Field Dissipation of Cloransulam-methyl at Four Sites in the U.S. Soybean Market

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The soil dissipation of cloransulam-methyl was studied using ^{14}C-labeled and non-radiolabeled material in Wisconsin, Indiana, Mississippi, and North Carolina between 1993 and 1995. The test substance was pre-emergence broadcast-applied at target rates of 50 and 61.5 g ai ha^{-1} for the ^{14}C-labeled and the non-radiolabeled studies, respectively. Bromide was used to track water movement at the NC and WI sites. The degradation of cloransulam-methyl was rapid and best characterized by a two-compartment model resulting in initial-rate half-lives ranging from 2.5 to 4.8 days at the MS, IN, and WI sites and by a first-order degradation model at the NC site with a half-life of 11.2 days. The rapid dissipation rates, metabolite formation patterns, and sorption characteristics obtained in this field study were consistent with the existing laboratory data generated for cloransulam-methyl. Rapid degradation rates and the increasing sorption to soil over time resulted in low persistence and mobility of this compound.

Keywords: *Cloransulam-methyl; triazolopyrimidine sulfonanalide; soil dissipation*

INTRODUCTION

Properties of Cloransulam-methyl. 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 soybeans through acetolactate synthase (ALS) inhibition (DowElanco, 1994; Jachetta et al., 1994; Hunter et al., 1994). Proposed application methods for the molecule include pre-plant incorporation and post-emergent treatment at maximum label rates of 44 and 17.5 g ai/ha, respectively. Physical properties of cloransulam-methyl are given in Table 1 (DowElanco, 1994). Aerobic soil half-lives under laboratory conditions were 9 and 13 days, respectively, in the Cecil loamy sand and Hanford loam soils for data fit to a two-compartment model and 16 and 21 days, respectively, for data fit to a first-order degradation rate model (Wolt et al., 1996). Degradation was observed to be biphasic in nature, with the rate of dissipation slowing with increasing soil adsorption. Soil sorption coefficients of 0.18−0.83 mL/g have been reported for the compound, with an average adsorption K_d of 0.38 mL/g. The average soil half-life ranged from 13 to 28 (mean ± SD = 18 ± 4 days) on 16 soils representative of the Southern and Midwestern U.S. where apparent K_d ranged from 0.19 to 4.89 L kg^{-1} and apparent K_d increased with time (Wolt et al., 1996).

Aerobic soil metabolism laboratory studies on the fate of this compound indicate the primary degradation products are cloransulam [*N*-(2-carboxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide], 5-hydroxycloransulam-methyl [*N*-(2-carbomethoxy-6-chlorophenyl)-5-hydroxy-7-fluoro[1,2,4]-triazolo[1,5-*c*]pyrimidine-2-sulfonamide], and 5-hydroxy-cloransulam [*N*-(2-carboxy-6-chlorophenyl)-5-hydroxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide]. Photolysis products, sulfonic acid [5-ethoxy-7-fluoro[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonic acid] and

sulfonamide [*N*-(2-carboxy-6-chlorophenyl)-1-methyl-5-(2-fluoroethenyl)[1,2,4]triazolo-3-sulfonamide], observed in laboratory studies, were possible degrades under field conditions. Breakdown pathways of cloransulam-methyl have been given by Wolt et al. (1996). A summary of the kinetic data for major dissipation routes of cloransulam-methyl is given in Table 2.

The objectives of these studies were as follows: (1) Obtain soil dissipation data for cloransulam-methyl and follow rates of formation and decline of the degradation products under field conditions using [^{14}C]cloransulam-methyl and non-radiolabeled cloransulam-methyl. (2) Evaluate movement of cloransulam-methyl and its degrades through the soil profile. (3) Track the water movement and establish the maximum potential leaching depth for the duration of the study.

MATERIALS AND METHODS
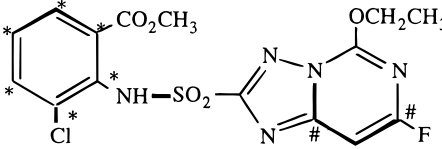
Two small plot field dissipation studies using [^{14}C]cloransulam-methyl were initiated at sites near Wayside, Mississippi (MS), and Greenfield, Indiana (IN), in 1993. Two additional field scale dissipation studies using non-radiolabeled cloransulam-methyl were initiated in the Southern Piedmont soybean growing region, near Durham, North Carolina (NC), and another representative of a colder climate soybean growing region near Arkansaw, Wisconsin (WI), in 1995.

Study Sites. The IN site was located at the DowElanco Greenfield Field Research Station in the City of Greenfield, Hancock County in central IN (32 km east of Indianapolis, 39° N, 85° W). The study site was located in the Crosby series soil (fine, mixed, mesic, Aeric Ochraqualfs). This series consists of deep and somewhat poorly drained, nearly level (0−3% slope) soils. The field was tiled to enhance drainage. Soil texture adjacent to the test plots ranged from loam (0−30 cm), to silty clay (30−45 cm), clay (45−75 cm), and clay loam (75−90 cm). Organic matter generally decreased from 1.68% at the surface to 0.38% at 90 cm.

The MS site was located at the DowElanco Wayside Field Research Station in Wayside Township, Washington County (north western MS, 33° N, 90° W). The study site was located in the Commerce series soil (fine-silty, mixed, nonacid, thermic, Aeric Fluvaquents). This series consist of nearly level (0.5−2% slope), moderately well-drained to somewhat poorly drained

Table 1. Properties of Cloransulam-methyl

common name	cloransulam-methyl
chemical name	N-(2-carboxymethyl-6-chlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
chemical structure[a]	

molecular formula	$C_{15}H_{13}N_5O_5SFCl$
molecular weight	429 g mol^{-1}
water solubility (20 °C)	pH 5, 3 mg L^{-1}; pH 7, 184 mg L^{-1}
DI water solubility	16 mg L^{-1}
solubility in acetone	4360 mg L^{-1}
solubility in acetonitrile	5500 mg L^{-1}
pK_a	4.81 at 20 °C
vapor pressure	4×10^{-14} Pa at 25 °C
Henry's law constant	9.23×10^{-16} atm m^3 mol^{-1} at pH 7
CAS Registry Number	147150-35-4

[a] Note: AN- and TP-label were present in different molecules. The asterisks refer to cloransulam-methyl UL-^{14}C phenyl label (AN-label), while the pound signs refer to cloransulam-methyl 7,9-^{14}C pyrimidine label (TP-label).

