Aerobic Metabolism of Diclosulam on U.S. and South American Soils

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Degradation of the sulfonanilide herbicide diclosulam was studied on nine soils from three countries to determine the rates and products of aerobic metabolism. Diclosulam was applied to four agricultural soils from the United States, three from Argentina, and two from Brazil at a rate of 0.1 ppm, equivalent to approximately twice the maximum field application rate of 52 g of active ingredient/ha. U.S. and Brazilian soils were incubated in the dark at 25 °C at 75% 0.3 bar moisture; Argentinean soils were incubated in the dark at 20 °C and 45% moisture holding capacity. Samples were analyzed up to one year after treatment. Two-compartment DT_{50} and DT_{90} values averaged 28 ± 12 and 190 ± 91 days, respectively. Three soil metabolites reached levels of >10% of applied in at least one soil and were identified as the 5-hydroxy analogue of diclosulam (5-OH-diclosulam), aminosulfonyl triazolopyrimidine (ASTP), and the 8-chloro-5-hydroxy analogue of diclosulam (8-Cl-diclosulam). The terminal products of diclosulam soil metabolism were mineralization to CO_2 and bound soil residues. Apparent sorption coefficients (K_d) were determined on a subset of samples by extraction with a 0.01 M $CaCl_2$ solution followed by an acidified acetone extraction. Initial sorption coefficients were similar to those obtained in a batch equilibrium study and averaged 1.1 L/kg for the six soils tested. K_d coefficients for the metabolites, when available, tended to be slightly lower than that for diclosulam. Sorptivity of diclosulam and degradates increased with time.

Keywords: *Diclosulam; 5-OH-diclosulam; 8-Cl-diclosulam; ASTP; aerobic soil metabolism; aged mobility*

INTRODUCTION

Diclosulam [*N*-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-*c*]pyrimidine-2-sulfonamide] is a new herbicide registered for the control of broad-leaf weeds in soybeans in Argentina and Brazil and is under development for use in the United States on soybeans and peanuts. Diclosulam is a member of the triazolopyrimidine sulfonanilide family of chemistry, which also includes metosulam, flumetsulam, florasulam, and cloransulam-methyl. Diclosulam and related sulfonanilides show excellent crop selectivity and broad-spectrum weed control at much lower application rates than traditional herbicides.

Diclosulam does not target soybeans and peanuts at field rates but is very active against such weeds as *Ambrosia artemisiifolia* (common ragweed), *Abutilon theophrasti* (velvetleaf), and *Xanthium strumarium* (cocklebur) (Bailey et al., 1999; Shaw et al., 1999). The mode of action for diclosulam in plants is inhibition of the enzyme acetolactate synthase (ALS). ALS is located in the chloroplast, where it catalyzes the first committed step in branched-chain amino acid biosynthesis (Singh and Shaner, 1995). This enzyme catalyzes the condensation of two molecules of pyruvate to form acetolactate, which is converted through a series of reaction steps into valine and leucine. A similar reaction, producing acetohydroxybutyrate for the production of isoleucine, is also catalyzed by ALS when α-ketobuterate and pyruvate are used as substrates.

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Application of diclosulam is pre-plant incorporated, surface pre-plant, or pre-emergence with a maximum global use rate of 52 g of active ingredient (ai)/ha; however, typical use rates are in the 17.5−35 g/ha range.

As diclosulam is a soil-applied herbicide with broad-leaf weed control, the potential for carry-over to injure subsequent crops, such as corn, cotton, or other crops rotated with soybeans and peanuts, must be evaluated. Degradation rate and sorptivity are key factors in ascertaining carry-over probability and also affect a chemical's potential to migrate into groundwater.

Diclosulam has a molecular mass of 406 g/mol. It is an off-white powder with a vapor pressure of 5×10^{-15} mmHg (25 °C). Water solubility of diclosulam is pH dependent, ranging from ∼100 ppm at pH 5 and 7 to >4000 ppm at pH 9. The pK_a is 4.09 at 20 °C, indicating that diclosulam exists in its ionic form in most natural water systems, and its octanol/water partition coefficient ranges from $\log K_{ow} = -0.448$ at pH 9 to $\log K_{ow} = 1.42$ at pH 5.

