order kinetics by regression of the natural logarithm of cloransulam-methyl on time using Delta Graph (DeltaPoint, Monterey, CA) software.

RESULTS AND DISCUSSION

Metabolism Study. *Material Balance.* The average material balances over the time course of the study were 94 ± 7% of applied ^{14}C for the Hanford loam and 97 ± 6% of applied ^{14}C for the Cecil loamy sand (Tables 3 and 4).

Radiocarbon Distribution. The distribution of radiocarbon observed with time after application of [^{14}C]-cloransulam-methyl to soil is summarized in Tables 3 and 4 for Hanford loam and Cecil loamy sand, respectively. The data presented for each ring label represent the average of duplicate treatments.

Table 3. Product Distribution and Material Balance for Hanford Loam Fortified with [^{14}C]Cloransulam-methyl

		% of applied radiocarbon							
time, DAT	ring label	parent	acid	hydroxy	hydroxy acid	other	CO_2	bound	total
0	phenyl	92	0	0	0	3		6	100
	pyrimidine	103	0	0	0	1		6	110
3	phenyl	70	1	4	1	0	0	9	85
	pyrimidine	69	2	2	0	4	0	17	94
7	phenyl	77	3	3	0	2	1	12	98
	pyrimidine	76	2	2	0	4	1	10	95
14	phenyl	56	6	5	3	2	1	19	91
	pyrimidine	57	5	5	1	3	3	20	93
21	phenyl	36	9	7	0	7	1	22	82
	pyrimidine	36	8	8	0	6	4	27	88
28	phenyl	19	8	11	7	7	2	26	81
	pyrimidine	31	14	10	5	3	4	25	92
56	phenyl	15	21	11	9	2	3	41	103
	pyrimidine	16	21	10	5	7	6	31	95
129	phenyl	5	11	5	11	5	7	47	90
	pyrimidine	7	16	7	8	7	8	45	99
224	phenyl	4	15	6	11	4	4	49	93
	pyrimidine	3	14	6	10	7	5	56	101
357	phenyl	3	14	6	10	7	11	45	96
	pyrimidine	2	10	2	6	13	10	44	87

Table 4. Product Distribution and Material Balance for Cecil Loamy Sand Fortified with [^{14}C]Cloransulam-methyl

		% of applied radiocarbon							
time, DAT	ring label	parent	acid	hydroxy	hydroxy acid	other	CO_2	bound	total
0	phenyl	96	1	0	0	1		1	98
	pyrimidine	104	1	0	0	0		1	107
3	phenyl	69	12	3	0	1	0	7	93
	pyrimidine	73	9	5	0	2	0	6	95
7	phenyl	64	14	6	0	2	1	9	97
	pyrimidine	57	23	7	0	1	0	8	96
14	phenyl	39	26	4	0	7	1	9	86
	pyrimidine	39	18	17	2	1	1	8	86
21	phenyl	23	32	9	0	6	2	22	95
	pyrimidine	22	31	11	1	7	2	20	95
28	phenyl	13	37	8	3	2	2	32	97
	pyrimidine	22	29	16	0	3	2	23	96
56	phenyl	12	23	10	4	8	3	43	103
	pyrimidine	7	26	6	4	5	5	45	97
129	phenyl	5	12	5	2	7	5	61	97
	pyrimidine	4	18	3	4	5	6	50	91
224	phenyl	4	12	3	2	5	4	65	95
	pyrimidine	6	13	4	3	5	6	62	99
357	phenyl	2	10	2	0	7	7	78	106
	pyrimidine	2	10	1	2	6	11	74	108

1. Hanford Loam. The aerobic degradation of cloransulam-methyl was rapid in Hanford loam, for which the recoverable [^{14}C]cloransulam-methyl averaged 2−3% of applied radiocarbon at 357 DAT (Table 3). The similarity in the patterns of parent and metabolites observed from the differently ring-labeled substrates indicated that metabolic separation of the phenyl and pyrimidine rings by sulfonanilide bridge cleavage did not occur. Mineralization of the ring structures resulted in the evolution of 10−11% of applied radiocarbon as $^{14}CO_2$ on average by 357 DAT. Bound radiocarbon not extracted by acidified acetone steadily increased as soils aged, reaching 44% of applied radiocarbon at 357 DAT.

