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Photodegradation of Penoxsulam

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This study was carried out to characterize the photodegradation of penoxsulam and to evaluate the significance of photolysis for its fate and dissipation. Degradation studies of ^{14}C-labeled isotopes of penoxsulam in a "merry-go-round" reactor suggest that aqueous photodegradation proceeds via three possible pathways: cleavage of the sulfonamide bridge, stepwise degradation of the triazolopyrimidine system and its substituents, and photooxidation of the sulfonyl group. Seven major photoproducts were found, and six were identified. Two of the identified photodegradation products seem to be either rapidly biodegraded when formed or not formed in significant amounts in environmental conditions.

KEYWORDS: Aqueous photochemical degradation; environmental fate; Granite; triazolopyrimidine sulfonamide

INTRODUCTION

Penxosulam (**Figure 1**), manufactured by Dow Agrochemicals LLC and distributed under the trade name Granite, is an ALS (acetolactate synthase) inhibitor intended for postemergence control of annual grasses, sedges, and broadleaf weeds in rice culture (*1*). Chemically, it belongs to the triazolopyrimidine sulfonamide (sulfonanilide) herbicides, which also include the ALS inhibitors cloransulam, cloransulam-methyl, diclosulam, florasulam, flumetsulam, and metosulam (*2*).

As an ALS inhibitor, penoxsulam targets an enzyme found only in plants and microorganisms and is therefore not expected to pose a threat to wildlife or humans (*3*). The U.S. Environmental Protection Agency has therefore determined penoxsulam as a reduced risk pesticide but has also concluded that there are uncharacterized risks, particularly to plants and microbial communities (*4*).

Currently, there is little information on the environmental fate of penoxsulam that is available in the open literature and potential degradation pathways and kinetics have not been fully characterized (*4*). The current study is intended to provide information on the mechanism of aqueous photochemical transformation of penoxsulam. Specific objectives of this work were to (i) characterize the occurrence and photochemical kinetics of degradation products and (ii) describe possible photochemical transformation pathways.

MATERIALS AND METHODS

Chemicals. Penoxsulam [XDE-638, 98.8% active ingredient (a.i.)], XDE-638-TP-^{14}C (28.1 mCi/mol; 97.1% a.i.), XDE-638-Ph-UL-^{14}C (98% a.i.), ^{13}C-XDE-638, and reference standards for the transformation products 5-OH-XDE-638 (purity >99%), BSTCA (>98%), BST (>99%), BSTCA-methyl (99%), sulfonamide (100%), BSA (92%), TPSA (99%), 2-amino-TP (99%), and 5-OH-2-amino-TP (98%) were supplied by Dow AgroSciences LLC. High-performance liquid chromatography (HPLC) analysis grade solvents (methanol, acetonitrile, and water) were purchased from Burdick & Jackson (Muskegon, MI), and acetic acid was from EMD Chemicals Inc. (Gibbstown, NJ). Strata-X 30 mg/1 mL solid phase extraction cartridges were purchased from Phenomenex (Torrance, CA), and Minispike Acrodisk Syringe Filters were from Pall Gelman (East Hills, NY).

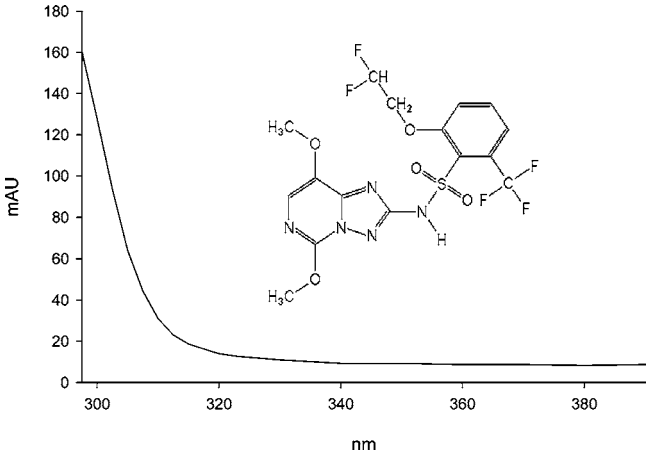

Figure 1. Chemical structure and photochemically relevant UV/vis spectrum of penoxsulam.

