Chlorimuron Dissipation in Water and Soil at 5 and 25 °C

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Chlorimuron, 2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid ethyl ester, was added to water (pH 7.5, hardness = 110 mg of $CaCO_3$/L) and soil (sandy loam, pH 5.2) to determine the rates of dissipation at 5 and 25 °C. Radioactivity of both pyrimidine- and phenyl-^{14}C-labeled chlorimuron was quantitatively recovered from water after incubation for 112 days. Greater than 85% of the radioactivity was recovered from the soil treatments after 56 days of incubation. Extractable radioactivity in the soil decreased with time. The rate of degradation of chlorimuron in water followed zero-order kinetics ($R^2 > 0.95$). Less than 7% of the chlorimuron degraded at 5 °C, and the slope of the zero-order constant did not differ from zero. Half-life for chlorimuron in water at 25 °C ranged from 388 to 725 days, depending upon treatment. Dissipation of chlorimuron appeared to be greater in light than dark treatments. In soil, chlorimuron dissipation was described by first-order kinetics and half-life ranged from 17 to 22 days. Probable degradation products (saccharin, ethyl benzoate sulfonamide, and pyrimidine amine) in soil and water were identified in the methanol eluate by thin layer chromatography. Ethyl benzoate sulfonamide and pyrimidine amine are hydrolysis products of chlorimuron. Less than 1% of the radioactivity from water was evolved as carbon dioxide. Three to 5% of the radioactivity was evolved as carbon dioxide from the nonsterile soil treatment. Temperature appears to be a significant factor affecting chlorimuron dissipation in soil and water. Light may also enhance chlorimuron dissipation in water.

Keywords: *Sulfonylurea; environmental fate; biotic and abiotic dissipation*

INTRODUCTION

Chlorimuron is a sulfonylurea herbicide used for pre- and postemergence broadleaf weed control in soybean [*Glycine max*. (L.) Merr.] (Brown, 1990). Field application of chlorimuron will result in deposition to soil and vegetation, where it can move to surface water or leach through soil.

Previous studies on the dissipation of sulfonylurea herbicides in water have determined, for instance, that sulfometuron methyl, 2-[[[[(4,6-dimethyl-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]benzoic acid methyl ester, is rapidly hydrolyzed in water at pH 5 (half-life 2 weeks) but stable at pH 7 (13% loss in 30 days), with the methyl benzoate sulfonamide identified as the major metabolic product (Harvey et al., 1985). Other sulfonylurea herbicides are also rapidly hydrolyzed in water at pH <6, with the rate of hydrolysis greatly reduced at higher pH (Sabadie, 1990, 1991; Thomas and Harrison, 1990; Smith and Aubin, 1993; Schneiders et al., 1993; Cambon and Bastide, 1996). Increasing incubation temperature resulted in faster hydrolysis. For chlorimuron, hydrolysis of the sulfonylurea bridge to ethyl 2-(aminosulfonyl)benzoate (ethyl benzoate sulfonamide) and 2-(4-chloro-6-methoxy)pyrimidine amine (pyrimidine amine) occurred in water at pH <8 and was more rapid at 50 than 30 °C (Sabadie, 1995).

Sulfonylureas also photolyze in water. Irradiation with 300−400 nm light resulted in rapid loss of the phenyl ring of sulfometuron methyl as CO_2 (Harvey et al., 1985). Photolysis of chlorimuron involved hydrolysis of the sulfonylurea bridge characterized by first-order reaction kinetics. Photoreactive additives or naturally occurring photosensitizers such as riboflavin may affect photolysis of chlorimuron (Venkatesh et al., 1993). Nonionic surfactants increased the rate of hydrolysis of chlorimuron in water but not on glass plates (Thomas and Harrison, 1990).

