Effects of Soil pH and Soil Water Content on Prosulfuron Dissipation

Ryan P. Hultgren,*,† Robert J. M. Hudson,† and Gerald K. Sims‡

Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, Illinois
61801, and Agricultural Research Service, U.S. Department of Agriculture, Urbana, Illinois 61801

The sulfonylurea herbicide prosulfuron, 1-(4-methoxy-6-methyltriazin-2-yl)-3-[2-(3,3,3-trifluoropropyl)-phenylsulfonyl]urea, is used for the selective control of broadleaf weeds in corn, sorghum, and cereal grains. To investigate its fate in soils, this study examined the effects of soil pH and water content on the rates of dissipation processes and the products formed under aerobic conditions. Radiometry and chromatography analyses were used to quantify the degradation products and bound residues formed in incubations of 10 different soils. The pH-dependent hydrolysis of the sulfonylurea bridge to form phenyl sulfonamide was the primary transformation process. Significant microbial degradation of prosulfuron occurred in 2 of the 10 soils, yielding $^{14}CO_2$ and desmethyl prosulfuron among the major products. The time required for 50% dissipation of the herbicide (DT_{50}) was determined for each soil and water content treatment. At equivalent water contents, prosulfuron DT_{50} values were positively correlated with soil pH ($P < 0.0001$), varying from 6.5 days at pH 5.4 to 122.9 days at pH 7.9. Soil pH and water content strongly influence the fate of sulfonylurea herbicides in agricultural fields. Differences in the effect of soil water content on dissipation kinetics in a comparison of two soils were attributed to differences in soil pH, texture, and the ability of indigenous microorganisms to transform the herbicide.

KEYWORDS: Prosulfuron; environmental fate; aerobic dissipation; soil pH; soil water content; DT_{50}

INTRODUCTION

The sulfonylurea herbicide prosulfuron [1-(4-methoxy-6-methyltriazin-2-yl)-3-[2-(3,3,3-trifluoropropyl)phenylsulfonyl]-urea] is used for selective postemergence control of broad-leaved weeds in corn, sorghum, and cereal crops. The mode of action for this herbicide is inhibition of the production of the enzyme acetolactate synthase (ALS). ALS-inhibiting herbicides, including all of the sulfonylurea herbicides, exhibit extremely high herbicidal potency but have low acute and chronic toxicity to animal species and do not bioaccumulate in nontarget organisms. These properties make them very competitive as alternatives to conventional herbicides that are applied at much higher rates and have higher nontarget toxicity (*1*, *2*). Application rates for prosulfuron are low, typically ranging from 10.1 to 40.4 g of active ingredient (ai) ha^{-1} (*3*). In 2000, ~11000 kg of prosulfuron was applied to corn in the United States, treating 1.1 million ha (*4*). The principal problem associated with ALS-inhibiting herbicides is that some may cause carry-over damage in soybeans when used in a corn/soybean rotation, most commonly in alkaline soils. Therefore, understanding the factors governing the dissipation of prosulfuron is important to predicting where this herbicide can be most beneficially employed.

Soil pH is the major environmental determinant of both abiotic and biological processes affecting the fate of sulfonylurea herbicides. These compounds are weak acids ($pK_a = 3.3-5.2$) and thus exist predominantly in the dissociated form (anion) in agronomic soils (pH >6). Sulfonylurea herbicides are generally weakly sorbed by soil, with sorption decreasing with increasing pH as the amount of anionic species increases in solution (*1*, *5*). The major transformation process affecting sulfonylureas in soil is the hydrolysis of the sulfonylurea bridge. This process is also pH-dependent as the neutral sulfonylurea molecule is more susceptible to cleavage resulting from the nucleophilic attack by H_2O on the carbonyl C (*1*, *2*, *5*). Thus, the hydrolysis half-life ($t_{1/2}$, days) values for many sulfonylurea herbicides in aqueous solution are several hundred times shorter under acidic conditions than at pH >7 (*6−8*). A similar pH dependence of sulfonylurea hydrolysis has been found in soil incubation studies. Degradation half-lives for chlorsulfuron [1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea] under aerobic conditions range from 20 days at pH 3.9 to 147 days at pH 7.0 (*9−14*). Soil pH also affects the rate of microbial transformations of sulfonylureas in the environment. Studies with both sulfometuron-methyl [methyl 2-[[[[(4,6-dimethylpyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate] (*15*) and chlorsulfuron (*11*) have indicated biological degradation in alkaline soils controls the overall rate of degradation because abiotic hydrolysis is so slow. Taken together, these findings suggest that the

* Address correspondence to this author at the School of Civil Engineering, Purdue University, W. Lafayette, IN 47907 (e-mail hultgren@ecn.purdue.edu).
† University of Illinois.
‡ U.S. Department of Agriculture.

Prosulfuron Dissipation

J. Agric. Food Chem., Vol. 50, No. 11, 2002 **3237**
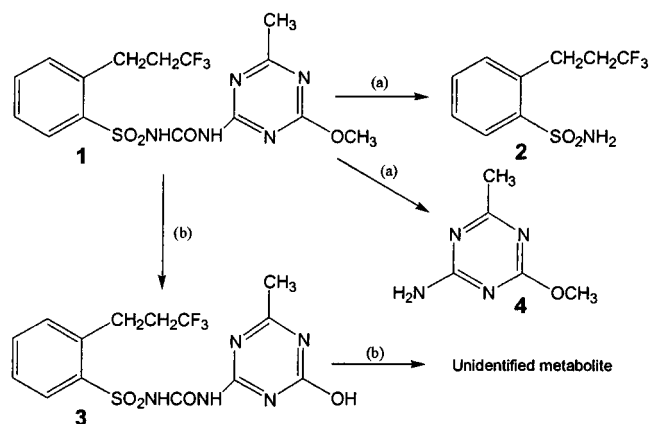
Figure 1. Structures of prosulfuron (**1**), phenyl sulfonamide (**2**), desmethyl prosulfuron (**3**), and amino triazine (**4**). Only **1–3** were traceable in this study. Proposed degradation pathways of prosulfuron in soil: (a) chemical hydrolysis and (b) microbial degradation. See text for discussion of degradation product of **3** detected in soil incubations.

pH will be the major predictor of the environmental fate of sulfonylurea herbicides in soil.

