Concurrent Patterns of Sorption−Degradation for Oryzalin and Degradates

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Sorption and degradation are linked, dynamic processes which largely govern the potential for herbicides and their degradation products to reach groundwater. Patterns of concurrent degradation and sorption of the dinitroaniline herbicide oryzalin (3,5-dinitro-N^4,N^4-dipropylsulfanilamide) and its degradates were determined on four soils representative of typical use areas. Radiolabeled oryzalin was applied to soil at either 1.64 or 3.14 μg/g and incubated at 25 °C under aerobic conditions for up to 6 months. The time required for 50% and 90% degradation of oryzalin ranged from 24 to 42 and 79 to 140 days, respectively. The radiocarbon was rapidly incorporated into the soil organic matter; up to 57% of the applied radiocarbon was recalcitrant to extraction after 6 months. The degradation pathway deduced is similar to that for the related dinitroaniline herbicide trifluralin. Apparent distribution coefficients were measured separately for the pool of material in the soil solution (K_{ss}, determined from a 5-min desorption) and the total desorbable pool of material (K_d, determined from a 24-h desorption). Sorption coefficients increased by a factor of 3 over 6 months, indicating that the total pool of extractable oryzalin became less available for desorption and degradation. Values of K_{ss} remained constant over time, indicating that material in the soil solution and the desorbable pool were in equilibrium. The amount of oryzalin and degradates in soil solution was a function of the desorption energy from the surface and was not limited by solubility. Similar, though less consistent, trends were observed for oryzalin degradation products.

Keywords: *Oryzalin; aerobic soil metabolism; sorption; aerobic soil degradation*

INTRODUCTION

Consideration of the environmental fate of herbicides frequently involves the evaluation of potential for occurrence in groundwater. Degradation and sorption are the principal processes driving the potential for herbicides to be mobile in soil environments and are the focus of assessments for leaching potential (Jury et al., 1986; Gustafson, 1989). They are often studied as discrete processes, while in reality the sorption and degradation of organic molecules are concurrent, linked processes (Scow and Johnson, 1997). In general, increasing sorption results in decreasing availability for degradation by soil microbes (Sims et al., 1991, 1992).

In terms of protection of groundwater resources, the fate and behavior of the products of degradation as well as that of the herbicide itself are of interest. Definitive data detailing the sorption and degradation of herbicide metabolites in soil are not always available because of the difficulty in obtaining radiolabeled standards for conduct of such studies. Additionally, laboratory sorption and soil metabolism studies conducted by fortifying soil with neat metabolites may lead to misleading interpretations, since the products of herbicide degradation occur in soil under dynamic conditions. The in situ formation of metabolites may significantly impact patterns of sorption and degradation relative to dosing soil with pure metabolites and consequently alter the interpretation of metabolite mobility.

Oryzalin (3,5-dinitro-N^4,N^4-dipropylsulfanilamide) is an herbicide used to control broadleaf weeds in turf, ornamentals, fruit and nut crops, and vineyards. Oryzalin is applied by spray or broadcast methods to the soil surface and is typically incorporated into soil by rainfall or irrigation. Use rates vary from 2.25 to 7.72 kg ha^{-1}. Typical annual use of oryzalin (as reported for 1991) is between 670 000 and 870 000 kg applied to 410,000 to 770,000 ha of crops (United States Environmental Protection Agency, 1994). Oryzalin is unique among the dinitroaniline herbicides in that it has an ionizable functionality (it is weakly acidic with a pK_a of 8.6), which gives it a higher water solubility (2.6 ppm at 25 °C) and a lower vapor pressure ($<1.4 \times 10^{-6}$ Torr at 25 °C) than most dinitroanilines (Weber and Monaco, 1972). Aerobic soil half-lives of oryzalin have previously been reported as 40 and 130 days at 30 and 15 °C, respectively (Gingerich and Zimdahl, 1976), and 60 days at 24 °C (Graper and Rainey, 1989).

In this study we present a methodology for interpretation of sorption−degradation relationships of the herbicide oryzalin and its principal soil degradation products. This study was conducted to determine degradation rate and sorptivity for oryzalin and its aerobic soil degradates under environmentally relevant concentrations. In addition, the temporal variation in sorptivity of individual compounds was determined. This study also adds to knowledge of the degradation rate and pathways of oryzalin in aerobic soil systems.

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Table 1. Physical and Chemical Characteristics of the Soils Used in This Study

property	soil			
	Fox	Traver	Hanford	Millhopper
pH	5.6	6.9	7.3	6.0
CEC, cmol(+)/kg	5.29	11.30	5.99	2.04
organic carbon, %	0.65	0.74	0.69	0.73
water holding capacity at 33 kPa, %	10.53	23.74	11.39	2.92
textural class	sandy loam	loam	sandy loam	sand
sand, %	60.8	51.6	60.8	92.8
silt, %	26.0	29.6	34.0	6.0
clay, %	13.2	18.8	5.2	1.2

series	taxonomic class
Fox	fine-loamy, mixed, mesic Typic Hapludalfs
Traver	coarse-loamy, mixed, thermic Natric Haploxeralfs
Hanford	coarse-loamy, mixed, nonacid, thermic Typic Xerothents
Millhopper	loamy, siliceous, hyperthermic Grossarenic Paleudults

