Photolytic Degradation of Florasulam on Soil and in Water

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The rate and pathway of degradation in the presence of light for the triazolopyrimidine herbicide florasulam was determined on soil and in aqueous systems. Florasulam was exposed to natural sunlight for up to 32 days; solar irradiance was measured with either chemical actinometers or by radiometry. The quantum yield for direct photodegradation in a sterile, buffered aqueous solution was determined to be 0.096; an analogous quantum yield for the sum of direct and indirect photodegradation on soil was 0.245. The quantum yields were used to estimate half-lives due to photodegradation as a function of season and temperature. Estimated half-lives due to photodegradation in summer at 40° N latitude were 14 days on soil and 36 days in sterile, buffered water. Photodegradation was much faster in a natural water system, with a measured half-life of 3.3 days in summer at 51.5° N latitude, indicating that indirect photolytic processes will be important contributors to photodegradation of florasulam in aqueous environments.

Keywords: *Florasulam; 5-OH-florasulam; aqueous photolysis; natural water photolysis*

INTRODUCTION

Florasulam (*N*-(2,6-difluorophenyl)-5-methoxy-8-fluoro-(1,2,4)-triazolo-[1,5c]-pyrimidine-2-sulfonamide) is a systemic herbicide to be used in Europe and Canada for the postemergence control of broadleaf weeds in cereals and pasture; its mode of action is through acetolactate synthase (ALS) inhibition. Florasulam is a member of the triazolopyrimidine family of chemistry, which also includes metosulam, flumetsulam, cloransulam-methyl, and diclosulam. Florasulam is highly selective to wheat, barley, and turf but very active on weeds in the plant families Compositeae, Polygonaceae, Caryophyllaceae, Rubiaceae, and Crucifereae. Florasulam is a low use rate herbicide, with proposed maximum application rates of 7.5 g/ha in Europe and 5 g/ha in Canada. The vapor pressure of florasulam is 1×10^{-5} Pa (Richardson, 1995), and its pK_a is 4.54 at 23 °C (Richardson, 1996). Because of the ionizable nature of florasulam, its aqueous solubility is a strong function of pH, ranging from 0.084 g/L at pH 5, to 6.36 g/L at pH 7, and to 94.2 g/L at pH 9 (Richardson, 1995).

Although florasulam is rapidly degraded by microorganisms in soil (DT_{50} < 9 days, Krieger et al., 2000; Jackson et al., 2000), abiotic degradation by photolysis is also of interest to determine the impact of florasulam on the environment. Florasulam has no aquatic uses; however, it could potentially enter surface water by spray drift during application or runoff after application. Therefore, determination of the rate and route of photolytic degradation in water is crucial in defining the environmental impact of florasulam application. The rate and route of photolysis of pesticides can be significantly different in natural waters containing humic substances and other photosensitizers (Frimmel and Hessler, 1994; Tsao and Eto, 1994; Hapeman et al., 1998; Mansour et al., 1997), so we examined the photolytic degradation of florasulam in both pure buffered water and a natural water system. Because of its rapid microbial degradation, photolysis on soil is not likely to be a major route of dissipation of florasulam under normal circumstances. However, photodegradation on soil surfaces may be important in environments where soil microbial activity is low. Therefore, characterization of the photolytic fate of florasulam on soil is also important.

MATERIALS AND METHODS

Experimental Design. To determine the rate of photolytic degradation on soil, florasulam was applied to a moist, viable soil and an air-dried soil at rates of 134 or 315 ppb, respectively, and exposed to natural sunlight for up to 30 days. Soil moisture was maintained at a level of 75% of 1/3 bar for the moist soil, while the soil temperature was held constant at 25 °C. Dark control samples were treated in an identical manner, except they were incubated in the dark to account for nonphotolytic degradation.

To determine the rate of photolytic degradation in water, florasulam was applied to a sterile pH 5 buffer at a rate of 100 ppb and exposed to natural sunlight for up to 32 days. The temperature of the samples was held constant at 25 °C. This experiment was conducted at pH 5 because florasulam showed no degradation due to hydrolysis at pH 5 and pH 7 (20 °C) over 30 days; at pH 9, florasulam slowly degraded with a half-life of 100 days (Jackson, 1996). Florasulam was also applied to a natural lake water at a rate of 8.3 ppb and exposed to natural sunlight for 30 days. Dark control samples were treated in an identical manner to account for degradation due to hydrolysis and biotic degradation in the natural water samples.

Test Material and Reference Compounds. Radiolabeled florasulam was acquired from the Specialty Synthesis group of Dow AgroSciences. Two radiolabeled test substances were used to track degradates containing each of the ring structures of florasulam. For both the soil and buffered water photolysis experiments, separate applications were made using the 9-^{14}C-triazolopyrimidine florasulam (referred to as TP-labeled florasulam) and the uniformly labeled ^{14}C aniline-florasulam (referred to as AN-labeled florasulam). The natural water

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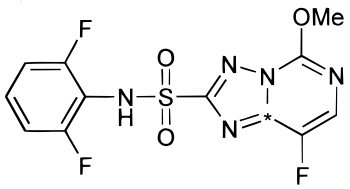

Figure 1. Structure of florasulam; location of the radiolabeled carbon atom in the triazolopyrimidine-labeled test material is indicated with an asterisk. The aniline-labeled test material was uniformly radiolabeled in the phenyl ring.

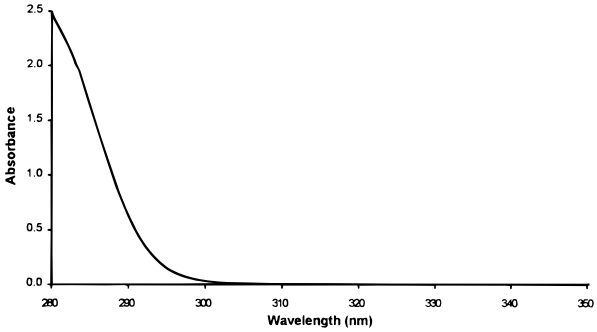

Figure 2. UV-visible absorbance spectrum of a 5×10^{-4} M aqueous solution of florasulam. Florasulam has no significant absorbance at wavelengths greater than 310 nm.

photolysis experiments used only TP-radiolabeled florasulam as the test material. The specific activity of the TP-labeled florasulam was 9.07×10^{11} Bq/mol (1.51×10^{11} dpm/g), and the specific activity of the uniformly AN-labeled florasulam was 2.03×10^{12} Bq/mol (3.39×10^{11} dpm/g). The radiochemical purity was >97% for all test materials. The structure of florasulam and the location of the radiolabeled carbon atoms are shown in Figure 1. The UV−visible absorbance spectrum of florasulam is shown in Figure 2.

