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Soil Photolysis of Herbicides in a Moisture- and Temperature-Controlled Environment

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The problem of maintaining the moisture content of samples throughout the course of a soil photolysis study is addressed. The photolytic degradations of asulam, triclopyr, acifluorfen, and atrazine were independently compared in air-dried soils and in moist (75% field moisture capacity at 0.33 bar) soils maintained at initial conditions through the use of a specially designed soil photolysis apparatus. Each pesticide was applied at 5 μg/g. The exposure phase extended from 144 to 360 h, depending on the half-life of the compound. A dark control study, also using moist and air-dried soils, was performed concurrently at 25 °C. The results showed significant differences in half-life. The dissipations generally demonstrated a strong dependence on moisture. In most cases, photolytic degradation on air-dried soil was longer than in the moist dark control soils. Half-lives in dry soil were 2−7 times longer, and in the case of atrazine, the absence of moisture precluded significant degradation. Moist soil experiments also tended to correlate more strongly with linear first-order degradations. The dark control experiments also demonstrated shorter half-lives in moist soil. Moisture was also observed to affect the amount of degradate formed in the soils.

KEYWORDS: Soil photolysis; asulam; triclopyr; acifluorfen; atrazine; moisture; half-life

INTRODUCTION

In the United States, 1.2 million tons of herbicides were applied to crops in 1999 (*1*), but this represents only one area of application for weed control. In addition to farmland, target applications also include parks and recreational areas, roadsides, residences, and businesses, which are also areas of activity where people conduct their daily lives. It is extremely important then that the fate of these chemicals is well-documented before they are approved for use in these areas. For health and ecological reasons, it is necessary to know how long these compounds will remain in the environment, the degradates that they form upon exposure, and the persistence of these degradates themselves. The possibility exists that the degradates formed in the environment could equal or exceed the parent compound in toxicity, persistence, or bioavailability (*2*−*5*).

With this in mind, it becomes essential that laboratory studies investigating the fate and metabolism of herbicides are as representative as possible in regards to the environmental conditions to which the chemicals are exposed. Specifically, in the environment, soil is kept moist through equilibrium with the atmosphere, cooler nighttime temperatures, precipitation, groundwater supply, and irrigation. In a laboratory soil photolysis study, Frank et al. (*6*) have shown that initially moist soil can reach air-dried equivalent conditions within 30 min of irradiation. Adjustment of soil moisture at each sampling was detrimental to obtaining meaningful degradation data, as this caused the soil surface to harden considerably.

The importance of soil moisture on pesticide degradation has been brought to the forefront in several publications. Increasing soil moisture content is known to increase the degree of mineralization of herbicides under aerobic conditions (*7*−*9*). Increasing soil water content causes increases in biological activity and stimulates microbial degradation of pesticides (*8*−*14*). With less water available, the mobility of the chemical is affected. There is more herbicide sorption and less diffusion in drier soils (*15*). The presence of moisture also allows for greater interactivity with microorganisms, since pesticides in solution are more available for microbial degradation than when sorbed onto the soil (*15*−*17*). The presence and variety of microbes in the soil can also determine the type of degradates formed (*18*). A complementary effect between soil and water has also been reported, resulting in the enhancement of hydrolytic degradation in soil systems as compared to that in pure water alone. The outcome is that moisture can affect the amount and type of degradation products formed (*6*, *11*). If laboratory photolysis studies do not include the maintenance of soil moisture content, different degradation patterns may arise as compared to what will occur in the field, resulting in misleading half-lives and the formation of different or no degradates. This can result in incorrect regulatory decisions regarding uses of that compound.

The test compounds for this study are shown in **Figure 1**. Asulam, methyl *N*-(4-aminobenzenesulfonyl)carbamate, manufactured by Aventis (formerly Rhone-Poulenc), is a systemic

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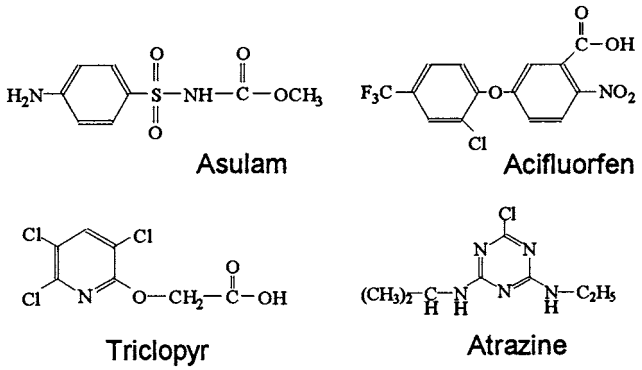

Figure 1. Structures of herbicide test substances.

herbicide used in reforestation, pine tree, noncropland, turf, cereal grain, and ornamental areas (*19*, *20*). It receives extensive use in Florida and Louisiana on sugar cane (*21*).