Table 2. Rates and Half-Lives for Environmental Degradation of Cloransulam-methyl

dissipation mechanism	half-life (days)	rate (days^{-1})
aerobic soil		
at 25 °C	16,[a] 21[b]	0.043,[a] 0.033[b]
at 5 °C	263	0.0026
γ-irradiated	186	0.0037
sixteen-soil study	13[c]	0.053
	28[d]	0.025
anaerobic aquatic	16	0.043
hydrolysis		
pH 5	>365	0.0019
pH 7	118−231	0.0031
pH 9	3	0.23
natural water, pH ~8	10	0.069
soil slurry, pH ~6.5	67	0.010
aqueous photolysis	0.015	44.76
soil photolysis (moist)	~13	0.053

[a] Value for Cecil loamy sand. [b] Value for Hanford loam. [c] Low value of the range. [d] High value of the range.

medium-textured soil. Soil texture adjacent to the test plots ranged from silt loam (0−15 cm), to loam (15−30 cm), and silty clay loam (30−90 cm). Organic matter ranged from 0.61−0.88%.

The NC site was located at a research farm in the City of Durham, Durham County (approximately 36° N, 79° W). The soil at the site was a Granville series sandy loam (fine-loamy, siliceous thermic Typic Hapludalts), a well-drained soil. There was no appreciable slope at the site. The soil adjacent to the test plots was a sandy loam (0−15 cm) overlaying a sandy clay loam through the rest of the profile to a depth of 120 cm. Organic matter content ranged from approximately 1% in the surface layer (0−15 cm) to <0.1% in the deepest segments.

The WI site was located at a research farm near Arkansaw, Pepin County, in west-central WI (45° N, 92° W). The study site was located in the Burkhardt sandy loam (sandy, mixed mesic Typic Hapludolls), an excessively drained soil with no appreciable slope. The soil adjacent to the test plots is a sandy loam to loamy sand to the 60 cm depth. Below 60 cm the profile becomes a sand (>95% sand). Organic matter content in the top 30 cm was approximately 2.3%, decreasing to approximately 0.15% in the deepest segments. Guelph Permeameter measurements were made at the WI site to determine soil hydraulic conductivity at depths of 20 and 40 cm (Reynolds and Elrick, 1990). Volumetric soil water content was measured at the WI site using a time domain reflectometry (TDR) system (Topp et al., 1980). A Campbell TDR system was used with an array of thirty, 30 cm long horizontally installed probes at depths of 15, 30, 45, 60, and 90 cm. Five replicate probes were placed at each depth in an area adjacent to the treated plot, and one replicate of each depth

was placed in an area adjacent to the control plot. The system logged soil water content at 1 h intervals from the day prior to application of the test substance until approximately 5 months after treatment.

Meteorology. Weather was monitored at each field site, within 10 m of the test plot, using a Campbell 21X weather station (Campbell Scientific, Logan, UT) configured to measure rainfall, air temperature, solar radiation, and soil temperature at depths of 2.5, 10, and 100 cm. Measurements taken every second were used to calculate daily maxima, minima, and mean values.

Irrigation. Plots were irrigated via hand held sprinklers in MS and IN and by center pivot irrigation in WI and NC on a semimonthly basis during the growing season to ensure that total precipitation plus irrigation amounts were at least 125% of the 30-year monthly average rainfall amounts reported by the nearest NOAA weather stations. Surplus rainfall plus irrigation exceeding the monthly target was not carried over into subsequent months.

^{14}C-Labeled Test Substances. [*pyrimidine*-7,9-^{14}C]Cloransulam-methyl (specific activity 26.9 mCi/mmol; labeled in the 7- and 9-positions of the pyrimidine ring; hereafter referred to as the TP-label) and [*phenyl*-UL-^{14}C]cloransulam-methyl (specific activity 29.3 mCi/mmol; uniformly labeled in the phenyl ring; hereafter referred to as the AN-label) were acquired from the specialty synthesis group of DowElanco. The radiochemical purity of the test substances was greater than 99% with the exception of TP-label at Indiana which was greater than 91%. The positions of ^{14}C labeling are shown in Table 1. Each labeled material was applied to separate plots at each site. Use of labeling on each ring system provided information on the cleavage of the sulfonamide bridge and subsequent formation of products unique to each ring. The degradates identified in the laboratory studies, cloransulam, 5-hydroxycloransulam-methyl, and 5-hydroxy cloransulam, can be observed in both labels while the sulfonamide and sulfonic acid can only be observed in the TP-label. The test substance was formulated on the day of application by first dissolving it in acetonitrile and then adding water to form a 50:50 mixture of acetonitrile and water. The inert materials included in the label formulation (NAF-75) were then added.

Non-Radiolabeled Test Substance. Cloransulam-methyl was used as the test substance in the end-use product formulation NAF-75. The lot used in this study contained 84.3% cloransulam-methyl, the percentage of active ingredient indicated on the product label. The tank mix (approximately 130 ppm of NAF-75 dissolved in water) was agitated for approximately 5 min prior to application.

^{14}C-Labeled Test Plot Description. Two bordered treatment plots (122 cm × 520 cm) were prepared at each radiolabeled site (IN, MS), one for the AN-labeled material and one for the TP-labeled material. All plant matter was removed

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Table 3. Test Substance Application Dates and Soil Sampling Days after Treatment (DAT) for the MS, IN, NC, and WI Sites

MS June 9, 1993	IN July 8, 1993	NC April 26, 1995	WI June 7, 1995
1	1	1	1
3	4	3	3
8	12	7	7
14	21	14	14
21	27	21	22
28	42	28	28
42	98	49	43
92	155	70	75
152	300	100	100
299	458		
453			

from the plots prior to application of the test substance. Each plot was equipped with a runoff collection system designed to prevent ponding of water in the plots during heavy rains. A 91 cm × 244 cm control plot was located upwind relative to the prevailing winds to minimize the possibility of spray drift contamination. The control plot did not have a containment wall or water collection system.

Non-Radiolabeled Test Plot Description. At the NC and WI sites the study consisted of a treated plot approximately 972 and 796 m² in area, respectively, including treated buffer areas. Control plots were established with areas of 56 and 195 m² at the NC and WI sites, respectively. Approximately 25 m separated the treated and control plots.

Application of ¹⁴C-Labeled Test Substance. [¹⁴C]Cloransulam-methyl was applied on June 9, 1993, at Wayside, MS, and on July 8, 1993, at Greenfield, IN, as a broadcast spray in a single application at a target rate of 50 g ai ha⁻¹ (1.14× the maximum label rate of 44 g ai ha⁻¹ for a pre-emergent application). A pressurized nitrogen hand boom sprayer was used with two flat fan nozzles on 51 cm centers. Guide wires were used to maintain the proper height and position over the plots. Two passes were made over the plot with the sprayer to obtain a uniform application. Approximately 10 mL of each tank mixture was analyzed immediately prior to the application to verify tank mixture integrity. Nine filter paper disks were placed in the plots to determine the uniformity of the application.