Under conditions yielding slow hydrolysis, the environmental factors that affect herbicide biodegradation likely control the fate of sulfonylureas. Because pesticides in solution are more available for microbial degradation than when sorbed (*16–18*), pH and soil water content, which determine the sorption and diffusion of herbicides in soil, control rates of biodegradation. Increasing soil water content is known to stimulate the microbial degradation of several sulfonylureas (*19–21*), as demonstrated by the mineralization of sulfometuron-methyl under laboratory conditions (*15*). Similarly, mineralization of other herbicides such as clomazone [2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone] (*22*) and cloransulam-methyl [*N*-(2-carbomethoxy-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo-[1,5-*c*]pyrimidine-2-sulfonamide] (*23*) has been shown to increase with soil water contents under aerobic conditions.

The limited published research addressing the fate of prosulfuron in the environment is consistent with what is known of the sulfonylureas in general. Hydrolysis in aqueous solution is pH sensitive, with half-lives at 25 °C decreasing from approximately 330 to 0.97 days between pH 7.5 and 2 (*6*). Aqueous hydrolysis is also highly responsive to temperature changes, with half-lives decreasing 70-fold from 15 to 55 °C. The major hydrolysis products of prosulfuron (**Figure 1**) were identified by Bray et al. (*24*) as phenyl sulfonamide and amino triazine. Minor products include desmethyl prosulfuron (resulting from the O-demethylation of the parent compound) and its two subsequent transformation products (*24*). Prosulfuron biotransformation was observed in pure cultures of soil microorganisms, with desmethyl prosulfuron as the major product (*25*). Hydroxylation at multiple reactive sites appears to be the primary degradation pathway, leading to the formation of nine different byproducts including phenyl sulfonamide and amino triazine as minor products.

To date, no studies of prosulfuron transformation in soils have been reported in the literature. The purpose of this work was to fill this gap by examining how prosulfuron dissipation processes, including transformation and bound residue formation, vary as a function of soil pH and water content. A total of 10 different soils were selected for aerobic soil incubation studies to examine the effects of these variables.

MATERIALS AND METHODS

Soils. Ten field soils were sampled from the top 15 cm of the profile in fall of 1998 and spring of 1999 from several locations in Georgia, Illinois, and Texas. The history of herbicide applications to these fields is not known. All soils were passed through a 2 mm diameter mesh sieve and stored in plastic bags at 5 °C until use. Physical characteristics of the soils were determined by A&L Great Lakes Laboratories, Inc., Fort Wayne, IN, and are shown in **Table 1** along with sampling locations.

Chemicals. Prosulfuron and its metabolites were supplied as gifts by Syngenta Crop Protection, Greensboro, NC. Radiolabeled [^{14}C-UL-*phenyl*]prosulfuron was used in all soil incubation experiments as the herbicide source. The chemical had a specific activity of 1.88 MBq mg^{-1} and a radiochemical purity of 97.8% and was used without any further purification. Unlabeled prosulfuron and two metabolites, CGA-159902 [**Figure 1**; **2**; 2-(3,3,3-trifluoropropyl)phenyl sulfonamide] and CGA-300406 [**Figure 1**; **3**; *N*-[[(1,4-dihydro-6-methyl-4-oxo-1,3,5-triazin-2-yl)amino]carbonyl]-2-(3,3,3-trifluoropropyl)benzenesulfonamide], were used as reference materials for analytical methods. Optima grade acetonitrile, ethyl acetate, and water, used for processing and analyzing soil samples, and Scintiverse scintillation cocktail used for liquid scintillation spectrometry (LSS) were obtained from Fisher Scientific (Fair Lawn, NJ).

Aerobic Soil Incubation Experiments. Unless otherwise indicated, the following procedures applied to all incubation studies. Bulk soil samples were allowed to dry at room temperature for ~24 h. Mason jars (480 mL) were used as soil biometers according to the methods described by Mervosh et al. (*22*). In the bottoms of jars a 50 μL aliquot of a [^{14}C]prosulfuron spiking solution (0.17 MBq of prosulfuron mL^{-1}) in acetonitrile was combined with a sufficient volume of water to achieve equivalent gravimetric water contents for a matric potential of −100 kPa (**Table 1**). Soil samples (50 g dry wt basis) were transferred to the biometers and allowed to equilibrate with the water and herbicide mixture for ~4 h prior to thorough mixing with a stainless steel spatula. The herbicide level, ~88.5 ng of prosulfuron g^{-1} of soil, was equivalent to 4.4 times the maximum field application rate of prosulfuron (40.4 g of ai ha^{-1}), assuming a soil bulk density of 1.33 g cm^{-3} and a soil mixing depth of 15 cm. The higher herbicide rate was used to enable better detection of ^{14}C in soil extracts and base traps. A 20 mL scintillation vial containing 5 mL of 0.2 M NaOH for trapping evolved carbon dioxide (CO$_2$) was suspended from the Mason jar lid above the soil. The base traps were sampled and replaced with fresh solution on a weekly basis throughout the study for aeration purposes, in addition to each soil-sampling time point. The combination of the sealed biometer and dilute NaOH trap minimizes loss of soil water. Three replicate biometers were prepared for each soil and treatment. All biometers were incubated in the dark at 25 °C in a constant-temperature room.

All soils were stored for several months at 5 °C in plastic bags before use. To assess the activity of the microbial populations, three randomly selected soils (Drummer-3, Tabor, and Xenia-2) were treated with [^{14}C]glucose and ^{14}CO$_2$ evolution with time was monitored. This approach has been used previously for soil incubation studies with cloransulam-methyl (*26*). Three replicates of 5g dry wt basis samples of each soil, adjusted to −100 kPa water contents, were treated with 1400 Bq of [^{14}C]glucose and stored in 1 pt Mason jars with base traps for 28 days under the same conditions as used for the prosulfuron experiments. After 2 days, ~40% of the applied radioactivity had been recovered as ^{14}CO$_2$ in Drummer-3 and Xenia-2 soils, whereas 50% of the radiolabeled glucose had been mineralized in Tabor soils, which is similar to what is typically observed in fresh soils.

Effects of Soil pH. For this study, eight soils were selected to represent four soil pH ranges (pH 5.9, 6.2–6.3, 6.9–7.1, and 7.9–8.0), with two soils of different organic carbon contents in each pH range (**Table 1**). Soil samples were taken at 1, 4, 8, 14, 27, 49, 80, and 104 days after treatment (DAT).