The primary metabolite extracted from Hanford loam was cloransulam, which reached 21% of applied radiocarbon by 56 DAT and then declined (Table 3). Both 5-hydroxycloransulam-methyl and 5-hydroxycloransulam were identified at peak concentrations of 11% of applied radiocarbon and declined to ≤10% of applied radiocarbon by 357 DAT. Other chromatographic peaks typically occurring at <5% of applied radiocarbon were observed sporadically throughout the study. A peak eluting with the same retention time (RT) as *N*-methylcloransulam-methyl was frequently observed at ≤1% of applied radiocarbon but its occurrence was inconsistent. A poorly retained polar peak eluting with an RT of approximately 4 min was observed during later stages of the study and accounted for upward to 11% of applied radiocarbon by 357 DAT. Subsamples from 357 DAT extracted with acetone/1 M HCl and chromato-

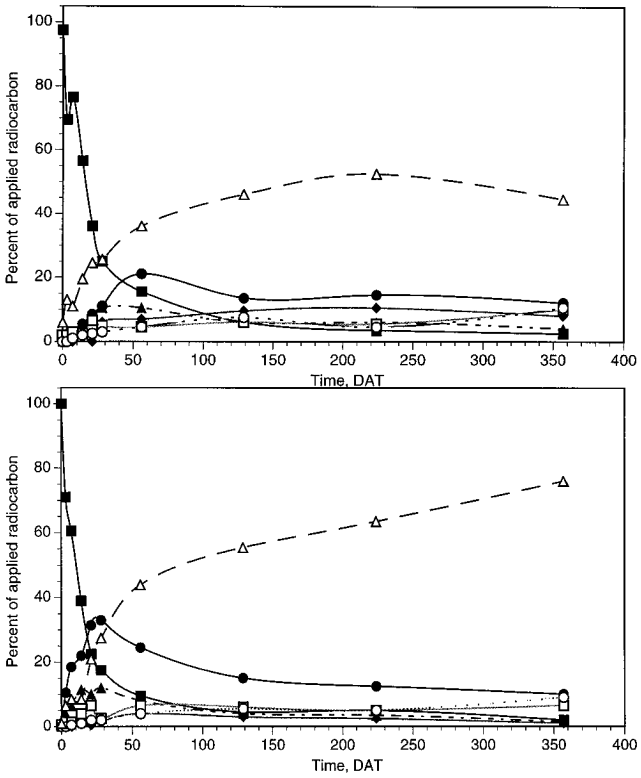


Figure 3. Average distribution of cloransulam-methyl and aerobic soil metabolites on (a, top) Hanford loam and (b, bottom) Cecil sandy loam: cloransulam-methyl, ■; cloransulam, ●; 5-hydroxycloransulam-methyl, ▲; 5-hydroxycloransulam, ◆; other, □; CO_2, ○; bound, △.

graphed by an extended gradient showed the early-eluting peak to be comprised of multiple products.

Figure 3a shows the pattern of parent and metabolite distribution with time for [^{14}C]cloransulam-methyl applied to Hanford loam. The patterns of rise and decline of principal extractable metabolites are established in the initial 129 DAT.

2. Cecil Loamy Sand. The aerobic degradation of cloransulam-methyl was rapid in Cecil loamy sand, for which the average recoverable [^{14}C]cloransulam-methyl averaged 2% of applied radiocarbon at 357 DAT (Table 4). The similar patterns of parent and metabolites observed from differently ring-labeled substrates indicated that metabolic separation of the ^{14}C-labeled phenyl and pyrimidine rings did not occur. Mineralization of the ring structures resulted in the evolution of 7 and 11% of applied radiocarbon as $^{14}CO_2$ on average for [*Ph*-^{14}C]- and [*Pyr*-^{14}C]cloransulam-methyl, respectively, by 357 DAT. Bound radiocarbon not extracted by acidified acetone steadily increased as soils aged, reaching 74−78% of applied radiocarbon at 357 DAT.