Nonradiolabeled standards of 5-OH-florasulam [*N*-(2,6-difluorophenyl)-8-fluoro-5-hydroxy(1,2,4)triazolo(1,5c)-pyrimidine-2-sulfonamide], DFP-ASTCA [*N*-(2,6-difluorophenyl)-5-amino-sulfonyl-1H-1,2,4-triazole-3-carboxylic acid], ASTCA [5-(aminosulfonyl)-1H-1,2,4-triazole-3-carboxylic acid], and ASTP [8-fluoro-5-methoxy (1,2,4)triazolo-(1,5c)pyrimidine-2-sulfonamide] were used as chromatographic reference standards.

Test Systems. A moist, viable Catlin silt loam soil (pH 6.8, 2.92% organic matter, fine-silty, mixed, mesic Oxyaquic Agriudolls) was used for the soil photolysis experiments. The Catlin silt loam is one of the soil types used in an aerobic soil degradation study of florasulam (Jackson et al., 2000). Approximately 2 g (dry weight) of soil samples was placed in sterilized 10-mL quartz Erlenmeyer flasks, and water was added to raise the moisture level to 75% of the 1/3 bar moisture potential. The flasks were equipped with a trap designed to collect volatile organics (with activated carbon) and CO_2 (with ascarite); a layer of molecular sieve/indicating silica gel was also included to prevent water vapor from reaching the ascarite layer. Glass wool was used as a separator before and after each layer. The bottom layer was acid-washed activated carbon, followed by molecular sieves (5A) and Grade 42 indicating silica gel, topped with Ascarite II, 20-30 mesh. The open tops of the traps were covered with Parafilm and wrapped in aluminum foil to keep rainwater from entering the trap and to maintain the traps in the dark.

Soil moisture was maintained at approximately 75% of 1/3 bar by periodically determining the amount of water lost from the test system (gravimetrically) and then adding deionized water to return the test system to its initial weight. Dark control samples were prepared in Pyrex flasks under identical conditions; they were placed in a darkened incubator set at 25 °C. Air-dried soil samples were prepared by weighing approximately 2 g of soil into quartz (for exposed samples) or Pyrex (for dark control samples) flasks. The flasks were placed in an incubator set at 35 °C for 2 h to partially air-dry the soil before dosing. No traps were used with the air-dried test systems to more effectively exclude water. Sample flasks were stoppered and sealed with Parafilm.

Table 1. Physical and Chemical Characterization of the Natural Lake Water Used in This Study

property	value
turbidity	2.3 FTU
suspended solids	7 mg/L
BOD + ATU (5 day)	<2 mg/L
COD (filtered)	<20 mg/L
hardness (total as Ca)	98 mg/L
alkalinity as HCO_3^-	242 mg/L
pH	7.8
total coliforms	67 cfu/100 mL

The moist, viable soil samples were dosed with florasulam at either 134 ppb (AN-labeled, equivalent to a field application rate of 16 g/ha) or 315 ppb (TP-labeled, equivalent to a field application rate of 38 g/ha). The air-dried soils were dosed with AN-labeled florasulam at a rate of 133 ppb (equivalent to a field application rate of 16 g/ha).

For buffered aqueous photolysis experiments, florasulam was dosed into 10-mL quartz test tubes containing a buffer solution of 0.01 M sodium acetate in HPLC grade water adjusted to pH 5 with 1 N HCl. The buffer solution and glassware were sterilized by autoclave prior to use. Dark control samples were prepared in an identical manner but were wrapped completely in aluminum foil prior to insertion into the water bath. Test systems were dosed either with AN- or TP-labeled florasulam at a rate of 100 ppb. Test systems that were dosed with AN-labeled florasulam were prepared with traps as described for the moist soil photolysis samples, while those dosed with TP-labeled florasulam were capped without traps.

All soil photolysis and buffered aqueous photolysis samples were placed in a stainless steel water bath on the roof of Dow AgroSciences Building 306 in Indianapolis, IN, USA (approximately 39.9 °N latitude). Samples were exposed to natural sunlight for up to 32 days. Soil samples were exposed in May and June of 1997, while buffered aqueous samples were exposed in either May (AN-label) or June 1997 (TP-label). Samples in the water bath faced south to receive maximum sunlight. Soil temperature was monitored using a thermocouple thermometer placed on the surface of the soil inside a flask. The temperature of the water bath was varied to maintain the soil temperature at an average temperature of 25 ± 1 °C. Aqueous samples were placed in a separate water bath that was maintained at 25 ± 1 °C.

For natural water photolysis experiments, water was obtained from 20 to 30 cm below the surface of Letcombe Lake, Letcombe Regis, Wantage, Oxfordshire, U.K. Physical and chemical characterization of the lake water are given in Table 1. The biological characteristics of the lake water were typical of surface water for the Upper Thames region (Pond Action, 1997). A solution of ^{14}C-florasulam was prepared in Letcombe lake water at a concentration of 8.33 μg/L. Approximately 100-mL aliquots of the fortified lake water were transferred into 80 × 45 mm i.d. quartz tubes, which were then capped. Six tubes were covered with aluminum foil to serve as dark controls, while 10 tubes were left uncovered. All samples were placed outside at the Dow AgroSciences Letcombe Laboratory, Letcombe Regis, Wantage, Oxfordshire, U.K. (approximately 51.5° N latitude) on June 30, 1998. After application, the samples were maintained in a metal tray containing water to a depth of ~5 cm. The temperature of the water in the tray was monitored throughout the study. The average water temperature was 19.4 °C, with a maximum temperature of 31.4 °C on day 20 and day 25, and a minimum temperature of 9.9 °C on day 3 of the study.