Application of Non-Radiolabeled Test Substance and KBr. Cloransulam-methyl and KBr were broadcast applied on April 26, 1995, in NC and on June 7, 1995, in WI to bare soil plots at a target rate of 61.5 g ai ha⁻¹ (combined pre-emergence, 44 g ai ha⁻¹, and post-emergence, 17.5 g ai ha⁻¹) in a spray volume of approximately 270 L ha⁻¹. KBr was applied in a separate application at a rate of 79.8 kg ha⁻¹ (NC) and 101.1 kg ha⁻¹(WI) using the same spray volumes as for the test substance. Two passes over the plot were made using a tractor-mounted spray boom with flat-fan nozzles. After application of the test and control substance, the soil was rototilled (NC) or disced (WI) to a depth of approximately 5 cm to incorporate the material as directed in the product label for pre-emergence applications. No crop was planted on the treated or control plots and the plots were maintained weed-free during the growing season. KBr was not applied at the MS or IN sites.

¹⁴C-Labeled Plot Soil Sampling. At the IN and MS sites, a single two-stage (0–15, 15–90 cm) core was removed from one randomly selected grid in each of three subplots resulting in a total of three cores at each sampling event. As each stage was removed, a steel casing remained in the hole. Core diameters for the 0–15 cm segment were 5.7 cm (MS) and 11.4 cm (IN) and for the 15–90 cm segment were 3.2 cm (MS) and 2.2 cm (IN). The cores were placed in a freezer or on dry ice and kept in the dark. The equipment was decontaminated between each coring. Frozen soil cores were cut into 15 cm segments and analyzed individually. Sampling dates and days after treatment (DAT) are given in Table 3.

Non-Radiolabeled Plot Soil Sampling. At the NC and WI sites, a set of 15 two-stage (0–15, 15–90 cm) cores were taken. Core diameters for the 0–15 cm segment were 5.7 cm

(WI) and 5.6 cm (NC) and for the 15–90 cm segment were 4.5 cm (WI) and 4.2 cm (NC). Cores were frozen and segmented into 15 cm increments. The 0–15 cm core was further segmented into a 0–5 and 5–15 cm increments. Cores were then composited in groups of 5 to form three replicate composite cores at each depth for analysis. Twelve aluminum soil pans each with a surface area of 1734 cm² and containing a 1 cm layer of sieved soil were placed randomly in the plot prior to each of the test substance and KBr application at the NC and WI sites. The soil pan samples were collected to obtain greater precision in the estimate of the mass of cloransulam-methyl and KBr applied to the soil. Table 3 shows sample dates for the NC and WI sites.

The treated plots were sampled separately for bromide, using the same apparatus, at 7, 14, 42, and 100 DAT at NC and at 7, 14, 28, 42, and 70 DAT at the WI site. Sets of nine cores were sectioned into 7.5 cm segments from 0–45 cm and 15 cm segments from 45–90 cm and composited into three replicate samples for each depth and analyzed for bromide.

Travel Spikes. Travel spikes were prepared at all four sites to determine the stability of the cloransulam-methyl during shipping, sample preparation, and analysis. Spikes were prepared by dosing a preweighed mass of control soil with pre-weighed quantities of cloransulam-methyl to achieve the desired concentration in soil.

Analytical Methods for ¹⁴C-Labeled Residue. The analytical method for soil analysis consisted of three primary steps: combustion of the soil to determine total activity, extraction with individual component analysis (cloransulam-methyl and degradates), and post-extraction combustion to determine the insoluble fraction. Frozen soil cores were segmented and placed into metal cans to thaw. Approximately 15–20% by weight of deionized water was then added to each sample can. The samples were mixed thoroughly while chilled. Samples were then stored frozen at −18 °C until analysis. Biological oxidizers were used to combust aliquots of soil samples to CO_2 and H_2O. The CO_2 was trapped in a liquid scintillation counting (LSC) cocktail and then quantified by LSC. The component analysis consisted of multiple extractions with 90:10 acetone:1 N HCl, concentration, filtration, and high-pressure liquid chromatography (HPLC) to separate degradates from cloransulam-methyl. [¹⁴C]Cloransulam-methyl and its degradates were quantified using LSC of collected HPLC fractions. On the basis of the lab study data no degradates were formed where loss of the label occurred, resulting in a specific activity different from the labeled cloransulam-methyl. [¹⁴C]Cloransulam-methyl concentrations were also expressed as g ha⁻¹, ng g⁻¹ dry weight basis, or % of applied. The % of applied values are expressed as a percentage of the total radioactivity recovered in the 0 DAT 0–15 cm cores.

The limit of detection (LOD) and limit of quantitation (LOQ) for the soil combustion method were 9.1 and 37.9 dpm/g (approximately 300 parts per trillion), respectively. The primary purpose of the component analysis was to determine degradates in soil which approached or exceeded 10% of the applied cloransulam-methyl; therefore the LOQ for component analysis was set at 1% of applied on 0 DAT. The LOQ for the IN site was therefore 0.38 and 0.31 ng g⁻¹ for the AN- and TP-label, respectively, while at the Wayside, MS, site the LOQ was 0.42 and 0.20 ng g⁻¹ for the AN- and TP-label, respectively. The differences in LOQ's at each site are due to the difference in actual 0 DAT application rates and the specific activities for the AN- and TP-labeled material.

Analytical Methods for Non-Radiolabeled Residue. Frozen soil cores were segmented, composited, and ground using a hammermill equipped with a 3/16 in. screen. Samples were kept frozen throughout the grinding process by mixing with dry ice. A 200 g subsample was stored frozen at −18 °C until it was extracted and analyzed for cloransulam-methyl and cloransulam. Soil samples were analyzed for residues of cloransulam-methyl and cloransulam using DowElanco method GRM 95.10. Residues of cloransulam-methyl and cloransulam were extracted from the soil using acidified acetone, and co-extracted soil organics were precipitated by the addition of magnesium acetate. The residue was isolated using C_{18} solid-phase extraction (SPE). The eluant from the C_{18} SPE column

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was evaporated to dryness, and the analytes were derivatized with triethyloxonium tetrafluoroborate to form ethyl derivatives. Following derivatization and liquid−liquid partitioning, the residue was further purified using silica gel SPE. The eluant from the silica gel SPE column was evaporated to dryness and reconstituted in toluene containing the internal standard (*N*-methylcloransulam-methyl, >96% pure). The concentrations of *N*-ethylcloransulam-methyl and *N*-ethylcloransulam-ethyl were determined in the final solution by gas chromatography with mass selective detection (GC/MSD). The analyses of the soil samples for residues of cloransulam-methyl and cloransulam were conducted on a Hewlett-Packard GC/MSD system consisting of a 5890 Series II gas chromatograph, a 7673 autosampler, and a 5971A mass selective detector (MSD). Quantitation was performed using ethyl ester standards of cloransulam-methyl and cloransulam. The chromatographic data were collected and peaks integrated using a Hewlett-Packard Chemstation. The method had a validated LOQ of 1.0 ng g^{-1} and a statistical LOD of 0.3 ng g^{-1}. Degradation of cloransulam-methyl and the formation and decline of the cloransulam metabolite for the nonlabeled studies is expressed as a percentage of cloransulam-methyl applied, based on the 0 DAT 0−15 cm core concentrations.