Triclopyr, 3,5,6-trichloro-2-pyridyloxyacetic acid, is a Dow-Elanco product used to control woody plants and broad-leaved weeds in uncultivated fields and forests, industrial areas, and rice fields (*20*, *22*). Primary regions of use include Virginia, West Virginia, Oregon, and the lower Mississippi valley on pasture and rice (*21*). It is effectively degraded by soil microorganisms and has a moderate persistence in soil environments. Triclopyr is not strongly adsorbed to soil particles and has the potential to be mobile (*23*). The half-life in soil ranges from 30 to 90 days, depending on soil type and environmental conditions, with an average of ~46 days (*24*). The major metabolite of triclopyr in both soil (*25*) and fish (*26*) is 3,5,6-trichloro-2-pyridinol (TCP), a chemical similar in toxicity to triclopyr. The half-life of TCP in 15 soils ranged from 8 to 279 days, with 12 of the tested soils having half-lives of less than 90 days. Longer half-lives may occur in cold or arid conditions (*23*). The likelihood of concurrent exposure to TCP has resulted in a lowered U.S. EPA margin of exposure rating for triclopyr for women ages 13 and older (*27*).

Acifluorfen, 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, is a selective pre- and postemergence herbicide registered by Rohm and Haas and BASF for the control of annual broad leaf weeds and some grasses in peas, rice, peanuts, and soybeans (*28*, *29*). This chemical is used mostly in the Mississippi valley and on the mid-Atlantic seaboard (*21*). Acifluorfen has been reported to be moderately persistent in soils, with half-lives of 23 to over 112 days (*30*). Microbial action accounts for the majority of the compound's loss from soil. No leaching of the chemical below 3 in. was observed (*29*). No degradation of acifluorfen in water was observed in laboratory studies lasting up to 28 days. However, when it is exposed to sunlight, it degrades quickly (*31*). The half-life under continuous light was 92 (*31*) to 107 h (*32*) in water. Eleven photoproducts were isolated from aqueous solution by Vulliet et al., with only 1,4-nitrophenol positively identified.

Atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine, is an herbicide developed by Syngenta (formerly Ciba-Geigy) for the control of weeds in corn, sorghum, and other crops as well as unselective weed control in noncropland (*20*). It is used nationwide, but mostly in the Midwest (*21*). Atrazine is highly persistent in soil and moderately soluble in water. Chemical hydrolysis, followed by degradation by soil microorganisms, accounts for most of the breakdown of atrazine. Hydrolysis is rapid in acidic or basic environments but is slower at neutral pH values. Addition of organic material increases the rate of hydrolysis (*33*). Atrazine can persist for longer than 1 year under dry or cold conditions (*34*). Atrazine is moderately to highly mobile in soils with low clay or organic matter content. Because it does not adsorb strongly to soil particles and has a lengthy half-life (60 to >100 days), it has a high potential for groundwater contamination despite its moderate solubility in water (*35*). Atrazine is highly prevalent in private and community wells (*34*, *36*, *37*). A 5 year survey of drinking water wells detected atrazine in an estimated 1.7% of community water systems and 0.7% of rural domestic wells nationwide, and the recently completed National Survey of Pesticides in Drinking Water found atrazine in nearly 1% of all of the wells tested (*37*). Atrazine was also detected in each of 146 water samples collected at eight locations from the Mississippi, Ohio, and Missouri Rivers and their tributaries. For several weeks, 27% of these samples contained atrazine concentrations above the maximum contaminant level set by the U.S. EPA (*38*).

We examined the soil photolysis of asulam, triclopyr, acifluorfen, and atrazine using an innovative apparatus designed to maintain the moisture and temperature of the soil samples during exposure (*39*). An instrument of this type is better equipped to consistently maintain environmental conditions.

Table 1. Characteristics of Soil

organic matter	2.7%
pH	5.4
sand	87%
silt	8%
clay	5%
USDA textural class	loamy sand
cation exchange capacity	7.2 mequiv/100 g
bulk density	1.26 g/cm^3
base saturation data	
cation	
calcium	34.7%; 500 ppm
magnesium	11.6%; 100 ppm
sodium	2.1%; 35 ppm
potassium	2.9%; 81 ppm
hydrogen	48.8%; 35 ppm

MATERIALS AND METHODS

Test Substances. Asulam, triclopyr, acifluorfen, and atrazine (**Figure 1**) were received from AccuStandard, Inc. of New Haven, CT. The test substances were used without further purification. Stock solutions of reference substances were prepared in acetonitrile and stored in a freezer.