MATERIALS AND METHODS

Test Material and Reference Compounds. Radiolabeled oryzalin (OR-1; 3,5-dinitro-N^4,N^4-dipropyl[U-^{14}C]sulfanilamide; 19.5 μCi/mg; radiochemical purity 99%) was synthesized by Dow AgroSciences Specialty Synthesis. Reference standards for oryzalin degradates were synthesized at the Lilly Research Laboratories (Indianapolis, IN). The degradates were designated OR-2 (3,5-dinitro-4-propylaminobenzenesulfonamide), OR-4 (3-amino-4-(dipropylamino)-5-nitrobenzenesulfonamide), OR-13 (2-ethyl-7-nitro-1-propyl-1*H*-benzimidazole-5-sulfonamide), OR-15 (2-ethyl-7-nitro-1*H*-benzimidazole-5-sulfonamide), OR-20 (4-hydroxy-3,5-dinitrosulfanilamide), OR-41 (4-[(2-hydroxylpropyl)propyl amino]-3,4-dinitrobenzenesulfonamide), UN-1 (3,3′-azoxybis[4-(propylamino)-5-nitro]benzenesulfonamide), and UN-2 (2-ethyl-7-nitro-1-propyl-1*H*-benzimidazole-5-sulfonamide 3-oxide). These compound designations are those used in internal literature of Eli Lilly and Dow AgroSciences (the original discoverer and current manufacturer of oryzalin, respectively) and are used here to facilitate comparisons to the related dinitroaniline herbicide trifluralin. Trifluralin differs from oryzalin only by substitution of a trifluoromethyl group for the sulfonamide group. These designations parallel those for the degradates of trifluralin (Grover et al., 1997). These standards were used to identify soil degradates by comparison of thin-layer chromatography (TLC) characteristics.

Test System. The study was conducted using four soils of widely varied physicochemical properties (Table 1). Fox sandy loam soil was used for comparison to a previous aerobic soil metabolism study with oryzalin (Graper and Rainey, 1989), while the other soils are representative of major use areas in Florida and California. Moist, field-sampled soils at a workable consistency were passed through a 2-mm sieve and stored at 4 °C prior to use. Soils were stored for between 2 and 6 months prior to use.

Each sample was incubated in a biometer flask equipped with a side chamber containing 100 mL of 0.2 M NaOH solution for the collection of $^{14}CO_2$ released by microbial mineralization. A slight positive pressure of O_2 was supplied to the biometer flask to replace O_2 removed during oxidation of organic matter. Moist soil (50 g oven dry weight equivalent) was added to individual biometer flasks and moisture was adjusted to approximately 100 kPa water holding capacity.

Oryzalin was applied to the Fox, Traver, and Hanford soils at a rate of 3.14 μg/g and to the Millhopper soil at a rate of 1.64 μg/g (dry weight basis, equivalent to approximate field use rates of 2.09 and 1.09 kg/ha, respectively, assuming a 5-cm incorporation depth). Test systems were connected to oxygen manifolds in a darkened incubator set at 25 °C. Incubated samples of Fox, Traver, and Hanford soils were analyzed at 0, 1.8, 15, 29, 63, 90, 127, and 181 days after treatment (DAT), while the Millhopper soil samples were analyzed at 0, 2.5, 15, 34, 61, 98, 124, and 183 DAT.

Analytical Methods. Duplicate biometer flasks were removed from the incubator at each sampling time. One-milliliter aliquots of the NaOH solution were assayed for ^{14}C by liquid scintillation counting (LSC). All LSC measurements were performed on a Packard (Meriden, CT) 2500TR liquid scintillation counter; chemiluminescence was corrected for using the scintillation counter's on-board logic. Soil samples were transferred to centrifuge tubes and 100 mL of 0.01 N $CaCl_2$ solution was added; the samples were then mixed on a horizontal shaker for 5 min. The tubes were centrifuged at 900 RCF for 5 min, a 10-mL aliquot was removed, 10 mL of 0.01 N $CaCl_2$ was added, and the sample was mixed for an additional 24 h. After mixing, the tubes were again centrifuged and the supernatant was decanted. Three 1-mL aliquots from each of the desorption steps were analyzed for ^{14}C by LSC. The remaining soil was extracted three times with 75 mL (225 mL total) of 95% methanol/5% 0.1 N HCl (v/v) for samples analyzed through 63 DAT (34 DAT for Millhopper samples) or 95% acetone/5% 0.25 N HCl for subsequent samples. The supernatants from each organic solvent extract were combined; three 1-mL aliquots were analyzed for ^{14}C by LSC. After air-drying at room temperature, the extracted soil was ground to a uniform consistency (determined by visual examination) with a mortal and pestle and a subsample (three 1-g replicates) was combusted and analyzed by LSC to determine the amount of nonextractable ^{14}C.

Ten-milliliter aliquots of the organic extract were concentrated under a gentle stream of dry N_2 to approximately 0.5 mL, filtered through a 0.2 μm porosity PTFE syringe filter, and brought to a volume of 1 mL in a volumetric flask prior to TLC analysis. Five milliliters of the aqueous solutions from the 5-min and 24-h desorptions for samples through 90 DAT (61 DAT for Millhopper samples) were acidified with 0.25 mL of 1 *N* HCl and partitioned into either ethyl acetate or dichloromethane (3 × 4-mL aliquots). The aqueous phase was then diluted with methanol or water and also analyzed by TLC. The combined organic layers were concentrated to approximately 1 mL and filtered through a 0.2-μm porosity PTFE syringe filter prior to analysis by TLC. For sample timepoints >90 DAT (>61 DAT for Millhopper) aqueous samples were prepared by using 500 mg Waters (Milford, MA) C_{18} SepPak solid-phase extraction cartridges. Cartridges were precleaned with 5 mL of methanol and conditioned with 2 × 5 mL aliquots of 0.01 N $CaCl_2$. Five milliliters of the sample were loaded onto the cartridge and eluted with 10 mL of methanol, concentrated to approximately 0.5 mL under a gentle stream of dry N_2, brought to a volume of 1 mL in a volumetric flask, and analyzed by TLC.