Analytical Methods for Bromide. Soil samples from the field were weighed, mixed and a 5 g subsample extracted using 20 mL of deionized H$_2$O. Soil extracts were analyzed for bromide by ion chromatography with UV detection. The method had a LOQ of 1 μg g^{-1} (ppm) and a LOD of 0.3 ppm.

Statistical Methods and Kinetic Treatment of Data. Summary statistics for cloransulam-methyl, cloransulam, and bromide concentrations were determined using spreadsheet software. For the purposes of averaging, residue concentrations less than the LOD were assigned a value of zero. Degradation kinetics were based on the total % of applied material recovered from the entire soil profile using a first-order degradation model

$$C(t) = C_0 \exp^{-kt} \tag{1}$$

with a linear least-squares fit to the natural log (ln)-transformed data and also using a nonlinear fit to non-transformed data (NC and WI only) to obtain a degradation rate constant (*k*). Degradation constants (*k*) were converted to a half-life value in days (*T*$_{1/2}$) by

$$T_{1/2} = -0.693/k \tag{2}$$

Where appropriate, soil residue data were also fitted using a double exponential two-compartment model

$$S(t) = S_1 \exp^{-k_1 t} + S_2 \exp^{-k_2 t} \tag{3}$$

where k_1 and k_2 are the degradation rate constants representing the rapid degradation of the solution phase material (first compartment, S_1) and the slower degradation of the sorbed phase material (second compartment, S_2) respectively (Alexander and Scow, 1989). The double-exponential model was fit to the data using Sigmaplot at the NC and WI sites and using SimuSolv (Steiner et al., 1986) at the MS and IN sites. Times to 50% and 90% dissipation of cloransulam-methyl (DT$_{50}$, DT$_{90}$) are also discussed.

RESULTS AND DISCUSSION

Rainfall and Irrigation. Rainfall plus irrigation amounted to 139, 135, 149, and 151% of the 30-year normal precipitation at the IN, MS, NC, and WI sites, respectively, during the field phase of the studies. The MS and IN sites both received significant amounts of rainfall in the first 3 weeks following application of the test substance. Rainfall at MS in the month of July (first month after application) was 143% of the 30-year average. The first 3 weeks at the NC site were unusually dry, and most of the precipitation was added to the plots as irrigation. The NC site experienced several significant natural rainfall events after the initial 30 DAT, with 8.8 cm of rain over a 2-day period starting on 31 DAT, and 9.9 cm over 2 days starting at 63 DAT. Significant rainfall events at the WI site include a 4.3 cm rainfall over 3 days starting on 18 DAT, 6.8 cm of rainfall and irrigation on 23 DAT, and 7.3 cm of rain on 64 DAT.

Travel Spikes and Storage Stability. The recovery of total radioactivity was 100% and 94% for IN and MS, respectively, for 15 MAT travel spikes. [^{14}C]-Cloransulam-methyl represented 86% of the applied activity (average concentration = 38.6 ± 2.7 ng g^{-1}) at the IN site, while the insoluble fraction represented 13% of applied (average concentration = 5.8 ± 0.3 ng g^{-1}). Similar results were observed in the MS travel spikes where [^{14}C]cloransulam-methyl represented 88% of the applied activity (average concentration = 39.7 ± 1.3 ng g^{-1}) and the insoluble fraction represented 9% of applied (average concentration = 4.0 ± 0.7 ng g^{-1}). Mean concentrations of non-radiolabeled cloransulam-methyl from the four travel spike sets from WI and NC (DAT 0, 100 from each site), spiked at 50 ng g^{-1}, were 40.7, 58.9, 121.9, and 50.4 ng g^{-1}. The set with the 121.9 ng g^{-1} average concentration also exhibited the greatest variability between the three replicates indicating that the spiking material may not have been thoroughly homogenized with the soil sample. The travel spike results suggest that cloransulam-methyl did not significantly degrade during the shipping and handling conditions experienced during any of the studies. A storage stability study using non-radiolabeled material was conducted where soil samples were spiked and analyzed for cloransulam-methyl and cloransulam on the day of fortification and at 29, 89, 250, and 386 days after fortification. No degradation of either cloransulam-methyl or cloransulam was observed over this period of frozen storage.

Application Rate Validation and Uniformity. The application rate was validated using filter pads and 0 DAT soil cores at the ^{14}C study sites. Filter paper results from the IN site showed the average percent of the target application rate (50 g ha^{-1}) was 109% (±28%) and 106% (±32%) for AN- and TP-labeled plots, respectively, based on total radioactivity and 91% (±16%) and 70% (±24%) of target for cloransulam-methyl. Filter paper results from the MS site showed the average percent of the target application rate was 117% (±28%) and 98% (±22%) for the AN- and TP-labeled plots, respectively, based on total radioactivity and 117% (±18%) and 60% (±16%) of target for cloransulam-methyl. The lower recovery of [^{14}C]cloransulam-methyl in the soil samples may be due to the degradation of [^{14}C]cloransulam-methyl prior to sample collection on 0 DAT. In addition, approximately 12% of the total activity was unavailable for chromatographic analysis due to losses during cleanup and concentration or to non-extractability by the method used.