Photodegradation Experiments in a Merry-Go-Round Photoreactor. The formation and degradation kinetics of XDE-638-TP-^{14}C and XDE-638-Ph-UL-^{14}C were followed in samples using distilled water exposed in a Rayonet Mini Photoreactor (Southern New England Ultraviolet Company, Branford, CT) equipped with a merry-go-round and eight 4 W 350 nm UV lamps. The samples were irradiated

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continuously for 15 days. The average irradiation intensity was determined with a portable radiometer as 251 W/m^2. The reactor temperature was kept at 29 °C by means of a built-in air-cooling fan. The experiments were conducted using capped and Teflon-lined 4 and 12 mL borosilicate glass tubes.

Instrumental Analysis and Quantification. The LC system for chemical analysis of degradation products involved an Agilent model 1100 LC system and a 50 mm × 4.6 mm Luna 3 μm silica column (Phenomenex) with a SecurityGuard HPLC guard cartridge of the same material (Phenomenex). Analytes were eluted using a hydrophilic interaction liquid chromatographic approach (reverse gradient on a normal phase). For MS/MS analysis in positive ionization mode, the mobile phase consisted of acetonitrile (phase A) and 1% acetic acid in HPLC grade water (phase B). The following elution gradient was used at a flow rate of 0.75 mL min^{-1} and a total run time of 5 min: start (0 min, 75:25 phase A:B), step 1 (1 min, 75:25), step 2 (2 min, 40:60), step 3 (2.1 min, 75:25), and step 4 (5 min, 75:25). For MS/MS analysis in negative ionization mode, the mobile phase consisted of 50 mM ammonium acetate in methanol (phase C) and 50 mM ammonium acetate in HPLC grade water (phase D). The following elution gradient was used at a flow rate of 0.76 mL min^{-1} and a total run time of 6 min: start (0 min, 100:0 phase C:D), step 1 (3 min, 28:72), step 2 (3.1 min, 100:0), and step 3 (6 min, 100:0). The injection volume was 10 μL, and the oven temperature was set to 32 °C. The column eluate was split with 150 μL min^{-1} flowing to the source.

MS/MS analysis was performed on an MDS Sciex API 2000 MS/MS system with a TurboIonSpray source employing both positive and negative ionization with an ion spray (capillary) voltage of 5500 V in positive and 4500 V in negative mode. In positive mode, the declustering potential (DP; cone voltage) was 40 V, the focusing potential (FP) was 400 V, and the collision cell exit potential (CXP) was 7 V. The Q1/Q3 ions in positive ionization were 484/195 (penoxsulam), 487/198 (^{13}C-penoxsulam), and 196/111 (2-amino-TP). The optimized collision energies (CE) and collision cell entrance potentials (CEP) for the positive ion pairs were (CE/CEP) 40/36 (penoxsulam), 38/34 (^{13}C-penoxsulam), 58/29 (cloransula*m*-methyl), and 40/13.42 V (2-amino-TP). The Q1/Q3 ions in negative ionization were 465/386 (5-OH-XDE-638), 425/347 (BSTCA-methyl), 411/329 (BSTCA), 365/289 (BST), 302/97 (sulfonamide), 299/177 (BSA), and 267/165 (TPSA). 5-OH-2-Amino-TP was not analyzed due to analytical difficulties. In negative mode, the FP was 400 V and DP, CE, CEP, and CXP were optimized. The optimized voltages (DP/CE/CEP/CXP) for the negative ionization were 154/60/129/9 (5-OH-XDE-638), 26/33/17/9 (BSTCA-methyl), 20/21/17/9 (BSTCA), 24/22/15/9 (BST), 26/44/23/18 (sulfonamide), 26/35/17/9 (BSA), and 26/38/13/9 V (TPSA). The source temperature was 450 °C.