The primary metabolite extracted from Cecil loamy sand was cloransulam, which reached 37% of applied radiocarbon by 28 DAT and then declined (Table 4). Both 5-hydroxycloransulam-methyl and 5-hydroxycloransulam were identified at peak concentrations of 16 and 4% of applied radiocarbon, respectively, declining to ≤7% of applied radiocarbon by 357 DAT. Other chromatographic peaks typically occurring at <5% of applied radiocarbon were observed sporadically throughout the study. A peak eluting with the same RT as *N*-methylcloransulam-methyl was occasionally observed at ≤2% of applied radiocarbon, but its occurrence was inconsistent. The poorly retained polar peak observed for Hanford loam was also observed in Cecil loamy sand during later stages of the study. This accounted for ≤4% of applied radiocarbon by 357 DAT.

Figure 3b shows the pattern of parent and degradate distribution with time for [^{14}C]cloransulam-methyl applied to Cecil loamy sand. The patterns of rise and decline of principal extractable metabolites are well established in the initial 56 DAT.

Confirmation of Metabolites. Selected samples from 56 and 357 DAT were analyzed by normal phase TLC and compared against standards to confirm the presence of cloransulam-methyl and metabolites. The results were similar for TLC and HPLC with the exception that 5-hydroxycloransulam-methyl and 5-hydroxycloransulam were occasionally difficult to confirm by TLC. Further confirmation was obtained from derivatization and SIM of fragmentation patterns for cloransulam-methyl and metabolites in samples from 28 and 56 DAT.

Pathway of Cloransulam-methyl Aerobic Soil Metabolism. On the basis of the observed metabolites and patterns of degradation, the proposed pathway for aerobic soil metabolism of cloransulam-methyl is illustrated in Figure 4.

The principal metabolites occurring in both soils were CO_2, cloransulam, and bound residues; 5-hydroxycloransulam-methyl and 5-hydroxycloransulam also occurred but in lesser amounts. A peak corresponding to *N*-methylcloransulam-methyl was occasionally noted but occurred at concentrations below the minimum detectable level (MDL) of 2 ng g^{-1}. This peak occurred most frequently in the ^{14}C-Ph-labeled treatments and may be due to a contaminant or minor components eluted from the HPLC column at the end of the gradient run. On the basis of the product distributions reported in Tables 3 and 4 and the rates of fortification (60 and 69 ng g^{-1} for the pyrimidine and phenyl rings, respectively), the maximum concentrations of metabolites extractable with acetone/acetic acid occurring in either of the two soils studied were 25, 9, and 8 ng g^{-1} for cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam, respectively.

Metabolism of cloransulam-methyl by this pathway results in significant decrease in residue phytotoxicity. In vitro assays of barley root extracts indicated 50% ALS enzyme inhibition (I_{50}) values of 4.8, 470, and 1500 nmol L^{-1} for cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam, respectively, in comparison to 0.36 nmol L^{-1} for cloransulam-methyl (John Wright, personal communication). In this study, products of aerobic soil incubation in the dark gave no evidence for cleavage of the sulfonanilide bridge. However, data from field studies with surface-applied [^{14}C]cloransulam-methyl show evidence for limited bridge cleavage, apparently due to photolysis of cloransulam-methyl (P. Lewer and J. Zabik, personal communication).

