J. Agric. Food Chem. 1996, 44, 3393–3398

Abiotic and Biotic Degradation of Dithiopyr in Golf Course Greens

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Results of previous research have indicated that only a small fraction of dithiopyr [*S,S*-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioate] is lost in the surface water or by infiltration in soil leachate following application to golf course greens. The purpose of this research was to investigate the abiotic and biotic agents for dithiopyr loss from golf course greens. Growth chamber and laboratory studies were conducted to determine dithiopyr loss in response to volatilization, photodegradation, chemical transformation, and biological degradation in sterile and nonsterile rooting media (RM) and RM leachate collected from established golf course greens maintained in the greenhouse. Following application to RM, dithiopyr was lost primarily by volatilization which increased with increasing treatment period and temperature. The estimated half-life for dithiopyr in RM ranged from 68.8 days (sterile RM, dark, 20 °C) to 39.2 days (nonsterile RM, dark, 35 °C). Dithiopyr degradation in RM leachate was greater under UV radiation than in the dark and was faster than in distilled water under the same conditions indicating the potential for the presence of photosensitizers prompting photodegradation of dithiopyr in the RM leachate. The estimated half-lives for dithiopyr in RM leachate ranged from 515 days (sterile RM leachate, dark, 6.8 pH, 20 °C) to 0.8 days (nonsterile RM leachate, UV light, 6.8 pH, 20 °C). Results indicate a large effect of environmental variables on dithiopyr loss and its persistence in the turfgrass ecosystem.

Keywords: *Dithiopyr; biotic and abiotic degradation; photolysis; golf course; rooting media; leachate*

INTRODUCTION

Although agriculture is the largest user of pesticides in North America, turfgrass is typically the most intensively managed biotic system (Walker et al., 1990). The public demand for high-quality and uniform turf often requires the use of intensive management strategies to maximize pest control and nutrient availability (Potter et al., 1989) resulting in increased public awareness for pesticide use. The enhanced interest is, in general, a response to the increased use of pesticides and fertilizer since the 1960s and advancements in technology allowing scientists to detect their presence at very low concentrations (Lehr, 1988). The major concern for the impact of pesticides on the environment is their potential entrance into drinking water sources which is facilitated by movement in surface water and groundwater from the treated site (Pratt, 1985). The conclusive evidence of the health effects of long-term exposure to pesticides has yet to be obtained; however, there is intense public perception of risk concerning pesticides in drinking water (U.S. EPA, 1991).

Currently, there are over 14 300 golf courses in the United States, and assuming an average size of 48.6 ha/course (National Golf Foundation, 1991), there are over 0.7 million ha of turfgrass in the golf course industry. Additionally, the National Golf Foundation estimates that there are 21.7 million golfers in the United States, and by the year 2000, the number of players could easily exceed 30 million. To keep up with the demands of the rapidly increasing number of golfers, it is suggested that a new golf course must be opened every day over the next 10 years. Color, uniformity, and density of the turfgrass on these golf courses will be affected adversely by incursions of weeds, disease, and insects. Turfgrass of high-quality and uniform playing surface has become the expected necessity on golf courses, and this condition often requires the use of intensive management to control pests.

Assuming that 2% of a golf course is managed as putting greens, there are 14 thousand ha of greens in the United States which are constructed for maximum infiltration and percolation of water through the rooting medium. Rooting medium composition, generally, includes at least 80% by volume (97% by weight) coarse sand allowing for rapid water percolation and having an extremely low cation exchange capacity. Additionally, soil sterilization is recommended during construction for weed and disease management (Beard, 1982). The sterilization ultimately influences the soil microbial decomposition of applied pesticides. These characteristics of the rooting medium could result in rapid movement of pesticides through the rooting mixture allowing for a potential source of contamination of the effluent water from the greens.