Sulfonylurea herbicides dissipate in soil by chemical and biological pathways (Smith and Aubin, 1992; James et al., 1995). Dissipation of the sulfonylurea herbicides has been correlated to soil temperature, pH, and moisture content. Sulfometuron methyl dissipated more rapidly in acid than in alkaline soil (Cambon et al., 1992; Anderson and Dulka, 1985). Increasing temperature and moisture content increased the rate of dissipation. Metabolites, formed by cleavage of the sulfonylurea bridge, are mineralized to CO_2 by microorganisms. Actinomycetes and fungi were important in the dissipation of chlorsulfuron, but degradation occurred mainly by chemical hydrolysis, which was more rapid in acid than in alkaline soil (Joshi et al., 1985; Walker et al., 1989; Walker and Welch, 1989).

The stability of chlorimuron in soil has been reported by several investigators (Fuesler and Hanafey, 1990; Schroeder, 1994; Vencill and Banks, 1994; Reddy et al., 1995). Chemical hydrolysis of the sulfonylurea bridge appeared to be the main mode of dissipation, with faster hydrolysis in moist than in dry soil and at higher temperatures (Fuesler and Hanafey, 1990). Demethylchlorimuron and saccharin were identified as the major metabolites. Saccharin was formed by cyclization of the hydrolysis product, ethyl benzoate sulfonamide. Dissipation was described by first-order kinetics with a half-life of 5−20 days depending upon organic matter content of the soil, rain after application, and temperature (Vencill and Banks, 1994; Schroeder, 1994). Reddy et al. (1995) reported 10−16% loss of chlorimuron

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as CO_2 and calculated a half-life of >2 months from the first-order rate constant.

Chlorimuron's intended use in Canada requires information on the dissipation of this herbicide at temperatures <10 °C and at sterile conditions. Amidosulfuron, [[[(4,6-dimethoxypyrimidine)amino]carbonyl]sulfonyl]dimethylsulfonyl amine, was found to be stable (half-life > 500 days) at pH 9 and 10 °C compared to higher temperature and more acidic environments (Smith and Aubin, 1993).

In the current experiments, chlorimuron, ^{14}C-labeled in the phenyl or pyrimidine moiety, was added to water and soil and incubated under laboratory conditions at 5 and 25 °C to determine the effect of temperature on its rate of dissipation. A sterile water and soil treatment was included to determine the role of microorganisms in chlorimuron mineralization. The treatments were sampled at selected times for total and extracted carbon-14. Selected samples were screened by thin layer chromatography for detection of chlorimuron and its degradation products.

MATERIALS AND METHODS

Total microorganisms in soil and water were enumerated on R2A agar, actinomycetes on starch−casein agar, and fungi on rose bengal agar (Procedures 9215, 9250, and 9610, American Public Health Association, 1989). Enumeration was estimated from serial dilutions according to standard procedures. Radiochemical purity of chlorimuron dissolved in reagent acetone was determined by liquid scintillation counting techniques (LSC) and thin layer chromatography (TLC).

Water Characterization. Water was collected from a representative area in Ontario (Iona station) where chlorimuron is to be used. No suspended particles were present in the water, which was used as received. The water was tested for hardness, pH, and microbial activity when received and again prior to addition of the test substance. Hardness was determined by a titrimetric method with EDTA (Procedure 2340.C, American Public Health Association, 1989) and pH on a Sentron Model 1001 portable meter (Sentron Inc., Federal Way, WA).