Samples (typically 100-μL aliquots) were analyzed by single-dimension normal phase TLC using 90/10/1 (v/v) chloroform/2-propanol/acetic acid (solvent system A) and 70/30/1 (v/v) toluene/acetone/acetic acid (solvent system B). Sample timepoints >90 DAT (>61 DAT for Millhopper) were analyzed by using 55/45/1/1 (v/v) toluene/acetone/acetic acid/water (solvent system C) and 75/25/1/1 (v/v) toluene/acetone/acetic acid/water (solvent system D) solvent systems. Detection and quantitation was performed with a PhosphorImager SF (Molecular

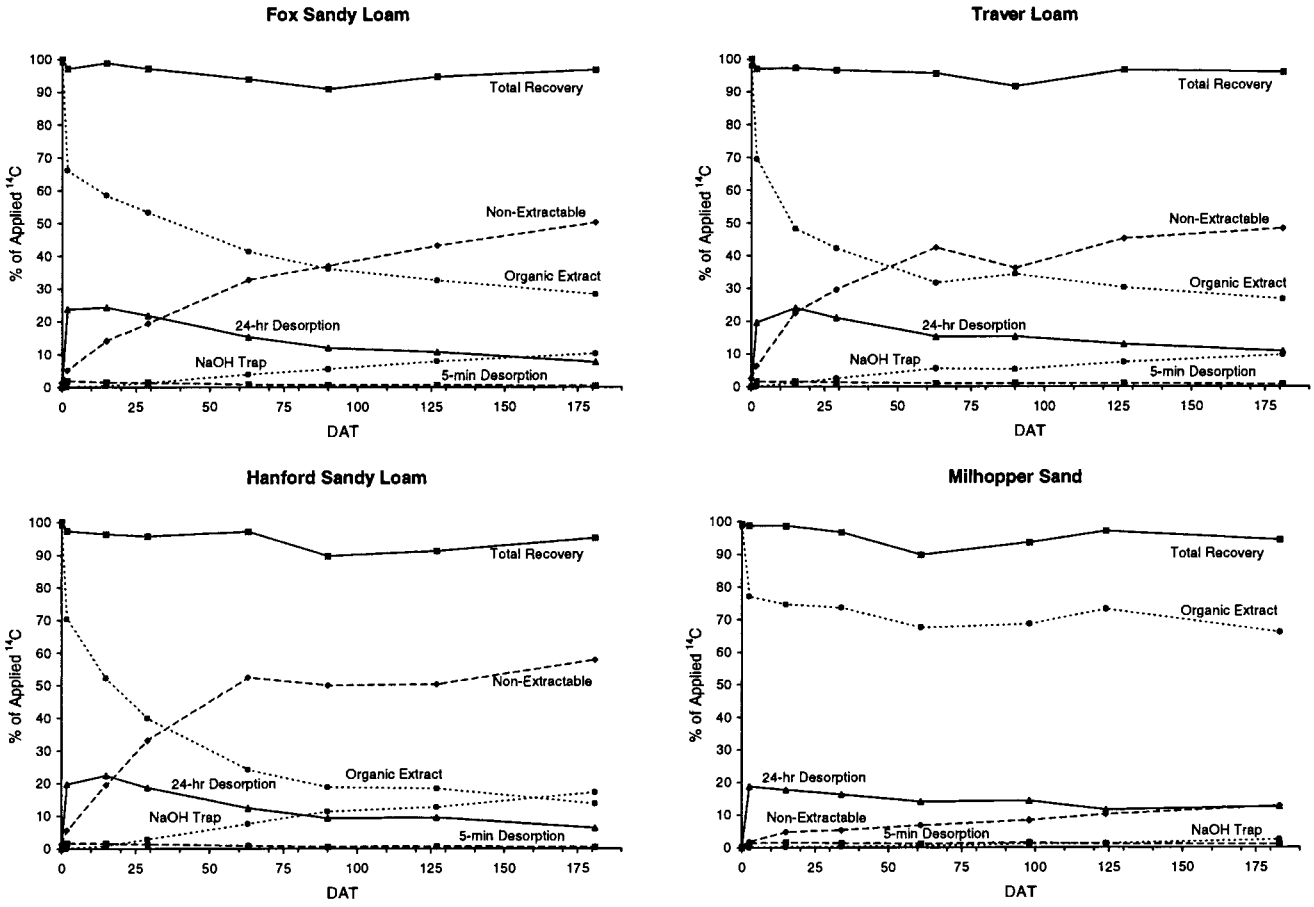

Figure 1. Distribution (%) of radiocarbon as a function of time and soil type. Values are the average of duplicate samples at each timepoint. Note that no aqueous desorptions were performed for 0 DAT samples.

Dynamics; Sunnyvale, CA) radiochemical scanner. TLC plates developed with solvent systems B and C were used for quantitation, while plates developed with solvent systems A and D were used to confirm identities of the degradates. Degradates OR-1 and OR-2 coeluted by using solvent systems B and C and were quantitated by using solvent systems A and D. Degradates OR-4 and OR-41 were not resolved with any of the TLC systems and were quantitated as a sum.

RESULTS AND DISCUSSION

Distribution of Radiocarbon and Material Balance. The distributions of radiocarbon among the NaOH traps, desorption solutions, organic soil extracts, and nonextractable material are shown in Figure 1. The average material balance for the Fox, Traver, Hanford, and Millhopper samples was 96.0%, 96.0%, 94.9%, and 96.0%, respectively, indicating that no volatile degradates (other than CO_2) were formed and that there was no dissipation of oryzalin by volatilization.

Patterns of radiocarbon distribution with time were similar for the Fox, Traver, and Hanford soils but were markedly different for the Millhopper soil. Mineralization of oryzalin to CO_2 reached levels of >10% of the applied radiocarbon and did not plateau by the end of the study period for the Fox, Traver, and Hanford soils. For the Millhopper soil, the cumulative $^{14}CO_2$ evolved after 6 months was 2% of applied. The quantity of radiocarbon in the rapidly desorbed pool was <2% in each soil throughout the study period and declined to <1% of that applied after 29 DAT on the Fox, Traver, and Hanford soils. For the Millhopper soil, however, rapidly desorbable radiocarbon remained at ≥1% of that applied throughout the study. The quantity of radiocarbon in the slowly desorbed pool (24-h desorption) also declined with increasing incubation time after approximately 15 DAT; the decline with time was somewhat greater for the Fox and Hanford soils than for the Traver and Millhopper soils. The amount of radiocarbon extractable with acidified organic solvent declined progressively with time on Fox, Traver, and Hanford soils, where respective concentrations were 28, 27, and 14% of applied at 181 DAT. There was a slight decline in organic extractable radiocarbon from the Millhopper soil; organic extractable radiocarbon ranged from 77 to 66% of applied from 2.5 to 183 DAT. The amount of radiocarbon that was recalcitrant to extraction was 48−57% by 181 DAT on the Fox, Traver, and Hanford soils but was only 13% on the Millhopper soil.