Dithiopyr [*S,S*-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioate] is the active ingredient in the formulated herbicide Dimension, marketed by Monsanto Co. (St. Louis, MO). It is registered for use in the control of crabgrass (*Digitaria* spp) in turfgrass (including greens) (Enache et al., 1991). Due to the increasing concern for the environmental fate of herbicides and their residues, a knowledge of the importance of physical, chemical, and biological processes on dithiopyr degradation is necessary. The low water solubility (1.38 mg/kg), high octanol−water partition coefficient (K_{ow} = 56 250), and organic carbon partition coefficient (K_{oc} = 1920) suggest a high potential of dithiopyr retention within the thatch, mat, and surface soil (Schleicher et al., 1995). We found that very small quantities of dithiopyr were lost in runoff water from golf course fairways and as leachate

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S0021-8561(95)00768-0 CCC: $12.00 © 1996 American Chemical Society

through golf course greens and only small fractions of the applied herbicide remained on the grass leaves. However, a larger fraction of the applied dithiopyr was found in the rooting medium (unpublished data). Degradation of pesticides does not abate upon egress from the soil environment as aqueous leachate. There is only limited information available on the abiotic and biotic degradation of dithiopyr in soil and water, especially in residence of the rooting medium of golf course greens and as leachate from golf course greens. The purpose of this research was to determine the effects of UV radiation, temperature, leachate pH, and medium sterilization on dithiopyr degradation in rooting medium (RM) and the aqueous environment.

MATERIALS AND METHODS

Chemicals. Analytical grade dithiopyr (98%) and the formulated emulsifiable concentrate of dithiopyr (Dimension) were supplied by Monsanto. A methanol solution of dithiopyr (50 mg/L) was scanned over a wavelength range of 190−1100 nm using a DU 640B spectrophotometer (Beckman Instruments, Fullerton, CA).

All solvents and anhydrous sodium sulfate (J. T. Baker, Phillipsburg, NJ) were resi-analysis grade. The anhydrous sodium sulfate was heated at 300 °C overnight; 1% KOH was prepared by dilution of 85% KOH (EM Science, Gibbstown, NJ) and distilled water, and 5% phosphoric acid was obtained by diluting 85% phosphoric acid (Fisher Scientific Co., Fair Lawn, NJ) with distilled water.

Rooting Media (RM) and RM Leachate. Miniature golf course greens were developed over lysimeters in the greenhouse during 1993 (USGA Green Section Staff, 1989). The simulated golf course greens had a well-established `Tifdwarf' bermudagrass [*Cynodon dactylon (L.) Pers.x C. transvaalensis Burttdavy*] sod. The RM consisted of 80% sand and 20% sphagnum peat moss (v/v) (96.83:3.17, w/w). The pH of the rooting medium was 5.5, and the maximum water-holding capacity was 17.4% (v/v). About 60 g of RM was packed loosely into glass Petri dishes (95 mm in diameter and 13 mm in depth). To simulate the sterilization of golf course greens RM, the RM in the Petri dishes was sterilized by autoclaving with steam for 1 h at 120 °C and 198 kPa. Before treating with dithiopyr, the sterility of RM was confirmed by checking for microorganism colony development for 1 week on nutrient agar which was inoculated with the supernatant from the autoclaved RM.

About 20 L of leachate was collected from a lysimeter base mounted below the miniature golf course greens located in the greenhouse. Leachate used for the abiotic treatment was steam-autoclaved for 1 h at 120 °C (198 kPa). The degree of sterilization of the leachate was confirmed by the lack of colony formation on nutrient agar. The pH of the original leachate was 5.5, and for pH treatments the pH was adjusted to 3.7, 6.8, and 9.4 using 5% phosphoric acid or 1% potassium hydroxide. The pHs were chosen to include the extremes and intermediate units common to leachate egressing from golf course greens. Formulated emulsifiable concentrate was diluted 3 million times with leachate for each pH. The total dilution occurred in four steps. The concentrate was diluted 100 times in each of the first three steps and three times in the fourth step. To ensure complete solvation the solution was shaken vigorously in the dark for 2, 4, 8, and 48 h during the respective steps. The final solution was sonicated (Mettler Electronics Corp., Hightstown, NJ) for 1 h. The final concentration of dithiopyr in the leachate at each pH was 500 μg/L. A distilled water solution of dithiopyr was similarly prepared.