Degradation Kinetics. Figure 3 shows [^{14}C]cloransulam-methyl to exhibit rapid biphasic decay in aerobic soil. The observed times to disappearance of 50% of applied cloransulam-methyl (DT_{50}) were <22 days on Hanford loam and <14 days on Cecil loamy sand (Tables 3 and 4). Therefore, a poor fit to the data through 357 DAT was obtained with simple first-order kinetics. Soil half-lives estimated in this manner (70 and 72 days for Hanford loam and Cecil sandy loam, respectively) were significantly longer than the observed DT_{50} values.

A better estimate of soil half-life was achieved when the fitting of a simple apparent first-order model was restricted to the initial rates observed in the first 56 DAT. The half-lives determined from initial rates are

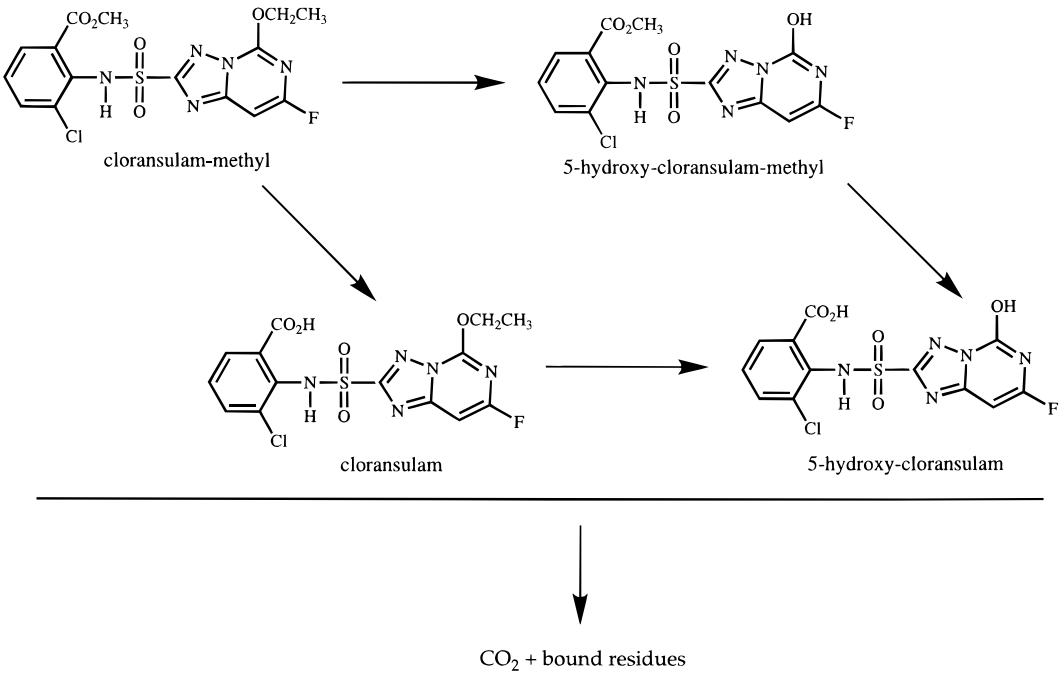
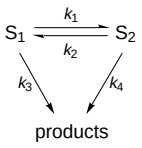


Figure 4. Pathway of aerobic soil metabolism of cloransulam-methyl.

much closer to the DT_{50} values actually observed ($t_{1/2}$ of 21 and 16 days for Hanford loam and Cecil sandy loam, respectively).

Because of the biphasic nature of cloransulam-methyl decay in these soils, the data can be best described by a two-compartment model that assumes partitioning of cloransulam-methyl between differentially reacting soil compartments. Data from Tables 3 and 4 were subjected to nonlinear modeling using SimuSolv to fit a two-compartment model. The solution used was a simplified two-compartment model (Alexander and Scow, 1989):



$$dS_1/dt = -(k_1 + k_3)S_1 + k_2S_2$$

$$dS_2/dt = k_1S_1 - (k_2 + k_4)S_2$$

S_1 and S_2 represent differentially reacting soil compartments of total parent X ($= S_1 + S_2$). The half-life of cloransulam-methyl is estimated from this model as $t_{1/2} = 0.693/(k_3 + k_4)$. This approach provided a superior fit to the data than did the simple first-order models and yielded half-lives of 13 and 9 days for Hanford loam and Cecil loamy sand, respectively. The various half-life estimates are summarized in Table 5.