Actinometry. Chemical actinometry was used to characterize the solar irradiance for the soil and buffered aqueous photolysis test systems. Actinometer solutions were prepared using *p*-nitroacetophenone and pyridine (PNAP/pyr) in sterile HPLC-grade water (Dulin and Mill, 1982). Actinometer solu-

tions of 1×10^{-5} M PNAP were prepared so that the theoretical half-life was approximately 6 days. Actinometer solutions were removed from the water bath at each sampling point and replaced with fresh solutions to allow the quantitation of sunlight intensity at each sampling point. Actinometer solutions were placed in the water bath to quantify the incident radiation received by the samples. Actinometer dark controls were placed in a darkened incubator set at 25 °C. For the natural water samples, total light intensity was measured between 300 and 400 nm using an Atlas Xenocal UV light sensor, provided by Alplas Technology, Oxford, U.K. The sensor was used to provide a continuous record of light intensity over the 30 days of the study. The samples were exposed to an average light intensity of 10.5 W m^{-2} day^{-1} over the 30 days.

Sampling and Analysis. For soil photolysis experiments, duplicate exposed and dark control samples were taken at 0, 1, 2, 5, 7, 13, and 30 days after treatment (DAT) for the AN-labeled samples; at 0, 1, 2, 5, 7, 14, and 30 DAT for the TP-labeled samples; and at 0, 3, 10, 22, and 30 DAT for the air-dried (AN-labeled) soil samples.

Soil samples were extracted with 10 mL of 90:10 acetone/0.1 N HCl on a mechanical shaker for 2 h. The solution was centrifuged for 15 min at 2000 rpm, and the liquid was decanted into a 25-mL volumetric flask. Approximately 7 mL of fresh extraction fluid was added to the soil, and the mixture was vortexed briefly to break up the soil mass and extracted for 0.5 h on a mechanical shaker. This solution was centrifuged, decanted, and combined with the initial extract. The extraction was repeated, and the total volume of the extract was brought to 25 mL. Two 1-mL aliquots of the extract were assayed for ^{14}C by liquid scintillation counting (LSC). Aliquots of sample extracts were concentrated and filtered prior to analysis by HPLC. Nonextractable residue was quantified by combustion of the extracted soil (after air-drying) followed by liquid scintillation counting.

For buffered aqueous photolysis experiments, duplicate exposed samples and dark control samples were taken at 0, 1, 4, 7, 14, 21, and 32 DAT. Immediately after sampling, the sterility of each sample was verified using trypticase soy broth. The sample pH was then checked, and two aliquots of each sample were assayed for ^{14}C by LSC. An aliquot of the sample was analyzed directly by HPLC.

Traps were separated into three components: activated carbon, silica gel and molecular sieves, and ascarite. The activated carbon component was extracted with 5 or 10 mL of acetone, and the ascarite component was extracted with 5 or 10 mL of water on a mechanical shaker for 1 h. After allowing the undissolved solids to settle, two aliquots (250 μL) of the supernatant were analyzed by LSC. The silica gel and molecular sieve components were not analyzed because they were expected to contain only water.

Duplicate samples of fortified, light-exposed natural water samples were analyzed at 0, 1, 3, 7, 15, and 30 DAT (only one replicate was analyzed at the 0 and 30 DAT timepoints). Single samples of the dark control samples were analyzed at the same timepoints as the light-exposed samples. Immediately after removal, triplicate aliquots of each sample were assayed by LSC. Natural water samples were prepared using solid-phase extraction (SPE) prior to analysis. A 1-g C_{18} SPE cartridge (International Sorbent Technology, Hengoed, U.K.) was conditioned with 5 mL of methanol/1.0 M HCl (99:1) followed by 5 mL of water. A 50 mL portion of the test solution was then passed through the cartridge. The cartridge was pulled dry and eluted with 5 mL of methanol/1.0 M HCl (99:1). The solvent was evaporated from the eluent and the residue reconstituted in acetonitrile/water (20:80) prior to HPLC analysis. At later timepoints for samples exposed to light, significant amounts of radioactivity were not retained by the column. For these samples, the aqueous eluent was frozen and then freeze-dried using an Edwards Modulyo freeze-drier. The residue was reconstituted in methanol (10 mL) and combined with the organic eluent from the C_{18} SPE cartridge. The solvent was evaporated and the residue reconstituted in acetonitrile/water (20:80) prior to HPLC analysis.

Chromatography. Soil extracts and buffered aqueous samples were separated using a binary HPLC mobile phase gradient where %A was initially 95% and was decreased to 40% at 30 min and held at this composition for an additional 10 min. Solvent A was water + 1% acetic acid, and solvent B was acetonitrile + 1% acetic acid. The gradient was linear at a constant flow rate of 1 mL/min, and the column was a YMC Pack ODS-AQ (250 × 4.6 mm, 5 μm particle size); HPLC hardware was a Hewlett-Packard 1050 system. Fractions (generally 1 min) were collected and counted by LSC. Actinometer solutions were analyzed using an isocratic mobile phase of 50:50 water/acetonitrile + 0.013 M pyridine on a Spherisorb ODS-2 column (250 × 4.6 mm, 5 μm particle size). Detection was by UV absorbance at 288 nm.

Because of the rapid degradation observed in the natural water photolysis experiments relative to the buffered water and soil photolysis experiments, additional chromatographic systems were required. Natural water samples were analyzed with either a Spherisorb ODS2 (250 × 4.6 mm, 5 μm particle size), Hypercarb (75 × 4.6 mm, 5 μm particle size), and Phenomenex Luna II C8 (250 × 4.6 mm, 5 μm particle size) HPLC column. Instrumentation consisted of a Varian 9010 pump, a Waters auto sampler (model 712 or 717), a Varian 9050 UV detector (set at 260 nm), and a Packard Radiomatic 515TR solid flow cell detector with associated data collection software. The binary mobile phase gradient used with the Spherisorb and Luna II columns was initially 80% solvent A, decreased to 50% A at 20 min and 0% A at 30 min; the flow rate was 1.0 mL/min. Solvent A was water/acetic acid (100:2 v/v), and solvent B was acetonitrile/acetic acid (100:2 v/v). The binary mobile phase gradient used with the Hypercarb column was initially 95% solvent A, decreased to 30% A at 30 min and 0% A at 35 min; the flow rate was 1.5 mL/min. Solvent A was water/trifluoroacetic acid (100:1 v/v), and solvent B was acetonitrile/trifluoroacetic acid (100:1 v/v).