Soil Acclimation. Soil was collected from Sauk County, WI, and classified by Agvise Laboratories (Northwood, ND) as loamy sand. The soil classification is detailed in **Table 1**. The moisture content of 75% at 0.33 bar FMC was determined as described previously (*6*). Prior to use, the soil was brought to 75% FMC at 0.33 bar and incubated at 25 °C. Oven drying resulted in a loss of 0.15 g of water per gram of natural soil. A portion of the natural soil was also air-dried for 3 days, causing a loss of 0.14 g of water per gram of natural soil. The soil was shown to be microbially active.

Test Systems. A Suntest photounit (Heraeus DSET Laboratories, Inc., Phoenix, AZ) equipped with a xenon lamp (Atlas, Linsengericht, Germany) was used to conduct the experiments. Lamp intensity was measured with a radiometer and photo detector assembly (International Light, Inc., Newburyport, MA) using 280, 365, and 440 nm sharp cut (high pass) filters and a wide eye quartz diffuser. The irradiated test vessel was an open top stainless steel chamber with a water jacket to maintain the soil temperature. A water bath circulated water through the floor of the photolysis chamber underneath the samples to control the temperature. The system was made airtight by sealing a quartz glass plate on the open top of the vessel. The photolysis chamber contained an air inlet to allow constant purging of the sample headspace. The soil trays were irradiated continuously by the xenon lamp 23 cm above the plates. The sample chamber was specifically designed to continuously monitor and maintain soil temperature and moisture at preset

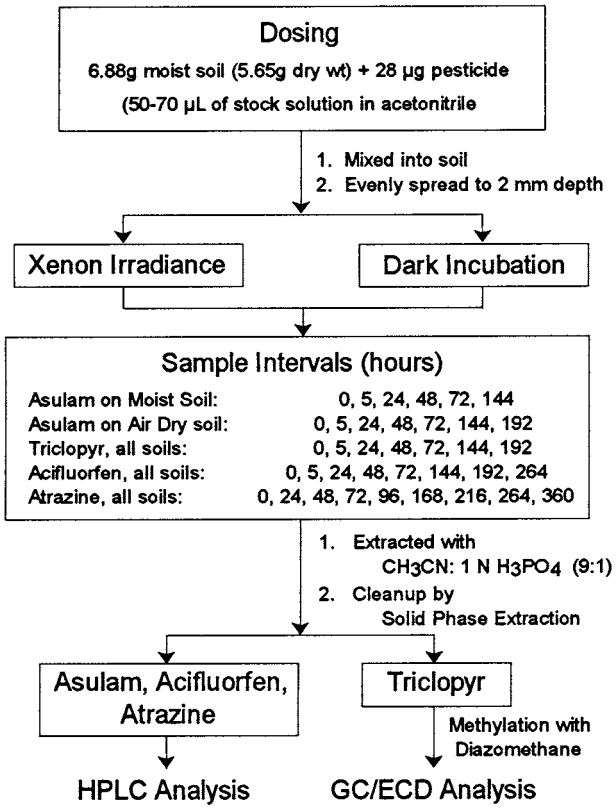

Figure 2. Dosing and sampling schematic.

values, with individual moisture control nozzles calibrated to spray each sample when the recorded soil moisture level fell below 75% FMC at 0.33 bar.

A reference plate containing incubated test soil was inserted into the photolysis chamber to obtain the moisture reference value. The initial reading of the instrument at 25 °C was 3.41 V. Soil temperature and moisture values were recorded every 6 min. If necessary, at each sampling, the weight of each soil tray was manually adjusted with water to ensure that the soil was being maintained at its initial weight and moisture content. No moisture control was performed in the air-dried soil study.

The dark control test samples were incubated in a stainless steel chamber with access ports for air circulation. The air inlet was diffused to maintain an even flow throughout the chamber. The test container was equipped with a stainless steel lid to provide an airtight dark system. The soil trays were similar to those of the irradiated test system. The test container with soil trays was sealed and placed in an incubator (Precision Scientific, Cleveland, OH) at 25 ± 1 °C.

Dosing Procedure and Study Initiation. The dosing solutions were prepared from a 5000 µg/mL stock solution by diluting with acetonitrile to a final concentration of ~500 µg/mL. The dosing solution concentration was verified by HPLC analysis.