Effects of Soil Water Content. Bulk samples of the Tabor and Xenia-2 soils were air-dried below equivalent −1500 kPa water-holding capacities (**Table 1**). Using the methods described above, soil samples were adjusted to −100 and −1500 kPa water contents with Optima

Table 1. Properties of Soils Used in [^{14}C]Prosulfuron Aerobic Incubation Experiments

soil series	taxonomic class	soil texture	soil pH	OC (%)	CEC (cmol/kg)	sand (%)	silt (%)	clay (%)	% water[e] (w/w) −100 kPa	−1500 kPa	air-dry
Dothan[a]	Plinthic Kandiudults	loamy sand	5.9	0.64	2.4	81	14	5	3.6		
Raub-2[b]	Aquic Argiudolls	clay loam	5.9	3.02	16.4	21	44	35	23.4		
Tifton[a]	Plinthic Kandiudults	loamy sand	6.2	0.64	2.4	79	12	9	4.0		
Raub-1[b]	Aquic Argiudolls	silty clay loam	6.3	2.15	13.7	17	50	33	20.5		
Drummer-3[c]	Typic Endoaquolls	silty clay	6.9	4.00	25.6	13	47	40	20.7		
Xenia-1[b]	Aquic Hapludalfs	silt loam	7.1	1.57	8.7	9	64	27	26.8		
Weswood[d]	Udifluventic Ustochrepts	loam	7.9	1.16	23.3	29	49	22	12.9		
Drummer-2[b]	Typic Endoaquolls	silty clay	8.0	3.42	29.5	7	48	45	26.6		
Tabor[d]	Oxyaquic Vertic Paleustalfs	sandy loam	5.4	0.70	3.4	67	26	7	5.6	3.3	1.0
Xenia-2[b]	Aquic Hapludalfs	silt loam	7.1	2.15	9.8	15	59	26	18.9	9.8	5.2

[a] Tifton, GA. [b] Champaign, IL. [c] Rochelle, IL. [d] College Station, TX. [e] % water in soil provided for −100 kPa matric potential for all soils and at −1500 kPa and air-dry for soils used in the soil water content study (Tabor and Xenia-2).

water and treated with [^{14}C]prosulfuron. Six additional replicates were prepared at the air-dry water content for each soil. For these samples, air-dried soil was transferred to biometers and spiked with herbicide solution (50 μL of 4.5 μCi of [^{14}C]prosulfuron mL^{-1} in acetonitrile) by surface application with a 100 μL syringe. At 17 DAT, the soil in three of the air-dry soil replicates was adjusted to −100 kPa water contents with water. These replicates are referred to as the "rewet" treatment. Soil was sampled for analysis at 2, 5, 8, 17, 27, 40, 59, and 110 DAT for the −100 and −1500 kPa and air-dry treatments. For the rewet soil treatment, soil was sampled at 2, 5, 19, 22, 27, 40, 59, and 110 DAT.

Respiration and Mineralization Analyses. As evidence for biotransformation of prosulfuron had been reported (*23*), sampling methods adapted from Mervosh et al. (*22*) and Anderson (*27*) were used to monitor total CO_2 respiration and mineralization of prosulfuron to [^{14}C]carbon dioxide ($^{14}CO_2$). Total CO_2 respiration was measured as an indication of microbial activity in the soil biometers, where CO_2 may be produced from the metabolism of plant and animal tissues, soil organic carbon, or other chemicals (e.g., prosulfuron) present in the soil. Total respiration was determined by titrating a 1 mL aliquot of the CO_2 trap solution, using phenolphthalein as an indicator, after the addition of 200 μL of 1.5 M $BaCl_2$, with 0.1 M H_2SO_4. Evolution of $^{14}CO_2$ was measured by combining a 1 mL aliquot of NaOH solution from the CO_2 trap with 15 mL of Scintiverse scintillation cocktail and counting with a Packard Tri-Carb 1900TR liquid scintillation analyzer (Packard Instrument Co., Meriden, CT) equipped for chemiluminescence correction.

Soil Extraction. Soil samples (5 g dry weight basis) were taken from each replicate after thorough mixing of the soil remaining in the biometer and extracted three times with a mixture of 10 mL of ethyl acetate and 100 μL of water in 50 mL Teflon centrifuge tubes. After each extraction, soil suspensions were centrifuged for 10 min at 7800g and 5 °C. Supernatants from the three extraction cycles were combined and evaporated to dryness. In the soil pH study, the soil was extracted overnight for ~24 h. In the water content study, the first extracting period was 4 h. In preliminary experiments, no significant differences were observed between using an initial extracting period of 4 vs 24 h; the change in method was made solely due to time constraints. The two subsequent extraction cycles were for 30 min each in both experiments. Dried extracts were dissolved in 5 mL of ethyl acetate, and two 100 μL aliquots were combined with 15 mL of Scintiverse scintillation cocktail and analyzed via LSS for total extractable radioactivity. Average recovery of the applied ^{14}C using these extraction methods was ~85% at 2 DAT in the soil water content study and ~90% at 1 DAT in the soil pH study. The remaining extract was quantitatively transferred to a 10 mL Reacti-vial and evaporated to dryness, dissolved in 250−500 μL of a 1:5 water to acetonitrile solution, and filtered through a 0.45 μm PTFE filter into a 1.5 mL glass vial for chromatography analysis.

Chromatography. The presence of ^{14}C-labeled prosulfuron and transformation products in the soil extracts was determined using high-performance liquid chromatography (HPLC). A Hewlett-Packard series 1050 HPLC (San Fernando, CA) was coupled to a Radiomatic 500TR

flow scintillation analyzer (Packard Instrument Co.). Chromatography conditions were as follows: injection volume, 200 μL; mobile phase flow rate, 1 mL min^{-1}; 4.6 × 250 mm, reverse phase C_{18} column (Econosil C_{18}, Alltech Associates, Inc., Deerfield, IL); and UV−vis detector wavelength, 224 nm. An isocratic mobile phase, consisting of 40% acetonitrile and 60% water, was used through the 40 DAT and 49 DAT soil sampling periods, respectively, in the soil water content and soil pH studies, to monitor the disappearance of prosulfuron and the presence of degradation products in the soil extracts. Both solvents in the mobile phase were acidified with 1 mL of 85% H_3PO_4 per liter of solution and degassed prior to use. For the later sampling points in each study, it was necessary to use a gradient mobile phase to achieve separation of the degradation products. Using the same acidified solvents as above, the gradient was the following (% water/% acetonitrile): 0 min, 100/0; 20 min, 70/30; 40 min, 40/60; 46−48 min, 0/100; 50−52 min, 100/0.