Analysis of soil contained in the 12 soil pans at each of the NC and WI sites indicate that the application of cloransulam-methyl was uniform across the treated plot and reached an average of 88.4% (±8.4%) of the target application rate in NC, and 93.9% (±10.3%) in WI. Better recovery of the test material was obtained from the soil pans than from the 0−15 cm soil cores collected on DAT 0 which showed average recovery of 83.1% (±14%) in NC and 84.2% (±25.8%) in WI. Higher
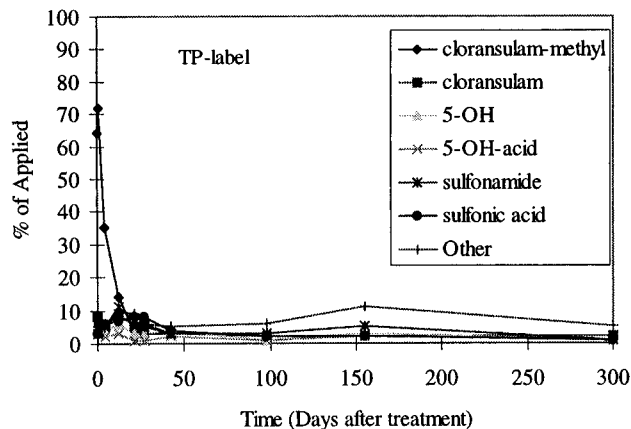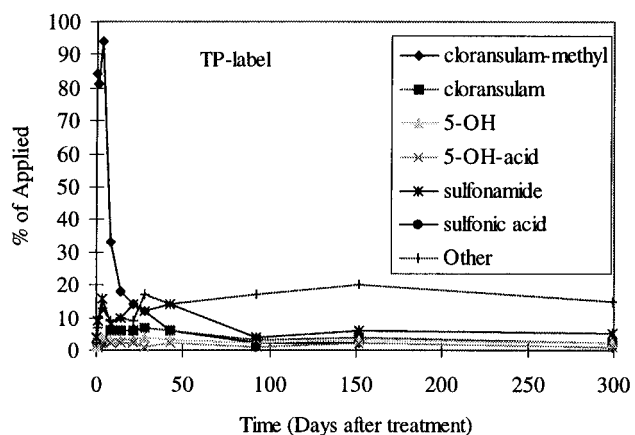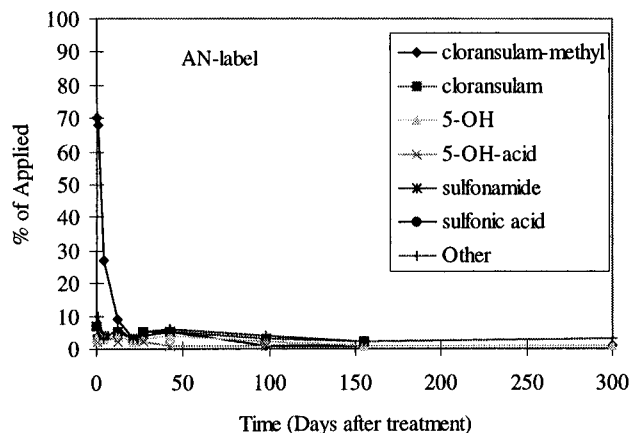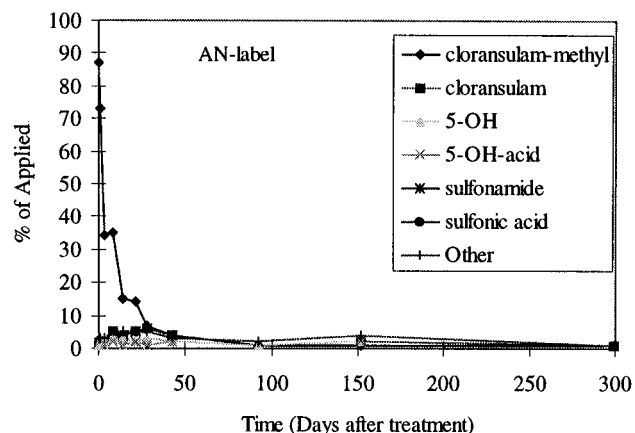
Figure 1. Percent of applied radioactivity as cloransulam-methyl and degradates vs DAT for the AN- and TP-label at the Mississippi site.

Figure 2. Percent of applied radioactivity as cloransulam-methyl and degradates vs DAT for the AN- and TP-label at the Indiana site.

average recoveries and lower variability in the soil pans than in the 0–15 cm soil cores are not surprising given the greater surface area and the higher surface area to volume ratio for the soil pans. The 12 soil pans covered a total surface area of approximately 20 808 cm^2 compared to 385 cm^2 for the 15 soil cores. Also, the soil pans were collected immediately after application and frozen, while the soil cores, by necessity, were sampled over a period of several hours after application, thus potentially allowing some degradation to occur.

^{14}C Mass Balance. Total ^{14}C activity within the soil declined to less than 30% of applied by 15 months after treatment (MAT). Total ^{14}C activity remaining was lower in the AN-label plots than in the TP-label plots. The decline in total ^{14}C activity is likely a result of losses due to ^{14}CO$_2$ evolution, rainfall/sediment runoff, and sampling. The average activity lost from the plots due to runoff was approximately 11% for IN and only 2% for MS. Most of the ^{14}C activity lost through runoff at IN was associated with sediment. The high sediment losses are attributed to the unusually high amount of rain that occurred during the month (July) following application, which eroded the recently tilled soil into the runoff collection trough. The remainder of the ^{14}C activity was apparently lost as ^{14}CO$_2$, since laboratory studies indicate significant mineralization of cloransulam-methyl. As much as 35.4% and 27.1% of the ^{14}C activity was lost through ^{14}CO$_2$ evolution in an aerobic soil metabolism laboratory study on the MS and IN soils, respectively (Cook, 1997). The soil photolysis laboratory study indicated that up to 7% and 9% ^{14}CO$_2$ was evolved from soil spiked with AN-label and TP-label

cloransulam-methyl, respectively. On the basis of the lab and field data up to 75% of the applied ^{14}C activity can be accounted for. The remaining ^{14}C activity was probably lost through ^{14}CO$_2$ evolution not predicted by the laboratory studies and can be attributed to two factors. First, in the field study multiple processes including metabolism and photolysis of cloransulam-methyl and degradates occurred simultaneously. Secondly, aerobic soil metabolism studies conducted in the lab underestimate the field degradation rate of the compound due to their artificial nature. Soil microbial population can decline rapidly under laboratory conditions where nutrient sources are limited and re-inoculation of the population is not possible (Frehse and Anderson, 1983). Thus, in the field, shorter half lives and greater CO$_2$ evolution would be expected as the result of a healthy soil microbial population combined with photolytic processes.

Rate of Cloransulam-methyl Dissipation. *1. First-Order Models.* The dissipation of cloransulam-methyl was rapid and biphasic at the MS and IN sites (Figures 1 and 2, respectively). Since cloransulam-methyl had entered the second phase of its biphasic degradation by 42 DAT at both sites, first-order fits were restricted to the initial 1.5 months post-application in order to describe the intrinsic rate of microbial degradation. The first-order half-lives based on initial rates were 9.6 days ($R^2 = 68.3\%$) and 8.1 days ($R^2 = 86.8\%$) for the AN- and TP-labeled plots, respectively at the IN site, and 10.2 days ($R^2 = 91.8\%$) and 10.5 days ($R^2 = 90.8\%$) for the AN- and TP-labeled plots, respectively in MS (Table 4). The relatively low R^2 for ln-transformed models indicates that cloransulam-methyl ter-

Table 4. Half-Life, DT$_{50}$, and DT$_{90}$ Estimates (in days) for Cloransulam-methyl

| site | half-life estimate ($T_{1/2}$) | | | DT$_{50}$ | DT$_{90}$ |
	linear first-order	nonlinear first-order[d]	two-compartment[e]		
MI	10.2[a] (92)[b], 10.5[c] (91)	6.7 (99)	4.8 (91)	<8	<25
IN	9.6[a] (68), 8.1[c] (87)	4.2 (98)	3.5 (84)	<5	<15
NC	11.2 (96)	11.4 (98)		<11	<40
WI	24.1 (92)	11.7 (96)	2.5 (99)	<7	<60