MATERIALS AND METHODS

Test Materials and Reference Compounds. Diclosulam contains two ring systems, a triazolopyrimidine ring and an aniline ring. The insertion of a ^{14}C label in each ring makes it possible to differentiate between metabolites formed by cleavage of the sulfonamide bridge. The structure of diclosulam shown in Figure 1 is marked with the placement of the radiolabeled carbons.

Soil samples were treated with either 7,9-[^{14}C]triazolopyrimidine (TP label) or uniformly labeled [^{14}C]aniline (AN) diclosulam. The specific activities for the two lots of [^{14}C]TP-labeled diclosulam were 23.2 mCi/mmol (U.S. and Brazilian

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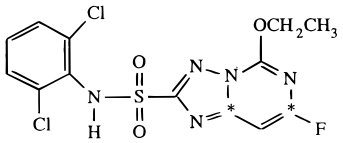

Figure 1. Structure of diclosulam. Location of the radiolabeled carbon atom in the TP-labeled test material is indicated with an asterisk (*). The AN-labeled test material was uniformly radiolabeled in the phenyl ring.

Table 1. Selected Characteristics of Soils Used for Diclosulam Aerobic Soil Metabolism

ID	location	texture	pH	% OC	soil moisture[a]
Norfolk[b]	Florence, SC	sandy loam	5.2	0.97	6.94
Commerce[b]	Wayside, MS	silty clay loam	7.8	0.99	21.31
Tama[b]	Henry, IL	silt loam	5.9	1.91	21.21
Norfolk II	Wilson, NC	sandy loam	6.0	1.19	11.04
Junin	Argentina	sandy loam	6.0	2.50	22.68
Pergamino	Argentina	silt loam	5.6	3.59	27.35
Tucuman	Argentina	silt loam	6.4	2.77	25.74
Cascavel	Brazil	clay	5.3	3.05	22.83
Londrina	Brazil	sandy clay loam	6.0	2.43	22.99

[a] Moisture at which samples were treated. Equivalent to 75% 1/3 bar for U.S. and Brazilian soils and 45% MHC for Argentinean soils. [b] U.S. soil taxonomic families: Norfolk, fine-loamy, siliceous, thermic Typic Kandiudults; Commerce, fine-silty, mixed, nonacid, thermic Aeric Fluvaquents; Tama, fine-silty, mixed, mesic Typic Argiudolls.

soils) and 30.5 mCi/mmol (Argentinean soils), whereas [^{14}C]-AN-diclosulam (U.S. soils only) had a specific activity of 24.2 mCi/mmol. The radiopurity for each lot of ^{14}C-labeled test substance was >97%.

Non-radiolabeled standards of diclosulam and its suspected metabolites were used as chromatographic standards and for mass spectral comparisons to isolated soil degradates. The purity of each standard was >98%. The standards included *N*-(2,6-dichlorophenyl)-5-hydroxy-7-fluoro[1,2,4]triazolo[1,5-*c*]-pyrimidine-2-sulfonamide, aminosulfonyl triazolopyrimidine, and *N*-(2,6-dichlorophenyl)-5-hydroxy-7-fluoro-8-chloro[1,2,4]-triazolo[1,5-*c*]pyrimidine-2-sulfonamide). In this paper these degradates will be designated 5-OH-diclosulam, ASTP, and 8-Cl-diclosulam, respectively. All other solvents or reagents used were of reagent grade or better and were typically obtained from Fisher Scientific (Pittsburgh, PA).

Soils. Soils were chosen from the soybean-growing regions of the United States, Argentina, and Brazil. These soils represented a wide range of chemical and physical characteristics as well as geographic locations (Table 1).

Analytical Methods. Two reverse phase high-performance liquid chromatography (HPLC) methods were used to analyze diclosulam soil metabolism samples. Brazilian and U.S. samples were analyzed using a linear gradient and a Waters μBondipak C_{18} column. Initial conditions were 95:5 A/B, where A = 1% acetic acid in water and B = 1% acetic acid in acetonitrile. The concentration of B was increased to 40:60 A/B in 40 min, then to 5:95 A/B at 51 min, and held until 60 min, before returning to the initial conditions for re-equilibration. The flow rate for this elution system was 1 mL/min.