Treatment of Water. Water was treated with phenyl- or pyrimidine-^{14}C-labeled chlorimuron at a concentration of 0.2 mg/L and 69 kBq/L. The treated water was divided into 100 mL aliquots to provide three treatments for incubation at 5 and 25 °C. Two replicates of each treatment were incubated in (1) light (aerobic), (2) dark (aerobic), and (3) dark flushed with He (anaerobic, 5 °C only) conditions. The aerobic treatments at 25 °C were fitted with potassium hydroxide (0.5 N) traps to absorb $^{14}CO_2$ and volatile degradation products. Air flow in the continuously aerated treatments was maintained from compressed air at a flow rate of 5−10 cm^3/min. The intensity of the cool white, fluorescent lights (GE F48T12/HO at 5 °C and Sylvania FT2T12/VHO at 25 °C) in the incubators was measured with a Li-Cor LI-188B integrating quantum radiometer photometer (Li-Cor, Inc., Lincoln NE). Photosynthetically active light intensity at 48 cm (midpoint of samples) was 66.9 ± 0.02 microEinsteins m^{-1} s^{-1} at 5 °C and 188.4 ± 9.4 microEinsteins m^{-1} s^{-1} at 25 °C. Spectral radiant power curves for fluorescent lamps have peak intensities at about 410, 440, 550, and 580 nm (Campbell et al., 1975). Dark and anaerobic treatments were protected from light by wrapping the containers in duct tape. Aerobic containers without air flow were closed with a polyurethane foam stopper, and samples were aerated twice each week by manual mixing. Anaerobic samples were sealed with a rubber septum, and oxygen content was determined weekly by sampling the head space with a gastight syringe and injecting into a gas chromatograph (Varian 3300, Varian Canada Inc., Georgetown, ON) fitted with a 5 Å molecular sieve column and thermal conductivity detector.

Individual samples (25 mL) of water were sterilized in an autoclave at 104 kPa for 18 min at 121 °C. Radiolabeled chlorimuron, in 1 mL of acetone, was added aseptically to each sample to provide a concentration of 0.2 mg/L (69 kBq/L). Sufficient samples were incubated at 5 and 25 °C to provide two replicates for analysis at each sampling date. Containers were closed with a polyurethane foam stopper to allow air exchange.

Evaporative losses from the treatments were adjusted prior to sampling by adding sterilized, distilled water to reach a predetermined weight.

Analysis of Water. Treatments were sampled at selected times for microbial enumeration and chemical analysis. At each sampling a 1 mL aliquot from each treatment was added directly to 10 mL of Ecolite scintillation fluor (ICN Biomedicals Canada Ltd., Mississauga, ON) and counted for 10 min in a Beckman Model LS1800 liquid scintillation counter (Beckman Instruments Inc., Toronto, ON) to determine total carbon-14 recovery. Count efficiency was determined by adding an internal standard of known radioactivity to selected samples and recounting.

A second 1 mL aliquot of each sample was added to a cyclohexyl C_6 Sep-Pak column (Bakerbond catalog no. 7212-03) preconditioned with 3 mL of methanol and three 1 mL aliquots of distilled water. After addition of the sample, the column was washed with 1.5 mL of distilled water, dried, and eluted with 3.5 mL of methanol (methanol eluate). The aqueous eluate from sample addition and the water wash were combined with 10 mL of Ecolite scintillation fluor. The methanol eluate was also added to 10 mL of Ecolite scintillation fluor. Carbon-14 in the water and methanol eluates was detected by LSC (10 min counts).

Soil Characterization. Soil (Granby sl) was collected from the Harrow Research Centre and stored at 5 °C without further preparation. Carbon content, pH, texture, and moisture tension release curve were determined using standard procedures. Carbon was determined on a Leco CR12 carbon determinator (Leco Corp., St. Joseph, MI). The pH was measured as a paste consistency with a Corning Model 130 pH-meter (Fisher Scientific Inc., Nepean, ON).

Treatment of Soil. Aliquots of the phenyl- or pyrimidine-^{14}C-labeled chlorimuron and unlabeled chlorimuron in acetone were added to 100 mL of water to provide a concentration in soil of 0.7 mg/kg and radioactivity of 77.3 kBq/kg. The samples were adjusted to 20% moisture content (85% field capacity), divided into two replicates, and incubated at (1) 5 and (2) 25 °C in the dark with air flow to measure $^{14}CO_2$ evolution and volatile degradation products retained in 0.5 N KOH. Soil for a third treatment was steam sterilized on three separate days at 120 °C and 104 kPa for 18 min. Chlorimuron was added aseptically to provide a concentration and activity similar to those of the unsterilized treatments.

