Terrestrial Field Dissipation of Diclosulam at Four Sites in the United States

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The soil dissipation of diclosulam was studied using ^{14}C-labeled and nonradiolabeled material in Mississippi, North Carolina, Georgia, and Illinois between 1994 and 1997. The test substance was preemergence broadcast applied at target rates of 35 and 37 g ai ha^{-1} for the ^{14}C-labeled and the nonradiolabeled studies, respectively. The degradation of diclosulam was rapid with half-lives ranging from 13 to 43 days at the four sites. Rapid degradation rates and the increasing sorption to soil over time resulted in low persistence and mobility of this compound. Metabolite formation and dissipation in the field reflected observations of photolysis, hydrolysis, and aerobic soil metabolism studies in the laboratory. The rapid field dissipation rates, metabolite formation patterns, and sorption characteristics obtained in these field studies were consistent with the laboratory data generated for diclosulam, and reflect the multiple concurrent degradation mechanisms occurring in the field.

Keywords: *Diclosulam; triazolopyrimidine sulfonanalide; soil dissipation*

INTRODUCTION

Diclosulam [*N*-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5 c]pyrimidine-2-sulfonamide] is the active ingredient in a triazolopyrimidine sulfonanilide herbicide effective in the control of broadleaf weeds in soybeans and peanuts. Its mechanism of action is through the inhibition of the enzyme acetolactate synthase (ALS). Diclosulam may be used at rates up to 52 g ha $^{-1}$ as pre-plant incorporation (PPI), preemergence (PRE), or post-emergence "rescue" application. Yoder et al. (*1*) have characterized the physical and environmental properties of diclosulam (Table 1) The key environmental parameters which may influence the degradation of diclosulam in the field appear to be microbial activity and hydrolytic degradation (>pH 7).

The objectives of this study were to (1) establish the rate of soil dissipation for diclosulam and follow the rates of formation and decline of degradates at 4 sites in the U.S.; (2) compare the degradates formed under field conditions with those detected in lab studies, and from these data determine which breakdown pathways dominate under field conditions; and (3) evaluate the movement of diclosulam and its degradates through the soil profile under typical use conditions.

MATERIALS AND METHODS

Two small-plot field dissipation studies using ^{14}C diclosulam were conducted at sites near Lucama, North Carolina (NC) and Wayside, Mississippi (MS) in 1995. Two additional field-scale dissipation studies using nonradiolabeled diclosulam were conducted in the southern coastal region near Meigs, Georgia (GA), and in the midwest near Carlyle, Illinois (IL), in 1997.

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Study Sites. The NC site was located at the American Agricultural Services research farm in Lucama, Wilson County (coastal plain of North Carolina, 35° N, 77° W). The study site was located on a Norfolk series soil (fine-loamy, siliceous, thermic, Typic Paleudult). Soil texture ranged from a sandy loam at the surface to a loam at 90 cm. Organic matter content was 1.58% at the surface and decreased to 0.27% at 90 cm. Undisturbed bulk density ranged from 1.3 to 1.5 g cm $^{-3}$, and soil pH ranged from 4.8 to 6.5 across the 90 cm.

The MS site was located at the Dow AgroSciences LLC Wayside Field Research Station in Wayside Township, Washington County (33° N, 90° W). The study site was located in the Commerce series soil (fine-silty, mixed, nonacid, thermic, Aeric Fluvaquents). Soil texture ranged from a silt loam (0 to 15 cm) to silty clay loam (at 90 cm). Organic matter content ranged from 1.03% to 0.70%. Undisturbed bulk density ranged from 1.1 g/cm^3 to 1.4 g/cm^3, and soil pH ranged from 6.8 to 8.1 across the 90 cm.

The GA site was located at Hickey's Agri-Services Laboratory facility in Mitchell County (31° N, 84° W). The study site was located in the Tifton series sandy loam soil (fine, smectitic, mesic Vertic Albaqualfs). The soil adjacent to the plot consisted of sandy loam (0−30 cm) overlaying sandy clay loam (30−120 cm). Organic matter ranged from 0.9% near the surface to 0.1% in the deeper layers. Soil pH ranged from 4.8 to 6.8.

The IL site was located at the Alvey Agricultural Research facility in Clinton County (39° N, 89° W). The study site was located in a Cisne silt loam series soil (Vertic fine-loamy, siliceous, thermic Plinthic Kandiudults). The soil adjacent to the test plot consisted of silt loam (0−45 cm) overlaying silty clay loam to clay (45−120 cm). Organic matter ranged from 2.2% near the surface to 0.3% in the deeper layers. Soil pH ranged from 4.5 to 6.9.

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, and solar radiation, as well as 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 NC and by center-pivot irrigation in GA and IL.