[a] Linear first-order fit to ln-transformed data, AN-label, first 45 days only. [b] Number in parenthesis is the R^2 of the regression. [c] Linear first-order fit to ln-transformed data, TP-label, first 45 days only. [d] Nonlinear first-order fit to non-transformed data (MI and IN data average for both labels). [e] Two-compartment (double-exponential decay) fit to non-transformed data (MI and IN data average for both labels).
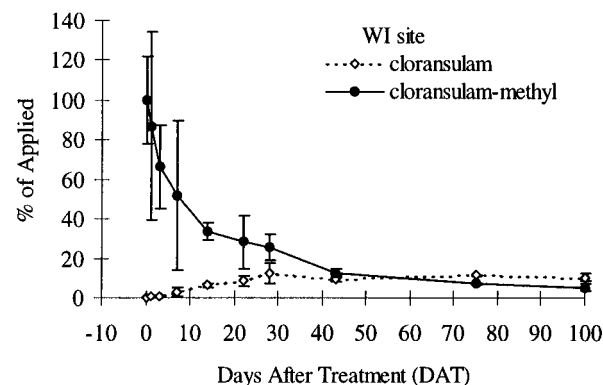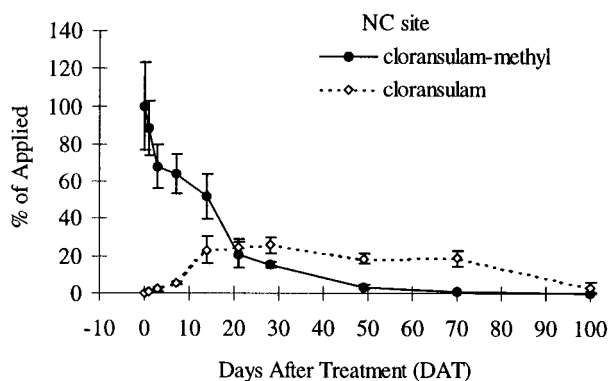
Figure 3. Concentration of cloransulam-methyl and cloransulam as a function of time for NC and WI.

Figure 4. Comparison of the fit to the simple first-order decay model using the linear regression on the ln-transformed data and the nonlinear regression on the non-transformed data for both sites.

restrial dissipation is not adequately described on the basis of simple first-order kinetics.

Dissipation of cloransulam-methyl also proceeded rapidly at both the NC and WI sites, with residues of cloransulam-methyl not detectable at NC (<0.3 ppb) after the 49 DAT sampling (Figure 3). A simple first-order degradation model (eq 1) with a nonlinear regression of the non-transformed data resulted in the best fit (R^2 = 97.5%, $T_{1/2}$ = 11.4 days) to the dissipation of cloransulam-methyl at the NC site (Figure 4). A linear fit to the ln-transformed data (R^2 = 95.9%, $T_{1/2}$ = 11.2 days) is also shown in Figure 4 for comparison. Both models fit the data equally well, suggesting that the dissipation of cloransulam-methyl at this site is indeed first-order.

Initial dissipation was rapid at the WI site, but slowed over time, with a small percentage of residual cloransulam-methyl remaining in the top 15 cm of the profile at levels less than 6% of applied (detections near the LOQ) at 100 DAT (Figure 3). Figure 4 also shows the fit of the simple first-order decay model using a linear regression of the ln-transformed data and the nonlinear regression of the non-transformed data for the WI site. The linear regression of the ln-transformed data (R^2 = 92.3%) overestimates the early dissipation of cloransu-

lam-methyl (<10 days) and underestimates the dissipation of cloransulam-methyl between 10 and 60 days. The regression is clearly weighted by the later time points. The fit to the data using nonlinear regression of the non-transformed data (R^2 = 96.0%) better describes the early degradation of the molecule but overestimates the dissipation rate after 20 days. This example shows the effect of the ln-transformation of the data on the relative weights of early and later time points on the regression compared to the nonlinear fit to the non-transformed data. As with the IN and MS sites, simple first-order kinetics does not adequately describe cloransulam-methyl dissipation at the WI site.

The nonlinear fit to the non-transformed data and the linear fit to the ln-transformed data are simply different techniques of fitting the parameters of the simple first-order decay model. The reason for the difference in the fits between the two methods of solving for the regression parameters is a mathematical artifact resulting from the ln-transformation of the data prior to minimizing the sum of squares of the regression. Transformation of the data results in greater weight being placed on later time points in the linear regression; hence those points will have a greater influence on the regression
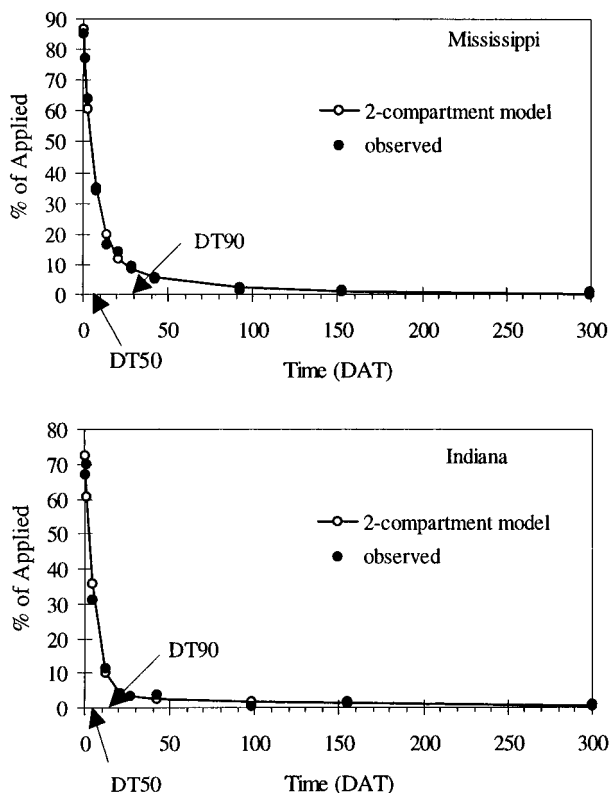
Figure 5. Two-compartment model fit to the average percent of applied radioactivity as cloransulam-methyl (TP- and AN-label) vs DAT for the Mississippi and Indiana sites.

line. If the process truly follows a simple first-order decay, then the two regression techniques will result in the same fit to the data. Conversely, the lack of agreement between the two fitting techniques for three of these sites indicates greater complexity in the dissipation pattern of cloransulam-methyl.

2. Two-Compartment Model. Clearly, the first-order model does not accurately describe the dissipation of cloransulam-methyl due to the biphasic nature of its degradation in most cases. To provide a clearer understanding of the dissipation rate for cloransulam-methyl, a nonlinear two-compartment model was used (eq 3). This approach allows the accurate description of the rates of dissipation for both the initial and final phases of cloransulam-methyl degradation. The two-compartment model was fitted to the average [^{14}C]cloransulam-methyl concentration of both labels for each site for the entire 10 months of data. The half-lives of the first compartment was 3.5 (R^2 = 84%) and 4.8 (R^2 = 91%) days, respectively, for IN and MS (Figure 5). Figure 6 shows the two-compartment model fit to the WI data where the first compartment half-life was 2.5 days (R^2 = 99.7%). Attempts at fitting a two-compartment model to the NC data did not significantly improve the R^2. The two-compartment model half-lives for cloransulam-methyl in the field (2.5−4.8 days) were much shorter than the two-compartment half-lives reported in the laboratory aerobic soil metabolism study (9−13 days). The shorter field half-lives are likely a result of multiple degradation processes (metabolic and photolytic) occurring in the field. The DT$_{50}$ for cloransulam-methyl, interpolated graphically from Figures 4−6, were 5, 7, 8, and 11 days, respectively for the IN, WI, MS, and NC sites. The DT$_{90}$ were 15, 25, 40, and 56 days at IN, MS, NC, and WI, respectively.