The increase in the amount of radiocarbon on Fox, Traver, and Hanford soil, relative to Millhopper soil, that was recalcitrant to extraction was most likely due to incorporation of degradation products into the soil organic matter. Organic matter contents were relatively similar in all four soils, but the Millhopper soil had a substantially greater sand content and consequently lower cation exchange capacity (CEC) and available water holding capacity than the other soils (Table 1). The differences observed in the degradation of oryzalin on the Millhopper sand (less CO_2 evolution and less nonextractable residue) were likely due to reduced microbiological activity as a consequence of limited moisture and nutrients. The small amount of nonextractable residue on the Millhopper sand combined with the relatively larger amount of oryzalin remaining on

Table 2. Distribution of Oryzalin and Degradates as a Function of Time and Soil Type[a]

	% of applied radiocarbon							
DAT	OR-1	OR-2	OR-4/41	OR-13	OR-15	OR-20	UN-1	UN-2
				Fox Sandy Loam				
0	98.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.8	90.5	0.2	0.0	0.2	0.0	0.0	0.0	0.1
15	73.2	0.0	0.0	0.9	0.7	2.6	0.0	1.6
29	61.6	0.0	0.0	1.9	1.7	2.0	0.5	2.2
63	35.2	0.1	0.4	3.3	2.2	1.1	1.4	5.7
90	20.1	2.4	0.5	3.0	2.9	1.0	1.2	5.5
127	15.5	1.0	1.6	3.3	3.4	0.6	0.6	5.0
181	13.5	0.6	0.3	4.1	4.1	0.2	1.9	3.9
				Traver Loam				
0	97.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.8	86.6	0.0	0.0	1.5	0.0	0.0	0.3	0.1
15	51.4	0.0	0.0	2.5	2.2	6.3	0.0	3.3
29	42.9	0.0	0.0	2.7	2.4	3.3	0.4	3.6
63	23.1	0.0	0.5	3.4	2.2	1.5	0.4	6.7
90	18.9	1.9	0.6	3.5	4.1	1.2	0.7	6.7
127	12.1	1.0	0.7	3.5	4.2	0.8	0.6	9.2
181	10.4	0.8	0.4	3.9	4.8	0.3	1.0	8.4
				Hanford Sandy Loam				
0	98.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.8	87.6	0.1	0.0	0.2	0.0	0.0	0.0	1.0
15	60.5	0.0	0.7	1.2	1.0	4.6	0.0	1.5
29	42.9	0.0	1.0	1.6	1.4	2.9	0.0	2.0
63	19.1	0.1	0.1	1.8	1.3	1.7	1.2	2.4
90	8.1	0.8	0.3	1.1	1.2	1.2	0.8	2.3
127	8.0	0.3	1.2	0.9	1.3	0.8	0.6	2.1
181	4.8	0.2	0.1	0.8	1.4	0.3	1.0	1.7
				Millhopper Sand				
0	97.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	93.1	0.0	0.0	0.0	0.0	0.0	0.0	0.8
15	88.4	0.2	0.0	0.0	0.0	0.5	0.0	0.0
34	85.6	0.0	0.0	0.2	0.0	0.8	0.3	1.1
61	64.1	0.0	0.0	1.0	0.4	0.7	0.8	1.8
98	61.2	1.9	1.3	1.7	1.0	0.5	0.8	1.9
124	60.6	0.8	0.0	1.0	0.3	0.3	1.4	1.9
183	61.4	1.6	0.0	1.2	0.9	0.3	1.5	2.3

[a] Values are the average of duplicate samples at each timepoint and are the sum of the desorbable and extractable pools.

this soil implies that the nonextractable residue observed on each of the soils was due to incorporation of oryzalin degradation products into soil organic matter and not simply a reflection of irreversible sorption of oryzalin.

Degradation Profiles. The total percentage of oryzalin and degradation products in each soil over time (Table 2) indicates the principal degradate on the Fox, Traver, and Millhopper soil was UN-2, which reached levels of 5.7, 9.2, and 2.3% of the applied radiocarbon at 63, 127, and 181 DAT, respectively. The principal degradate on the Hanford soil was OR-20, with a maximum level of 4.6% of the applied radiocarbon at 15 DAT. No single degradation product exceeded 10% of applied activity throughout the 6-month term of this study. Typical chromatograms are shown in Figure 2.

Degradate profiles on the Fox, Traver, and Hanford soils were similar. Although there was variation in the absolute levels and times of appearance for individual degradates, the overall degradation profile was consistent across these soils. The degradate profile on the Millhopper sand was difficult to interpret because of the slow rate of oryzalin degradation. The proposed degradation pathway for oryzalin in aerobic soil systems in given in Figure 3. The benzimidazole degradates (OR-13, OR-15, and UN-2) were among the first to form, despite their likely formation via degradate OR-4. This