Using the HPLC isocratic conditions, the respective retention times of prosulfuron, phenyl sulfonamide, desmethyl prosulfuron, and a third metabolite ("product C") were approximately 11, 7, 5, and 4.4 min. The retention times of these same compounds using the gradient mobile phase were approximately 35, 28, 25, and 21 min. The identificaton of prosulfuron and its transformation products in soil extracts was based on comparison of retention times of radioactive sample peaks with the analytical standards. Although additional radioactive peaks were occasionally observed, they occurred sporadically and accounted for little of the applied radioactivity, collectively <5%, and thus were not identified.

Unextractable ^{14}C. The extracted soil remaining in the centrifuge tubes was air-dried in a fume hood for 2 days and then ground to a fine powder using a mortar and pestle. Duplicate subsamples, weighing ~0.25−0.3 g, were each combusted for a 3 min cycle in a Harvey biological oxidizer (model OX500, R. J. Harvey Instrument Corp., Hillsdale, NJ). The combustion efficiency for each soil used was measured in triplicate by fortifying soil samples with [^{14}C]prosulfuron solutions of known activity immediately before combustion. Unextractable ^{14}C values were corrected on an individual soil basis using average percent recoveries of ^{14}C as $^{14}CO_2$, which ranged from 81 to 97%. Using this method, the specific identification of ^{14}C-labeled materials in the unextractable soil phase was not possible.

Statistical Analyses. Analyses of variance were conducted by the general linear models procedure of the SAS release 8.2 statistical package (SAS Institute Inc., Cary, NC). Comparisons of mean values in this study were accomplished using Fisher's protected least significant difference (LSD) methods at a confidence level (α) of 0.05 for soil pH, day, soil pH by day, water content, and water content by day interaction effects. The LSD values are typically represented as vertical bars in figures and as numerical values in tables. The influence of soil properties on prosulfuron dissipation rates was evaluated using the Pearson correlation and regression procedures in SAS.

RESULTS AND DISCUSSION

In the soil incubation studies, loss of prosulfuron and formation of degradation products were monitored by determin-

Prosulfuron Dissipation

J. Agric. Food Chem., Vol. 50, No. 11, 2002 **3239**

Table 2. Effects of Soil pH on ^{14}C Distribution 104 Days after [^{14}C]Prosulfuron Soil Treatment

soil: pH, % OC:	recovered radioactivity as % of applied [^{14}C]prosulfuron[a]								
	Dothan 5.9, 0.64	Raub-2 5.9, 3.02	Tifton 6.2, 0.64	Raub-1 6.3, 2.15	Drum-3 6.9, 4.00	Xenia-1 7.1, 1.57	Weswood 7.9, 1.16	Drum-2 8.0, 3.42	LSD[b]
mineralized	0.84	1.68	0.82	1.54	2.12	15.1	4.48	4.01	0.42
total extractable	39.1	59.3	29.8	62.2	55.0	34.1	55.1	47.0	3.7
prosulfuron	0.0	0.9	0.0	2.6	14.5	9.6	55.0	46.0	2.0
phenyl sulfonamide	39.1	57.8	29.8	57.6	39.3	17.1	0.0	1.1	4.4
desmethyl prosulfuron	0.0	0.4	0.0	0.5	0.8	0.0	0.0	0.0	0.6
product C	0.0	0.1	0.0	1.5	0.4	5.7	0.0	0.0	1.5
unextractable[c]	45.0	31.9	48.1	32.8	32.3	48.5	31.3	42.6	6.1
total	85.0	92.8	78.8	86.5	89.4	97.6	90.9	93.7	7.6

[a] Results are means of triplicate tests. [b] Least significant difference at $\alpha = 0.05$. [c] Corrected for ^{14}C oxidation efficiency using a soil-specific correction factor.

Table 3. Effects of Soil Water Content on ^{14}C Distribution 110 Days after [^{14}C]Prosulfuron Treatment

moisture content	recovered radioactivity as % of applied [^{14}C]prosulfuron[a]									
	Xenia-2, pH 7.1, 2.15% OC					Tabor, pH 5.4, 0.70% OC				
	−100 kPa	−1500 kPa	air-dry	rewet	LSD[b]	−100 kPa	−1500 kPa	air-dry	rewet	LSD[b]
mineralized	18.4	0.5	0.4	20.4	2.4	4.5	2.2	0.6	3.0	1.1
total extractable	31.8	56.6	61.3	32.2	3.7	54.6	58.9	54.7	69.6	7.2
prosulfuron	10.9	12.0	25.7	13.0	1.2	1.1	0.9	0.0	0.0	0.1
phenyl sulfonamide	8.3	44.1	35.5	7.7	2.2	52.0	57.7	54.4	69.5	6.9
desmethyl prosulfuron	1.25	0.13	0.00	0.22	0.08	0.81	0.08	0.04	0.00	0.09
product C	9.2	0.1	0.0	9.2	0.7	0.21	0.08	0.08	0.00	0.02
unextractable[c]	40.6	33.9	31.0	45.6	7.1	39.5	33.6	29.2	38.6	18.9
yotal	90.7	91.0	92.8	98.2	8.3	98.6	94.7	84.5	111.1	24.1

[a] Results are means of triplicate tests. [b] Least significant differences at $\alpha = 0.05$. [c] Corrected for ^{14}C oxidation efficiency using a soil-specific correction factor.

ing the quantities of ^{14}C-labeled compounds recovered in one of three pools: solvent-extractable compounds in the soil−water matrix, carbon dioxide trapped in the biometer, and unextractable residues bound to the soil. The final distributions of applied radioactivity among these pools are presented in **Table 2** for the eight soils used in the soil pH study and in **Table 3** for the water content study. Of the extractable ^{14}C-labeled compounds, typically 95% could be identified using HPLC as either prosulfuron or one of three related compounds. When all pools are summed, the average recovery of applied radioactivity for all replicates and sampling dates in the soil pH study was 97.4 ± 9.8%. The average recoveries of applied [^{14}C]prosulfuron for all water content treatments were 97.7 ± 7.8% (Xenia-2) and 95.2 ± 7.5% (Tabor).