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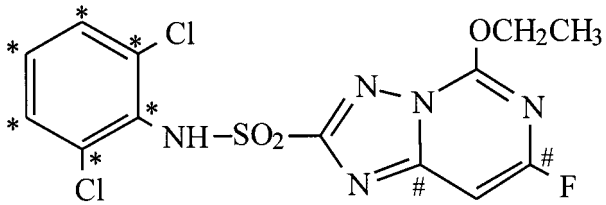
Table 1. Properties of Diclosulam (Yoder, 1996; ref *4*)

common name	diclosulam
chemical name	*N*-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro(1,2,4)triazolo[1,5 c] pyrimidine-2-sulfonamide
chemical structure	
molecular formula	$C_{13}H_{10}N_5O_3SFCl_2$
molecular weight	406.14 g mol^{-1}
water solubility (20 °C)	100 mg L^{-1} at pH 5 to 4000 mg L^{-1} at pH 9
D. I. water solubility (20 °C)	6.3 mg L^{-1}
pK_a (Yoder, 1996; ref *4*)	4.09 at 20 °C
vapor pressure (Yoder, 1996; ref *4*)	5×10^{-15} mm HG at 25 °C
CAS number	145701-21-9

*Anilline radiolabel of Diclosulam. # Pyrimidine radiolabel of Diclosulam.

Irrigation was performed on a semi-monthly 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, therefore each month was irrigated to meet 125% of the 30-year monthly average for rainfall.

^{14}C-Labeled Test Substances. Two different labels were used: [*phenyl*-UL-^{14}C] diclosulam (specific activity 25.5 mCi/mmol; uniformly labeled in the phenyl ring, hereafter referred to as the AN label) and [*pyrimidine*-7,9-^{14}C] diclosulam (specific activity 30.6 mCi/mmol; labeled in the 7- and 9-positions of the pyrimidine ring, hereafter referred to as the TP label)(Table 1). The radiochemical purity of the test substances was greater than 97%. 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 structure. The previously identified degradates (laboratory studies) 5-OH diclosulam (*N*-(2,6-dichlorophenyl)-5-hydroxy-7-flouro[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide), 8-Cl diclosulam (*N*-(2,6-dichlorophenyl)-8-chloro-7-flouro-5(6H)-oxo[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide), and TAAA (*N*-(2,6-dichlorophenyl)-3-[1,2,4]-triazoloacetic acid-5-sulfonamide) can be observed in both labels, whereas the ASTP (5-hydroxy-7-flouro[1,2,4]triazolo-[1,5-c]pyrimidine-2-sulfonamide) and TPSA (5-hydroxy-7-flouro[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonic acid) can be observed only in the TP label (Figure 1).

On the day of application at the Lucama, NC site the test substance was formulated by first dissolving it into acetonitrile and then adding water to form a 50:50 mixture of acetonitrile and water. Acetone was used at the Wayside, MS site in place of acetonitrile to help ensure resolubilization of the test substance. The inert materials that would be in the typical formulation were then added. Traditional formulating methods were not possible because of the small amounts of test substance required for each plot. The 50:50 mixture of acetonitrile (or acetone) and water was used in lieu of the typical 100% water solvent to ensure that the test substance was completely resolubilized after transport to the field site.

Nonradiolabeled Test Substance. Diclosulam was used as the test substance in the end use product formulation BF-309, a water-dispersible granule. The lot used in this study contained 82.4% of active ingredient as indicated on the product label.

^{14}C-Labeled Test Plot. Two bordered treatment plots (122 × 520 cm) were prepared at each radiolabeled site (NC, MS): one for the AN-labeled material and one for the TP-labeled material. Borders consisted of 5.08 × 30.5 cm boards extending approximately 10 cm into the ground. All plant material was removed from the plots prior to application of the test substance. Each plot was equipped with a runoff collection system designed to prevent ponding water in the plots during heavy rains. The runoff system consisted of a trough at one of end of the plot (lowest in elevation) which directed runoff via gravity feed into a buried containment tank. A 91 × 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.

Nonradiolabeled Test Plot. At the GA and IL sites, the study areas each consisted of one treated plot containing 5 subplots. Each subplot was separated by approximately 4 m of buffer area, and traffic on the plot was restricted within the buffer areas to ensure that the sampling subplots were not disturbed. Each subplot was divided into 20 sampling grid locations measuring approximately 152 cm × 152 cm. The plots were cleared of plant material before application. A control plot of approximately 457 cm × 457 cm was established at each location at least 2300 cm away from the treated plot.

Application of ^{14}C-Labeled Test Substance. ^{14}C-Diclosulam was applied on June 16, 1994, at Lucama, NC, and on June 22, 1994, at Wayside, MS, as a broadcast spray to bare soil plots at a target rate of 35 g a.i. ha^{-1}. A pressurized nitrogen hand boom sprayer (R&D Sprayers, Inc., Opelousas, LA) was used with one TeeJet 9502E even, flat fan nozzle (Spraying Systems Co., Wheaton, IL). Guide wires were used to maintain the proper height and position over the plots. Four passes were made over the plot with the sprayer to obtain a uniform application. Nine filter paper disks were placed in the plots to determine the uniformity of the application.

Application of Nonradiolabeled Test Substance. Diclosulam was broadcast applied to bare soil plots on June 13, 1996, at the Meigs, GA site, and on June 28, 1996, at the Carlyle, IL site at a target rate of 37 g a.i. ha^{-1} (105% of maximum label rate). Two passes were made over the entire plot to increase application uniformity. Three spray solution samples were collected at each site, two before application and one after application. After application the test substance was incorporated into the top 2.5 to 5 cm of soil at both sites.