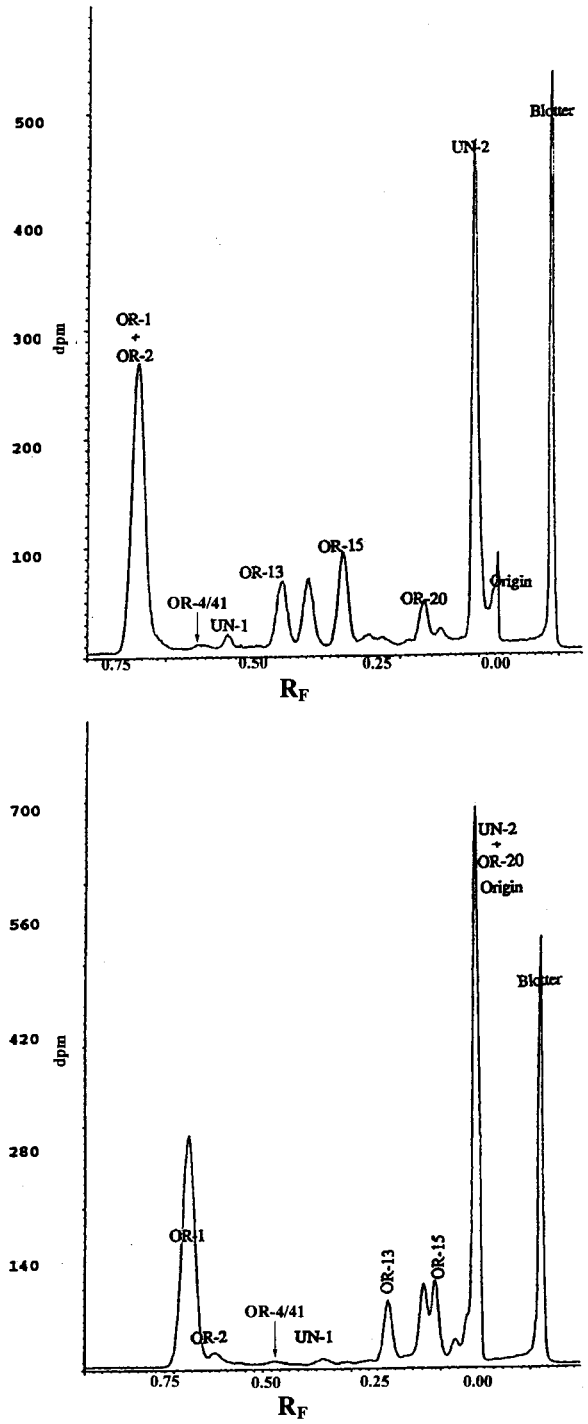

Figure 2. Typical TLC traces of oryzalin and degradates from 127 DAT 24-h desorption sample on Fox soil using solvent systems B (top) and C (bottom). The peak labeled blotter represents the material that remained on the absorbent strip below the origin of the stationary phase.

suggests that degradate OR-4 is short-lived and that the amount of material quantitated as the sum of OR-4 and OR-41 was likely predominantly OR-41.

Extractable radiocarbon that could not be attributed to known degradates (Figure 3) was approximately 10–15% of the applied radioactivity in each soil. This pool of material was immobile on the TLC systems used and could be composed of numerous degradates. Comparison of the proposed degradation pathway for oryzalin with that for trifluralin (Grover et al., 1997) is useful to elucidate other features of the degradation route and

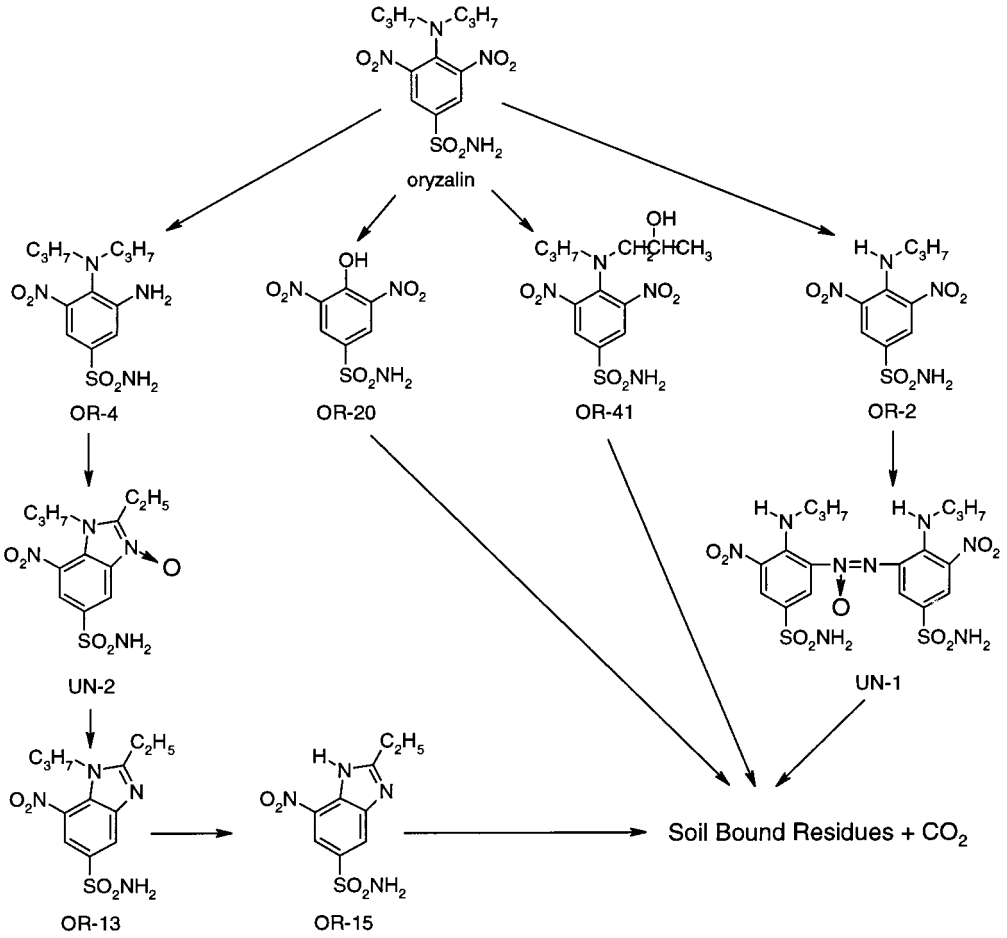

Figure 3. Proposed degradation pathway of oryzalin in aerobic soil systems.

to suggest what molecules may be in the pool of immobile material. Trifluralin differs from oryzalin by the substitution of a trifluoromethyl group for the sulfonamide group; however, in both molecules these groups are stable. All of the characterized oryzalin degradates have an analagous degradate in the degradation pathway for trifluralin. Thus, the unidentified soil degradates are likely intermediates in a degradation pathway leading toward a triamino-substituted benzenesulfonamide as a terminal product (the terminal product in soil degradation of trifluralin is a triamino-substituted trifluoromethylbenzene). By analogy, the 29 trifluralin degradates observed by Grover et al. (1997) suggests that the pool of unidentified oryzalin degradates should be composed of a number of discrete compounds.