The distribution of radioactivity at each timepoint was determined using the Spherisorb ODS2 column. This column gave good retention and separation of florasulam and 5-OH-florasulam. Other components observed at later timepoints eluted quickly from this column (<6 min), but reproducibility was good and separation of components was acceptable. The Hypercarb column contains a porous graphitic carbon stationary phase that can retain polar components more effectively than Spherisorb column. The Hypercarb column was used to examine the polar components that eluted quickly from the Spherisorb column. Separation of components on the Luna II C_8 column was good, but reproducibility was poor. Therefore, this column was used to separate components that coeluted in the Spherisorb column and for co-chromatography of isolated components with reference standards.

Liquid Scintillation Counting. All LSC measurements were performed on a Packard (Meriden, CT) 2500TR liquid scintillation counter; chemiluminescence was corrected using the scintillation counter's on-board logic. Reference ^{14}C standards obtained from the Packard Instrument Co. were used to frequently calibrate the counter. ^{14}C-Quench curves were generated once every 6 months. The quench curve was used to resolve sample efficiency and convert the raw counts per minute (cpm) to disintegrations per minute (dpm). Ultima Gold XR scintillation cocktail was added to each sample (excluding combustion samples) before counting. Combustion samples were collected in Harvey scintillation cocktail plus Permafluor. Samples were generally counted for 3 min. A vial containing only scintillation cocktail was counted for 10 min prior to each sample set; this "background" activity was subtracted from each sample by the counter.

Degradate Identification. The presence or absence of several known or proposed degradates of florasulam was determined by co-chromatography in one or more of the HPLC systems described above using nonradiolabeled reference standards. Confirmation of co-chromatography was shown by a characteristic retention time difference between peaks observed by the UV detector and those by the ^{14}C detector (0.1−0.2 min). Where possible, co-chromatography was demonstrated in two HPLC systems. Degradate identification

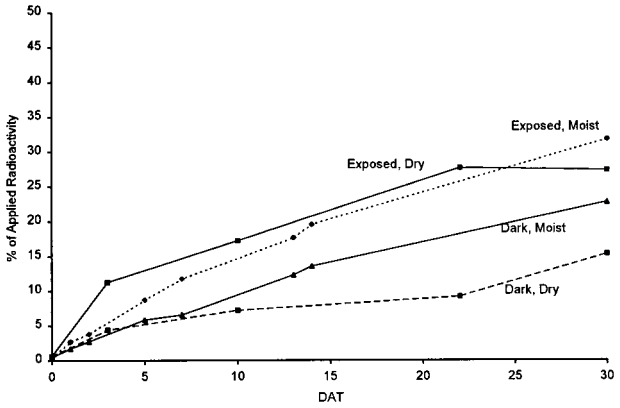

Figure 3. Amount of nonextractable residue as a function of time, sunlight exposure, and soil moisture.

described as tentative is based on the negative ion electrospray mass spectrum, obtained on a Finnigan TSQ 700 LC/MS.

RESULTS AND DISCUSSION

Distribution of Radiocarbon and Material Balance. For the soil photolysis experiments, the average material balance was 94.4 ± 4.5, 97.2 ± 3.8, and 95.5 ± 3.4% for the AN-labeled, TP-labeled, and air-dried (AN-labeled) test systems, respectively. The overall mass balance across all samples was 95.7 ± 4.1%; there was no significant difference in the material balance between the exposed and the dark samples for any of the three test systems. A maximum of 1.6% of the applied ^{14}C was found in the ascarite trap (assumed to be $^{14}CO_2$) for the aniline-labeled test systems, while the maximum found in the triazolopyrimidine-labeled test systems was 0.6%. The amount of ^{14}C detected on the activated carbon traps was <1% for all test systems. Therefore, no significant amounts of volatile degradates (including CO_2) were formed.

Applying a *t*-test to the regressions of material balance versus DAT shows that for the AN- and TP-labeled samples there is no decrease in mass balance over time at the 99% confidence level. There was a statistically significant decrease in mass balance over time for the exposed air-dried soil test systems, indicating the possible loss of a volatile degradate. These test systems did not contain activated carbon or ascarite traps to minimize moisture penetration. However, over the 30 day course of the study, the total decrease in radioactivity was small (<10%).

The amount of nonextractable residue increased with time and was higher in the exposed than in the dark control samples (see Figure 3). Nonextractable residues were 0.4 ± 0.3% at 0 DAT, indicating good extraction efficiency. This suggests either the formation of photoproducts that are more tightly bound to the soil surface than the soil metabolic degradates, or that the light and moisture cycling experienced by the exposed samples resulted in stronger adsorption. The same trend is apparent in the air-dried soil test systems, where the rate of metabolic degradation was significantly slower than the viable soil test systems. Regardless of the mechanism, this result suggests that sorption of florasulam and its degradates in the environment (where light exposure and moisture cycling will also occur) may be underestimated by laboratory batch equilibrium sorption studies.

To further characterize nonextractable residues, exposed and dark control samples from 30 DAT were treated with 1 N NaOH to determine partitioning of ^{14}C into humic acid, fulvic acid, and humin fractions. At 30 DAT, an average of 5.7, 45.5, and 48.9% of ^{14}C in the extracted soil was found in the humic acid, fulvic acid, and humin fractions, corresponding to 1.7, 13.6, and 14.6% of applied ^{14}C, respectively. There was no difference in humic acid, fulvic acid, and humin partitioning between the exposed and the dark control samples.