A linear gradient was also used to analyze the Argentinean samples using a YMC-PACK ODS-AQ, C_{18} column. Initial conditions for this method were 88:12 A/B, where A = 0.5% TFA in water and B = acetonitrile, with a flow rate of 1.5 mL/min. The initial conditions were held for 5 min before changing to 80:20 A/B over 40 min, then increasing to 100% B in 60 min, before re-equilibrating at the initial conditions.

Eluent fractions (30- or 60-s) were collected and analyzed by liquid scintillation counting (LSC); reconstructed radiochromatograms were then generated. All radioactivity measurements were performed using microprocessor-controlled Packard (Downers Grove, IL) liquid scintillation counters. Non-radiolabeled standards were monitored by UV detection at 254 nm.

Confirmatory chromatography for several samples selected at random was conducted by normal phase thin-layer chromatography (TLC). TLC was also used as a cleanup method for metabolite isolation and identification. Developed plates were scanned for radioactivity using an Ambis Radioanalytic imaging system (Scanlytics, San Diego, CA) or a Molecular Dynamics PhosphorImager (Sunnyvale, CA). For confirmatory metabolite identification procedures, samples and non-radiolabeled standards were spotted on a 20 × 20 normal phase, silica gel, phosphorescent plate (silica gel 60 F-254) and developed with a mobile phase consisting of 70:20:10 toluene/2-propanol/acetic acid. The plate was then scanned using the PhosphoImager or Ambis. The phosphorescent plate allowed for visualization at 254 nm of the non-radiolabeled standards for retention time comparisons to radioactive samples.

Diclosulam degradation products were identified by comparing the HPLC retention times and mass spectra of the isolated degradates with those of authentic standards. Radioactive samples and standards were analyzed using an HPLC with a Beta-Ram detector coupled with a Finnigan TSQ700 mass spectrometer (LC/MS) using electrospray ionization in both positive and negative ion modes.

Test Substance Application. Treating solutions were prepared so that a minimum volume of acetone was applied to each soil sample; in each case, <150 μL of acetone was applied to 50 g of dry weight of soil. The application rate was 0.1 mg/kg, or roughly twice the maximum field application rate of 52 g ai/ha, based on a 7.6 cm incorporation rate and a typical soil bulk density of 1.35 g/cm. To aid in identification of metabolites, additional samples were treated at a rate of 20−100 times (1−5 mg/kg) the maximum use. These high-concentration samples were not used for kinetics, degradate rise and decline profiles, or metabolic pathway determinations, but only for metabolite elucidation.

Approximately 50 g (oven dry weight equivalent) moist soil was weighed into one side of a two-chambered biometer flask. Each sample was treated with [^{14}C]diclosulam and mixed thoroughly with a metal spatula. Deionized water was added to the soil to bring the moisture content to 75% of 0.3 bar moisture (American and Brazilian soils) or 45% moisture holding capacity (Argentinean soils).

With the exception of day 0 samples, 100 mL of 0.2 N NaOH solution was added to one side of the biometer flask to collect evolved $^{14}CO_2$ as $^{14}CO_3^{2-}$. The biometers were sealed and connected to oxygen manifolds in a constant-temperature incubator. U.S. and Brazilian samples were incubated in the dark at 25 °C, whereas Argentinean samples were incubated in the dark at 20 °C. Day 0 samples were transferred to glass jars and frozen until analysis, up to 2 days after treatment.

Sampling Procedure. Samples were incubated for up to one year after treatment with diclosulam. At each sampling point (except day 0), aliquots of the NaOH solution were counted by LSC to determine mineralization to $^{14}CO_2$. The presence of $^{14}CO_2$ in several traps was verified by the addition of a saturated $BaCl_2$ solution to a portion of the trapping solution. The formation of a white carbonate precipitate and loss of radioactivity in solution confirmed the radioactivity in the NaOH traps was indeed $^{14}CO_3$.

After removal of the caustic trapping material, soil samples were transferred to glass jars. Samples were then either analyzed immediately or placed in frozen storage, typically for 1 or 2 days, before extraction. A representative portion of each sample (~5 g of wet weight) was extracted while the remainder was retained under frozen storage conditions. When necessary to confirm original results, additional aliquots of the soil sample were extracted.