Characterization of Bound Material. Bound residues typically comprise from 20 to 70% of applied pesticide in aged soils (Claderbank, 1991). A mineral acid extractant was used to increase the quantity of ^{14}C removed from aged soils for characterization of the bound residues. The choice of the acid component in the extraction medium had a limited effect on cloransulam-methyl recoveries from the bound pool but did recover 15% of applied ^{14}C as characterizable metabolites. That portion of bound residue subsequently extractable with citrate/dithionate (≈9% of applied) was shown to be associated predominantly with macromolecules with molecular masses >5000 Da (data not shown).

Table 5. Rates and Half-Lives for Cloransulam-methyl Degradation in Aerobic Soil As Determined by Various Estimation Methods

method of estimation	Hanford loam	Cecil loamy sand
k, Day^{-1}		
simple first order, 0−357 DAT	0.0103	0.00965
simple first order, 0−56 DAT	0.0333	0.0427
two compartment, 0−357 DAT	0.0527	0.0773
Variation Explained, %		
simple first order, 0−357 DAT	83	75
simple first order, 0−56 DAT	91	89
two compartment, 0−357 DAT	97	98
Half-Life, Days		
simple first order, 0−357 DAT	67	72
simple first order, 0−56 DAT	21	16
two compartment, 0−357 DAT	13	9
graphically interpolated DT_{50}	16	10

Effects of Low-Temperature Incubation and Soil Sterilization. Cloransulam-methyl applied to Hanford loam degraded under conditions of low-temperature (5 °C) incubation and sterilization, but at 10-fold lower rates than observed at 25 °C with viable soil (Table 6). Simple first-order fit of the data through 397 DAT produced half-life estimates of 263 and 186 days for low-temperature and sterile treatments, respectively. The degradation products observed for these treatments were the same as those observed for viable soil incubations at 25 °C.

The importance of degradation processes for the accumulation of bound materials is shown in significantly lower bound residue accumulation at 5 °C where both abiotic and biotic degradation processes were inhibited (Table 6). In comparison to sterile and viable incubations at 25 °C, bound residue amounts were from 1.5- to >10-fold lower for 5 °C incubations at comparable sampling times (Tables 3 and 6).

Multisoil Kinetics Study. *Radiocarbon Distribution.* The average material balance over the time course of the study was 96 ± 6% for applied ^{14}C. The distribution of ^{14}C over the 55-day time course of this study showed rapid degradation of cloransulam-methyl to

Table 6. Product Distribution and Material Balance for Hanford Loam Fortified with [^{14}C]Cloransulam-methyl and Incubated at 5 °C or Sterilized by γ-Irradiation and Incubated at 25 °C

time, DAT	% of applied radiocarbon						
	parent	acid	hydroxy	hydroxy acid	other	bound	total
Low-Temperature Incubation							
0	95	0	0	0	1	1	97
7	84	0	0	0	2	4	91
14	89	0	0	0	1	3	93
28	72	0	0	0	1	6	80
58	89	0	0	0	2	3	94
110	82	2	1	0	0	8	94
397	31	2	4	11	18	28	94
Sterile-Soil Treatment							
0	91	0	0	0	2	0	94
7	79	0	0	0	1	13	93
14	74	0	2	0	1	21	97
28	85	1	3	0	1	21	111
58	72	1	5	2	0	11	92
110	42	1	8	5	9	25	91
397	20	2	11	12	5	41	91