A schematic diagram of the dosing and sampling procedure is shown in **Figure 2**. For the 0 h samples, air-dried soil or preincubated soil at 75% FMC at 0.33 bar was brought to ambient conditions and dispensed into tared 40 mL vials. The calculated volume of dosing solution was added to the soil with a syringe to yield a concentration of 5 µg/g. The soils were thoroughly mixed after dosing.

For the remaining samples, soil was weighed into uniquely identified stainless steel trays. The dosing solution was dispensed evenly across the soil surface via syringe, applying ~30 drops per plate. The soils were mixed and uniformly distributed across the plate at a depth of 2 mm. The plates were then placed inside the photolysis apparatus and kept covered until all soil samples were dosed for irradiation.

Once all samples for irradiation were dosed, the test vessel was covered with a quartz glass plate and sealed. A continuous flow of compressed air at ~10 mL/min through the test chamber was established. The lamp was ignited, and the moisture control and monitoring program was started. The temperature of the soil, initially kept at 18 °C to prevent overheating, equilibrated under the lamp to 25 °C within ~20 min. The time and chronometer hours at lamp ignition were recorded.

Samples were removed according to the schedule of **Figure 2**. At each sampling, the lamp was shut off and the air flow was stopped. The selected samples were removed and weighed. The remaining soils were also weighed, and their moisture was adjusted if necessary. The soil plates were returned to the photolysis chamber and sealed. Air flow and irradiation were resumed.

A dark control experiment was conducted concurrently on moist and air-dried soils of 2 mm depth. Dosing was performed in the same manner as the irradiated soils. The moist and air-dried soils were kept separated in stainless steel chambers placed in the dark at 25 °C. Samples were removed correspondingly with the irradiated samples. If needed, the moist soils were brought back to their initial weight with water at each sampling.

Soil Extraction. After exposure, the samples were transferred into tared 40 mL vials and extracted three times with 7 mL portions of acetonitrile:1 N phosphoric acid 9:1 v/v by thoroughly vortexing, sonicating for 6 min in an ultrasonic bath, and centrifuging for 10 min. For the asulam samples, a 2 mL portion of the pooled extracts was neutralized with 1 mL of 0.05 N NaOH and concentrated by vacuum evaporation to a final volume of 1 mL. For triclopyr, acifluorfen, and atrazine, 2 mL aliquots of the pooled extracts were exchanged into 2.0 mL of reagent water under nitrogen.

SPE. Sample cleanup was performed by SPE using Supelco (Bellefonte, PA) Discovery DPA-6S 3 mL 250 mg cartridges. After it was conditioned with water, the sample was loaded at a low flow rate. Elution was with 6 × 1 mL acetone. In the case of asulam, the sample load was also collected for analysis. To avoid stability concerns with asulam in water, concentration, SPE, and analysis of asulam extracts were performed on the same day. Triclopyr eluents were taken to dryness under nitrogen and methylated with a 1 mL solution of diazomethane in ether. Methylation was allowed to proceed for 10 min, after which the excess diazomethane was removed under nitrogen and the ether solution was exchanged into hexane for GC analysis. Acifluorfen and atrazine eluents were exchanged into 1.0 mL of acetonitrile.

HPLC Analysis. Asulam, acifluorfen, and atrazine extract concentrates were analyzed by HPLC. A model 501 HPLC system (Waters, Milford, MA), configured with a model 715 WISP autosampler and a model 484 tunable UV detector, was used for the asulam and atrazine analyses. The specific HPLC conditions are presented in **Table 2**. Typical retention times were 18.4 min for asulam, 16.3 min for acifluorfen, and 17.7 min for atrazine. The quantitation of the test substances was by a five point calibration curve of the area response. The coefficient of determination was 0.9997 for asulam, 0.9999 for acifluorfen, and 0.9995 for atrazine. Limit of detection was ~2 ng injected. The degradation of the parent herbicide was followed by comparing the concentration at each sampling point to the 0 h concentration recovered.

GC Analysis. Triclopyr was analyzed by GC due to the strong response of the chlorine atoms on an electron capture detector (ECD). All triclopyr standards and extracts were first methylated using diazomethane in ether as described in the SPE section. A Hewlett-Packard (Wilmington, DE) model 5890A gas chromatograph with a model 19235 ECD and model 7673 autosampler was used. The column was an HP-1 (Agilent, Wilmington, DE), 25 m × 0.2 mm × 0.33 µm. The injection parameters were as follows: volume, 2 µL; temperature, 220 °C; helium carrier gas flow, 100 mL/min; column head pressure, 7 psi; septum purge flow, 3.5 mL/min; and septum purge on at 30 s. The oven was initially held at 40 °C for 0.5 min, ramped to 200 °C at 50 °C/min, held for 8 min, ramped to 270 °C at 50 °C/min, with a final hold of 3.9 min. The detector temperature was 290 °C. Nitrogen was used as the detector makeup gas, flowing at 40 mL/min. Calibration standards of triclopyr were prepared at 0.05, 0.125, 0.25, 0.5, 0.75, and 1.0 µg/mL and methylated before analysis. The resulting standard curve yielded a coefficient of determination of 0.996. The concentration of triclopyr at each sampling point was compared to the 0 h concentration to generate a decline curve.