HPLC was used in combination with liquid scintillation counting (LSC) to determine photoproducts and degradation kinetics of two radiolabeled isotopes of penoxsulam, XDE-638-TP-^{14}C and XDE-638-Ph-UL-^{14}C. The instrument was an HP 1090 (Agilent Technologies, Palo Alto, CA) equipped with a UV/diode array detector set at 199.4 and 230.4 nm. The column was a 50 mm × 4.6 mm Inertsil ODS 5 μm C-18 column (GL Sciences, Inc., Torrance, CA) with a guard column of the same material. The mobile phase consisted of acetonitrile (phase A) and 0.01% acetic acid in HPLC grade water (phase B). The following elution gradient was used at a flow rate of 1 mL min^{-1} and a total run time of 35 min: start (0 min, 15:85 phase A:B), step 1 (5 min, 40:60), step 2 (10 min, 70:30), step 3 (20 min, 15:85), step 4 (23 min, 15:85), and step 5 (35 min, 5:95). The injection volume was 20 μL.

At predetermined time intervals, two aliquots of 1.0 mL were withdrawn from duplicate test tubes. One aliquot was transferred directly to an 8 mL scintillation vial, mixed with 7 mL of Ultima Gold scintillation cocktail (PerkinElmer, Wellesley, MA), capped, and analyzed for ^{14}C by LSC with a TRI-CARB Liquid Scintillation Analyzer model 2000CA (Packard, Downers Grove, IL). The other sample was injected into the HPLC, and analytes were separated using the chromatographic conditions described in the previous section. The HPLC eluate was collected in scintillation vials with a Gilson model 203 fraction collector (Gilson, Middleton, WI) at 0.53 min intervals, and the fractions were analyzed for ^{14}C by LSC. Analytes in the fractions were identified based on retention time and comparison with a nonlabeled standard mixture that was injected and analyzed under the same HPLC conditions.