Formation and Decline of Metabolites. Cloransulam-methyl degraded rapidly into cloransulam, 5-hy-
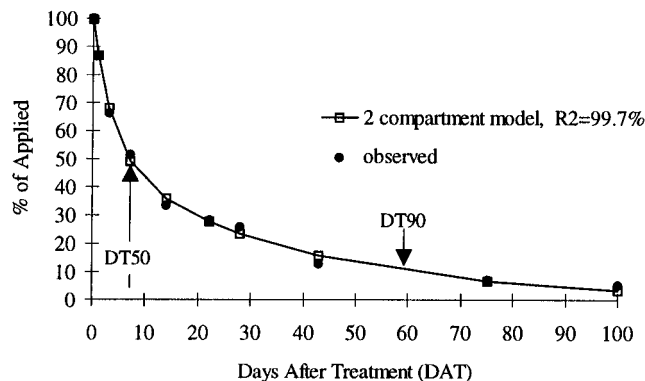

Figure 6. Two-compartment model fit to the cloransulam-methyl dissipation data at WI.

droxycloransulam-methyl, 5-hydroxycloransulam (all three observed in the laboratory aerobic soil metabolism study), and sulfonamide and sulfonic acid (both observed in the laboratory soil photolysis studies). The hydrolysis products identified in the laboratory study (cloransulam-methyl−imidate and cloransulam-methyl−acetic acid) were not observed in the field. Therefore, the key processes facilitating the degradation of cloransulam-methyl in the environment were microbial and photolytic. Only one metabolite, sulfonamide, reached >10% of applied at the MS and IN sites (16% and 11%, respectively); however, sulfonamide is of little phytotoxicological significance, with herbicidal activity 1000× less than parent (Schmitzer, 1996). Although cloransulam did not exceed 10% of applied in the ^{14}C studies (Figures 1 and 2), it reached 25.7% of applied parent at the NC site between 20 and 30 DAT and then declined to <10% of applied by 100 DAT. Cloransulam levels peaked at 12.4% of applied at the WI site then declined to 10.3% of applied by 100 DAT (Figure 3). Cloransulam has herbicidal activity approximately 10× less than cloransulam-methyl (Schmitzer, 1996). The rise and decline of cloransulam were especially well-defined at the MS and NC sites with estimated half-lives of 75.1 and 22.5 days, respectively. The pattern of cloransulam formation and decline at the IN and WI site did not allow for half-life estimates.

Mobility of Cloransulam-methyl and Degradates. Trace levels of ^{14}C activity at lower depths indicated that water moved downward from the soil surface to at least the depth at which ^{14}C was detected. On average, more than 98% and 90% of the ^{14}C activity remained in the 0−15 cm layer at the MS and IN sites, respectively. Approximately 4.7% of the applied ^{14}C activity was detected in the 30−45 cm depth increment on 27 DAT (IN), corresponding to concentrations of 0.6 and 1.4 ng g^{-1} for cloransulam-methyl and cloransulam, respectively. Maximum concentrations at depths below 15 cm during this sampling event were less than 1.5 ng g^{-1}. Although ^{14}C activity was detected at 90 cm, no cloransulam-methyl or degradates were found at levels above the LOQ below 45 cm. At the MS site, approximately 6% of the applied ^{14}C activity was detected in the 30−45 cm layer in one of six cores sampled during the 14 DAT event. ^{14}C was not detected at depths >30 cm in any other sample events, and the mass of ^{14}C in the 15−30 cm layer was always <10% of applied. These data indicate that although there was the potential for movement to depth of at least 90 cm at IN and 45 cm at MS, very little ^{14}C activity was actually mobile.

Mobility of Nonlabeled Cloransulam-methyl and Cloransulam. Cloransulam-methyl and cloransulam

were retained in the surface soil at both the NC and WI sites with only limited evidence of movement below 30 cm under conditions where water and bromide were very mobile in the soil profile. Most of the cloransulam-methyl was confined within the top 5 cm (incorporation depth) of the soil profile, even in the vulnerable, coarse-textured WI soil. Cloransulam-methyl was not detected below 30 cm at any time at the NC or WI site. Movement of cloransulam-methyl and cloransulam below 15 cm was sporadic and occurred at very low levels at both sites. Cloransulam was observed in the NC site 45−60 and 60−75 cm soil layer in a single composite sample at 70 DAT at levels <0.5 ng g^{-1}. At the WI site, cloransulam was detected in a single composite sample at levels <0.6 ng g^{-1} in the 30−45 cm soil layer on 28, 75, and 100 DAT. The fact that cloransulam-methyl was not observed at depths below 30 cm at either site suggests that this molecule sorbed strongly enough to these soils that, despite the extreme leaching conditions within the first month after treatment at the NC and WI sites, it was not significantly mobile.

Bromide Leaching. Sufficient water, through natural precipitation and irrigation, was applied to both the NC and WI sites to cause water and bromide tracer to move through the entire 90 cm soil profile during the first 100 DAT. At the NC site, soil samplings from 7 to 100 DAT show the pulse of bromide moving deeper into the profile with time. This is expected given the significant rainfall experienced by the site during the first 100 days of the study. The leading edge of the bromide tracer front was detected below 25 cm by 14 DAT and at 90 cm by 42 DAT. At the WI site, the bromide pulse moved deeper into the soil profile with time and completely leached through the profile by 70 DAT suggesting that there was significant movement of water through this soil profile and showing the vulnerability of this site in terms of leaching. Movement of bromide to the 90 cm depth was observed by 28 DAT indicating that the combined rainfall and irrigation that occurred at the site was sufficient to cause leaching through the entire soil profile within the first month after application.

TDR Data. Results of the TDR water content monitoring also indicate conclusively that water moved past the 90 cm depth and that response to rainfall was rapid at the WI site. Figure 7 shows the average water content change with time for the 15, 30, 45, 60, and 90 cm depths at the WI site for two separate precipitation events; one 0.9 cm rainfall on 6 DAT and one 2.2 cm rainfall on 54−55 DAT. Water movement to the 45 cm depth at 6 DAT is observed in Figure 7a and corroborates the presence of the leading edge of the bromide pulse at approximately 45 cm on 7 DAT at WI. The lagged response of water content increase due to the rainfall is evident with increasing depth, as the wetting front moves from the surface to the bottom of the profile. Infiltrating water moves rapidly through the soil profile as shown in Figure 7b where the water content at the 30, 45, and 60 cm depths respond in approximately 2, 3, and 8 h, respectively, to the 2.2 cm rainfall event. Increasing water content is observed in <24 h at the 90 cm depth. This is consistent with the average soil K_{fs} estimates of 49.5 and 65.8 cm h^{-1} at the 20 and 40 cm depths, respectively, and confirms the vulnerability of this site in terms of potential leaching.