^{14}C-Labeled Plot Soil Sampling. Soil samples were collected at 0, 1, 7, 14, 21, 28, 42, 60, 90, and 150 days after treatment (DAT). At the NC and MS sites, a single 3-stage (0−15, 15−30, and 30−90 cm deep) core was removed from one randomly selected grid in each of the three subplots, resulting in a total of three cores for each sampling event per plot, with the exception of 0 DAT when the cores taken were 2.5 cm deep and 10 cm in diameter. As each stage was removed a steel casing remained in the hole. Inner core diameters for the 0−15, 15−30, and 30−90 cm segments were 7.4, 4.9, and 3.2 cm, respectively. The cores were placed into a freezer or onto dry ice and kept in the dark until analyzed. All core holes

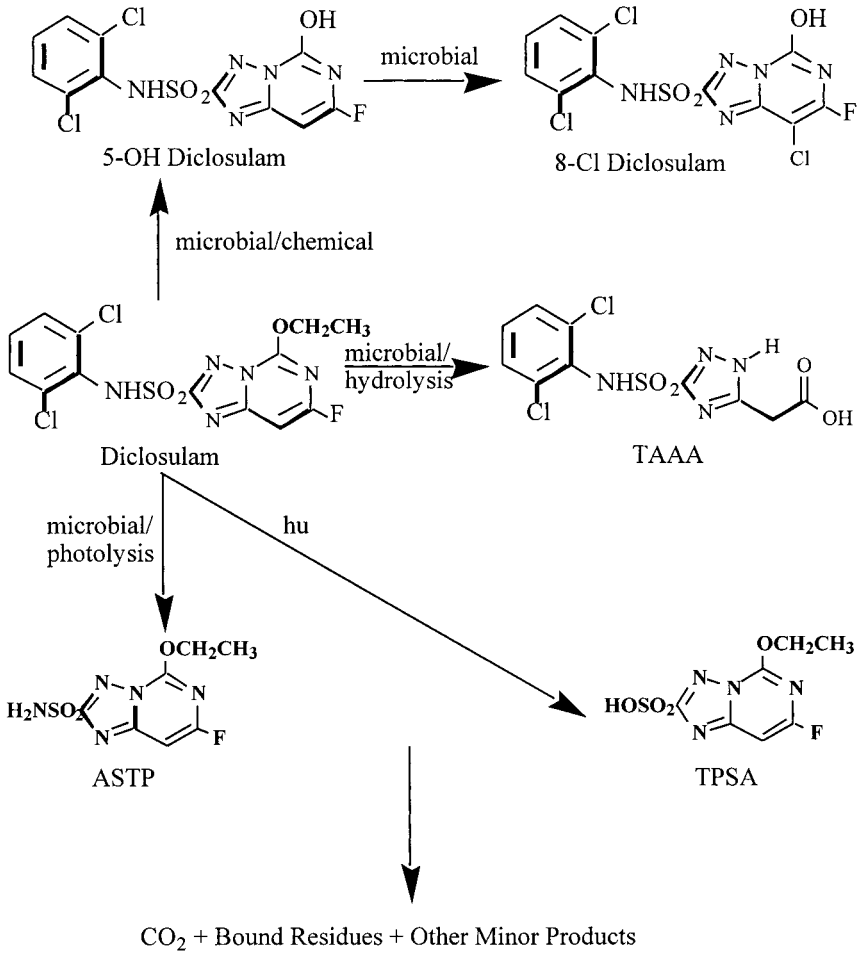


Figure 1. Structures of diclosulam and its metabolites and proposed pathway for the degradation.

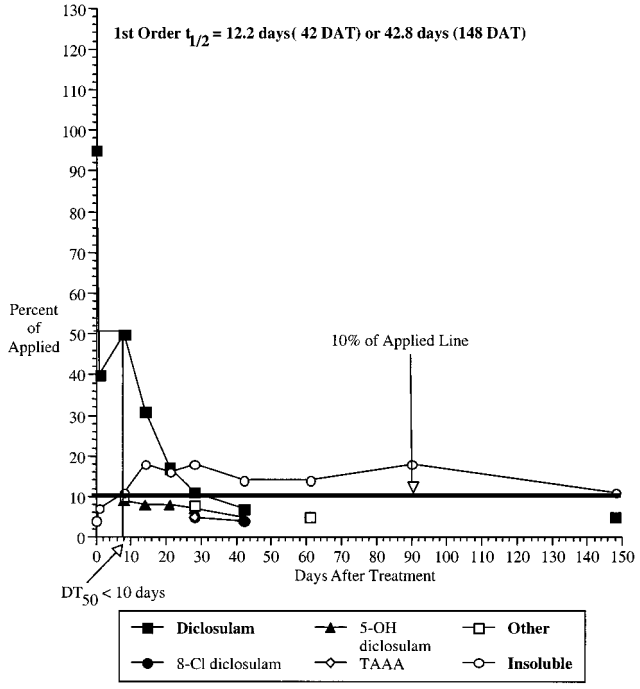


Figure 2. Patterns of degradation for diclosulam and its degradates for the AN label at the Lucama, NC site (days after treatment vs percent of applied material). Analytes exceeding 10% of applied material are printed in bold.

were back-filled with similar soil from an untreated area and marked with a flag. Frozen soil cores were cut into 15-cm segments and analyzed individually. During the first three months of the study, if adequate runoff water and sediment were available, sampling would be conducted of each matrix until radioactivity declined below 50 dpm/mL. Water samples were acquired from an underground tank that collected runoff water from one end of the plot. Prior to sampling, the water was thoroughly mixed and the volume of water was determined. After mixing, duplicate aliquots of water (approximately 100 mL each) were removed and placed into 250-mL brown glass containers with Teflon-lined caps and placed into metal cans for shipping.