Table 2. HPLC Operating Conditions

	asulam		acifluorfen		atrazine	
column	Lichrosorb C18[a] 250 mm × 4.6 mm		μBondapack C18[b] 300 mm × 3.9 mm		Microsorb-MV C18[c] 250 mm × 4.6 mm	
mobile phase	A, 0.1% acetic acid; B, CH_3CN		A, 0.1% acetic acid; B, CH_3CN		A, water; B, CH_3CN	
gradient 1 mL/min	min	% B	min	% B	min	% B
	0	5	0	15	0	30
	10	20	5	15	15	85
	20	20	17	57	16	100
	25	50	20	85	20	100
	30	5	25	85	25	30
			27	15		
detection	UV 254 nm		UV 296 nm		UV 296 nm	

[a] Alltech (Deerfield, IL). [b] Waters Corp. [c] Rainin (Woburn, MA).

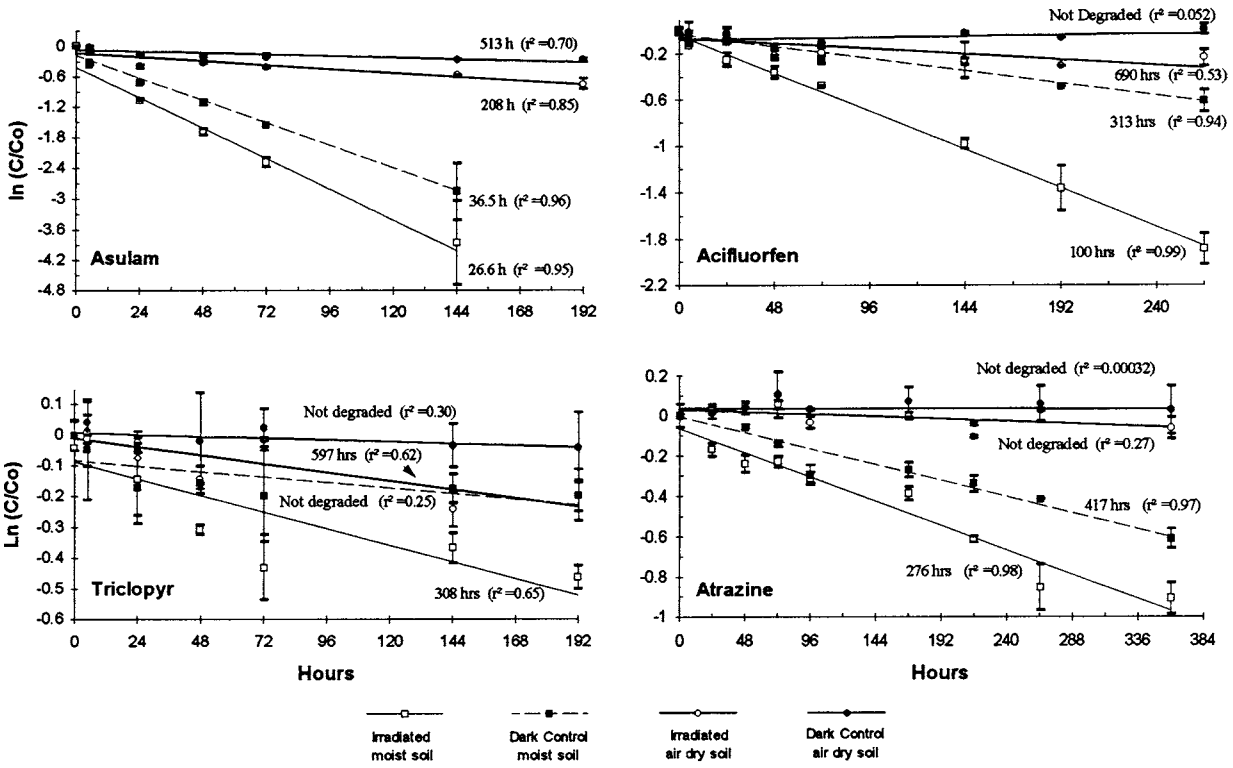

Figure 3. Decline of parent herbicides and corresponding half-lives. Vertical bars represent standard deviation of duplicate samples.