Comparison of Field and Laboratory Apparent K_d. The low mobility of cloransulam-methyl in the field
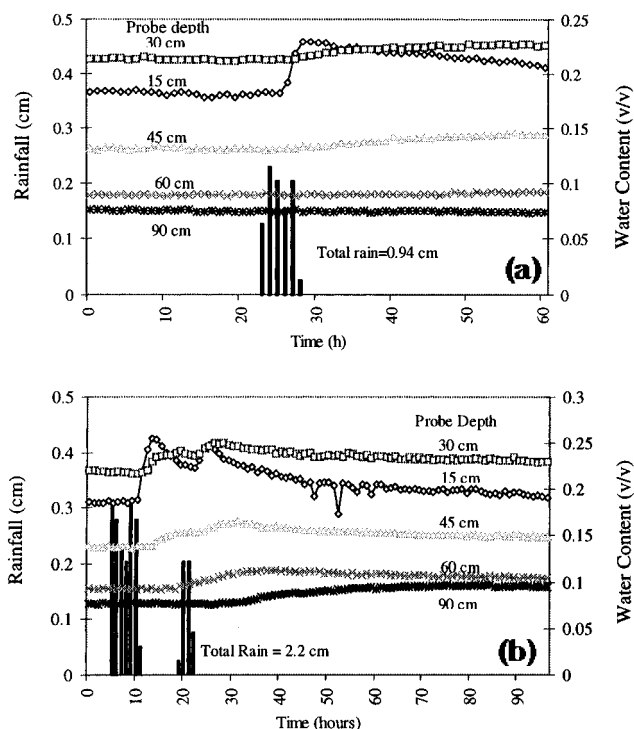

Figure 7. Volumetric water content measured by TDR for two events: (a) 0.94 cm on June 13, 1995 (6 DAT, $T = 0$ starts at 2:00 pm on 6/12/95), and (b) 2.2 cm on July 31 to August 1, 1995 (54−55 DAT, $T = 0$ starts at 12:00 noon on 7/31/95).

can be explained by its increased sorption and decreased bioavailability with increased soil contact time. Data which support this increase in the apparent K_d over time come from the multisoil kinetic study (Wolt et al., 1996) and an aged experiment involving phase partitioning concurrent with degradation over time. An independent estimate of apparent K_d can also be obtained from the field data in this study using

$$R = 1 + K_d \theta_g^{-1} \qquad (4)$$

and solving for K_d, where R is the retardation coefficient [R = ratio of the center of mass (COM) of the bromide tracer and the COM of cloransulam-methyl in the soil profile] and θ_g is the soil gravimetric water content (Freeze and Cherry, 1979). All of the parameters required to calculate R were measured in this study. Figure 8 shows the increase in apparent K_d with time for two laboratory experiments using a Hoyteville clay and an Appling sandy clay loam compared with the field apparent K_d values obtained from the Granville sandy loam (NC) and the Burkhardt sandy loam (WI) at several time points after application. Both the magnitude of apparent field K_d and the trend of increasing K_d over time are similar for the Hoyteville clay soil (laboratory) and the two field soils. Early time estimates of field K_d (<14 days) are less reliable due to the effect of low spatial resolution and thus difficulty in separating the true COM of bromide and cloransulam-methyl in the soil profile. Figure 8 clearly shows however that the increase in apparent K_d observed in the laboratory is manifested in the field through decreased mobility of cloransulam-methyl relative to the conservative and non-reacting bromide tracer.

CONCLUSIONS

The degradation of cloransulam-methyl was initially rapid, followed by slower degradation over time at three
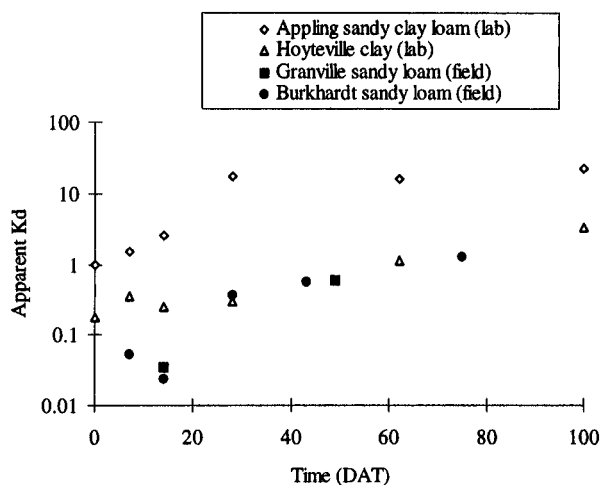
Figure 8. Apparent K_d values as a function of time for cloransulam-methyl for two laboratory soils and the NC and WI field soils.

of the four field sites (MS, IN, and WI) and was best characterized by a two-compartment model. The dissipation half-lives observed in this study (3–11 days) are shorter than the range of half-lives of 13–28 days observed in laboratory metabolism studies as a result of multiple concurrent degradation mechanisms in the field (microbial and photolytic). The range of cloransulam production in the field is consistent with the laboratory aerobic soil metabolism study which showed up to 37% cloransulam production. Phytotoxicity tests for cloransulam indicate that it possesses some herbicidal potential but at plant species-dependent levels of approximately $10\times$ lower than cloransulam-methyl. The concentration of cloransulam-methyl was below the EC_{25} (4 g ha^{-1}) for onion, the most sensitive terrestrial plant species, by 45 DAT at the MS, IN, and NC sites and by 100 DAT at the WI site. The rapid dissipation rates, metabolite formation patterns, and sorption characteristics obtained in these field studies are consistent with the existing laboratory data generated for cloransulam-methyl. The rapid degradation rate and the increasing sorption to soil over time results in low persistence and mobility of this compound.

ABBREVIATIONS AND SYMBOLS

$C(t)$, concentration at time t;

C_o, concentration at time $t = 0$;

$S_1(t)$, concentration of sorbed phase in two-compartment model;

$S_2(t)$, concentration of solution phase in two-compartment model;

$S(t) = S_1 + S_2$;

k, rate constant (day^{-1});

$t_{1/2}$, half-life (day);

DT_{50}, time for 50% of applied material to dissipate;

DT_{90}, time for 90% of applied material to dissipate;

K_d, soil sorption coefficient (L kg^{-1});

K_{fs}, field saturated soil hydraulic conductivity (cm h^{-1});

LOD, limit of detection;

LOQ, limit of quantification;

NOAA, National Oceanic and Atmospheric Administration;

R, retardation coefficient;

θ_g, gravimetric water content;

COM, center of mass.

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