Nonradiolabeled Plot Soil Sampling. Soil samples were collected at approximately 0, 1, 3, 7, 14, 20, 28, 64, 97, 120, 151, 181, 271, and 364 days after application. At the GA and IL sites, a set of 15 two-stage (0−15 and 15−90 cm deep) cores was taken. Core diameters for the 0−15 cm segment were 5.6 cm and for the 15−90 cm segment were 3.3 and 4.1 cm for the GA and IL sites, respectively. Cores were frozen and segmented into 15-cm increments. Cores from each subplot were composited in sets of 5 to form three composite cores at each depth for analysis.

Ten aluminum pans with surface areas of approximately 672 cm^2 at GA and 685 cm^2 at IL were filled with soil to a depth of approximately 2.5 cm and were placed within the buffer areas of the plot prior to application of the test substance. After application, the soil was stored frozen. The soil pan samples were collected to obtain greater precision in the estimate of the mass of diclosulam applied to the soil. At the IL site, 10 filter papers with a total surface area of approximately 1160 cm^2 were placed on the soil surface during application. The filter papers were collected and frozen for subsequent analysis.

Travel Spike. Travel spikes were prepared at all four sites to determine the stability of diclosulam and ASTP (GA and IL) during shipping, sample preparation, and analysis. Spikes

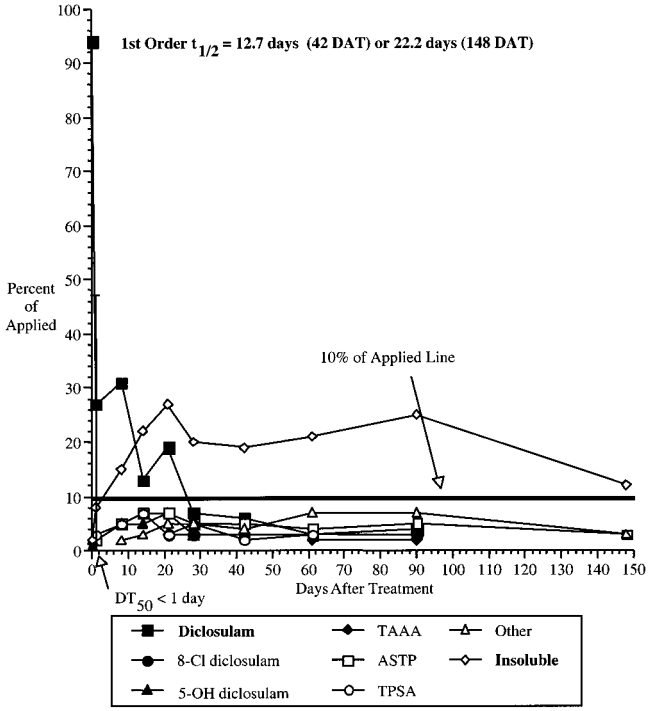


Figure 3. Patterns of degradation for diclosulam and its degradates for the TP label at the Lucama, NC site (days after treatment vs percent of applied material). Analytes exceeding 10% of applied material are printed in bold.

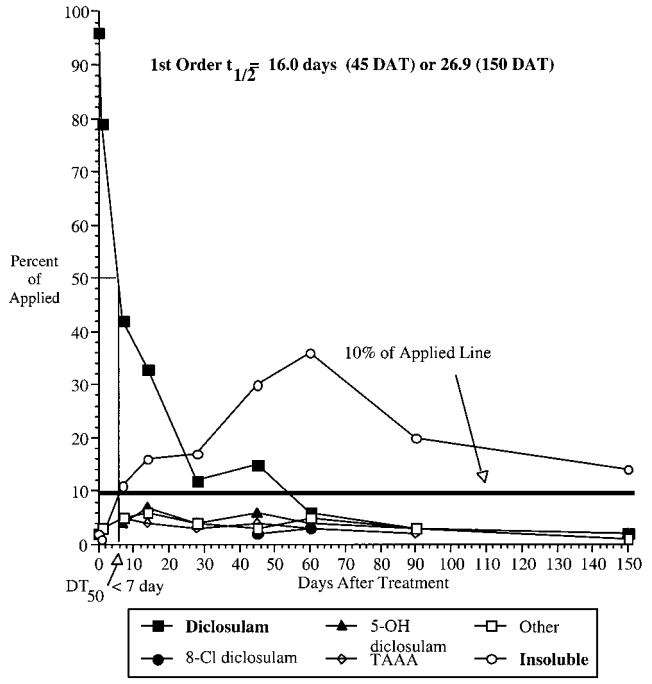


Figure 4. Patterns of degradation for diclosulam and its degradates for the AN label at the Wayside, MS site (days after treatment vs percent of applied material). Analytes exceeding 10% of applied material are printed in bold.

were prepared by dosing a preweighed mass of control soil with preweighed quantities of diclosulam to achieve the desired concentration in soil.