U.S. and Brazilian soil samples were extracted with 95:5 acetone/0.1 M HCl, whereas the Argentinean samples were extracted with a 90:10 acetone/1 M HCl solution. Samples were extracted on a mechanical shaker for 30−60 min. Samples were then centrifuged at 2000 rpm, and the supernatant was decanted. The extraction procedure was repeated twice more, combining supernatants. The combined extraction volume was determined (typically 25 mL) and aliquots of the extract were analyzed by LSC.

Aged Mobility. Several U.S. and Argentinean soil samples were first extracted with 2:1 0.01 M $CaCl_2$ solution/soil ratio to determine readily available material; extraction times ranged from 12 to 24 h. Samples were then extracted with an acidified acetone solution as previously described. Aqueous and organic extracts were analyzed separately by LSC and HPLC.

Apparent sorption coefficients (K_d) for diclosulam and available metabolites were generated using the equation

$$K_d = \frac{\%\ \text{sorbed}}{\%\ \text{solution}} \times \frac{\text{L of aqueous}}{\text{kg of soil}}$$

where the material sorbed was extracted with organic solvent and material in solution was extracted with 0.01 M $CaCl_2$. This K_d is termed apparent because the partitioning was not conducted under the conditions of a typical batch equilibrium experiment, where the test material is applied to the solution phase and then shaken with the soil to determine adsorption and desorption coefficients. This technique is useful in providing sorption data for soil metabolites as they are formed in situ as well as track changes in sorption over time.

Postextraction Soil Combustions. Portions of air-dried extracted soils were combusted to account for activity remaining in soils after extraction. Samples were combusted using a Zymate II Robot/Harvey OX400 biological oxidizer. The $^{14}CO_2$ generated from each combusted sample was collected in Harvey cocktail plus Permafluor, and the samples were assayed by LSC.

Bound Soil Residue Characterization. The bound residue for diclosulam was characterized in a series of extractions in several U.S. soil samples that contained a large amount (>20% of applied radioactivity) of radioactivity unextractable with the acidified acetone extraction solvent. First, 5-g wet weight samples were extracted with 95:5 acetone/0.1 M HCl, the original procedure used to extract the U.S. samples. Next, samples were extracted with two 10-mL extractions of 90:10 acetone/1 M HCl and brought to 25 mL final volume. The third step was a citrate−dithionate digestion. Sodium citrate dihydrate (40 mL of 0.3 M) plus 5 mL of 1 N sodium bicarbonate was added to the soil pellet. The slurry was warmed to 80 °C in a water bath, and ~1 g of solid sodium dithionate was added; the mixture was stirred constantly for 1 min and then occasionally for another 15 min. The mixture was removed from the water bath, and 10 mL of saturated sodium chloride solution was added. The slurry was then centrifuged and the supernatant decanted into a 100-mL volumetric flask. The digestion was repeated and the supernatants combined, counting 1-mL aliquots by LSC after the solution had been brought to volume.

The pellet was extracted with 24 mL of 1 N NaOH solution, shaken for 2 h, and then centrifuged. The supernatant was transferred to a 50-mL volumetric flask, and the extraction was repeated, combining the supernatants. The sample was brought to 50 mL total volume before aliquots were counted by LSC. The soil pellet was allowed to air-dry, and portions were combusted to obtain a material balance.

Metabolite Isolation. A series of cleanup steps was used to purify metabolites prior to identification by LC-MS. Samples that were treated at the 1 or 5 mg/kg application rate were extracted with organic solvent. These extracts were concentrated under a stream of nitrogen to remove the solvent and then loaded onto a C_{18} SPE cartridge. The metabolites were separated by washing the cartridge with solutions of acetonitrile and water, increasing the acetonitrile concentration with each elution. Acetic acid (1%) was also part of each elution solvent. Fractions were concentrated under a stream of nitrogen, and representative aliquots were spotted onto a TLC plate to determine the profile of each fraction.

Each SPE fraction containing a metabolite of interest was spotted onto a preparatory TLC plate and developed. A 1:1 hard copy of the image from this plate was used to determine the location of radioactivity on the plate. This area was scraped, and the silica gel was extracted with 80:20 acetonitrile/water. The extract was then fractionated by C_{18} HPLC. Fractions were collected, concentrated, and analyzed by LC-MS.