Table 3. First Order Rate Constants (h^{-1}) for the Photolytic Decline of the Herbicides Asulam, Triclopyr, Acifluorfen, and Atrazine in Moisture-Maintained (75% FMC at 0.33 bar) and Air-Dried Soil

soil type	asulam	triclopyr	acifluorfen	atrazine
irradiated moist	$2.60 \pm 0.42 \times 10^{-2}$	$2.25 \pm 1.05 \times 10^{-3}$	$6.90 \pm 0.46 \times 10^{-3}$	$2.51 \pm 0.35 \times 10^{-3}$
irradiated air-dried	$3.33 \pm 0.88 \times 10^{-3}$	$1.16 \pm 0.57 \times 10^{-3}$	$1.00 \pm 0.54 \times 10^{-3}$	nd[a]
dark control moist	$1.90 \pm 0.26 \times 10^{-2}$	nd	$2.22 \pm 0.32 \times 10^{-3}$	$1.66 \pm 0.26 \times 10^{-3}$
dark control air-dried	$1.35 \pm 0.56 \times 10^{-3}$	nd	nd	nd

[a] No degradation.

RESULTS AND DISCUSSION

Asulam. The decline of the test substances and their half-lives in the various phases of the study is displayed in **Figure 3**. Asulam degraded very rapidly under moist conditions (**Figure 3**, upper left panel). Irradiated and dark control moist samples containing asulam showed similar half-lives ($p = 0.025$), both under 40 h, with strong agreement to first-order rates of decline ($r^2 = 0.950$ and 0.964, respectively). The first-order reaction rates are presented in **Table 3**. In contrast, the disappearance of asulam in air-dried soils was more rapid during the first 24 h than during the remainder of the test period (**Figure 4**, top panel). The rate constant for the decline of asulam in irradiated air-dried soils from 0 to 24 h was 0.0161 h^{-1} ($r^2 = 0.982$), but the rate of disappearance slowed during the 24−192 h period, producing a rate constant of 2.42×10^{-3} h^{-1} ($r^2 = 0.864$). The average asulam concentration from 24 to 192 h in the air-dried irradiated samples was 61.9 ± 10.0%. Similarly, in the dark control air-dried soils, the rate constants were 7.65×10^{-3} (r^2

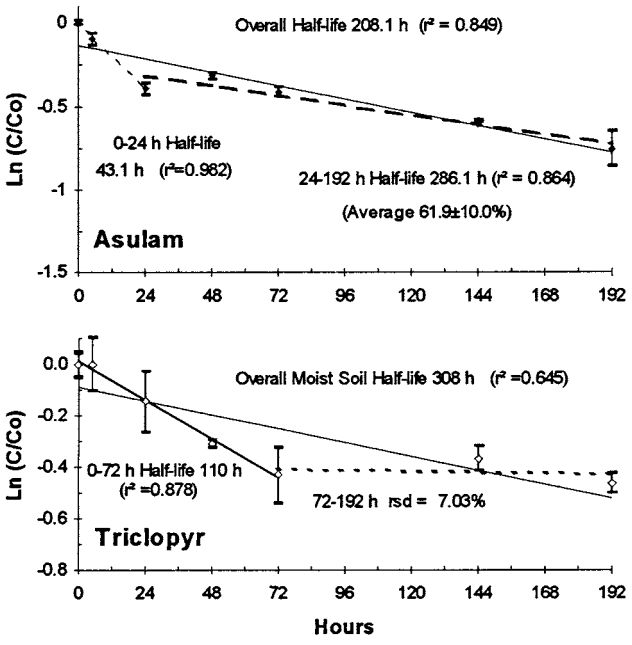

Figure 4. Photolysis of asulam on air-dried soils (top) and photolysis of triclopyr on moist soils (bottom) illustrating the biexponential nature of the degradation. Two different rates of reaction are indicated in both cases. The vertical bars represent the standard deviation of duplicate sample analyses.