Degradation Products and Pathways. A transformation scheme for prosulfuron in soil based on experimental data and literature results is illustrated in **Figure 1**. Mineralization of many herbicides, including sulfometuron-methyl (*15*), clomazone (*22*), and cloransulam-methyl (*23*), to CO_2 has been demonstrated to require biological activity by comparing sterile and nonsterile soil biometer treatments. Thus, we attributed $^{14}CO_2$ trapped in the experiments with prosulfuron to microbial degradation processes. Although sterile soil treatments were not investigated in this study, we attributed the formation of phenyl sulfonamide (**2**) predominantly to abiotic chemical hydrolysis of prosulfuron, as this was a major product observed under sterile aqueous solutions by Bray et al. (*24*). As will be discussed further, desmethyl prosulfuron (**3**) was observed in significant quantities only in two soils that also exhibited significant mineralization; thus, the formation of desmethyl prosulfuron was attributed to microbial transformation. Desmethyl prosulfuron was a common biotransformation product in pure culture studies conducted by Kulowski et al. (*25*). Of 72 soil microorganisms originally investigated, only 6 transformed prosulfuron to a significant degree, with desmethyl prosulfuron formed by 4 of

the 6 (*25*). A substantial quantity of a third prosulfuron transformation product, referred to as "product C", was observed in two soils that exhibited significant production of both **3** and $^{14}CO_2$, suggesting that it was also formed through biological processes. Product C appeared to increase in quantity in both soils as **3** decreased following a peak, suggesting that it may be a daughter product of the degradation of **3**. In aerobic soil incubation studies with chlorsulfuron, a metabolite structurally similar to desmethyl prosulfuron was further degraded to a product in which the triazine ring was cleaved (*14*). No attempt was made to identify the chemical structure of product C due to insufficient mass of the molecule recovered in this study. The formation of unextractable residues is thought to largely involve the diffusion of solutes into the interior of soil aggregates and/or formation of covalent bonds with soil materials (*28*).

Effects of Soil pH. The amount of [^{14}C]prosulfuron recovered in the soil extracts decreased over the duration of the study, with the extent and rate of decrease primarily dependent on soil pH (**Figure 2**). The dissipation of [^{14}C]prosulfuron in the four acidic soils (Dothan, Raub-2, Tifton, and Raub-1) was mainly due to the formation of phenyl sulfonamide through prosulfuron hydrolysis and the formation of unextractable residues (**Figure 2**). At the end of the study, phenyl sulfonamide represented 30−58% of the applied radioactivity in soil extracts, with <1% recovered as prosulfuron in three of the four acidic soils (**Table 2**). At 14 days, ∼30% of the ^{14}C was unextractable in all four soils (**Figure 2**), and after 104 days, a range of 31.9−48.1% of unextractable ^{14}C was measured (**Table 2**). For the duration of the experiment, extractable microbial transformation products accounted for at most 5.6 ± 1.2% of the applied radioactivity (Raub-1, 49 DAT). No more than 1% of the applied radioactivity was detected as microbial transformation products in the Dothan and Tifton soils.

The loss of prosulfuron was less rapid in the neutral pH soils, Drummer-3 and Xenia-1 (**Figure 2**), than in the acidic soils.

3240 *J. Agric. Food Chem.,* Vol. 50, No. 11, 2002

Hultgren et al.
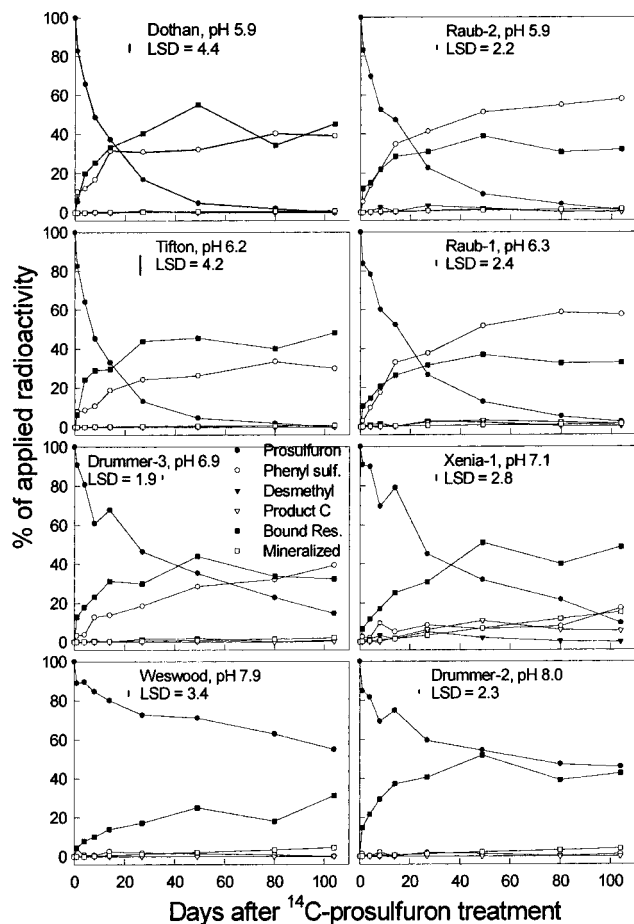
Figure 2. Distribution of ^{14}C in extractable, bound residue, and mineralized ($^{14}CO_2$) phases in soil pH study. Extractable phase represented by HPLC detection of ^{14}C-labeled compounds: prosulfuron, phenyl sulfonamide, desmethyl prosulfuron, and product C.

Hydrolysis and formation of ^{14}C residues dominated the dissipation of [^{14}C]prosulfuron in Drummer-3. Mineralized and extracted microbial transformation products combined for only slightly more than 3% of the applied ^{14}C in Drummer-3 (**Table 2**). In contrast, the transformation of prosulfuron in Xenia-1 occurred via a combination of microbial and chemical processes. In the extractable phase, a mixture of hydrolysis and microbial transformation products was observed beginning at 8 days and continuing throughout the study (**Figure 2**). At 104 days, ~21% of the applied [^{14}C]prosulfuron was recovered as microbial transformation products ($^{14}CO_2$, desmethyl prosulfuron, and product C) and 17% as phenyl sulfonamide.

The dissipation of [^{14}C]prosulfuron in both alkaline soils resulted primarily from the binding of ^{14}C residues to soil over time, thus contributing to the unextractable pool (**Figure 2**). At the 104 DAT soil sampling point, unextractable radioactivity accounted for approximately 31 and 43% of the applied [^{14}C]-prosulfuron, respectively, in Weswood and Drummer-2 (**Table 2**). The majority of the radioactivity in soil extracts was identified as prosulfuron throughout the study, with insignificant accumulation of transformation products.