Analytical Methods for ^{14}C-Labeled Residues. The filter papers were extracted with 90:10 acetone/1N HCl, and total radioactivity was determined by liquid scintillation counting (LSC). The soil method consisted of three primary steps: combustion of a soil subsample to determine total activity, extraction of a soil subsample with individual component analysis (diclosulam and degradates), and combustion of the

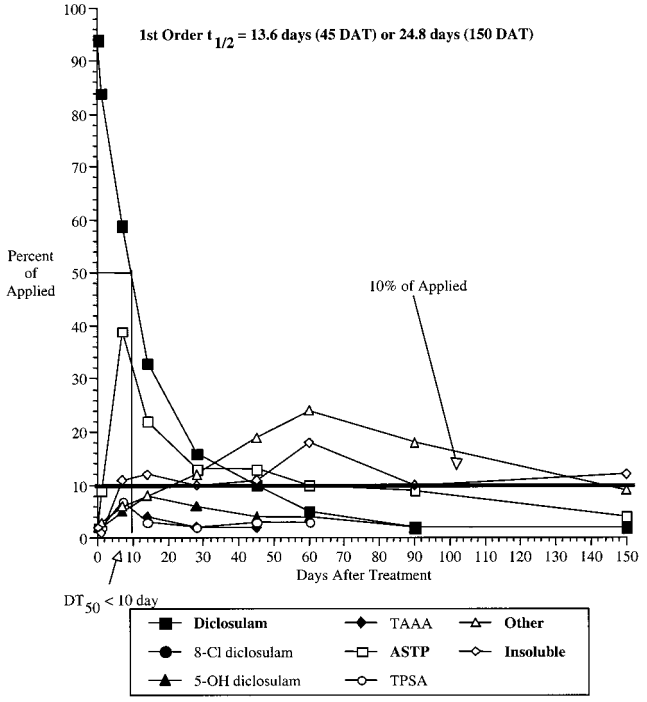


Figure 5. Patterns of degradation for diclosulam and its degradates for the TP label at the Wayside, MS site (days after treatment vs percent of applied material). Analytes exceeding 10% of applied material are printed in bold.

extracted soil to determine the insoluble (nonextractable) fraction. Frozen soil cores were segmented and placed in metal cans to thaw. Approximately 15−20 wt % of deionized water was added to each sample can. The samples were then mixed thoroughly while chilled. Samples were stored 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, then quantified by LSC. The component analysis consisted of three extractions with 90:10 acetonitrile/1N HCl, concentration, filtration (for samples containing large quantities of particulate), and a Waters high-pressure liquid chromatography (HPLC; Milford, MA) to separate degradates from diclosulam. Soil extracts were analyzed by reverse-phase liquid chromatography under the following conditions. Using a Waters C-18 Radial Pak 8 × 10 column (Milford, MA), components were eluted with a linear gradient using 99:1 water/acetic acid (mobile phase A) and 99:1 acetonitrile/acetic acid (mobile phase B). Fraction collection took place for 45 min with 0.5-min fractions collected. The gradient consisted of a 5 min hold at 100% A, linear gradient over the next 40 min to 40%:60% A/B, linear gradient over the next 5 min to 100% B, hold for 5 min at 100% B, and then reequilibrate with 100% A for 15 min before next injection. UV/vis detection at 254 nm was for retention check of nonradiolabeled material only. Diclosulam and degradates were quantified using liquid scintillation counting. The strong extracting solution was required to effectively remove aged residues of diclosulam and its degradates from soil. The method of detection for both the combustion analysis and component analysis was liquid scintillation counting.

The limit of quantification (LOQ) for the soil combustion method was 45 dpm g^{-1}. The LOQ for the Lucama, North Carolina site was <0.29 and <0.25 ng g^{-1} for the AN and TP labels, respectively. At the Wayside, Mississippi site the LOQ was <0.12 and <0.10 ng g^{-1} for the AN and TP labels, respectively. The LOQ for both water and sediment combustion was 37 dpm g^{-1}.

The soundness of the method was established by running analytical recoveries, travel spikes, and concurrent fortified controls with sample analysis. Analytical recoveries consisted of control soil fortified with TP labeled ^{14}C diclosulam and were >97% (98 ± 5%). Fortified controls were analyzed during the

Table 2. Simple First-Order $t_{1/2}$ for Diclosulam and Maximum Concentrations of Diclosulam Degradates at the North Carolina and Mississippi Sites Reported as Percent of Applied Material (and ng g^{-1})[a]

site/label	DT_{50}	$t_{1/2}$ of diclosulam at 5 months (first order)	LOQ	8-Cl	5-OH	TAAA	ASTP	TPSA	InSol
NC/AN label	<10	43 days	<4.3% (<0.29)	5% (0.5)	9% (0.9 ± 0.2)	5% (0.6)	NA	NA	18%
NC/TP label	<1	22 days	<1.9% (<0.25)	3% (0.8)	7% (1.4 ± 0.3)	3% (0.6 ± 0.3)	7% (1.1 ± 0.3)	7% (0.9)	27%
MS/AN label	<7	27 days	<1.3% (<0.12)	3% (0.4)	7% (1.0 ± 0.3)	5% (0.6 ± 0.3)	NA	NA	36%
MS/TP label	<10	25 days	<1.5% (<0.10)	<LOQ	8% (0.8 ± 0.5)	4% (0.4)	39% (2.5 ± 1.8)	7% (0.4 ± 0.3)	18%

[a] NA, not applicable; InSol, insoluble (not extracted by organic solvent); LOQ, limit of quantitation.