Degradation Kinetics. Degradation of oryzalin was described by an exponential decay model:

$$y = Ae^{-kt}$$

where y is the percent of oryzalin remaining at time t, k is the rate constant, and A represents the initial amount of oryzalin. The model was used to estimate the time required for 50% and 90% degradation (DT_{50} and DT_{90}, respectively) of oryzalin (Figure 4). Examination of the residuals from the exponential decay fit for each soil reveals that this simple model underestimates the initial rate of decay and overestimates the degradation rate at later timepoints. The net result is a overprediction of DT_{50} and an underprediction of DT_{90} values; these errors suggest that the degradation of oryzalin was actually biphasic in nature. This effect was most pronounced on the Millhopper soil, although it was also discernible on the other three soils. However, the high correlation coefficients for the regressions imply that the absolute magnitude of the errors are small and the model is adequate for predicting the dissipation of oryzalin in aerobic soil systems.

The DT_{50} values (24−42 days) determined in this study on three soils were less than the simple first-order half-life of 60 days previously reported for oryzalin (Graper and Rainey, 1989). The reason for the substantially slower rate of degradation of oryzalin on the Millhopper soil is attributable to the high sand content and consequently lower CEC and water holding capacity which should support a smaller, less active microbial community due to limiting moisture and nutrient availability.

Sorption. Apparent sorption coefficients (K_d, L/kg) were determined at each sampling point; apparent sorption coefficients reported here do not assume a steady-state phase distribution. Sorption coefficients were calculated from the expression

$$K_d = S/C \text{ (L/kg)}$$

where S is the concentration of material released upon extraction of the soil (mg/kg) and C refers to the concentration released to aqueous solution (mg/L). With two desorption periods it was necessary to modify the

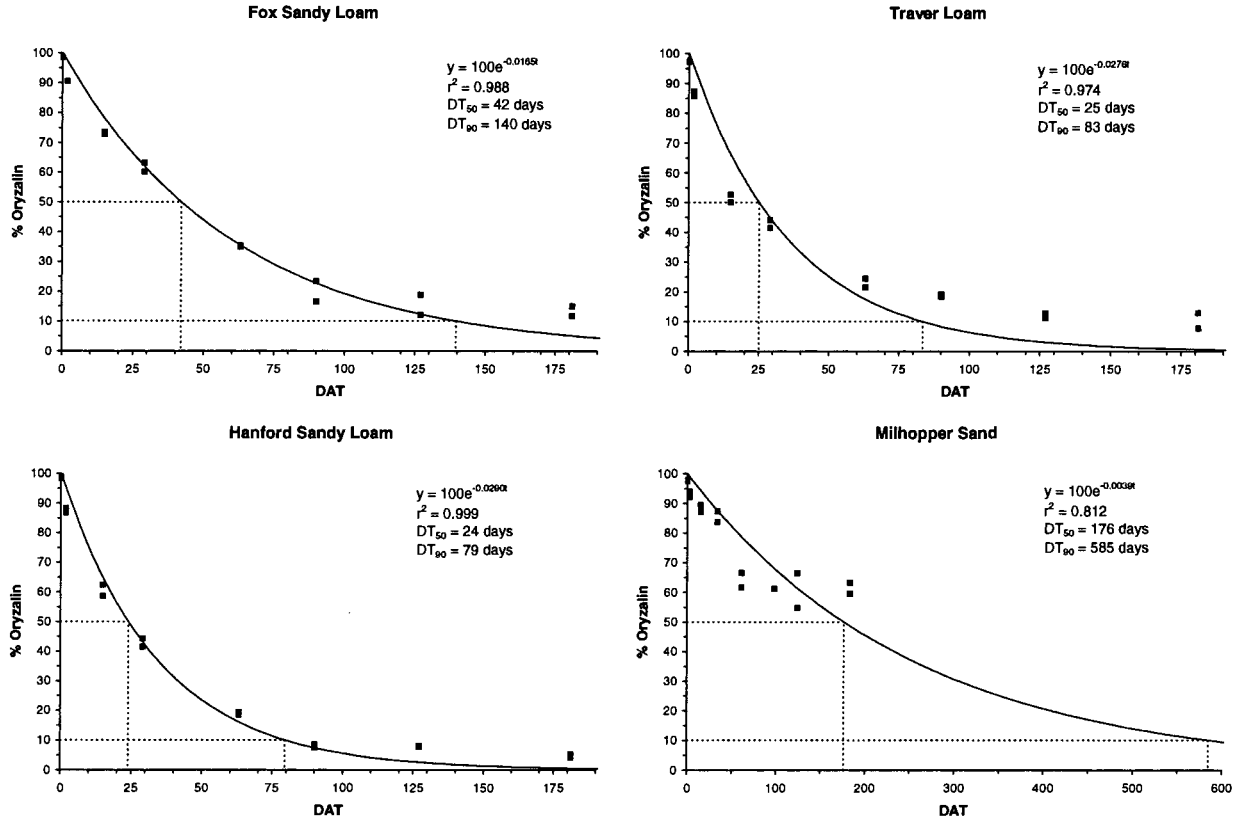

Figure 4. Degradation kinetics of oryzalin in aerobic soil systems.

above expression (for 24-h desorption) to

$$K_{\mathrm{d}} = \frac{[\mathrm{OR}_x]_1}{\frac{\mathrm{OR}_{x2} + \mathrm{OR}_{x3}}{V}}$$

where $[\mathrm{OR}]_x$ refers to the concentration of compound (mg/kg), OR_x refers to the quantity of a compound (mg), V refers to the volume of the aqueous solution (L), and the subscripts refer to different phases: 1 = material extracted from soil after desorption, 2 = 24-h desorption period, and 3 = 5-min desorption period.