Analysis of Soil. *Extractable Residues.* Soil was extracted for 1 h on a rotary shaker (New Brunswick Scientific Inc., Model V, New Brunswick, NJ) with a 1:1 mixture of methanol/0.1 N NaOH at a soil/solution ratio of 1:4 (Reddy et al., 1995). Methanol in the extract was removed by evaporation, the pH adjusted to <3, and the volume brought to 100 mL with distilled, deionized water. The samples were filtered (Whatman 934-AH glass microfibre filters, catalog no. 1827-090) to remove the precipitated humic acids before volume adjustment. A 1 mL aliquot of the extractant was added to 10 mL of Ecolite scintillation fluor to determine total extracted radioactivity. The extracts were added to a C_6 Sep-Pak column preconditioned with methanol and distilled water. After loading, the column was dried and eluted with 3.5 mL of methanol. The water and methanol eluates were adjusted to 5 and 4 mL, respectively, and a 1 mL aliquot was added to 10 mL of Ecolite fluor. A sample of the unextracted soil at each sampling date was stored at −10 °C for combustion analysis.

Nonextractable Residues. Soil at each sampling time was dried and analyzed in a Harvey Biological oxidizer (Model OX-600, R. J. Harvey Instrument Corp., Hillsdale, NJ) for total ^{14}C content. Carbon dioxide was trapped in 10 mL of Carbosorb E and mixed with 10 mL of Permafluor E+ (Packard Instrument Co. Inc., Downers Grove, IL) for LSC. Recovery averaged 95 ± 2 and 89 ± 1% for phenyl- and pyrimidine-^{14}C-

labeled chlorimuron, respectively. Unextracted radioactivity was the difference between activity in soil before and after extraction.

Chlorimuron Mineralization. The nonsterile treatment at 25 °C was fitted with an alkali trap (0.5 N KOH) to absorb volatilized $^{14}CO_2$ resulting from microbial degradation of chlorimuron. Continuous air flow (5−10 cm^3/min) was maintained over the soil by compressed air. At selected sampling times a 1 mL aliquot of the trap solution was removed for ^{14}C analysis in 10 mL of Ultima-Flo AF (Packard Instrument Co.) by LSC.

TLC. A 3 mL aliquot from each water sample was partitioned on a C_6 cyclohexyl column using the above procedure; the column eluates were analyzed by TLC to determine unchanged chlorimuron and degradation products. The methanol eluate was reduced to dryness and the residue dissolved in acetone (0.25 mL). Soil extracts were reduced to dryness on a rotary evaporator, and the residue was dissolved in acetone. For both water and soil, these acetone solutions were transferred by syringe to Polygram Sil G/UV254 precoated plates (Mandel Scientific Co. Ltd., Guelph, ON; Part No. 805023). Unlabeled reference compounds [chlorimuron, saccharin, aminosulfonyl benzoate, a pyrimidine amine analog [2-(4-chloro-6-methyl)pyrimidine amine]] and a degraded chlorimuron standard in ethanol (Sabadie, 1995) were added to each plate to provide chromatographic comparison. The plates were developed to 10 cm in a chromatography tank with acetonitrile/ethyl acetate/formic acid, 150:50:1.5 (v/v/v), or methylene chloride/methanol/ammonium hydroxide, 144:50:6 (v/v/v) (Anderson and Dulka, 1985), as developing solvents. After development, the chromatography plates were viewed at 254 nm with a UV lamp to identify location of the reference standards and separated into their corresponding sections. Each section was placed in scintillation vials with 10 mL of Ecolite fluor, and radioactivity was determined by LSC. Reference standards for the hydrolysis products of chlorimuron (pyrimidine amine and ethyl benzoate sulfonamide) were not available, but R_f was determined from TLC of the corresponding radiolabeled aged chlorimuron standard in ethanol. Three compounds identified as chlorimuron, pyrimidine amine, and ethyl benzoate sulfonamide were identified by viewing the developed plates at 254 nm with a UV lamp and sectioning of the respective areas for quantification by LSC. Chlorimuron, like sulfometuron methyl, is rapidly hydrolyzed in ethanol and methanol to form a carbamate alcoholysis product with ethyl benzoate sulfonamide (Sabadie and Bastide, 1990; Sabadie, 1995).