Mineralization of prosulfuron to $^{14}CO_2$ was generally very slow, accumulating to <5% of the applied radioactivity after 104 days for seven of the eight soils (**Table 2**). Evolved $^{14}CO_2$ from Xenia-1 was significantly greater than that from the other seven soils at 8 DAT and continued to be greater throughout the study, with an average of 15.1 ± 0.2% of the applied radioactivity recovered as $^{14}CO_2$ at 104 DAT (**Figure 3A**). The
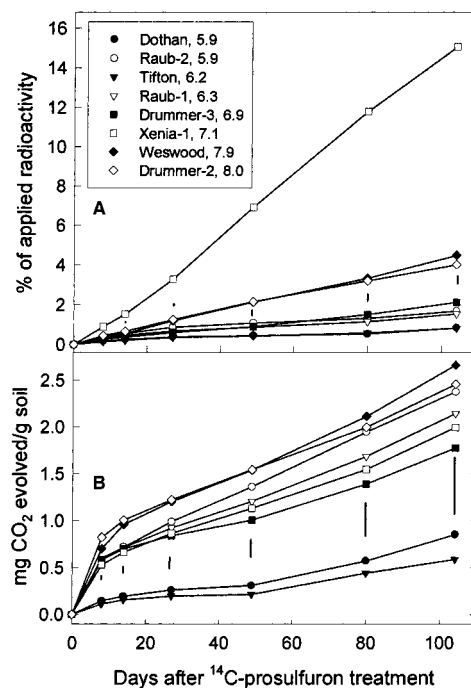
Figure 3. Effects of soil pH on (A) cumulative mineralization ($^{14}CO_2$) and (B) total CO_2 respiration. Vertical bars represent LSD values at $\alpha = 0.05$ at each sampling time point.

results indicate that mineralization was independent of specific soil properties. A plausible reason for the significantly greater mineralization observed in the Xenia-1 soil is that more potential prosulfuron degraders, such as those examined by Kulowski et al. (25) were present in this soil than the others. However, no attempts were made to isolate the microorganisms responsible for mineralization of prosulfuron in our soil incubation studies. Six of the eight soils exhibited similar amounts of total CO_2 respiration, ranging from 1.8 ± 0.05 to 2.7 ± 0.9 mg of CO_2 evolved g^{-1} of soil. The Xenia-1 soil, which produced much more $^{14}CO_2$ than the other soils, did not evolve significantly more total CO_2 (**Figure 3B**). Simple correlation analyses comparing respiration and mineralization found no significant relationships (data not shown). This indicates that gross soil microbial activity, as estimated by respiration, is not a good predictor for how rapidly indigenous soil microorganisms can mineralize prosulfuron.

Effects of Soil Water Content. As with other herbicides (*15, 19−23*), increasing soil water contents (reducing tensions) caused increases in biological activity and degradation of prosulfuron. In Xenia-2, an apparent water content threshold was observed in the mineralization data (**Figure 4A**) but not in total microbial respiration results (**Figure 4B**). At −100 kPa, ~20% of the applied ^{14}C was recovered as $^{14}CO_2$, whereas <1% was detected from both −1500 kPa and air-dry treatments (**Table 3**). This large difference between the wetter and drier soils may have been a result of more herbicide sorption and less diffusion in drier soils (*17*) and, thus, more bioavailability constraints at the lower water contents. The rewet treatment resulted in a dramatic increase in both mineralization and respiration after rewetting on day 17, with both attaining levels similar to the −100 kPa treatment by 110 DAT (**Figure 4**). Production of $^{14}CO_2$ was 46 times greater in the rewet than in air-dry soils (**Table 3**). Both the −100 kPa and rewet soils exhibited significant production of microbial transformation (desmethyl prosulfuron and product C) and hydrolysis (phenyl sulfonamide) products throughout the course of the study
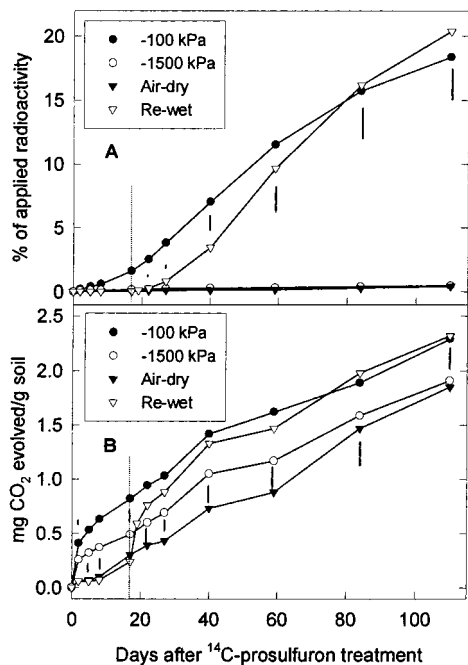
Prosulfuron Dissipation

J. Agric. Food Chem., Vol. 50, No. 11, 2002 **3241**

Figure 4. Effects of water content in Xenia-2 soil on (A) cumulative mineralization ($^{14}CO_2$) and (B) total CO_2 respiration. Vertical bars represent LSD values at $\alpha = 0.05$. Vertical dashed line indicates 17 DAT rewetting.

(**Figure 5**). In contrast, the -1500 kPa and air-dry treatments produced at most 4% of applied ^{14}C as biotransformation products (**Figure 5**), whereas the hydrolysis product represented ~40% of the applied radioactivity at 110 DAT (**Table 3**). It is interesting to note that more radioactivity was extractable from the -1500 kPa and air-dry soils than from the -100 kPa and rewet soils from 40 DAT until the end of the study (**Figure 5**). This may be explained by the ~20% of applied radioactivity lost via mineralization in the latter two soils versus <1% in the drier soils. Also, the key processes thought to contribute to loss of extractability (covalent binding and intraparticle diffusion) would be expected to depend on water availability for a nonvolatile compound.