$= 0.955$) during the first three samplings and 6.76×10^{-4} h^{-1} ($r^2 = 0.812$, average concentration 79.8 ± 3.9%) for the 24−192 h period. Each of these sampling periods exhibited good correlation to first-order kinetics, with r^2 values ranging from 0.81 to 0.98. Such a pattern of initial, relatively rapid degradation followed by a period of slower kinetics is suggestive of a biexponential model (*40*). Because soil microbial activity has been shown to be vastly affected by the lack of moisture (*8*−*11*), this decrease in the rate of decline would appear to be a result of either a depletion in the microbial population after 24 h in dry soil or lack of hydrolysis, or both, since photon penetration and indirect photolysis are inapplicable to the dark control samples. The differences between the moist and the dry experiments ($p = 0.00413$ for irradiated samples and $p = 0.00180$ for dark control) and the irradiated to dark control experiments ($p = 0.367$ for moist samples and $p = 0.0111$ for air-dried samples) illustrated further the relative importance of moisture over photolysis in asulam degradation. Taking the difference between the irradiated and the dark control rate constants allowed calculation of the half-life due to photolysis, which for asulam was 98.2 h in the moist samples, 3.7 times the irradiated moist half-life. In air-dried soils, the half-life due to photolysis was 350 h. Conversely, the half-life due to increased activity from moisture in irradiated samples was 30.5 h, and in dark control samples, it was 39.3 h, both in close agreement with the respective overall half-lives.

Triclopyr. The slope of the least squares, best-fit line of the natural logarithmic decline of triclopyr over time resulted in half-lives of 308 h for irradiated moist soils and 597 h for irradiated air-dried soils (**Figure 3**, lower left panel). However, the rates of reaction were not well-represented by first-order kinetics (**Figure 4**) and not statistically different from each other ($p > 0.05$). Overall, in the four experiments, the coefficients of determination ranged from 0.25 to 0.65. In the moist soil, photolytic degradation of triclopyr occurred more rapidly during the first five samplings, thereafter maintaining an equilibrium value. The decline of triclopyr in moist soil from 0 to 72 h of irradiation demonstrated a linear correlation ($r_{\mathrm{Im},0-72}^2 = 0.878$, $k_{\mathrm{Im},0-72} = 6.30 \times 10^{-3}$ h^{-1}) whereas the average percent of initial concentration from 72 to 192 h was 65.8 ± 4.6%. The irradiation of triclopyr on dry soils resulted in a coefficient of determination of 0.621. The irradiated air-dried samples showed a similar but slower decline pattern to the moist experiments, except that the 72 h sample showed an unexpectedly high percentage of triclopyr. Nevertheless, triclopyr reached equilibrium at ~80% at the 144 and 192 h samplings. The rate of reaction from the 0 to 48 and 144 h data was 1.71×10^{-3} h^{-1} with $r^2 = 0.829$. We attribute the differences in the amount and rate of degradation in the moist and dry photolysis experiments to several possible factors, including the ability of light to penetrate the soil, greater mobility of triclopyr into the photolytic zone of moist soil, and indirect photolysis (*2*, *6*), although further experimentation would be necessary for verification.

The overall first-order rates of reaction for the dark control samples were indistinguishable from zero for both the moist ($p = 0.0687$) and the air-dried ($p = 0.376$) experiments. However, a noticeable trend was seen in the dark control moist samples. Triclopyr declined linearly ($r_{\mathrm{Dm},0-24}^2 = 0.9991$, $k_{\mathrm{Dm},0-24} = 6.97 \times 10^{-3}$ h^{-1}) through the first 24 h and then maintained a constant level of 83.7% (rsd = 6.8%) to the end of the study. In the dark control air-dried samples, triclopyr did not appreciably degrade at all. After 192 h of incubation, there remained 96% of the initial concentration of parent material, and the rsd of the percent of initial throughout this phase of the study was only 6.92%. Therefore, the major degradation pathway for triclopyr occurred by photolysis.

Acifluorfen. The decline curves for acifluorfen are shown in the upper right panel of **Figure 3**, and the first-order rates of decline are presented in **Table 3**. The moist soil experiments produced excellent agreement with first-order kinetics, with an irradiated half-life of 100 h ($r^2 = 0.986$) and a dark control half-life of 313 h ($r^2 = 0.942$). This results in a half-life due to photolysis of 148 h in moist soil. Conversely, the experiments performed on air-dried soil had coefficients of determination less than 0.6, and the rate of reaction for the dark control air-dried experiment was not statistically differentiated from zero. The photolytic degradation of acifluorfen was influenced by the moisture content of the soil ($p < 0.005$). Whereas the half-life in irradiated air-dried soil was 690 h, the half-life due to moisture was 118 h. The poor coefficient of determination in the irradiated air-dried experiment was due to a change in the factors affecting degradation. Like asulam, the air-dried soil photolysis of acifluorfen was more rapid during the first 48 h ($k_{\mathrm{Id},0-48} = 4.25 \times 10^{-3}$ h^{-1}, $r^2 = 0.700$) than from 48 h through the end of the study ($k_{\mathrm{Id},48-264} = 2.91 \times 10^{-4}$ h^{-1}, rsd = 7.2%), during which time further degradation of acifluorfen essentially no longer occurred ($p = 0.34$). This is speculated to be due to decreased microbial activity and/or depletion of acifluorfen in the photolytic zone of the soil without replenishment through transport from underlying depths by convection of moisture. The solubility of acifluorfen in water is 120 mg L^{-1} (*41*). This additional dependence, whether related to microbial activity or acifluorfen availability, results in degradation that is not successfully modeled by first-order kinetics.