Table 2. Final Distribution of Activity for Diclosulam Degradation on Aerobic Soil

soil	last point (days)	% diclosulam	% CO_2	% bound
Junin	119	13.0	22.0	12.0
Tucuman	119	11.0	26.0	12.0
Cascavel	140	30.8	1.9	34.4
Londrina	140	13.5	8.9	50.3
Norfolk (AN)	140	11.8	15.5	38.4
Commerce (AN)	140	5.7	31.1	51.2
Tama (AN)	140	21.1	7.1	43.0
Pergamino	168	24.0	10.0	13.0
Norfolk (TP)	182	8.5	6.6	23.7
Commerce (TP)	182	3.9	26.7	42.0
Tama (TP)	182	15.7	8.2	42.5
Norfolk II	365	2.7	46.9	31.7

RESULTS AND DISCUSSION

Material Balance. Material balance was determined by the ^{14}C activity recovered as extractable, as mineralized to $^{14}CO_2$, and as bound residues recovered by postextraction combustions. Recoveries for samples averaged 96.7 ± 7.6% across all soils and time points, indicating that no volatile degradation products other than CO_2 are formed during diclosulam aerobic soil degradation.

Radiocarbon Distribution. Extractable material decreased over time while radioactivity recovered in the CO_2 traps and by combustion increased, suggesting that mineralization to CO_2 and bound soil residues are the terminal products of the metabolism of diclosulam in soil. Radioactivity recovered as $^{14}CO_2$ and as bound soil residues varied greatly by soil type, reaching levels as high as 47 and 32%, respectively, one year after treatment in the Norfolk II soil. Degradation of diclosulam was less complete in other soils; the Cascavel clay soil generated only 1.9% CO_2 140 days after treatment. See Table 2 for the range of $^{14}CO_2$ and bound residue concentrations, as well as the amount of extractable diclosulam.

Kinetics. Diclosulam soil degradation is best described as biphasic, characterized by a rapid initial degradation followed by a slower degradation over time. Two-compartment models have been used previously to describe the biphasic degradation of pesticides in soil. A model presented by Hill and Schaalje (1985) proposed that a "deposited residue" is rapidly dissipated through losses due to photochemical degradation, volatilization, and other surface processes while pesticide present as a "retained residue" is more slowly degraded by chemical or biological mechanisms.

The degradation of cloransulam-methyl, a triazolopyrimidine herbicide structurally related to diclosulam, was studied on several aerobic soils (van Wesenbeeck et al., 1997). The degradation of cloransulam-methyl was fitted using a double-exponential two-compartment model. The degradation rate constants represented rapid degradation of the solution phase material and the slower degradation of the sorbed phase material. Sigmaplot (SPPS, Chicago, IL) and SimuSolv (Dow AgroSciences, Indianapolis, IN) software were used to solve the double-exponential models.

Unlike these models, the two-compartment model used here to describe diclosulam degradation assumes a partitioning of diclosulam between an aqueous and a

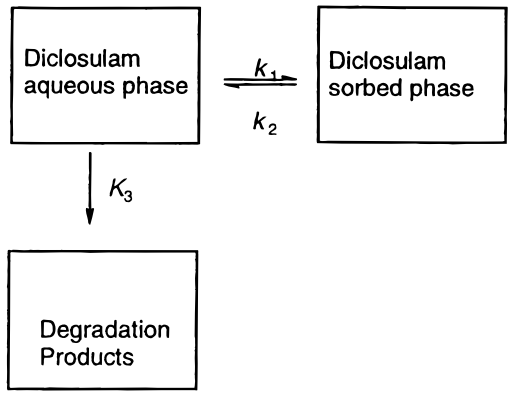

Figure 2. Diclosulam two-compartment degradation model.

sorbed phase (k_1 and k_2), where diclosulam degradation (k_3) is presumed to take place only from the aqueous phase (Figure 2). Diclosulam in the aqueous pool is assumed to be the material readily extractable from soil, whereas the sorbed pool is the diclosulam that is more tightly sorbed. The total amount of diclosulam extracted from the soil is the sum of diclosulam in the two pools. ModelMaker software (Cherwell Scientific, Oxford, U.K.) was used to fit this two-compartment model by solving for the degradation rate and equilibrium constants:

$$\frac{d[\text{diclosulam}_{aq}]}{dt} = k_2[\text{diclosulam}_{sorb}] - k_1[\text{diclosulam}_{aq}] - k_3[\text{degradation products}]$$

$$\frac{d[\text{diclosulam}_{sorb}]}{dt} = k_1[\text{diclosulam}_{aq}] - k_2[\text{diclosulam}_{sorb}]$$