Mineralization and respiration responded positively to increasing water contents in Tabor soils; however, no water content threshold was observed for prosulfuron mineralization (**Figure 6**). The overall extent of mineralization was much less than that in Xenia-2, accumulating to at most $4.5 \pm 0.9\%$ of the applied ^{14}C as $^{14}CO_2$ in the Tabor -100 kPa treatment (**Figure 6A**). Although the water contents in both Xenia-2 and Tabor soils were equivalent, ~3 times greater mass of water was present in the Xenia-2 than in the Tabor soil due to differences in the texture of the two soils (**Table 1**). This may have led to more prosulfuron occurring in the bioavailable soil solution phase. In addition, sandy soils typically contain less microbial biomass than more finely textured soils. Addition of water on day 17 caused a 5-fold increase in $^{14}CO_2$ production relative to the continuously air-dry soils (**Figure 6**; **Table 3**). The major transformation process occurring in all four water content treatments was the hydrolysis of prosulfuron (**Figure 5**), indicating that the increases in mineralization rates in wetter soils were not as important as abiotic processes in the transformation of prosulfuron. Phenyl sulfonamide ranged from 52.0 to 69.5% of the applied ^{14}C in Tabor soils at 110 DAT (**Table 3**). The significant differences in extractable radioactivity observed in Xenia-2 were not present in Tabor, possibly due to the decreased overall levels of $^{14}CO_2$ produced.
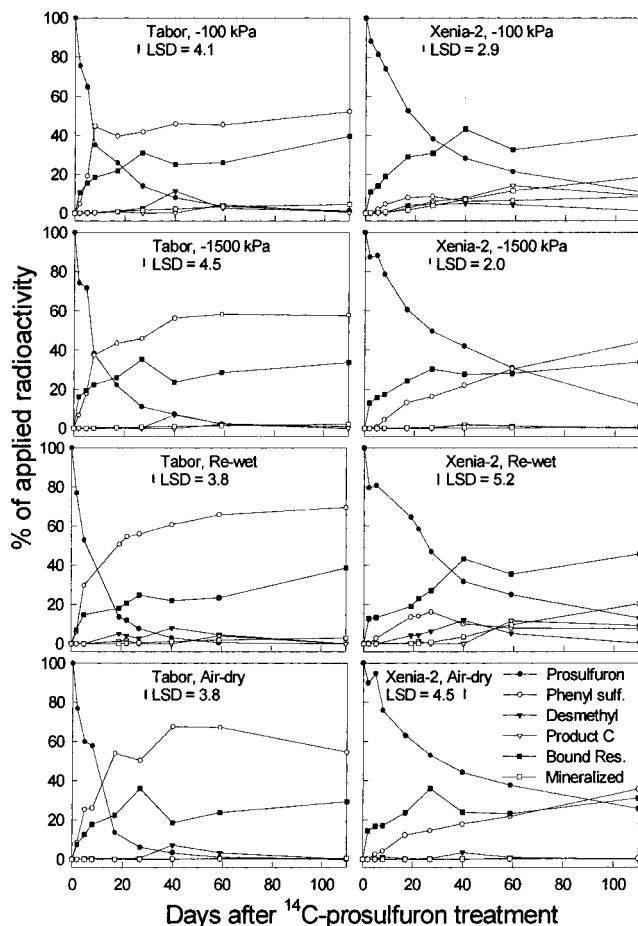

Figure 5. Distribution of ^{14}C in extractable, bound residue, and mineralized ($^{14}CO_2$) phases in soil water content study. Extractable phase represented by HPLC detection of ^{14}C-labeled compounds: prosulfuron, phenyl sulfonamide, desmethyl prosulfuron, and product C.

Dissipation DT_{50}. The time required to dissipate 50% of the initially applied [^{14}C]prosulfuron, DT_{50} (**Table 4**), was estimated for each soil and water content treatment, except for rewet Xenia-2 and Tabor treatments. The DT_{50} values were estimated graphically by interpolating the percent recovered [^{14}C]prosulfuron values between successive sampling time measurements, an approach adapted from that of Sarmah et al. (*29*). In that study, DT_{50} values were used to describe the degradation of two sulfonylureas in Australian soils because experimental data did not follow first-order kinetics. Although a number of authors have used either first-order (*9, 10, 13, 15, 19, 20*) or biexponential (*2, 14, 21*) kinetics to describe the degradation of sulfonylurea herbicides in soil, neither approach adequately described the dissipation of [^{14}C]prosulfuron in all treatments. The first-order approach produced linear correlation coefficients, r^2, >0.9 for many of the soils and water content treatments; however, calculated half-life values ($t_{0.5}$, days) tended to overestimate the DT_{50} values (**Table 4**). Attempts to use the biexponential model for the present study were also unsuccessful as model parameters proved to be statistically insignificant for many of the treatments.

The DT_{50} values for prosulfuron dissipation increased strongly with soil pH, ranging from 6.5 days at pH 5.4 to 122.9 days at pH 7.9 (**Table 4**). Although sampling time points were different in the soil pH and soil water content studies, the preparation and incubation methods for all biometers at the -100 kPa treatment were the same. Thus, comparisons of DT_{50} values and soil properties were conducted with all 10 soils together.

3242 *J. Agric. Food Chem.,* Vol. 50, No. 11, 2002

Hultgren et al.
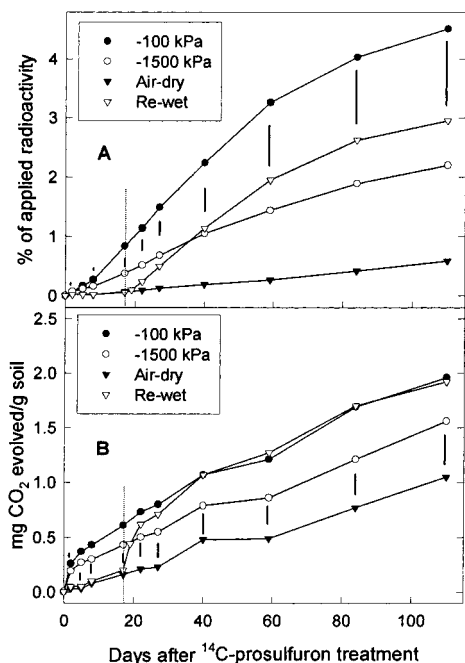
Figure 6. Effects of water content in Tabor soil on (A) cumulative mineralization ($^{14}CO_2$) and (B) total CO_2 respiration. Vertical bars represent LSD values at $\alpha = 0.05$. Vertical dashed line indicates 17 DAT rewetting.