produce CO_2, extractable metabolites (cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam), and a sizable pool of bound ^{14}C recalcitrant to aqueous and organic extractions. Table 7 summarizes the product distribution observed at 55 DAT (data for other sample times not presented). Mineralization of cloransulam-methyl resulted in the evolution of 1−18% of applied radiocarbon as $^{14}CO_2$. At 55 DAT, the cloransulam-methyl concentration had declined in all soils. The remaining [^{14}C]cloransulam-methyl ranged from 6 to 24% of applied at 55 DAT. Cloransulam was the major degradate; it reached peak concentrations of 3−22% of applied ^{14}C. In most cases, cloransulam concentrations peaked at 20−27 DAT and subsequently declined. Exceptions were soils M378, M388, M393, M398, and M403 for which increasing cloransulam concentrations were noted throughout the 55-day term of the study. The secondary metabolites, 5-hydroxycloransulam-methyl and 5-hydroxycloransulam, occurred in later stages of the study. 5-Hydroxycloransulam-methyl frequently reached peak concentrations of 2−12% of applied from 20 to 27 DAT and then declined. The 5-hydroxycloransulam typically was detected only at the 55-day sample point, when it reached a peak concentration of 6% of applied ^{14}C. Results were consistent with the aerobic soil metabolism study in which cloransulam-methyl was incubated in two soils for up to 1 year. Significant bound residue accumulation was observed. At 55 DAT the bound residue concentration ranged from 45 to 64% of applied ^{14}C.

Kinetic Treatment of Data. Simple first-order kinetics were used to estimate aerobic soil half-lives for cloransulam-methyl on the 16 soils. The half-lives ranged from 13 to 28 days with R^2 ranging from 0.88 to 0.99 (Table 7). The mean soil half-life on these 16 soils was 18 ± 4 (SE) days.

K_d of Parent and Metabolites. The average apparent K_d for cloransulam-methyl and the metabolites is summarized in Table 7. The general trend was for the apparent K_d of cloransulam-methyl to increase as much as 10-fold with time. The time-averaged apparent K_d of cloransulam-methyl over the 55-day period of soil aging ranged from 0.19 to 4.89 L kg^{-1} (0.84 ± 1.14 L kg^{-1}, n = 16). The time-averaged apparent K_d values for metabolites were not significantly different from those for the parent. When averaged across soils and times of sampling, apparent K_d values were 0.65 ± 0.76 L kg^{-1} (n = 16), 0.81 ± 1.25 L kg^{-1} (n = 13), and 0.25 ± 0.15 L kg^{-1} (n = 5) for cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam, respectively. Soil M378 exhibited a unique combination of low pH and high OC that resulted in markedly higher sorptivities for cloransulam-methyl and metabolites than did other soils. When sorption coefficients were expressed as a function of fractional soil organic carbon content ($K_{OC} = K_d$/OC), the resulting K_{OC} ranged from 12 to 262 L kg^{-1}.

CONCLUSION

Aerobic soil metabolism is a significant route of cloransulam-methyl dissipation in the terrestrial environment. Cloransulam-methyl exhibited a biphasic pattern of degradation over the 357-day time course of the study. Average aerobic soil half-lives in the metabolism study were 9 and 13 days, respectively, on Cecil loamy sand and Hanford loam when data were fit to a nonlinear two-compartment model. Comparable aerobic soil half-lives of 16 and 21 days, respectively, on Cecil loamy sand and Hanford loam were obtained when data were described by an apparent first-order initial rate model. These aerobic soil half-lives are corroborated by the multisoil kinetic study with cloransulam-methyl in

Table 7. Product Distribution (at 55 DAT), Time-Averaged Apparent K_d, and Simple First-Order Half-Life for Cloransulam-methyl Metabolism in 16 Soils