Influence of UV Light, Sterilization, and Temperature on Dithiopyr Loss from RM. The emulsifiable concentrate of dithiopyr was diluted 10-fold with water and sprayed evenly on the surfaces of the RM in the sterile and nonsterile Petri dishes at 0.56 kg ai/ha using a precision spray chamber. Each dish with RM received 13 $\pm$ 1 μg of dithiopyr. Following treatment, water was added onto the surface of RM at 6.5 mL/dish. The RM moisture was maintained at field capacity of 15.4%. The dishes were covered with one layer of plastic film (No. 9076, Nugget Distributor, Stockton, CA) to maintain sterility. This plastic film does not interfere with the transmission of UV light in the wavelength range desired for this study (Falb et al., 1990), nor does it eliminate the movement of O_2 (0.6 mL/cm^2/24 h), H_2O vapor (0.4 g/cm^2/24 h), N_2 (0.2 mL/cm^2/24 h), CO_2 (2.4 mL/cm^2/24 h), and other simple molecules. The covered Petri dishes were placed in an incubator under UV lights or in the dark at 20 $\pm$ 2 °C.

The UV light was furnished by a bank of four 40 W Voltarc UV fluorescent tubes (Voltarc USA FS40T12-ERE-BP, Ultraviolet Resources International, Cleveland, OH) with a spectral range of 270−400 nm and a peak output at 310 nm. The lamps were located 15 cm apart in the bank, and the bank was located 60 cm above the surfaces of the RM in dishes. The intensity of UV light at the surface of the RM was estimated to be 0.7−1 W/m^2 (Ultraviolet Resources, Cleveland, OH). To determine the influence of temperature on dithiopyr loss from RM, an additional set of Petri dishes containing nonsterile and sterile RM and dithiopyr was incubated in the dark at 20, 30, and 30 °C.

Water was added to the RM in the dishes based on the weight loss. At 0, 17, 28, and 55 days after treatment (DAT), three Petri dishes were removed from the sterile and nonsterile treatments maintained under the UV light and dark conditions. The samples were immediately extracted in preparation for dithiopyr analyses.

In an additional experiment, 30 mL of dithiopyr solution was placed in 50 mL poly(propylene) centrifuge tubes. For temperature treatments, the tubes were placed in a refrigerator at 4 °C or an incubator maintained in the dark at 20, 30, or 35 °C. The centrifuge tubes contained covers with small holes and were placed in a plastic bag with open containers of water to maintain a high level of humidity in the closed plastic bag to restrict the loss of dithiopyr by volatilization from the centrifuge tube. The air space inside the bag, containing the tubes, was ca. 0.5 times the volume of the sample tubes and open water containers.

UV light treatments were conducted under a UV light at 20 $\pm$ 2 °C. The same procedures were conducted under aseptic and nonsterile conditions. The solution in each tube was sampled once and discarded. The poly(propylene) centrifuge tubes were determined, using a DU 640B spectrophotometer (Beckman Instruments, Fullerton, CA), to transmit ca. 50% of the light in the wavelength range of 260−400 nm and 100% of the light in the wavelength range 400−1000 nm. The UV light source was the same as previously described. The lamps were located 60 cm above the capped tubes placed horizontally on a plate. The UV light intensity on the side wall of the tubes was estimated to be 0.7−1 W/m^2 (Ultraviolet Resources, Cleveland, OH). The treatments (Table 1) were repeated three times.