Table 4. DT_{50} and $t_{0.5}$ Values for All Soil and Water Content Treatments in [^{14}C]Prosulfuron Dissipation Studies

Effects of Soil pH

soil	pH	$DT_{50}{}^b$ (days)	$t_{0.5}{}^a$ (days)	R^2
Tabor	5.4	6.5 ± 0.1 A	14.3	0.86
Tifton	6.2	7.0 ± 0.4 A	11.3	0.93
Dothan	5.9	8.1 ± 1.0 A	12.6	0.95
Raub-2	5.9	11.3 ± 2.9 B	15.6	0.98
Raub-1	6.3	15.1 ± 0.9 C	18.5	0.97
Xenia-2	7.1	18.6 ± 2.6 D	29.6	0.89
Drummer-3	6.9	24.8 ± 0.4 E	35.5	0.93
Xenia-1	7.1	25.1 ± 0.6 E	31.5	0.96
Drummer-2	8.0	67.3 ± 2.6 F	73.7	0.49
Weswood	7.9	122.9 ± 3.4 G	110.0	0.68
	LSD	3.2		

Effects of Soil Water Content

soil	θ_w	$DT_{50}{}^c$ (days)	$t_{0.5}{}^a$ (days)	R^2
Tabor	−100 kPa	6.5 ± 0.1 a	14.3	0.86
	−1500 kPa	7.0 ± 0.6 a	13.4	0.86
	air-dry	9.2 ± 1.7 b	8.2	0.96
	LSD	2.0		
Xenia-2	−100 kPa	18.6 ± 2.6 a	29.6	0.89
	−1500 kPa	27.0 ± 2.1 b	34.5	0.98
	air-dry	32.3 ± 0.9 c	47.1	0.82
	LSD	3.9		

[a] Half-life ($t_{0.5}$, days) values calculated from first-order exponential decay equation. [b] Mean DT_{50} values followed by the same capital letter were not significantly different at $\alpha = 0.05$ in the soil pH study. [c] Mean DT_{50} values followed by the same lower case letter were not significantly different at $\alpha = 0.05$ in the soil water content study. Separate LSD values are used for DT_{50} comparison in each soil.

Pearson correlation analyses between DT_{50} or log DT_{50} values and the soil properties provided in **Table 1** were significant ($\alpha = 0.05$) for only pH and log DT_{50} ($r^2 = 0.86$) and CEC and DT_{50} ($r^2 = 0.44$). The correlation between pH and CEC precluded the performance of a regression analysis with both CEC and pH as independent variables. The effect of pH on prosulfuron dissipation kinetics was presumably due to enhanced hydrolysis of prosulfuron at the lower pH values, as observed
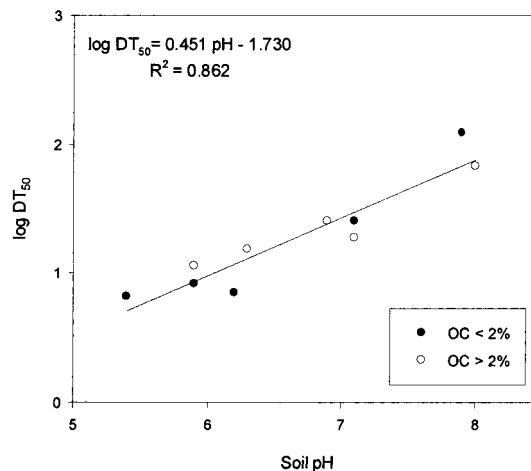
Figure 7. Effect of soil pH on DT_{50} values for prosulfuron dissipation in 10 soils. Soil organic carbon content (OC): <2% (●); >2% (○).

in soil-free systems (*6*). Note, however, that the DT_{50} values observed here are on average ~8-fold lower than the half-life in solution at the same pH (*6*). Because ~50% of the dissipation at low pH is typically due to hydrolysis in these soils, hydrolysis appears to be enhanced in the soil systems relative to pure water. In addition, other processes such as irreversible sorption and mineralization act to enhance the overall dissipation rate, particularly at higher pH. Although soils were originally selected to provide a range of OC at a given soil pH, no significant correlations were found between DT_{50} or log DT_{50} values and OC either by itself or in combination with pH, the main controlling variable (see also **Figure 7**).

The range of DT_{50} values was comparable to first-order kinetics half-life values reported for chlorsulfuron, 20−147 days, and metsulfuron-methyl [methyl 2-[[[[(4-methoxy-6-methyl-pyrimidin-2-yl)amino]carbonyl]amino] sulfonyl]benzoate], 17−135 days, in soils with pH values of 3.9 and 7.0, respectively (*9*). In Xenia-2 soil, the combination of chemical and microbial degradation of prosulfuron in the −100 kPa treatment resulted in a significantly shorter DT_{50} than that for soils with −1500 kPa and air-dry soil water contents in which chemical hydrolysis was the dominant transformation mechanism. In contrast, the dissipation of prosulfuron in Tabor soils was not significantly enhanced by increasing water contents, with similar DT_{50} values at −100 and −1500 kPa matric potentials, and only a slightly longer DT_{50} in air-dry soil (**Table 4**). Water content has been shown to not significantly affect the dissipation rates of other sulfonylureas in soils where hydrolysis is the dominant transformation pathway (*21, 30*).

Conclusions. The potential for carry-over damage to sensitive crops from excessive persistence and off-site transport has increased the need to examine the transformation and transport mechanisms of the sulfonylurea herbicides in the soil and plant environment (*2, 31*). This research has demonstrated the influence of prosulfuron dissipation on soil pH in a broad range of soils. Although significant microbial degradation of prosulfuron was observed in only two soils, total respiration in incubated soils was not a good predictor of the ability of indigenous microorganisms to transform or otherwise degrade prosulfuron. In the absence of significant microbial transformation in soils, hydrolysis of prosulfuron was the dominant degradation pathway. The effects of soil water on the degradation of prosulfuron were variable in the two soils examined and appeared to be dependent on soil pH and texture. At a neutral pH, where chemical hydrolysis may have been limited due to

Prosulfuron Dissipation

J. Agric. Food Chem., Vol. 50, No. 11, 2002   **3243**

ionization of prosulfuron, an apparent biodegradation water content threshold was observed in Xenia-2 soils between wet and dry treatments, possibly due to bioavailability restrictions related to soil texture. Although mineralization of prosulfuron increased with increasing water content, dissipation rates were not significantly affected by water content in the acidic Tabor soil, due to the predominance of pH-dependent hydrolysis. In both soils, increasing water contents after 17 days from air-dry to −100 kPa resulted in a stimulation of microbial activity and transformation of the herbicide.

Although no studies were performed to examine the fate of prosulfuron under field conditions, on the basis of our results, application of prosulfuron in an alkaline, coarse-textured soil in a dry season has the greatest potential for persistence of this herbicide. If populations of microbial degraders were present in such a soil, our results suggest that sufficient rainfall to raise soil water levels after herbicide application could enhance the biodegradation and dissipation of prosulfuron. Incubation studies, such as this, provide dissipation data for prosulfuron in a relatively large collection of soils representing a broad range of soil properties. These data can also be used to derive rate constants for use in fate and transport models to predict the behavior of prosulfuron and structurally similar compounds in the soil and plant environment.

ACKNOWLEDGMENT

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