Additionally, a partition coefficient, K_{ss}, was determined from the 5-min desorption period and represents the distribution of a compound between the soil solution and pool of material available for desorption:

$$K_{ss} = \frac{\mathrm{OR}_{x2}/W}{\mathrm{OR}_{x3}/V_{ss}}$$

where W is the weight of the soil (kg), V_{ss} is the volume of the soil solution (L), and the other variables are the same as defined for K_{d}. The soil solution distribution coefficient (L/kg) is dependent on the strength of sorption and the aqueous solubility of a compound. An increase in K_{ss} indicates an increased magnitude of the pool of sorbed compound; this pool is not readily desorbable into the soil solution. Thus, we have defined three pools of material based on the desorption and extraction procedures used: (1) the soil solution pool, defined by the material measured in the 5-min desorption, (2) the surface desorbable pool, defined by the material in the 24-h desorption, and (3) the extractable pool, defined by the material in the acidified organic solvent extraction.

The apparent sorption coefficients (K_{d}, L/kg) and soil solution distribution coefficients (K_{ss}, L/kg) for oryzalin and its degradation products as a function of time are shown in Table 3. Coefficients are presented for compounds where the quantity of radiocarbon in each pool was at least 0.02% of the applied radioactivity.

Values of K_{d} for oryzalin increased between 29 and 63 days after treatment on the Fox, Traver, and Hanford soils but not on the Millhopper soil. The average increase in K_{d} over the 6-month study period was a factor of 3 on the Fox, Traver, and Hanford soils but less than a factor of 2 on the Millhopper soil. Values of K_{d} increased concurrently with decreasing degradation rates for oryzalin, suggesting that increasing sorption decreased the amount of oryzalin readily available for degradation. The K_{d} of OR-20 increased as a function of incubation time. Values of K_{d} for UN-2 did not vary systematically across soil types or with increasing incubation time with the exception of the 63 DAT sampling point. The other benzimidazole degradates, OR-13 and OR-15, both had higher sorptivities and a trend toward increasing sorptivity with increasing incubation time. This latter trend was lacking for the *N*-oxide UN-2.

Regressions of K_{ss} versus time were not significantly different from zero at the 99% confidence limit for any of the molecules in this study; indicating that there was no temporal trend in K_{ss}. Therefore, the equilibrium between the rapidly desorbed/soil solution pool (5-min desorption) and the slowly desorbed pool of material (24-h desorption) was rapid. Average values of K_{ss} for oryzalin and each degradate are given in Table 4. Although the magnitude of K_{ss} for a given molecule varied across soil types, trends in K_{ss} between molecules were consistent across soil types. Thus, averaging K_{ss}

Table 3. Apparent Soil Solution Distribution Coefficients (K_{ss}, L/kg) and Sorption Coefficients (K_d, L/kg) for Oryzalin and Degradates on Each Soil and at Each Timepoint[a]

		5-min desorptions (K_{ss})				24-h desorptions (K_d)			
	DAT[b]	Fox	Traver	Hanford	Millhopper	Fox	Traver	Hanford	Millhopper
oryzalin	15	1.11	2.03	1.05	0.22	5.72	7.48	7.26	8.14
	29	1.08	1.95	1.54	0.24	5.52	7.44	7.44	9.78
	63	1.00	2.15	0.79	0.24	9.71	11.09	10.45	8.43
	90	1.12	2.11	0.99	0.18	7.96	9.48	8.21	9.32
	127	1.05	1.60	0.91	0.19	13.49	15.11	9.67	12.03
	181	0.98	1.36	0.45	0.24	18.86	22.36	22.71	14.26
OR-2	15				0.76				
	29								
	63	1.25	1.21	1.89					
	90	2.03	2.18	1.37		16.94	8.26	6.46	6.88
	127	0.59	1.98	0.53	0.28	14.69	8.67	4.89	5.35
	181	1.35	6.60	1.61	0.41	11.25	7.67	7.51	9.37
OR-4/41	15								
	29								
	63								
	90					80.31		3.89	
	127	1.45	1.09			47.65	17.00	19.40	
	181	0.98				11.11	9.75		
OR-13	15	0.48	1.62	0.84		4.14	7.68	3.96	
	29	1.57	2.89	2.86		3.45	4.92	2.29	
	63	1.12	2.15	1.23		5.51	7.34	2.49	4.97
	90	1.37	1.74	0.97	0.34	6.81	8.85	2.85	12.35
	127	0.99	1.86	1.01	0.47	8.94	11.44	4.63	6.05
	181	1.51	2.16	1.00	0.34	14.48	13.41	6.92	7.23
OR-15	15	1.13	2.38	1.45		3.01	2.89	2.78	
	29	1.69	3.40	2.52		5.41	5.24	2.62	
	63	1.26	2.77	1.11		5.68	3.70	2.51	5.42
	90	1.38	2.12	1.34	0.09	9.05	9.02	3.08	11.64
	127	1.04	1.77	1.05	0.75	6.92	8.53	4.58	5.09
	181	1.62	2.19	1.18	0.47	8.39	9.58	4.65	5.66
OR-20	15	0.80	3.24	1.04	0.42	1.33	0.63	0.56	
	29	2.65	3.50	6.68	0.86	1.02	0.69	0.59	0.74
	63	2.39	2.63	3.64	0.76	1.30	1.53	0.95	1.86
	90	3.99	2.92	4.26	0.40	2.17	1.40	1.12	2.25
	127	1.53		3.76	0.45	2.66	6.38	1.75	
	181	1.35		1.17	0.62	1.56	2.09	1.13	
UN-1	15								
	29								
	63					25.26		13.62	
	90	2.06				17.28		16.47	
	127	0.43	1.50	0.20		7.78	14.32	20.87	
	181	1.50	2.28	0.99		41.61	39.53	8.31	
UN-2	15	1.06	2.23	0.71		1.20	1.44	1.62	
	29	2.31	3.66	2.26	0.22	1.47	1.69	1.05	3.62
	63	1.27	2.07	0.96	0.36	4.52	4.49	3.05	3.68
	90	3.66	2.37	1.26	0.41	3.10	1.42	1.64	1.78
	127	1.40	2.08	1.40	0.52	1.39	1.27	0.89	2.05
	181	1.52	1.77	1.02	0.55	2.23	2.16	2.20	1.29

a Values are the average of duplicate samples at each timepoint [b] Day after treatment for Fox, Traver, and Hanford soils. Corresponding timepoints were 15, 34, 61, 98, 124, and 183 DAT for Millhopper.