RESULTS AND DISCUSSION

The water had a pH of 7.45 and hardness of 110 mg of $CaCO_3$/L. Bacteria, actinomycetes, and fungi were present in the water at 10^2, 10^1, and 0 colony forming units (cfu), respectively. Reanalysis of the water before addition of test substance showed no change in pH, hardness, or microbial numbers, except fungi were detected at 10^1 cfu. During the study, total plate counts for bacteria in the water varied from 1.3×10^2 to 2.9×10^5 cfu depending upon storage and treatment conditions. No microorganisms were detected in the sterile treatments in any of the samplings.

Radiochemical purity of the test substance was determined by TLC and LSC. Analysis by TLC with acetonitrile/ethyl acetate/formic acid solvent (solvent 1) found >95% of the phenyl- and pyrimidine-^{14}C-labeled chlorimuron associated with the test substance at R_f 0.77 (Table 1). In this solvent system the pyrimidine amine hydrolysis product of chlorimuron chromatographed at an R_f 0.74. The corresponding pyrimidine amine analog, which had a methyl instead of methoxy group at position 6 of the pyrimidine ring, had an R_f 0.54. The ethyl benzoate sulfonamide, saccharin, and benzoate sullfonamide products cochromatographed at an R_f similar to that of chlorimuron (0.76). In solvent 2 (methylene chloride/methanol/ammonium hydroxide), chlorimuron had an R_f 0.62, with the pyrimidine amine, pyrimidine amine analog, ethyl benzoate sulfonamide, saccharin, and benzoate sulfonamide appearing at R_f 0.84, 0.83, 0.52, 0.39, and 0.10, respectively.

Table 1. R_f for Chlorimuron and Selected Degradation Products (Figure 1) in Two Solvent Systems[a] on Polygram Sil G/UV 254 Precoated Plates

compound	solvent 1	solvent 2
chlorimuron	0.77	0.62
pyrimidine amine	0.74	0.84
pyrimidine amine analog	0.54	0.83
ethyl benzoate sulfonamide	0.76	0.52
benzoate sulfonamide	0.76	0.10
saccharin	0.76	0.39

[a] Solvent 1, acetonitrile/ethyl acetate/formic acid (150:50:1.5, v/v/v); solvent 2, methylene chloride/methanol/ammonium hydroxide (144:50:6, v/v/v).

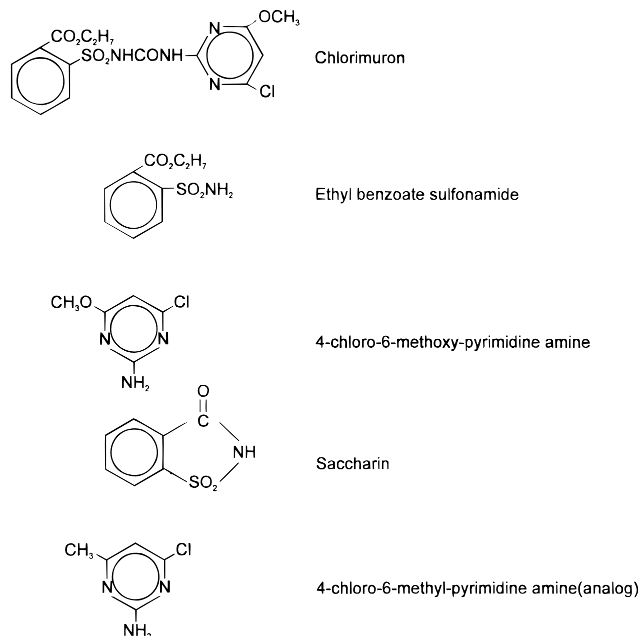

Figure 1. Chlorimuron, suggested degradation products, and pyrimidine amine analog structures.