Table 2. Amount of Florasulam and Degradates at Each Sampling Point in Soil Photolysis Experiments[a]

DAT	florasulam	5-OH-florasulam	DFP-AST + DFP-ASTCA + ASTP	non-extractable residue
		Moist, Viable Soil		
dark				
0	88.6	0.0	0.4	0.4
1	70.7	19.5	0.0	1.7
2	59.3	33.1	0.0	2.7
5	28.4	55.7	2.9	5.8
7	27.3	54.4	3.9	6.5
13	6.7	59.3	8.7	12.2
14	24.0	46.6	5.9	13.5
30	8.5	51.2	8.9	22.7
exposed				
1	79.1	12.6	0.0	2.7
2	65.2	18.2	1.0	3.8
5	53.6	22.5	4.5	8.7
7	51.0	22.7	6.2	11.7
13	12.8	40.7	13.8	17.6
14	22.6	28.1	12.9	19.5
30	11.1	23.9	19.9	31.8
		Air-Dried Soil		
dark				
0	85.7	0.0	0.0	0.6
3	92.0	0.5	0.5	4.4
10	88.9	0.5	0.0	9.0
22	84.9	1.1	0.0	9.2
30	76.5	1.4	0.0	15.3
exposed				
3	83.7	0.0	0.0	11.3
10	73.9	1.6	1.3	17.2
22	58.4	2.0	2.7	27.7
30	55.7	2.1	2.8	27.4

[a] Results are expressed as a percentage of the applied radioactivity and are typically the average of two to four samples.

For the buffered aqueous photolysis experiments, recoveries averaged 103.0 ± 3.7, 97.0 ± 4.6, 99.6 ± 1.3, and 99.1 ± 1.5% for AN-labeled exposed, AN-labeled dark control, TP-labeled exposed, and TP-labeled dark control samples, respectively. Less than 1% of applied radioactivity was found in any trap.

For the natural water samples exposed to sunlight, recoveries were >97% up to 7 days after treatment (DAT). At 15 DAT, 94.6% was recovered and at 30 DAT 88.4% was recovered. This slightly lower recovery could have been due to the production of a volatile product as degradation proceeded or perhaps a degradation product that had adsorbed to the glassware. In the dark control samples, recoveries were 95.6−100.0% indicating there was no significant loss of radioactivity at any timepoint.

Degradation Profile. Florasulam degraded quickly in the soil systems, forming two degradates that reached significant concentrations. The amount of florasulam and degradates observed at each sampling point is given in Table 2. Typical chromatograms of a soil extract from an exposed and a dark control sample are shown in Figure 4. The same degradates were observed both in the exposed and the dark control samples, indicating that the degradates were formed by nonphotolytic

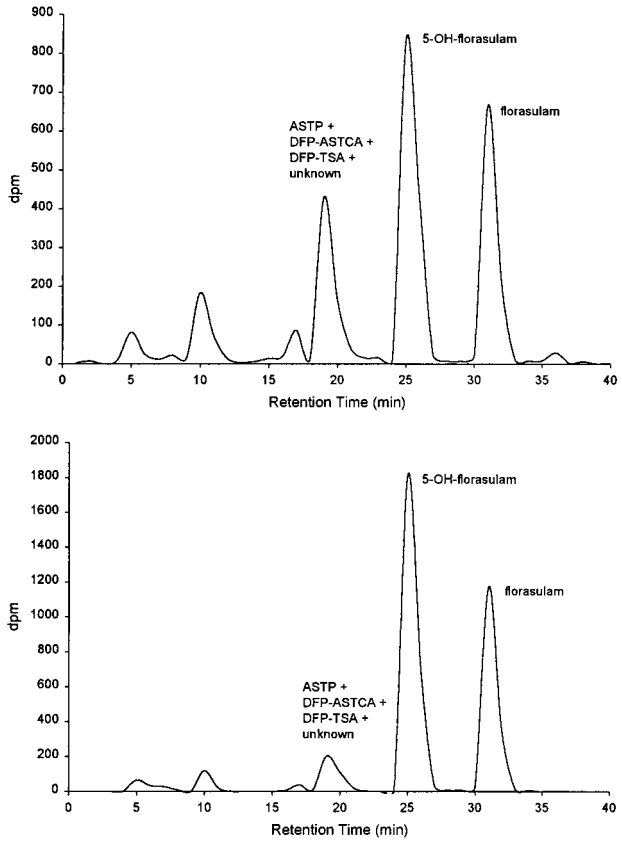

Figure 4. Radiochromatogram of triazolopyrimidine-labeled samples that had been exposed to sunlight for 14 days (top) or incubated in the dark for 14 days (bottom) on moist, viable soil.

degradation. One of these degradates was identified as the 5-OH analogue of florasulam (conversion of the methoxy to a hydroxy group on the pyrimidine ring). The 5-OH-florasulam reached up to 46.5% of applied in the exposed samples and 68.4% of applied in the dark control samples. The amount of 5-OH-florasulam peaked between 5 and 14 days and had begun to decline in each of the moist soil systems by 30 days. The 5-OH-florasulam is also the major degradate observed in the aerobic soil metabolism of florasulam (Jackson et al., 2000). The rate of decline of 5-OH-florasulam was more rapid in the exposed samples, indicating that the rate of photolysis of 5-OH-florasulam was significant relative to the rate of microbial degradation.

The second peak to reach a significant concentration in the soil photolysis experiments eluted at 19 min. LC-MS analysis of this peak revealed it to contain four components that were not resolved within the 1-min fractions collected and analyzed by LSC. Three of the components of the this peak were tentatively identified as the aminosulfonyltriazolopyrimidine (ASTP) of florasulam, the difluorophenyl aminosulfonyltriazolo carboxylic acid (DFP-ASTCA), and the difluorophenyl triazolosulfonamide (DFP-TSA). The 5-OH-florasulam, DFP-ASTCA, and DFP-TSA degradates have been observed as degradates of florasulam in an aerobic soil metabolism study (Jackson et al., 2000), while the ASTP was not. The maximum amount of these degradates observed was 2.6, 10.4, 3.2, and 5.1% of applied for the unknown component, ASTP, DFP-ASTCA, and DFP-TSA, respectively. The proposed degradation pathway for florasulam on soil in the presence of light is shown in Figure 5. Note that since this study had a duration