Dithiopyr Analysis. The RM was transferred from the Petri dishes to 300 mL wide-mouth brown bottles. The dishes and covering plastic film were rinsed with 20−30 mL of methanol three times. The rinsing solutions plus 30 g of dehydrated sodium sulfate were added to the bottles. Additional methanol was added until there was about 20 mL of methanol above the RM in the bottles. The bottles were covered with Teflon-lined caps and placed on a rotary shaker set at 300 rpm for 8 h. The methanol layer was transferred to a 50 mL poly(propylene) centrifuge tube and centrifuged for 20 min at 5000 rpm. A 3 μL sample of the supernatant was injected directly into a gas chromatograph/mass spectrometer (GC/MS). If the instrument signal was not in the linear range for dithiopyr quantification, the supernatant was condensed or diluted accordingly. The recovery of dithiopyr from spiked samples of RM was determined to be 92−102%. The minimum concentration investigated was 0.2 μg/kg of soil.

The aqueous solution was filtered through LC-18 SPE (6 mL) tubes that had been previously conditioned by elutriating 10 mL of acetone and 10 mL of distilled water through the column before saturating the column with distilled water. SPE was accomplished on a vacuum manifold (Supelco, Inc., Bellefonte, PA) using LC-18 SPE extraction tubes (Supelco,

Table 1. GC/MS (SIM Mode) Operation Conditions

component	description	operation conditions	
		RM leachate	RM
gas chromatograph			
instrument	Hewlett-Packard 5890, HP-5 (5% phenyl methyl silicone), 0.25 μm, 30 m × 0.25 mm + 5 m × 0.25 mm		
capillary column	silica guard column, changing the guard column and transfer line every 100 samples		
injection	splitless, using automatic sampler HP 7673 (μL)	3	3
carrier gas	helium (psi)	10	10
temperature and holding time			
	transfer line (°C)	310	310
	inlet, with silanized glass wool (°C)	260	260
	oven initial (°C)	180	150, 2 min
	oven final (°C)	isotherm	164, 0 min
	rate (°C/min)		0.5
	solvent delay (min)	6.5	25
mass spectrometer			
instrument	Hewlett-Packard 5971A		
ion source	electron impact (eV)	70	70
	source temperature (°C)	210	210
detection	selective ions monitoring on ions	286, 306, 354	286, 306, 354
manual tune	perform daily using perfluorotributylamine (PTFBA) with ions	219, 264, 414	219, 264, 414
dwell time (ms)		500	500
EMV (V)		2500	2500

Inc.). A 75 mL poly(propylene) sample reservoir was connected to the top of each LC-18 SPE 6 mL tube by an adapter. Following vacuum filtration of the aqueous sample through the SPE tube, the tubes were dried by drawing hot (40−50 °C) air through the tubes for 15 min. The retained dithiopyr was elutriated from the LC-18 adsorbent with 3 mL of methanol. A 3 μL sample of the methanol effluent was injected into the gas chromatograph for dithiopyr quantification. Dithiopyr recovery from the leachate was determined to be between 95% and 101% for the dithiopyr concentration range of 0.03−300 μg/L.

The methanol extracts from RM and the methanol elutriation effluent from the LC-18 tube were analyzed by a Hewlett-Packard (Sunnyvale, CA) GC coupled to a Hewlett-Packard MS in the selective ion-monitoring (SIM) mode (Hong and Smith, 1995). Different programs were used for analyzing dithiopyr extracted from the RM and the leachate (Table 1). The retention times for dithiopyr extracted from the RM and leachate were 27.2 and 8.28 min, respectively.

Statistical Analyses. The data were analyzed by the general linear model procedure of SAS Release 6.08 (SAS Institute Inc., Cary, NC). The test methods were F test and T test (Fisher's protected least-significant difference values at the level of 0.05).