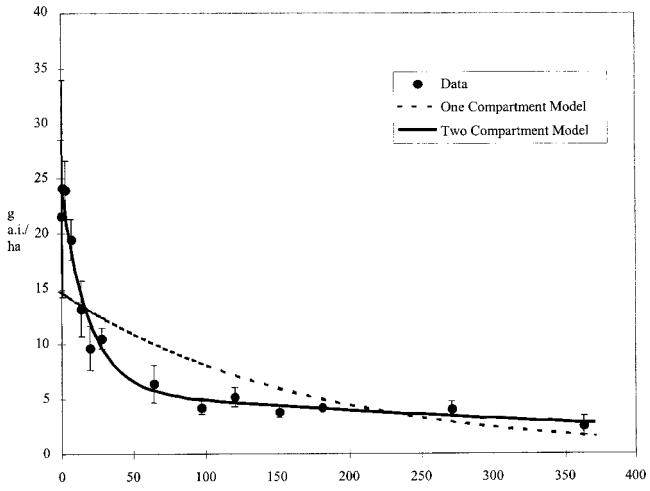


Figure 6. Dissipation of diclosulam at the GA site.

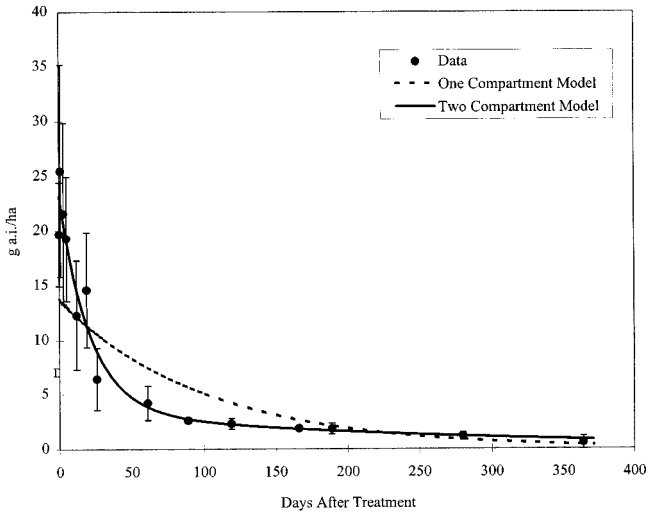


Figure 7. Dissipation of diclosulam at the IL site.

same time period as the samples. No degradation of the parent molecule was observed in either (greater than 98 ± 1%) indicating the parent molecule was stable during the course of the analysis. Mass spectral confirmation was performed by LC/MS on a Hewlett-Packard 1050 series HPLC and a Finnigan TSQ700 utilizing an electrospray ionization mode with selected reaction monitoring (SRM). The presence of diclosulam, 8-Cl diclosulam, ASTP, 5-OH diclosulam, and TPSA at both Lucama, NC (42 DAT sample) and Wayside, MS (45 DAT sample) were confirmed in 0−15 cm cores against a mixed standard containing diclosulam, 8-Cl diclosulam, ASTP, 5-OH diclosulam, and TPSA.

Analytical Methods for Nonradiolabeled Residues. Frozen soil cores were segmented and composited, and ground using a hammermill equipped with a 5-mm 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 diclosulam and ASTP.

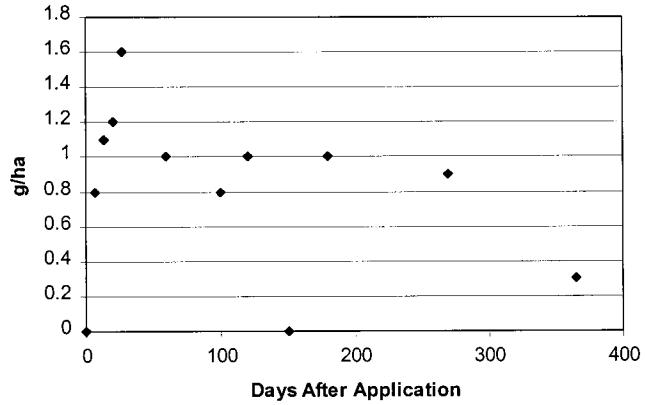


Figure 8. Formation and decline of ASTP at the GA site.

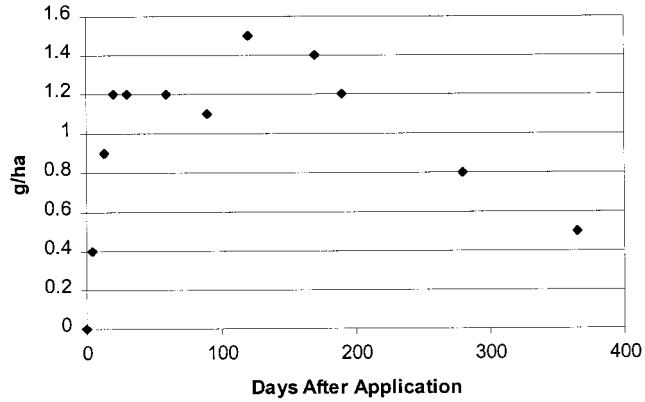


Figure 9. Formation and decline of ASTP at the IL site.

Soil samples were analyzed for residues of diclosulam and its metabolite ASTP using gas chromatography with mass selective detection (GC/MSD) with a limit of detection (LOD) of 0.3 ppb and a limit of quantitation (LOQ) of 0.8 ppb.