soil	product distribution at 55 DAT, % of applied radiocarbon								time-averaged apparent K_d, L kg^{-1}				
	parent	acid	hydroxy	hydroxy acid	other	CO_2	bound	total	parent	acid	hydroxy	hydroxy acid	parent half-life, days
M345	6	11	1	1	0	23	45	88	0.82	0.78	ND[a]	ND	14
M354	6	5	2	2	2	14	59	90	0.40	0.38	0.52	ND	14
M355	7	13	7	2	2	6	54	91	0.49	0.40	0.38	ND	14
M356	11	16	6	1	1	4	54	92	1.45	0.68	1.22	ND	17
M369	15	5	5	1	4	5	63	97	0.32	0.29	0.26	ND	21
M373	14	3	4	1	3	9	60	95	0.21	0.29	0.30	ND	21
M378	16	18	9	1	1	4	45	94	4.89	3.39	4.84	ND	22
M388	6	7	5	4	3	9	54	89	0.29	0.46	0.28	0.21	13
M393	24	14	7	0	0	2	48	95	1.06	0.69	ND	ND	28
M395	8	13	2	5	4	7	59	98	0.45	0.42	0.36	0.30	15
M396	11	22	6	3	0	6	54	101	0.97	0.49	0.60	ND	17
M398	11	13	6	5	0	6	64	103	0.29	0.28	0.27	0.13	17
M400	10	8	0	0	0	18	64	100	0.33	0.25	ND	ND	18
M403	13	11	7	2	5	4	62	103	0.19	0.35	0.21	ND	18
M404	15	17	5	6	0	4	56	102	1.06	0.99	1.09	0.49	20
M405	14	8	5	4	9	4	61	104	0.25	0.25	0.18	0.13	19

[a] ND, not determined; insufficient radiocarbon recovery to assay either the aqueous or organic phase extract.

which apparent first-order half-lives ranged from 13 to 28 days (18 ± 4 days, $n = 16$) on soils representative of the projected market region for cloransulam-methyl. Rates of cloransulam-methyl degradation decreased ≈10-fold when soils were incubated at 5 °C or when sterilized by γ-irradiation. Degradation from sterile and low-temperature treatments indicated that abiotic processes are consequential as secondary routes of cloransulam-methyl dissipation from the terrestrial environment.

Mineralization, resulting in evolved $^{14}CO_2$, accounted for up to 10% of applied radioactivity by 357 DAT. The average material balances over the time course of the study were 98 ± 5% of applied ^{14}C for the Cecil loamy sand and 95 ± 7% of applied ^{14}C for the Hanford loam.

Extractable metabolites were cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam. These occurred at maximum concentrations of 25, 9, and 8 ng g^{-1}, respectively, corresponding to 38% of applied ^{14}C at 28 DAT, 17% of applied ^{14}C at 14 DAT, and 11% of applied ^{14}C at 129 and 224 DAT. Degradation resulted in extractable metabolites with markedly reduced phytotoxicity relative to the parent molecule. Significant bound residue (^{14}C recalcitrant to extraction with acidified acetone) accumulation was observed by 357 DAT, averaging 44% of applied ^{14}C on Hanford loam and up to 79% of applied ^{14}C on Cecil loamy sand. The pool of bound residues at 357 DAT was reduced to ≤8% of applied ^{14}C by sequential extraction of representative samples with acetone/1 M HCl (28−53% of applied ^{14}C), citrate/dithionate (7−12% of applied ^{14}C), and 1 M NaOH (≤3% of applied ^{14}C). Acetone/HCl extraction recovered ≤2, ≤33, and ≤26% of applied ^{14}C as cloransulam-methyl, cloransulam-methyl metabolites, and multiple low-level peaks, respectively. That portion of bound residue extractable with citrate/dithionate was shown to be associated predominantly with macromolecules with molecular masses >5000 daltons.

In the multisoil kinetic study, degradation rates and product profiles were consistent with the soil metabolism study. The apparent K_d values, determined from two-phase extractions, ranged from 0.19 to 4.89 L kg^{-1} when averaged over the 55-day term of this study. Average apparent K_d values for metabolites were 0.64, 0.80, and 0.25 L kg^{-1} for cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxycloransulam, respectively. There was a trend for increased K_d values (as much as 10-fold) with time for both the parent molecule and metabolites.

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Received for review June 14, 1995. Accepted October 2, 1995.[⊗]

JF9503570

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.