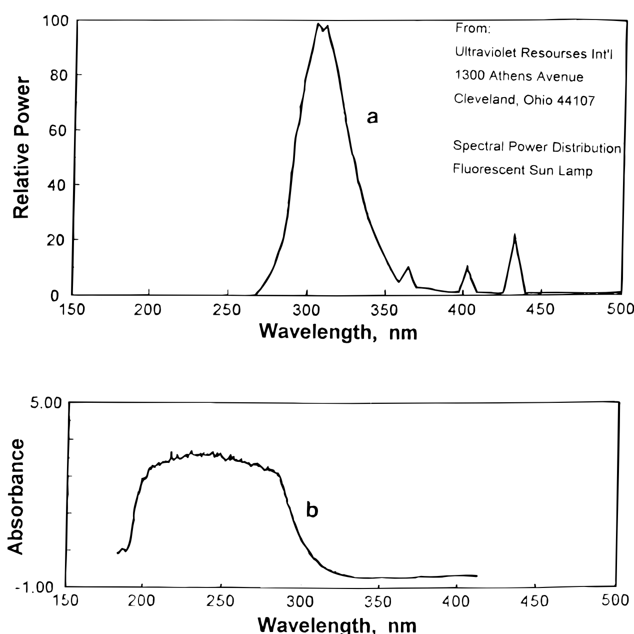

Figure 1. Emission spectrum (a) of the UV lights and absorption spectrum (b) of dithiopyr in methanol.

RESULTS AND DISCUSSION

Dithiopyr Degradation by UV Radiation on RM. Maximum light emission for the UV light source was in the wavelength range of 275−350 nm (Figure 1a), and the maximum light absorption range for dithiopyr was determined to be between 200 and 316 nm (Figure 1b). This should allow for the photolysis of dithiopyr (Zepp et al., 1977; Wolfe et al., 1990).

Generally, dithiopyr loss from the RM increased with increasing temperature and sampling period after treatment (Table 2). The highest dithiopyr loss occurred in samples taken at 55 DAT from the 35 °C treatments in the dark. More than 50% of the dithiopyr was lost from samples maintained at temperatures of 30 °C and higher for 55 DAT. It is apparent that UV light did not increase dithiopyr loss compared to dark treatments at 20 °C indicating that the dithiopyr was moved into the RM matrix while adding the water or the RM retarded the photodegradation of dithiopyr under UV light. The reduction effect of soil on photolysis of some pesticides has been reported before (Niles et al., 1975; Miller et al., 1983). Sterilization of the RM did not influence the rate of dithiopyr loss compared to the nonsterile RM. Since dithiopyr loss increased in response to increases in temperature and DAT in both the sterile and nonsterile RM, it would infer that the loss is probably due to volatilization from the surface of the soil. It was necessary to use a film covering for the Petri dishes that would allow gaseous exchange for microbial activity. Therefore, analyte volatility could not be controlled.

The equation that most closely describes dithiopyr loss from RM over time (t) is $100 - \text{loss (\%)} = 100(10^{kt})$ (k is constant). Equations for predicting the half-life ($t_{0.5}$) for dithiopyr in RM were developed for the four sampling dates against dithiopyr remaining (Table 3). The longest half-lives were for the 20 °C treatments, and the shortest were determined for samples incubated at 35 °C. UV light did not decrease the half-life for dithiopyr compared to the dark treatment at the same temperature. Additionally, sterilization of the RM did not increase the half-life for dithiopyr compared to the nonsterile treatment conducted at the same tempera-

Table 2. Dithiopyr Loss (%) in Sterile (S) and Nonsterile (N) RM Samples in the Dark, under UV Light, and at Three Temperatures[a]

	20 °C				dark			
	UV light		dark		30 °C		35 °C	
DAT	S	N	S	N	S	N	S	N
0	0	0	0	0	0	0	0	0
17	19.7ab	26.2a	6.6c	12.1bc	20.9ab	24.8a	16.4abc	27.6a
28	40.0ab	34.7ab	14.7c	33.8ab	25.4ab	48.1a	25.1ab	46.1a
55	49.8bc	46.2bc	41.4c	45.7bc	61.1abc	55.8ab	54.2ab	61.6a

[a] Means, in the same row, followed by different letters are significantly different ($p \leq 0.05$).