This two-compartment model produces a DT_{50}, the time it takes for 50% of the diclosulam to degrade, rather than a half-life. The DT_{50} takes into account both degradation of diclosulam from the aqueous pool and movement of diclosulam between the aqueous and sorbed phases. In addition to a DT_{50}, a DT_{90} (10% diclosulam remains) was also calculated. The average DT_{50} and DT_{90} of diclosulam on the nine soils tested were 28 ± 12 and 190 ± 91 days, respectively. Table 4 presents the degradation rates for diclosulam on each soil type tested.

Metabolite Identification. Three metabolites were identified by LC retention time matches to authentic standards and by mass spectral analysis. ASTP, 5-OH-diclosulam, and 8-Cl-diclosulam were measured at >10% of applied in at least one test system. One of the primary routes of diclosulam degradation is the dealkylation of the ethoxy moiety in the 5-position on the triazolopyrimidine ring (to 5-OH-diclosulam), followed by the biochlorination of 5-OH-diclosulam to 8-Cl-diclosulam. A parallel pathway involves the cleavage of the sulfonamide bridge of diclosulam to ASTP. These degradates as well as other minor products are then further degraded to CO_2 and incorporated into the soil organic matter as bound soil residues. The proposed aerobic soil metabolic pathway for diclosulam degradation is presented in Figure 3. The maximum concentration of each metabolite and the time point of the maximum are presented for each soil in Table 5.

The appearance of 8-Cl-diclosulam was unexpected, as chlorination of a xenobiotic organic compound is not a typical breakdown mechanism in soil metabolism. To confirm that 8-Cl-diclosulam was not an artifact of the extraction method (which employed acetone containing HCl), several samples were extracted using nonchlorinated solvents. In each case, 8-Cl-diclosulam was identified from the extract. 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 (Gribble, 1998). These organisms produce halogenated substances as part of their defensive or food-gathering strategies. The formation of 8-Cl-diclosulam in aerobic soils is the first known example of a sulfonanilide that has undergone biochlorination.

Bound Residue. Triazolopyrimidine sulfonanilides as a family of compounds characteristically exhibit a large increase in unextractable residues over time (Wolt et al., 1996, Krieger et al., 1999). Diclosulam also exhibits this behavior of decreased extractable residue. It was therefore considered to be important to characterize this bound pool of radioactivity.

The day 112 samples (both AN- and TP-labeled) from the Commerce silty clay loam (U.S. soil) were selected to characterize the bound residue fraction. The Commerce soil was chosen because of the large amount of radioactivity (up to 51% at 140 days) remaining in the soil after extraction with 95:5 acetone/0.1 M HCl. Additionally, samples of the South Carolina Norfolk sandy loam and the Tama silt loam were sequentially extracted with the 0.1 M HCl/acetone solution followed by extraction with 1 M HCl/acetone. Even though up to 25% more of the applied activity was extracted with 90:10 acetone/1 M HCl, neither diclosulam nor its metabolites were released from this rigorous extraction process; the majority of ^{14}C activity was recovered as polar components each in small quantities by HPLC. Although the Argentinean samples were extracted with 90:10 acetone/1 M HCl and the U.S. and Brazilian soil samples with 95:5 acetone/0.1 M HCl, the measured degradation rates are still comparable as no further diclosulam or metabolites were extracted using the 1 M HCl solvent.

Aged Mobility. Samples from three U.S. and three Argentinean soils were used to determine apparent desorption coefficients for diclosulam and its soil metabolites. Analysis of time 0 samples produced apparent K_d values for diclosulam comparable to sorption coefficients obtained in a batch equilibrium study. The average time 0 K_d for diclosulam on all tested soils was 1.1 ± 1.1 L/kg, which is similar to that of related sulfonamides (Lehman et al., 1992; Krieger et al., 1999; Wolt et al., 1996). The low K_d of diclosulam indicates that the potential for mobility through soil exists. However, other factors, such as degradation rate and increased sorption over time, also affect soil mobility.