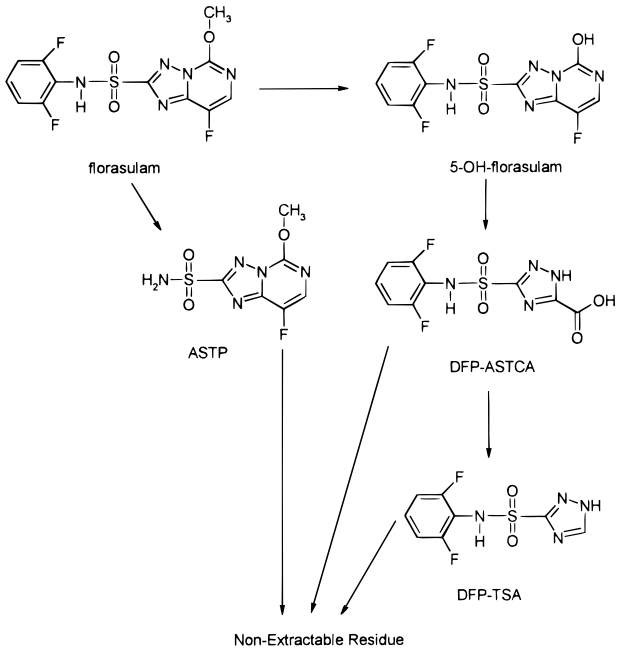

Figure 5. Proposed pathway for the degradation of florasulam in moist, viable soil after exposure to natural sunlight.

of only 30 days, some of the degradates observed in longer-term soil degradation studies would not have had time to form in this study.

The degradates shown in Figure 4 that elute at 6 and 11 min reached maximum levels of 5.9 and 6.9% of the applied radioactivity, respectively, at 30 DAT. These degradates were only observed in the TP-labeled samples, indicating that the sulfonamide bridge had been cleaved. No further information regarding the nature of these degradates was obtained.

The amount of florasulam and each degradate in the buffered and natural water systems is given in Table 3. In the buffered water aqueous photolysis study, only one degradate was found at greater than 10% of the applied radioactivity. Typical chromatograms from an exposed and a dark control aqueous sample are shown in Figure 6. This degradate was tentatively identified by LC-MS as the triazolopyrimidine sulfonic acid (TPSA) of florasulam; it reached a level of 18% of the applied radioactivity after 32 days. An analogous TPSA degradate was identified as a product of aqueous photolysis for a structurally related sulfonamide herbicide, diclosulam (Concha et al., 1994). Florasulam accounted for over 70% radioactivity at the end of the study.

A substantially different route of degradation was observed in the natural water system; TPSA was not observed in any sample. The proposed route of degradation for florasulam in natural water exposed to sunlight is shown in Figure 7. Florasulam was transformed to two different degradation products. 5-OH-florasulam was formed by conversion of the methoxy group on the triazolopyrimidine ring to a hydroxy group. Alternatively, loss of the difluorophenyl moiety by cleavage of the phenyl carbon−nitrogen bond yields ASTP. 5-OH-florasulam subsequently degraded by two different routes. One route occurred by opening of the pyrimidine ring to form DFP-ASTCA and then loss of the difluorophenyl moiety to form ASTCA. The other route of degradation occurred by loss of the difluorophenyl moiety first to form the 5-OH-ASTP, followed by opening of the pyrimidine ring to form ASTCA. ASTP formed

Table 3. Amount of Florasulam and Degradates at Each Sampling Point in Buffered Aqueous and Natural Water Photolysis Experiments[a]

DAT	florasulam	5-OH-florasulam	ASTP	DFP-ASTCA	5-OH-ASTP	ASTCA	TPSA
			Buffered Aqueous, TP Label (June)				
0	91.7	nd[b]	nd	nd	nd	nd	3.2
1	95.8	nd	nd	nd	nd	nd	1.9
4	93.1	nd	nd	nd	nd	nd	4.0
7	92.1	nd	nd	nd	nd	nd	5.1
14	87.3	nd	nd	nd	nd	nd	9.2
21	75.3	nd	nd	nd	nd	nd	15.0
32	75.7	nd	nd	nd	nd	nd	17.0
			Buffered Aqueous, AN Label (May)				
0	97.8	nd	nd	nd	nd	nd	nd
1	97.6	nd	nd	nd	nd	nd	nd
4	96.7	nd	nd	nd	nd	nd	nd
7	95.0	nd	nd	nd	nd	nd	nd
14	92.8	nd	nd	nd	nd	nd	nd
21	90.6	nd	nd	nd	nd	nd	nd
32	88.9	nd	nd	nd	nd	nd	nd
			Natural Water (June)				
0	94.4	nd	nd	nd	nd	nd	nd
1	96.0	nd	nd	nd	nd	nd	nd
3	52.1	16.6	6.4	nd	15.1	7.3	nd
7	17.3	13.0	6.8	8.9	28.9	23.0	nd
15	6.0	nd	6.2	6.3	24.0	49.4	nd
30	nd	nd	9.8	nd	14.6	53.8	nd

[a] Light-exposed samples only. Results are expressed as a percentage of the applied radioactivity. Exposure times are not corrected for sunlight intensity. [b] Not detected.

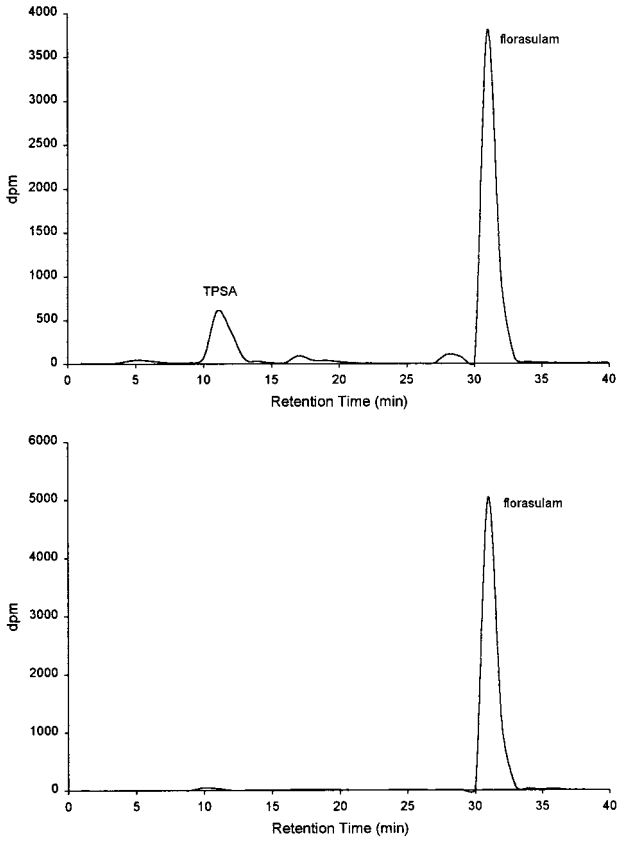

Figure 6. Radiochromatogram of triazolopyrimidine-labeled samples that had been exposed to sunlight for 32 days (top) or incubated in the dark for 32 days (bottom) in a buffered aqueous solution.