Table 3. Estimated Half-Life ($t_{0.5}$) of Dithiopyr on Sterile (S) and Nonsterile (N) RM by Semilog Regression[a]

RM	radiation	temp (°C)	k	r^2	$t_{0.5}$ (days)
S	dark	20	−0.004372c	0.8582	68.8
N	dark	20	−0.005071bc	0.8912	59.3
S	dark	30	−0.005571ab	0.9113	54.0
N	dark	30	−0.006613ab	0.8319	45.5
S	dark	35	−0.006231ab	0.9254	48.3
N	dark	35	−0.007668a	0.9134	39.2
S	UV light	20	−0.005616ab	0.8516	53.6
N	UV light	20	−0.006500ab	0.7858	46.3

[a] The semilog regression equation is $\log_{10}$(remaining (%)) = $\log_{10}(100) + k \times$ DAT, with squared coefficient r^2. k values followed by different letters are significantly different ($p \leq 0.05$).

Table 4. Dithiopyr Degradation[a] (%) in Sterile (S) and Nonsterile (N) RM Leachate in the Dark

pH	temp (°C)	S/N	DAT 0	17	28	55
3.7	4	S	100	1.3bc	1.4f	3.1fg
3.7	4	N	100	2.1bc	2.9ef	5.9efg
3.7	20	S	100	4.0abc	4.3ef	8 e
3.7	20	N	100	5.2abc	6.1de	11.3def
3.7	30	S	100	2.8abc	6.0ef	8.8 de
3.7	30	N	100	4.8abc	7.8cde	11.1de
3.7	35	S	100	0.3c	4.5def	10.5de
3.7	35	N	100	4.4abc	9.8abc	11.0de
6.8	4	S	100	0.4c	4.3ef	5.6efg
6.8	4	N	100	1.5bc	1.8f	5.8efg
6.8	20	S	100	2.5bc	3.2ef	7.2ef
6.8	20	N	100	6.6ab	14.4a	17.1b
6.8	30	S	100	2.5abc	6.0cde	9.2de
6.8	30	N	100	8.6a	12.9ab	22.1a
6.8	35	S	100	1.6bc	4.2ef	8.9de
6.8	35	N	100	6.8ab	12.7ab	16.3bc
9.4	4	S	100	0.9bc	3.0ef	6.3fg
9.4	4	N	100	0.8c	5.3cde	0g
9.4	20	S	100	1.7bc	3.3ef	7.7ef
9.4	20	N	100	2.4bc	3.8ef	8.9de
9.4	30	S	100	1.0bc	5.1cde	7.7ef
9.4	30	N	100	3.6bc	7.2cde	10.4de
9.4	35	S	100	4.4abc	9.0bcd	11.4cde
9.4	35	N	100	2.5 bc	5.8cde	11.2de

[a] Means, in the same column, followed by different letters are significantly different ($p \leq 0.05$).

ture. The differences are based on the differences determined for the slope (k) for the lines. The Q_{10} (ratio for degradation constants at 10 °C increments), comparing the loss rates in RM at 20 and 30 °C, was 1.2.

Calculated half-lives for dithiopyr ranged from 68.8 days (20 °C) to 39.2 days (35 °C) in golf course greens RM in sealed containers in the dark. Schleicher et al. (1995) estimated the half-life for dithiopyr in soil under turfgrass at Mead, NE, to be 35 days. Adams and Cowell (1990) reported a range of half-lives for dithiopyr, in soil under turfgrass observed over a range of locations across the United States, to be from 4 to 49 days. In these field experiments loss by photodegradation and volatility was not controlled. Dithiopyr has a vapor pressure of 5.3×10^{-6} kPa (Schleicher et al., 1995), and pesticides with vapor pressures $\geq 5.2 \times 10^{-9}$ kPa at 25 °C have been classified as moderately to highly volatile in the field (Kennedy and Talbert, 1977).