Statistical Methods and Kinetic Treatment of Data. Degradation kinetics were based on the total percent of applied material recovered from the entire soil profile using a first-order degradation model:

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

with a linear least-squares fit to the natural log(ln)-transformed data. Degradation constants (k) were converted to a half-life value in days ($T_{1/2}$) by

$$T_{1/2} = -0.693/k \quad (2)$$

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

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

where k_1 and k_2 are the degradation rate constants representing the rapid degradation of the solution-phase material (1st compartment, S_1) and the slower degradation of the sorbed-

phase material (2nd compartment, S_2) respectively (*2*). The double-exponential model was fit to the data using Deltagraph at the GA and IL sites. Interpolation from the modeled results was used to determine the time to 50% and 90% dissipation of diclosulam (DT_{50}, DT_{90}).

RESULTS AND DISCUSSION

Climatological Conditions. Rainfall plus irrigation amounted to 117, 134, 137, and 117% of the 30-year normal precipitation at the NC, MS, GA, and IL sites, respectively, during the field phase of the studies. Both the NC and MS sites received 140 and 302% of the 30 year average rainfall during the month following application.

Travel Spikes and Storage Stability. The average percent recovery for the component analysis was 96% ± 9% for three travel spikes using radiolabeled diclosulam. No significant degradation was observed in the radiolabeled travel spike analysis, indicating that degradates observed in field samples were the result of "in field" degradation of diclosulam. Diclosulam recoveries from 4 field spikes using nonradiolabeled diclosulam averaged 89% of expected and ASTP recoveries averaged 114% of expected at the GA site. Recoveries were 88% and 124% of expected for the diclosulam and ASTP at the IL site. These results suggest that neither diclosulam nor ASTP experienced significant degradation during shipping, handling, and preparation. The field spikes were reanalyzed 61, 189, 230, and 265 days after the initial analysis. No degradation of diclosulam or ASTP was observed over this period of frozen storage.

Application Rate. The application rate was validated using filter papers and 0-DAT soil samples. Filter paper results from the NC site indicated that the average percent of target application in terms of total ^{14}C activity was 62 ± 10% and 76 ± 13% for the AN and TP plots, respectively. Day of application soil samples indicated the average percent of target application was 59% and 98% for the AN and TP plots, respectively. Filter paper results from the MS site indicated that the average percent of target application was 83 ± 13% and 74 ± 9% for the AN and TP plots, respectively. Day of application soil samples indicated the average percent of target application was 65% and 51% for the AN and TP plots, respectively.

Analyses of the soil pans indicated that the application of diclosulam was uniform across the treated plot and reached 70 ± 4% of the target application rate in GA and 84 ± 6% in IL. The 0−15 cm soil cores from the day of application indicated that 63 ± 20% of the target application rate had been reached in GA and 57 ± 14% in IL. The filter papers indicated that 97 ± 5% had been applied at IL.

^{14}C Mass Balance. Total ^{14}C activity within the soil declined over time to less than or equal to 50% of that applied. Yoder et al. (*1*) reported up to 47% of the ^{14}C activity was lost through $^{14}CO_2$ evolution in a laboratory soil aerobic metabolism study with diclosulam. Therefore, a majority of the activity lost over time in the field study is likely the result of CO_2 evolution from the plots. This is similar to the results and conclusions drawn for the field dissipation of a related sulfonanalide compound, cloransulam-methyl (*3*).

Rate of Diclosulam Dissipation. The degradation of diclosulam was initially rapid and biphasic at all sites. The degradation observed at the NC, MS, GA, and IL sites is illustrated in Figures 2 and 3, 4 and 5, 6, and 7, respectively.

Radiolabeled. For the radiolabeled studies, first-order half-lives were calculated. Although visual inspection of the data reveals a biphasic degradation, the variability in the data precluded determination of half-lives using a two-compartment model. At the NC site the first-order half-life was 43 and 22 days for the AN and TP labels, respectively (Table 2). At the MS site the first-order half-life was 27 and 25 days for the AN and TP labels, respectively (Table 2). As a result of multiple dissipation processes, the half-life for diclosulam in the field was shorter than the half-lives reported in the laboratory aerobic soil metabolism study (*1*). Although the half-life of diclosulam in the aerobic soil metabolism laboratory study ranged from 33 to 77 days, the half-life in the field ranged from 22 to 43 days.

Nonradiolabeled. The double exponential or two-compartment decay curve fitted to the data ($R^2 = 0.97$ for GA and 0.95 for IL) is plotted on the figure. This model provides an excellent fit for the data, and can be conceptualized as describing diclosulam degradation in two phases: the soil solution phase and the sorbed phase. The majority of the diclosulam exists in the solution phase where degradation is rapid, as evidenced by the sharp decline in diclosulam concentrations near the day of application; the remainder of the diclosulam is sorbed to the soil and breaks down more slowly. Using this conceptual model, the half-life for the solution phase is approximately 13 days in Georgia and 14 days in Illinois. The sorbed half-lives are approximately 350 days for Georgia and 140 days for Illinois. Using this model, the DT_{50} and DT_{90} values (the time for 50% and 90% of the material to dissipate) for GA are approximately 19 days and 440 days. For IL, the DT_{50} and DT_{90} values are approximately 18 days and 130 days. From a biological perspective, the sorbed material is unavailable for exposure and if it desorbs would degrade rapidly as shown by the rapid solution phase kinetics.