Analysis of later time samples monitored the mobility of the metabolites relative to that of diclosulam as they are formed in situ and also any changes in diclosulam sorption with time. The sorption partition coefficients of diclosulam increased with time of soil contact (Table 6). This increase in apparent K_d substantiates the biphasic model of diclosulam metabolism: diclosulam is initially degraded quickly from the pool of activity in the aqueous phase; over time, as K_d values increase, less diclosulam resides in the aqueous pool and degradation slows. Although a small amount of diclosulam is extractable from soil even one year after treatment, this

Table 3. Percent of Applied Diclosulam Remaining as a Function of Time

day	Norfolk	Commerce	Tama	Norfolk II	Junin	Pergamino	Tucuman	Cascavel	Londrina
0	95	90	103	98	103	97	103	91	89
1	86	92	93	–[a]	–	–	–	–	–
3	87	86	90	–	–	–	–	–	74
7	73	76	74	- -	79	67	67	90	70
14	56	62	66	53	61	65	61	70	51
21	–	–	–	–	69	66	57	–	–
28	41	44	56	35	55	39	41	64	40
42	31	29	44	–	–	–	–	–	–
56	28	23	39	–	34	41	33	52	27
70	22	16	30	–	–	–	–	–	–
84	18	12	28	11	–	–	–	–	–
91	–	–	–	–	20	33	20	–	–
112	14	8	22	–	–	–	–	–	–
119	–	–	–	–	13	19	11	–	–
140	12	6	21	–	–	–	–	31	14
168	–	–	–	–	–	24	–	–	–
182	9	4	16	6	–	–	–	–	–
280	–	–	–	4	–	–	–	–	–
365	–	–	–	3	–	–	–	–	–

[a] No sample was analyzed at this time point.

Table 4. Rates of Sorption and Degradation of Diclosulam on Nine Soils

soil	k_1[a] (days^{-1})	k_2[b] (days^{-1})	k_3[c] (days^{-1})	r^2	P value[d]	DT_{50} (days)	DT_{90} (days)
Norfolk	0.0116	0.0111	0.0609	0.997	<0.001	18	152
Commerce	0.0025	0.0091	0.0367	0.992	<0.001	22	93
Tama	0.0041	0.0043	0.0283	0.987	<0.001	34	302
Norfolk II	0.0063	0.0093	0.0669	0.996	<0.001	16	136
Junin	0.0600	0.0312	0.0737	0.714	0.005	32	136
Pergamino	0.0049	0.0096	0.1029	0.877	<0.001	35	210
Tucuman	0.0266	0.0225	0.0608	0.855	<0.001	24	132
Cascavel	0.0165	0.0085	0.0267	0.997	<0.001	54	373
Londrina	0.0340	0.0140	0.0677	0.787	0.036	16	174
						av = 28	190
						SD[e] = 12	91

[a] k_1 is the adsorption rate constant. [b] k_2 is the desorption rate constant. [c] k_3 is the degradation rate constant. [d] P value is the probability the model is fit by chance—a smaller number is a better fit. [e] Standard deviation.

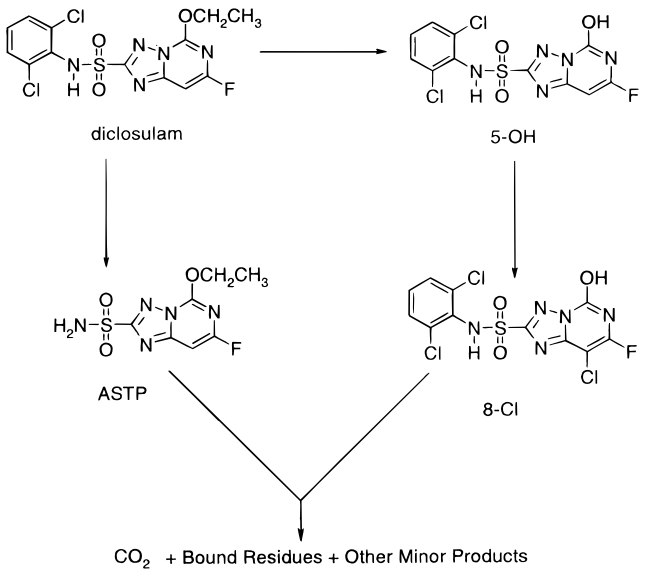

Figure 3. Proposed aerobic soil metabolic pathway for diclosulam.

material is more tightly sorbed to soil and is less available for movement through soil.