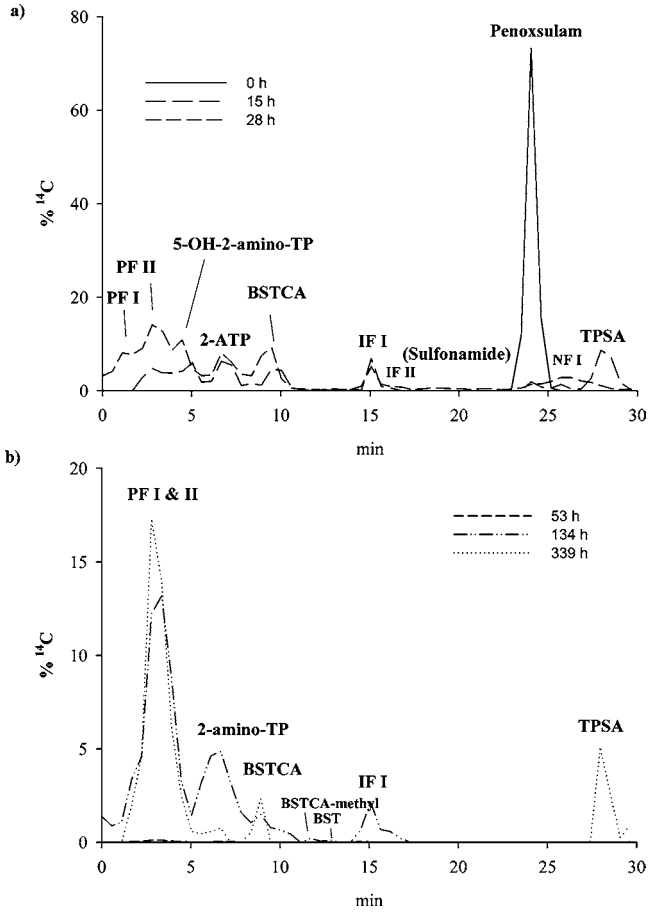

Figure 2. ^{14}C HPLC profile of an aqueous solution of radiolabeled penoxsulam (XDE-638-TP-^{14}C) and its photodegradation products after (**a**) 0, 15, and 28 and (**b**) 53, 134, and 339 h of irradiation with simulated solar light. Full compound names are given in the Materials and Methods section. Unidentified fractions: PF I and II, polar fractions I and II; IF I and II, intermediate fractions I and II; and NF I, nonpolar fraction I.

RESULTS AND DISCUSSION

Photodegradation Pathway and Products. The formation of photodegradation products was measured in photoreactor studies under simulated solar irradiation. Photodegradation products were determined with HPLC/^{14}C radiodetection (**Figure 2**). Partial liquid chromatography/tandem mass spectrometry (LC-MS/MS) scans of standards of the identified degradation products are shown in **Figure 3**.

By using ^{14}C-radiolabeled penoxsulam (XDE-638-TP-^{14}C) in photoreactor experiments, four photodegradation products—2-amino-TP, 5-OH-2-amino-TP, BSTCA, and TPSA—were identified and found to occur in significant amounts during the course of the degradation study. 2-Amino-TP reached a maximum level of 24.1% of the initial ^{14}C after 28 h of continuous irradiation and declined to 1.8% at 339 h. BSTCA and 5-OH-2-amino-TP reached maximum levels of 20.7 and