As shown in Figures 6 and 7, a first-order kinetic model does not fit the data as well as the double exponential model ($R^2 = 0.74$ for GA and 0.86 for IL). The predicted first-order half-lives for diclosulam, approximately 120 days for Georgia and 70 days for Illinois, are much longer than the observed DT_{50} because of the slower dissipation of diclosulam once concentrations reach lower levels.

Formation and Decline of Metabolites. *Radiolabeled Study.* Figures 2, 3, 4, and 5 depict the formation and decline of degradates at the NC and MS sites. The degradates 5-OH diclosulam, 8-Cl diclosulam, ASTP, TPSA, and TAAA were observed in these studies at less than 10% of applied material (Table 2). No new degradates were identified in the field studies. The 5-OH diclosulam was observed in the aerobic soil metabolism, hydrolysis, soil photolysis, anaerobic aquatic, and aerobic aquatic laboratory studies (*4*). 8-Cl diclosulam was observed in the aerobic soil metabolism laboratory study (*1*). The appearance of 8-Cl-diclosulam was unexpected, as chlorination of a xenobiotic organic compound is not a typical breakdown mechanism in soil metabolism. Although unusual, biochemical halogenation of organic substrates has been noted for numerous life forms, with examples from organisms as diverse as bacteria, fungi, algae, higher plants, insects, and mammals (*5*). These organisms produce halogenated substances as part of their defensive or food gathering strategies. The forma-

tion of 8-Cl-diclosulam in aerobic soils is the first known example of a sulfonanilide that has undergone biochlorination. ASTP was observed in the aerobic soil metabolism and soil photolysis laboratory studies (*4*). TPSA was identified in the laboratory aqueous and soil photolysis studies (*4*). TAAA was observed in the hydrolysis, anaerobic aquatic, and aerobic aquatic laboratory studies (*4*). The key processes facilitating the degradation of diclosulam in the environment were microbial and photolytic. Figure 1 illustrates the proposed pathway for the degradation of diclosulam.

Nonradiolabeled Study. Figures 8 and 9 depict the formation and decline of ASTP at the GA and IL sites. ASTP began forming after approximately 4 days, and peaked at a concentration of approximately 7% and 6% of the highest observed diclosulam concentration at the GA and IL sites, respectively. The concentration at the GA site peaked at about 1 month after application, whereas the concentration at the IL site reached a peak after approximately 4 months.

Mobility of Diclosulam and Degradates. *Radiolabeled Study*. The majority of the ^{14}C activity remained in the top 15 cm of soil. Diclosulam and degradates were below the LOQ at 45 cm and greater depths. The limited mobility of diclosulam is most likely related to aging effects resulting in increased adsorption. Yoder et al. (*1*) reported apparent K_d values for diclosulam in 6 soils increasing by factors of up to 7.5× after 56 to 119 days of aging. Sorption to soil has been shown to increase over time in both lab and field studies for cloransulam-methyl (*3*) and florasulam (*6*), both similar sulfonanilide molecules.

Nonradiolabeled Study. At the IL and GA sites, the majority of both diclosulam and ASTP residues was confined to the 0−15-cm layer. Movement of diclosulam and ASTP below 15 cm was sporadic and occurred at very low levels. At the Georgia site, only one detection of diclosulam occurred in the 15−30-cm layer. This detection, at 4 months after application, occurred in only one of the three composite samples for this date. There were no detections of diclosulam below the 15−30-cm layer.

At the Illinois site, diclosulam was detected at levels below the LOQ in the 15−30-cm soil layer at two sampling points (3 days and 2 months after application). In both cases, only one of the three composite samples contained detectable residue levels. A single composite sample at one time point (2 months after application) contained residues in the 45−60-cm soil layer and may have reflected an isolated preferential flow event due to a soil macropore or crack. No ASTP residues were detected below the 0−15-cm soil layer at the GA or IL sites.

The fact that the majority of applied diclosulam at all four study sites remained in the top 15-cm soil layer suggests that the molecule sorbed strongly enough to soil that, despite the extreme leaching conditions at these sites during the first 2−3 months after application, it was not significantly mobile.

CONCLUSIONS

The degradation of diclosulam was bi-phasic, with initial rapid degradation slowing over time, and was best characterized by a two-compartment model. The first-order dissipation half-lives (solution phase) observed in this study (13 to 43 days) are shorter than the range of similarly calculated half-lives observed in the laboratory metabolism studies (33 to 77 days) as a result of multiple, concurrent degradation processes occurring in the field. Diclosulam degraded rapidly into 5-OH diclosulam, 8-Cl diclosulam, TAAA, ASTP, and TPSA. The observed degradates were consistent with those found in the laboratory studies and were indicative of microbial, photolytic, and hydrolytic processes occurring in the field. No new degradates were observed in the field studies. In the radiolabeled studies, the majority of the ^{14}C activity was confined to the top 0 to 15 cm of the soil profile. Analysis of selected lower depths indicated that diclosulam and degradates were below the LOQ (<0.5 ng g^{-1}) at depths $>$ 45 cm. In the nonradiolabeled study diclosulam was detected only sporadically below 15 cm, with the majority of the mass remaining in the top 15 cm of soil. The ASTP degradate was not detected below 15 cm at the GA or IL sites. The limited mobility of this compound observed in these studies is likely a result of the rapid dissipation rate, and the increasing sorption to soil over time.

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