It can be expected that pH would play an important role in diclosulam sorption due to its ionic nature (pK_a = 4.1). Such a correlation was not seen in the study, but this data set of only six soils may be too small to draw any conclusions. A batch equilibrium study conducted internally for Dow AgroSciences LLC found a correlation between diclosulam sorption and soil pH. A similar correlation between pH and sorptivity was determined (Wolt et al., 1994; Lehmann et al., 1992) for the related sulfonanilides cloransulam-methyl and flumetsulam. Although this correlation was not observed for this data set, the soil with the lowest K_d had the highest pH (Commerce silty clay loam). Additionally, the soils with the largest magnitude of increase over time (Commerce silty clay loam and Tucuman silt loam) tended to have a higher pH values (Table 6).

Table 5. Diclosulam Metabolite Maximum Concentrations and Time of Maximum

soil	% 5-OH-diclosulam	time (days)	% 8-Cl-diclosulam	time (days)	% ASTP	time (days)
Norfolk	11.0	14	15.0	182	15.4	7
Commerce	6.4	28	5.9	70	3.3	56
Tama	16.6	140	7.5	140	3.2	182
Norfolk II	6.1	14	8.1	21	4.2	28
Junin	4.0	7	11.0	56	4.0	56
Pergamino	17.0	168	nd[a]		9.0	56
Tucuman	11.0	28	7.0	91	6.0	28
Cascavel	11.0	40	nd		7.2	140
Londrina	9.2	140	nd		7.9	56

[a] Below level of detection.

The relationship between K_d and organic carbon content resulted in an r^2 value of 0.73, by which greater organic carbon contents resulted in higher sorption coefficients.

Metabolite sorption coefficients were comparable to that of diclosulam, that is, generally <2 L/kg (Table 6), and also showed an increase in sorptivity over time.

Table 6. Apparent K_d Values (Liters per Kilogram) of Diclosulam and Metabolites

soil	day	diclosulam	magnitude of change	ASTP	5-OH-diclosulam	8-Cl-diclosulam
Norfolk	0	0.58		–[a]	–	–
	14	1.20		0.67	0.78	1.31
	28	1.57		0.92	1.03	1.47
	56	2.14	3.7×	1.03	0.97	1.38
Commerce	0	0.04		–	–	–
	14	0.16		0.38	0.13	0.19
	28	0.23		0.73	0.18	0.21
	56	0.30	7.5×	0.53	0.17	0.27
Tama	0	0.36		–	–	–
	14	0.63		–	0.45	–
	28	0.70		1.75	0.55	0.81
	56	1.09	3.0×	2.26	0.64	1.01
Junin	0	1.82		–	–	–
	28	4.58		–	–	5.44
	119	8.16	4.5×	–	–	8.21
Pergamino	0	2.93		–	–	–
	28	4.51		2.91	3.17	–
	119	9.75	3.3×	3.88	5.52	–
Tucuman	0	0.89		–	–	–
	28	2.25		4.26	1.55	–
	119	5.63	6.3×	–	–	–

[a] Insufficient material present in aqueous and/or organic extracts to calculate a K_d.

However, the magnitude of change was smaller in diclosulam degradate sorption over time than for diclosulam, probably for several reasons. First, the degradates are less polar than diclosulam and therefore more likely extracted in aqueous solution. Second, the degradates have less contact time with soil. Third, the degradates were formed in much smaller quantities than diclosulam and in some cases were undetectable in either the aqueous or organic extracts, so no K_d could be calculated—therefore, fewer data points were available for comparison.

Conclusions. Diclosulam degrades quickly under laboratory aerobic soil conditions with an average DT_{50} < 30 days. Apparent desorption coefficients suggest that diclosulam is less available for movement as well as degradation over time. In the field, other factors such as photolysis and temperature and moisture changes can also contribute to diclosulam dissipation. Diclosulam is not expected to accumulate in the environment or move into ground or surface waters.

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