Chlorimuron Dissipation in Water. At all sampling dates, radioactivity was quantitatively recovered from all water treatments incubated at 5 and 25 °C (Figure 2). Recovery of radioactivity ranged from 94 to 114% from the water treatments incubated at the two temperatures with no significant differences among treatments or time of incubation. Mineralization of chlorimuron to CO_2 was <1% of added radioactivity measured up to 112 days from the nonsterile treatment with light at 25 °C. Microorganisms were absent from the sterile treatment when tested with the various growth media.

The methanol eluate from the C_6 column contained 98−100% of the radioactivity from all water treatments incubated at the two temperatures (Tables 2 and 3). Chlorimuron eluted in the methanol fraction. The water eluate contained <2% of the radioactivity with greater amounts in treatments incubated at 25 °C than at 5 °C. The quantitative recovery of radioactivity from the water treatments indicates mineralization of chlorimuron did not occur in any of the treatments.

The methanol eluate from the treatments at 5 and 25 °C for all samples up to 112 days of incubation were

Table 2. Radioactivity Recovered (Percent of Total) from Chlorimuron in Water after 112 Days of Incubation at 5 °C ($n = 2$)

	recovery		water		methanol		chlorimuron	
treatment	Pyr[a]	Phe	Pyr	Phe	Pyr	Phe	Pyr	Phe
light/nonsterile	105	109	0.1	0.2	100	100	96	95
dark/nonsterile	105	109	0.2	0.1	100	100	95	95
light/sterile	99	103	0.2	0.2	100	100	94	95
anaerobic/nonsterile	105	104	0.1	0.3	100	100	97	96

	probability > F			
test variable	recovery	water	methanol	chlorimuron
treatment (T)	0.04	NS[b]	NS	0.08
label (L)	0.09	NS	NS	NS
T × L	NS	<0.01	<0.01	NS

[a] Pyr, [*pyrimidine*-^{14}C]chlorimuron; Phe, [*phenyl*-^{14}C]chlorimuron. [b] NS, F statistic > 0.10.

Table 3. Radioactivity, Chlorimuron, and Metabolites Recovered (Percent of Total) from Water after 112 Days of Incubation at 25 °C ($n = 2$)

	recovery		water		methanol		chlorimuron		hydrolysis products[a]		saccharin	
treatment	Pyr[a]	Phe	Pyr	Phe	Pyr	Phe	Pyr	Phe	Pyr	Phe	Pyr	Phe
light/nonsterile	103	104	1.7	0.4	99	100	85	86	4	2	NA[b]	6
dark/nonsterile	105	106	0.3	0.4	100	100	91	83	5	1	NA	12
light/sterile	95	100	1.9	1.3	98	99	82	76	11	3	NA	15

	probability > F					
test variable	recovery	water	methanol	chlorimuron	hydrolysis products	saccharin
treatment (T)	<0.01	0.07	0.07	<0.01	<0.01	NS
label (L)	0.09	NS[c]	NS	0.02	<0.01	NA
T × L	NS	NS	NS	NS	0.03	NA

[a] Pyr, [*pyrimidine*-^{14}C]chlorimuron; Phe, [*phenyl*-^{14}C]chlorimuron. [b] NA, not applicable. [c] NS, F statistic > 0.10.