Effects of UV Radiation on Dithiopyr Degradation in RM Leachate. At 4 °C in the dark, dithiopyr loss was not significant until 55 DAT at a pH of 3.7, 6.8, or 9.4 (Table 4). The dithiopyr degradation at this temperature is probably due to abiotic chemical transformation not catalyzed by the acid pH. We tested the influence of UV light on dithiopyr degradation in sterile and nonsterile RM leachate that had been adjusted to pH values of 3.7−9.4 at ≥20 °C. Dithiopyr concentration in RM leachate at the first sampling (17 DAT) was near the minimum detectable limit (MDL) of 0.03 μg/L. The maximum concentration for all treatments at 17 DAT was 0.1% of the initial concentration of 500 μg/L. The treatment differences were not significant due to the final concentrations being near the MDL (data not included). These data indicate that dithiopyr is rapidly degraded by UV light over a pH range of 3.7−9.4 in sterile and nonsterile RM leachate. It can be concluded that the effect of UV light on dithiopyr degradation in RM leachate masked the effects of sterilization and pH at 17, 28, and 55 DAT.

In a separate experiment designed to determine the half-life for dithiopyr under different environments, it was determined that the predicted half-life for dithiopyr in distilled water under UV light was 1.7 compared to 0.8 days in RM leachate (Table 5). This difference could be due to the presence of photosensitizers prompting the photodegradation of dithiopyr in the leachate (Choudhry and Webster, 1985). Additionally, our data indicate that the predicted half-life for dithiopyr in the dark at 20 °C in nonsterile RM leachate was 200 days (Table 5). Under UV light, dithiopyr in RM leachate degrades to a concentration near the MDL at 17 DAT, whereas in the dark it is degraded less than 15% at 28 DAT and less than 25% at 55 DAT (Table 4).

Dithiopyr Degradation in RM Leachate in the Dark. Dithiopyr was not readily degraded under dark conditions. No more than 22% of the dithiopyr, in the RM leachate, was degraded in all treatments included in Table 4. Degradation was highest in the nonsterile RM leachate at 55 DAT in treatments including a pH of 6.8 and at temperatures between 20 and 35 °C (Table 4). There is no difference in degradation between sterile and nonsterile RM leachate at 55 DAT at pH 3.7 and 9.4. The Q_{10} for the degradation rate for dithiopyr in nonsterile RM leachate at the pH of 6.8 and between the temperatures of 20 and 30 °C is 1.3. The degradation of dithiopyr in sterile RM leachate over the 55 day treatment period (Table 4) is probably due to a chemical reaction and not to volatilization since the reactions occurred in air-tight vessels. Additionally, the 7.2% dithiopyr degradation at a pH of 6.8 and 20 °C in

Table 5. Estimated Half-Life ($t_{0.5}$) of Dithiopyr in RM Leachate by Semilog Regression[a]

radiation	pH	temp (°C)	sterilization	k ($\times 10^{-4}$)	r^2	$t_{0.5}$ (days)
dark	3.7	20	sterilized	−6.27ef	0.6757	470
dark	6.8	20	sterilized	−5.85f	0.8377	515
dark	9.4	20	sterilized	−6.40ef	0.6891	466
dark	3.7	20	nonsterile	−9.15def	0.7499	322
dark	6.8	20	nonsterile	−15.08cd	0.7444	200
dark	9.4	20	nonsterile	−7.43ef	0.5978	402
dark	3.7	30	sterilized	−7.44ef	0.8521	398
dark	6.8	30	sterilized	−7.81ef	0.7864	380
dark	9.4	30	sterilized	−8.58def	0.7084	349
dark	3.7	30	nonsterile	−9.23def	0.7877	318
dark	6.8	30	nonsterile	−19.55c	0.9479	151
dark	9.4	30	nonsterile	−8.79def	0.8348	335
dark	3.7	35	sterilized	−9.40def	0.7842	320
dark	6.8	35	sterilized	−7.57ef	0.7717	394
dark	9.4	35	sterilized	−9.67def	0.7931	303
dark	3.7	35	nonsterile	−9.40def	0.7995	311
dark	6.8	35	nonsterile	−13.94cd	0.8286	208
dark	9.4	35	nonsterile	−9.64def	0.8592	309
UV	6.7	20	distilled water	−1821.6b	0.7838	1.7
UV	5.5	20	nonsterile	−3578.4a	0.9280	0.83