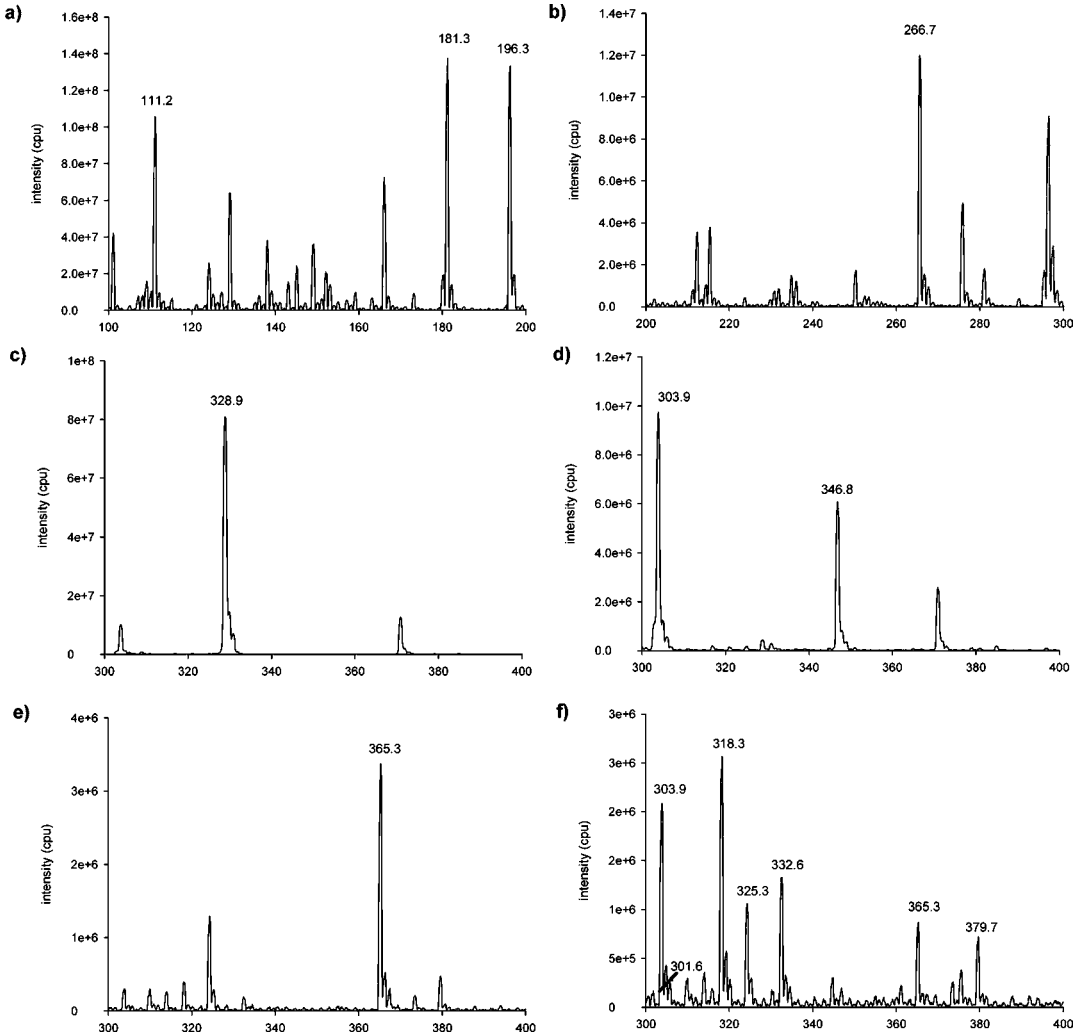

Figure 3. Partial LC-MS/MS scans of penoxsulam degradation products: (**a**) 2-amino-TP, (**b**) TPSA, (**c**) BSTCA, (**d**) BSTCA-methyl, (**e**) BST, and (**f**) sulfonamide.

18.7% of the initial ^{14}C after 2−3 days of continuous irradiation and declined to 0 and 2.8% at 339 h (**Figure 2**). At the final time point of 339 h, TPSA was still present at 8.9% of the initial ^{14}C.

Two minor degradation products, BSTCA-methyl and BST, occurred at maximum levels of 1.3 and 0.4% (**Figure 2**) and are not expected to occur at substantial levels in the environment. An additional peak of intermediate polarity with a retention time of 15.0 min (IF 1 in **Figure 2**) accounted for 9.7% of the total initial ^{14}C of penoxsulam at $t = 28$ h but could not be matched with any of the available standards. Unidentified polar compounds accounted for 67.6% of the total ^{14}C at $t = 28$ h. Photoreactor experiments with XDE-638-Ph-UL-^{14}C did not reveal any further insights into the photodegradation process, but the results were in agreement with the data reported here.

None of the degradation products were detected in an ad hoc LC-MS/MS analysis of a rice field water sample taken 6 weeks after penoxsulam treatment and containing a residual concentration of 0.025 mg/L. Although the LC-MS/MS method did not provide the required sensitivities to detect BSTCA and 5-OH-2-amino-TP in the field samples, it would have permitted the detection of TPSA and 2-amino-TP if present in amounts proportional to those observed in the experiments (limits of detection for TPSA and 2-amino-TP were 0.0026 and 0.0006 mg/L).

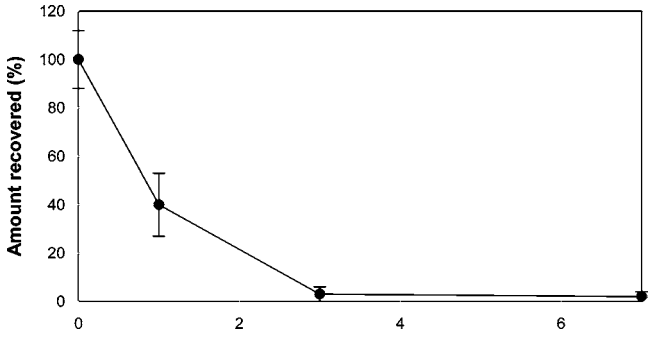

Figure 4. Biodegradability of 2-amino-TP.