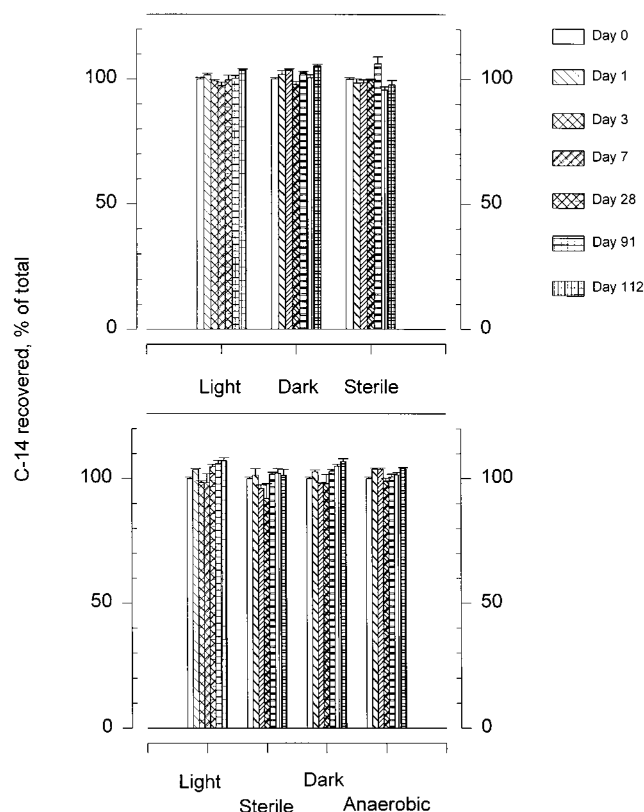

Figure 2. Recovery of radioactivity from chlorimuron in water at 25 (top) and 5 °C (bottom). Vertical bars = standard error ($n = 2$).

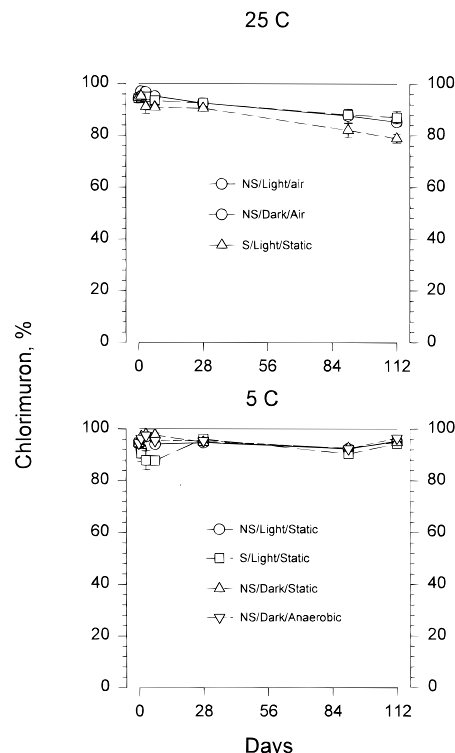

Figure 3. Chlorimuron dissipation in water at 25 (top) and 5 °C (bottom). Vertical bars = standard error ($n = 2$).

subject to TLC using solvent system 2. The concentration of chlorimuron decreased with incubation time at 25 °C (Figure 3). TLC of the treatments at 25 °C sampled at 112 days identified 76−91% of the radioactivity as intact chlorimuron (Table 3). Loss of chlorimuron at 5 °C was <7% after 112 days (Table 2). At 25 °C, the proportion of intact chlorimuron was larger ($P = 0.02$) from the treatments receiving the chlorimuron labeled in the pyrimidine moiety (86%) compared to that which was phenyl labeled (82%). This may be because the pyrimidine amine hydrolysis metabolite of chlorimuron further degrades to products that may cochro-

Table 4. Chlorimuron and Metabolites Recovered (Percent of Total) from Water after Incubation for 112 Days at 5 °C (n = 2)

	light/nonsterile		dark/nonsterile		light/sterile		anaerobic/nonsterile		probability > F		
product	Pyr[a]	Phe	Pyr	Phe	Pyr	Phe	Pyr	Phe	treatment (T)	label (L)	T × L
chlorimuron	96	95	95	95	94	95	97	96	0.08	NS	NS
hydrolysis products[b]	3	1	2	1	4	2	2	1	NS[c]	<0.01	NS
saccharin	NA[d]	2	NA	2	NA	2	NA	2	NS	NA	NA

[a] Pyr, [*pyrimidine*-^{14}C]chlorimuron; Phe, [*phenyl*-^{14}C]chlorimuron. [b] Pyrimidine amine for [*pyrimidine*-^{14}C]chlorimuron, ethyl benzoate sulfonamide for [*phenyl*-^{14}C]chlorimuron. [c] NS, F statistic > 0.10. [d] NA, not applicable.