[a] The semilog regression equation is $\log_{10}$(remaining (%)) = $\log_{10}(100) + k \times$ DAT, with squared coefficient r^2. k values followed by different letters are significantly different ($p \leq 0.05$).

sterilized RM leachate at 55 DAT is similar to that at 4 °C in the dark indicating that there is some abiotic chemical transformation in the RM leachate. Degradation of dithiopyr by chemical and biological systems appears to be equally as important at the pH of 6.8.

Generally, there was no temperature influences on dithiopyr degradation at pH 3.7, 6.8, and 9.4 in the sterile RM leachate (Table 4), and temperature did not influence dithiopyr degradation in the nonsterile RM leachate adjusted to pH 3.7 and 9.4. However, dithiopyr degradation in nonsterile RM was maximum at pH 6.8 and 30 °C. Maximum degradation of dithiopyr occurred at a pH of 6.8 and a temperature of 30 °C in the nonsterile RM leachate.

The half-lives of dithiopyr in RM leachate under dark conditions were estimated by extrapolating the semilog regression of the data (Table 5). The semilog equation, $\log_{10}$[remaining (%)] = $\log_{10} 100 + k \times$ DAT, was a best fit for the data. Degradation of dithiopyr in RM leachate appeared to follow first-order kinetics. On the basis of the estimated half-lives, it appears that dithiopyr degrades fastest under UV light in the RM leachate and distilled water. A short dithiopyr half-life at pH 6.8 and 20 or 30 °C indicates biological degradation. The degradation at pH 6.8 and 30 °C also implies abiotic mediated chemical degradation of dithiopyr (Tables 4 and 5). Similar data in Table 4 indicates that degradation by biotic and abiotic systems is very similar when comparing dithiopyr loss from sterile (7.2%) and nonsterile (17.1%) samples at 55 DAT, 20 °C, and a pH of 6.8. In summary these data indicate that the order of degradation agents on dithiopyr in RM leachate in descending order is UV light, biotic chemical conversion, and abiotic chemical transformation.

Conclusions. Pesticides begin to disperse from the target area immediately after application. Partitioning of the pesticides in the environment and potential loss of pesticides to groundwater and surface water is determined by innumerable interacting factors and conditions. Results of our research on the potential movement of dithiopyr following application to simulated golf course greens indicated that dithiopyr is lost from the greens environment very rapidly. Less than 1% of the applied analyte is transported through the rooting medium of the simulated greens (unpublished data). Results of this research indicate that following application of dithiopyr to the sod and soil surface, it is rapidly lost by photodegradation and volatilization. Upon entry into the RM, biotic and abiotic mediated degradation occurs at a much slower rate compared to loss by volatilization (Table 2). Upon exiting the golf course greens in the solution, the analyte can be further degraded by UV light and biological and abiotic mediated processes (Tables 4 and 5). Based on the availability of the molecules to these processes, the estimated half-life could be very different (ranging from 0.8 to 515 days) (Tables 3 and 5). For example, if immediately following dithiopyr application a rainstorm event occurs and the dithiopyr infiltrates into the soil or RM, very little photodegradation or loss by volatility would occur. The half-life would be much longer compared to the dithiopyr remaining on the foliage surface, in spray droplet form, for volatilization and phototodegradation.

ACKNOWLEDGMENT

We thank Mr. Nehru Mantripragada, Miss Deborah Dumas, and Mr. Klay Kilrease for technical assistance, Dr. David Bridges for providing important advice and the UV radiation device, and Mrs. Dianne Brooks for statistics assistance.

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Received for review November 20, 1995. Revised manuscript received August 7, 1996. Accepted August 8, 1996.[⊗] This research was supported by grant funds received from the United States Golf Association and Georgia Golf Course Superintendents Association.

JF950768G

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.