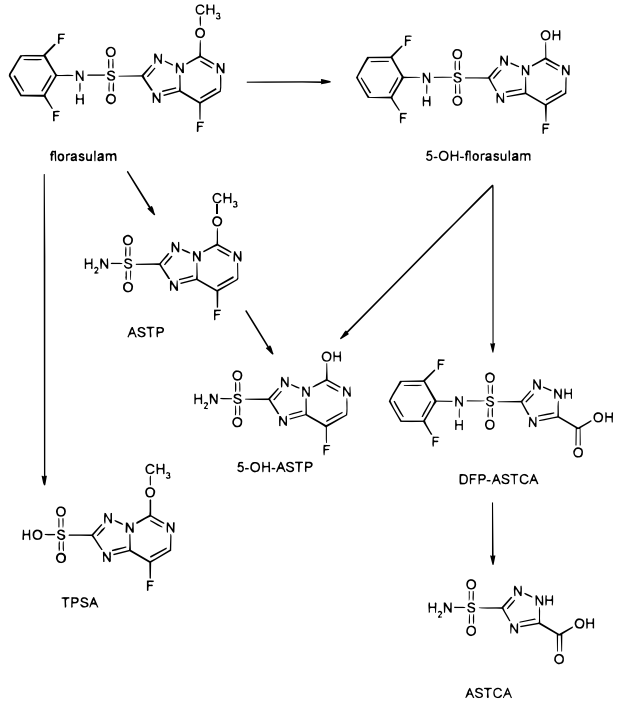

Figure 7. Proposed pathway for the degradation of florasulam in water after exposure to sunlight.

directly from florasulam can also potentially degrade to the 5-OH-ASTP by conversion of the methoxy group on the triazolopyrimidine ring to a hydroxy group.

The relative importance of the different routes of degradation is difficult to interpret from the data set in this study alone. The slow increase in amount of ASTP with time as compared to the degradation rate of florasulam indicates either a slow formation rate or a transient metabolite. ASTP is still present at 9.8% AR when all florasulam has degraded, which indicates that this degradate is formed at a slow rate and also degrades at a slow rate. This in turn implies that the major source of 5-OH-ASTP is from degradation of 5-OH-florasulam. The major route from 5-OH-florasulam to ASTCA could be either through 5-OH-ASTP or through DFP-ASTCA. As 5-OH-ASTP reached 28.9% and its major precursor appears to be 5-OH-florasulam, the route through 5-OH-ASTP is most likely to be the major route. However, there is no doubt that the major

Table 4. First-Order Degradation Kinetics of Florasulam and 5-OH-Florasulam on Soil and in Water under Natural Sunlight[a]

	florasulam			5-OH-florasulam		
test system	k ($\times 10^2$ day^{-1})	r^2	$t_{1/2}$ (days)	k ($\times 10^2$ day^{-1})	r^2	$t_{1/2}$ (days)
moist, viable soil						
exposed	13.7	0.909	5.0	13.9	0.412	5.0
dark	22.8	0.941	3.0	3.9	0.826	18
photolysis				10.0		6.9
air-dried soil						
exposed	2.4	0.961	30			
dark	0.88	0.540	79			
photolysis	1.5		47			
buffered aqueous						
TP, exposed (June)	0.95	0.812	73			
AN, exposed (May)	0.42	0.933	164			
natural water						
exposed (July)	19.5	0.970	3.3			

[a] Uncorrected for incident radiation.

terminal degradation product in this study was ASTCA. There was some evidence that further degradation occurred as small amounts of other polar degradation products were seen in the 30 DAT sample.

Degradation Kinetics. The amount of florasulam and degradates present at each timepoint in the soil photolysis experiments are shown in Table 2. First-order rate constants (uncorrected for sunlight intensity as determined by the chemical actinometry) for the degradation of florasulam were fit to the simple first-order exponential decay model:

$$C = C_0 e^{-kt}$$

where C is the concentration of florasulam at time t, C_0 is the initial concentration of florasulam (set to 100%), and k is the degradation rate constant. To calculate the degradation rate of 5-OH-florasulam, we assumed that all of the florasulam that degraded was converted to 5-OH-florasulam (Krieger et al., 2000; Jackson et al., 2000). The degradation rate of 5-OH-florasulam was then determined using the expression:

$$[\text{5-OH-florasulam}]_t = k_a[\text{florasulam}]_0\left(\frac{e^{-k_a t} - e^{-k_b t}}{k_b - k_a}\right)$$

where k_a is the degradation rate of florasulam, and k_b is the degradation rate of 5-OH-florasulam. The rate of degradation of 5-OH-florasulam (k_b) was determined by nonlinear curve fitting to the actual data set, using the rate of degradation independently determined for florasulam (k_a) and a value of 100% for $[\text{florasulam}]_0$. The rate of degradation due to photolysis was taken to be the difference between the rate of degradation in the exposed and dark test systems. Rate constants and corresponding half-lives are given in Table 4.

There was no significant difference in the degradation rate constants for florasulam between the exposed and the dark control samples for the moist, viable soils. This is not surprising considering the rapid metabolic degradation of florasulam (Jackson et al., 2000). The rate of photolytic degradation would have to approach the rate of metabolic degradation for a meaningful degradation rate constant due solely to photolysis to be derived. Consequently, a meaningful rate constant for degradation by photolysis cannot be derived from this data set. However, the air-dried soil sample set showed a difference in the degradation rate between the exposed and the dark control samples, probably due to a decline in the biological activity of the air-dried soil. The difference in the rate constants can be interpreted as the rate due to photolysis. This degradation rate corresponds to a half-life due to photolysis on soil (uncorrected for sunlight intensity) of 47 days.