Atrazine. In **Figure 3**, the atrazine experiments are presented in the lower right panel. Good correlation of the moist soil experiments was again observed, with r^2 values of 0.936 for the irradiated system and 0.922 for the dark controls. The half-lives for these experiments were 276 and 417 h, respectively. The first-order rates of decline are presented in **Table 3**. No

degradation of atrazine took place in samples lacking moisture. For the irradiated air-dried experiment, $r^2 = 0.27$ and $p = 0.026$. In the dark control air-dried system, $r^2 = 3.2 \times 10^{-4}$ and $p = 0.94$. Only a slight dependence on photolysis was seen in atrazine degradation. The half-life due to photolysis was 818 h ($k_{ph} = 8.47 \times 10^{-4}$), three times the overall half-life.

In the chromatograms of the atrazine samples, there appeared a peak U1 at 19.5 min that was not observed in blank soil extracts. Three primary metabolites of atrazine have been reported in the literature. Atrazine can be hydrolyzed chemically by soil humus and clay minerals (*42*, *43*) and by the bacteria *Pseudomonas putida* (*44*, *45*) to hydroxyatrazine. Microbial degradation yields desethylatrazine and desisopropylatrazine (*46*). Loss by volatilization may also occur (*47*). Although no attempt was made in the present experiment to compare U1 to these compounds, several observations can be made about its formation. In the irradiated moist soil experiment, U1 was first observed in the 24 h samples with an area of 2.8% of that of 0 h atrazine. U1 steadily increased in area 330-fold by the end of the study, with an area 930% of 0 h atrazine. The overall rate of formation was 30 290 h^{-1} with $r^2 = 0.904$. U1, however, formed at a slower rate from 0 to 168 h ($k_{U1,0-168} = 11\,210$ h^{-1}, $r^2 = 0.810$), then was produced more rapidly during the remainder of the study ($k_{U1,168-360} = 45\,980$ h^{-1}, $r^2 = 0.935$). In the dark control moist samples, U1 was again first noticed in the 24 h sample and increased in area 6-fold throughout the study from 2.8 to 17% of 0 h atrazine. The rate of formation was 508 h^{-1} with a good r^2 value of 0.920. In the dry soils, U1 was observed in the 0 h samples at 1.6% of the atrazine area but was not detected from 48 to 96 h. The degradate reappeared at 168 h and persisted to the end of the study but never reached 1% of the 0 h atrazine area.

Each of the herbicides used in the study showed distinct differences in the rate of degradation depending upon the soil moisture content. With the exception of triclopyr, which was not degraded in the control samples and does not degrade by first-order kinetics, each chemical degraded slower in air-dried irradiated soil than in moist soils in the dark, and the correlation to first-order kinetics was better in the moist samples than in the corresponding air-dried samples. Triclopyr under irradiation exhibited an initial rapid decline followed by a period of equilibrium, with the dry soils showing a slower initial rate than the moist soils. Photolytic declines can be highly moisture-dependent, as exhibited by asulam and atrazine. Asulam photodegradation in moist soil was very similar to the dark control, while the half-lives in the air-dried soils increased by 8−14 times. Atrazine degraded under moist conditions but not significantly on air-dried soil, and it exhibited a difference between the two soils in the amount of degradate formed. Moisture can affect the degree of linearity of degradation. Although the photolysis of acifluorfen on moist soil was linear, the air-dried photolysis was not. Its decrease in degradation on air-dried soils could be due to decreased microbial activity or the depletion of acifluorfen in the photolytic zone. All in all, thoroughly different conclusions are drawn from photolysis on moist soil and photolysis on air-dried soil. To obtain agreement between laboratory data and field observations, control of moisture is a very important factor in soil photolysis.

ABBREVIATIONS USED

ECD, electron capture detection; FMC, field moisture capacity; GC, gas chromatography; HPLC, high performance liquid chromatography; rsd, relative standard deviation; SPE, solid phase extraction.

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