The absence of TPSA and 2-amino-TP from the field samples could be the result of microbial degradation processes. The biodegradability of 2-amino-TP was tested in a flooded Willows clay soil (**Figure 4**) and yielded a half-life of 1.25 days. The result indicates that 2-amino-TP will not occur in significant amounts in rice field waters due to rapid biodegradation.

On the basis of the identified photoproducts and the sequence of their formation during the experiments, we suggest that aqueous photodegradation of penoxsulam proceeds via three possible pathways (**Figure 5**): cleavage of the sulfonamide

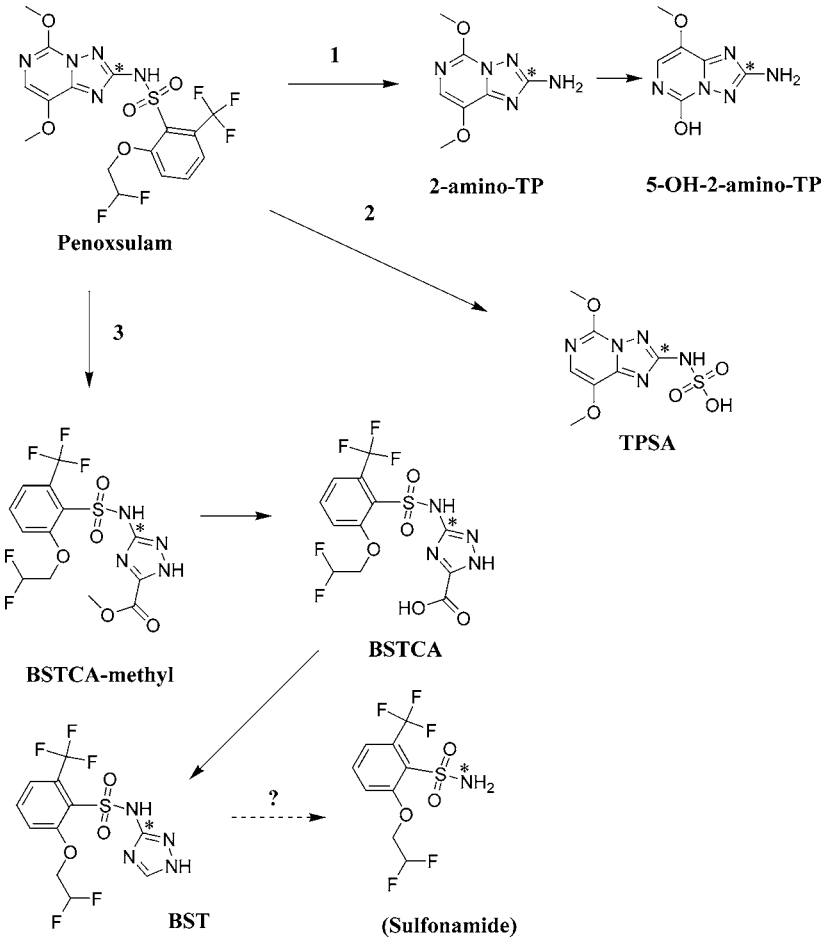

Figure 5. Suggested aqueous photodegradation pathways of penoxsulam: 1, cleavage of the sulfonamide bridge; 2, photooxidation of the sulfonyl group; and 3, stepwise degradation of the triazolopyrimidine system and its substituents. * = position of ^{14}C atom in XDE-638-TP-^{14}C radioisotope and its products.

bridge, stepwise degradation of the triazolopyrimidine system and its substituents, and photooxidation of the sulfonyl group.

Conclusion. The results of this study suggest that penoxsulam is rapidly photodegraded. However, photodegradation products of penoxsulam may have longer residual times and are more difficult to detect in the environment than the original compound. The uncharacterized risk of photodegradation products of penoxsulam to aquatic plant and microbial communities needs to be more fully addressed.

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