The rate of degradation of 5-OH-florasulam in soil is slower than that of florasulam; thus, meaningful data on the rate of degradation due to photolysis on moist soil surfaces can be obtained for 5-OH-florasulam. The derived photolytic half-life of 5-OH-florasulam, 6.9 days, is substantially shorter than that of florasulam. There is considerable uncertainty in our calculation on the photolytic degradation rate of 5-OH-florasulam, as evidenced from the poor correlation coefficient (0.412) for the exposed, moist-soil data set. However, it is apparent from the data in Table 2 that the maximum amount of 5-OH-florasulam is lower in the exposed test systems than in the dark controls, which implies that the photolysis rate must be significant relative to the dark soil degradation rate.

Dark controls were stable over the kinetics period for both aqueous test systems, indicating hydrolysis or biotic degradation (in the natural water system) was not a factor in degradation. Buffered aqueous samples were exposed to sunlight at two different times, May and June. The observed half-lives (uncorrected for sunlight intensity) were different (Table 4) due to differences in the amount of incident radiation over the exposure periods. Once corrected for incident irradiation, the degradation rates in the buffered system for florasulam were the same. The degradation rate in the natural water systems was significantly faster (>20×) than in the buffered aqueous solutions. Clearly, florasulam is subject to enhanced photodegradation in aqueous systems due to indirect photolytic processes.

Quantum Yield. The quantum yield for florasulam can be calculated using the known quantum yield of the PNAP/pyr actinometer, which is dependent upon the concentration of pyridine in solution, as shown by the equation:

$$\phi_{da} = 0.0169[\text{pyr}]$$

The quantum yield of florasulam (ϕ_{dc}) can be calculated from (Leifer, 1988)

$$\phi_{dc} = (k_{dc}/k_{da})\left(\sum_\lambda \epsilon_{\lambda a} L_\lambda / \Sigma_\lambda \epsilon_{\lambda c} L_\lambda\right)(\phi_{da})$$

where k_{dc} = degradation rate constant for florasulam,

Table 5. Estimated Photolytic Half-Lives (Days) for Florasulam as a Function of Season and Latitude on Soil and in Sterile, Buffered Aqueous Systems

latitude (°N)	spring	summer	fall	winter
		Soil		
20	12	10	15	23
40	24	14	48	180
60	94	29	600	12000
		Buffered Aqueous		
20	29	25	39	59
40	62	36	120	41
60	240	73	1500	29000

k_{da} = degradation rate constant for PNAP/pyr actinometer, $\sum_\lambda \epsilon_{\lambda a} L_\lambda$ = day-averaged specific light absorption rate constant for sunlight absorption by PNAP as a function of season and latitude, $\sum_\lambda \epsilon_{\lambda c} L_\lambda$ = light absorption rate constant for florasulam calculated from UV spectra, and ϕ_{da} = quantum yield for the actinometer.

On air-dried soil, the degradation rate constant due to photolysis for florasulam was 0.015 day^{-1}, while the degradation rate constant for the appropriate actinometers was 0.035 day^{-1}. Assuming that the test systems were exposed to typical summer sunlight, then $\sum_\lambda \epsilon_{\lambda a} L_\lambda = 532$. The value of $\sum_\lambda \epsilon_{\lambda c} L_\lambda$ for florasulam in summer is 0.2021; substitution of these values into the equation for quantum yield gives $\phi_{dc} = 0.245$.

This quantum yield should be considered a sum of the quantum yield from direct photolysis and other processes such as indirect photolysis. This quantum yield should also be considered the quantum yield for the system (florasulam on this specific soil type and moisture conditions) and may vary with soil type and moisture conditions. However, this system-specific quantum yield can still be used to estimate the photolytic half-life of florasulam on soil at various temperatures and seasons. The expressions for half-life and photolytic rate constant, $t_{1/2} = \ln 2/k$ and $k = \phi(\sum_\lambda \epsilon_{\lambda c} L_\lambda)$, can be combined to give the following:

$$t_{1/2} = \ln 2/\phi(\Sigma_\lambda \epsilon_{\lambda c} L_\lambda)$$

Substituting in appropriate values of $\Sigma_\lambda \epsilon_{\lambda c} L_\lambda$ (Leifer, 1988) yields estimated photolytic half-lives as a function of season and latitude for florasulam on soil (Table 5).

In the buffered water systems, the degradation rate constants due to photolysis for florasulam were 0.0042 and 0.0095 day^{-1} for the AN- and TP-labeled samples, respectively. The degradation rate constants for the appropriate actinometers were 0.035 and 0.059 day^{-1}. (Differences in the degradation rates of the different labeled materials are due differences in sunlight intensity during the exposure period; the AN-labeled samples were exposed in May, while the TP-labeled samples were exposed in June.) Assuming that AN-labeled samples were exposed to typical spring sunlight (May) and TP-labeled samples were exposed to typical summer sunlight (June), then $\Sigma_\lambda \epsilon_{\lambda a} L_\lambda = 431$ and 532, respectively. $\Sigma_\lambda \epsilon_{\lambda c} L_\lambda$ was calculated for florasulam for both spring (0.1169) and summer (0.2021). Substitution into the equation for quantum yield gives $\phi_{dc,AN} = 0.098$ and $\phi_{dc,TP} = 0.093$, for an average quantum yield of 0.096. Half-lives at various seasons and latitudes due to direct photolysis in water were calculated using the quantum yield of 0.096 and are given in Table 5. Given that rate of photolytic degradation was substantially faster in natural water systems, these estimated half-lives are conservative because they do not account for indirect photolysis processes that can occur in natural waters.

CONCLUSIONS

Soil photolysis rates for florasulam in the summer were high enough that there will be a photolytic contribution to the environmental dissipation of florasulam, although this contribution will be small relative to that of biodegradation because of the short soil half-life of florasulam due to biological degradation. However, the rate of photolytic degradation of 5-OH-florasulam was fast relative to its rate of biodegradation in soil, and therefore photolysis should contribute to the dissipation of 5-OH-florasulam in the soil environment. Photolytic processes also increased the percentage of irreversibly bound material present on soil, although whether this was due to light and moisture cycling or formation of specific, strongly sorbed photoproducts is not clear. Florasulam degraded much faster in natural water than in sterile, buffered water, even after adjusting for differences in the relative light intensities. Clearly, indirect photolytic processes will be important contributors to the photolytic degradation of florasulam in aqueous environments.

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