Table 4. Average Values of K_{ss} as a Function of Soil Type for Oryzalin and Degradates[a]

	K_{ss}, L/kg				
	Fox	Traver	Hanford	Millhopper	overall av
oryzalin	1.03	1.85	0.95	0.22	1.01
UN-1	1.33	1.89	0.60		1.28
OR-13	1.17	2.07	1.42	0.38	1.39
UN-2	1.87	2.36	1.24	0.41	1.52
OR-15	1.35	2.44	1.44	0.44	1.56
OR-2	1.44	2.99	1.22	0.48	1.57
OR-20	1.88	2.49	3.02	2.54	1.94

[a] Values are averages across all timepoints on each soil and the overall average for each molecule across all timepoints and soils.

across soil types allows us to see the trends in K_{ss} as a function of molecular structure. The hydroxylated degradate OR-20 exhibited the highest value of K_{ss}, while the less polar oryzalin and dimer UN-1 had the lowest values; the benzimidazole degradates were intermediate. Therefore, the percentage of oryzalin available for desorption that was in soil solution was greater than the concomitant percentage of OR-20 available for desorption that was in soil solution.

There was a direct correlation between the soil water holding capacity and the average value of K_{ss} on that soil. That is, as the total volume of the soil solution increased, the concentration of material in the soil solution decreased. Therefore, the mass of material in the soil solution was determined by its concentration in the surface desorbable pool and not by the volume of the soil solution pool.

We can verify the conclusion that desorption and not solubility was responsible for the amount of material in soil solution by comparing the theoretical maximum of oryzalin in solution to the observed values. The aqueous solubility of oryzalin is 2.6 ppm; aqueous solubilities of oryzalin degradates are unknown. The application rates of oryzalin in this study, 3.14 μg/g (157

μg applied) for the Fox, Traver, and Hanford soils and 1.64 μg/g (82 μg applied) for the Millhopper soil, were high enough to potentially saturate the total pool of soil moisture. For example, the Traver soil had the highest moisture content of the soils used in this study, with approximately 8.9 mL of H_2O per 50 g of soil. Given an aqueous solubility of 2.6 ppm (μg/mL), the maximum mass of oryzalin in the aqueous phase would have been 23.1 μg, leaving 133.9 μg sorbed to the soil matrix (resulting in a minimum K_d value of 1.03 L/kg). However, the highest concentration of oryzalin observed in the soil solution on any soil (estimated by the 5-min desorption) was 1.0 μg/mL, well below the aqueous solubility limit. This exercise also suggests that aqueous solubility was not a limiting factor in the value of K_{ss} for oryzalin and was unlikely to be limiting for its degradates, which were present at lower concentrations and should have higher water solubilities. Thus, differences in K_{ss} between molecules were likely due to differences in sorption energetics. The relative values of K_{ss} are therefore a surrogate for the strength of the sorption interaction between a molecule in solution and the soil surface.

Comparing structural features with relative sorptivities (average K_{ss}, Table 4) allows us to determine the impact of changing functional groups on the strength of sorption. Oryzalin and its degradates were grouped into three structural classes: (1) substitution on the tertiary amine group (oryzalin, OR-2, and UN-1), (2) substitution of the tertiary amine group (OR-20), and (3) ring closure to form the benzimidazole structure (OR-13, OR-15, and UN-2). Substitution of the dipropylamino group with a polar hydroxyl group (OR-20) yielded the strongest sorption of the oryzalin degradates. Ring closure to form the benzimidazole degradates yielded intermediate sorption. The similar sorptivities among the benzimidazole degradates suggests that their principal structural feature controlling sorption is the planar benzimidazole ring and not their aliphatic substituents. Oryzalin exhibited the weakest sorption. Comparison of sorptivity of OR-2 and UN-1 relative to oryzalin revealed that sorption strength decreased when the propyl substituent is replaced with a hydrogen. Therefore, the strength of sorption for degradates formed by substitution on the tertiary amine is determined by the substituents on the amine functionality.

These conclusions are not the same as one would reach by simply looking at the K_d results. For example, oryzalin and UN-1 had the highest K_d values in this data set, but they also had the lowest K_{ss} values. Conversely, OR-20 had the lowest K_d values but the highest K_{ss} value. Thus, molecules that were more weakly bound to the surface desorbable pool of material (low K_{ss}) were also more tightly bound to the surface organic extractable pool (high K_d). Keep in mind that these two distribution coefficients describe partitioning between physically different pools of material. One is a liquid−solid partitioning (K_{ss}), while the other is principally a distribution between different surface sites (K_d). (The calculation of K_d does also include the pool of material in soil solution, but since the absolute magnitude of this pool was ≤2% of the applied material, it is not significant in the calculation of K_d.) This apparent contradiction implies that the mechanisms controlling distribution between the soil solution and desorbable pools are not the same as those controlling distribution between the desorbable and extractable pools. The explanation for these differences in sorption strengths may lie in the microbiological mechanism and physical location of the in situ formation of the degradates relative to the surface application of oryzalin.

CONCLUSIONS

Since the value of K_{ss} showed no clear trend with time for a given molecule, we assume that an equilibrium existed between the soil solution and surface desorbable pool of material. While the relative distribution of oryzalin and degradates between the soil solution and desorbable pool was constant over time (equilibrium was rapid), the relative distribution between the total desorbable pools and the total extractable pool (K_d) changed. Thus, there was a decreasing percentage of the total extractable pool available for desorption and degradation as incubation time increased.

Apparent K_d values for oryzalin, OR-2, UN-1, and OR-4/41 indicated that they have low potential mobility within the soil profile. Sorption on finer textured soils and soils with more organic matter would be expected to be greater than for the coarse-textured soils investigated in this study. Degradates OR-13, OR-15, and OR-2 (the benzimidazole degradates) exhibited intermediate sorptivity that increased with time. Therefore, the tendency for these molecules to migrate through the soil profile will decrease with soil contact time and will be overestimated by simple transport models using time-invariant sorption coefficients.

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