Table 5. Slope, Intercept, R Square (R^2), F Statistic, and Half-Life ($t_{1/2}$) for Linear Regression of Chlorimuron Dissipation in Water Incubated at 25 °C

treatment	slope	intercept	R^2	$P > F$	$t_{1/2}$[a]	CI[b]
light/nonsterile	−0.095 ± 0.009	96	0.95	<0.01	526	420−704
dark/nonsterile	−0.069 ± 0.004	95	0.99	<0.01	725	611−833
light/sterile	−0.129 ± 0.014	94	0.95	<0.01	388	305−532

[a] $t_{1/2}$ (days) = 50/slope. [b] CI, 95% confidence interval.

Table 6. Extracted Radioactive Carbon-14 (Percent of Total) from Granby sl after 0 and 56 Days of Incubation with Chlorimuron [Proportion of Total Radioactivity Recovered in the Water and Methanol Eluate from a Cyclohexyl Column (n = 2)]

treatment	days	extracted	water	methanol
sterile/25 °C	0	107	6	94
	56	90	36	64
nonsterile/25 °	0	103	8	92
	56	57	37	63
nonsterile/5 °C	0	104	8	94
	56	85	16	84

	probability > F		
test variable	extracted	water	methanol
treatment (T)	<0.01	0.05	0.05
days (D)	<0.01	<0.01	<0.01
T × D	<0.01	0.03	0.03

matograph with chlorimuron (Table 3). This is evidenced by the sum of saccharin and ethyl benzoate sulfonamide from phenyl-^{14}C-labeled chlorimuron being greater (P < 0.01) than the proportion of pyrimidine amine from pyrimidine-^{14}C-labeled chlorimuron (Table 3). Harvey et al. (1985) reported that the hydrolysis products of sulfometuron methyl produced many unidentified metabolites never exceeding 10% of the total radioactivity in solution.

The major products identified in the methanol eluate of the water samples were the hydrolysis products of chlorimuron (pyrimidine amine and ethyl benzoate sulfonamide), saccharin, and intact chlorimuron (Table 3). Saccharin was detected in all treatments with the phenyl-^{14}C-labeled chlorimuron because it forms from cyclization of the ethyl benzoate sulfonamide (Harvey et al., 1985). There was no difference in the amount of saccharin recovered from the nonsterile and sterile treatments at 25 °C, but more pyrimidine amine (P < 0.03) was recovered from the sterile than nonsterile treatment, indicating that microorganisms are involved in dissipation of this product. Previous studies have indicated that saccharin but not chlorimuron is utilized by microorganisms (Harvey et al., 1985). Sabadie (1995) also reported that the hydrolysis of chlorimuron involved only the sulfonylurea group.

A dissipation rate for chlorimuron was calculated at 25 °C from the regression of chlorimuron with time (Figure 3). The rate of disappearance of chlorimuron was zero order (R^2 > 0.95) with the rate constant ranging from −0.069 to −0.129%/day (Table 5). No improvement in R^2 was noted when the rate of dissipation was fitted to the first-order rate expression. Light may have affected the rate of dissipation of chlorimuron since dissipation was faster in the sterile than in the dark/nonsterile treatment. From these rate constants, it was estimated that the half-life of chlorimuron in water at 25 °C ranged from 388 days in the sterile treatment with light to 725 days in the dark/nonsterile treatment. Half-life for chlorimuron dissipation at 5 °C would be >800 days.

Soil Properties. The soil had organic carbon content of 1.2%, pH 5.05, and sand, silt, and clay contents of 72.5, 17.7, and 9.8%, respectively. Water content at field capacity was 25%. Total microorganisms averaged 7.2×10^5 and 3.4×10^5 cfu prior to and after initiation of the study, respectively. No microorganisms were detected in the sterile treatment at any time during the study. The extraction procedure without soil resulted in 100% recovery of radioactivity added but 25% loss of

Table 7. Proportion (Percent of Total) of Radioactive Carbon-14 Products from Granby sl after 0 and 56 Days of Incubation with Chlorimuron

treatment	days	chlorimuron	metabolites[a]	saccharin	unextracted
sterile/25 °C	0	63	16	8	−11
	56	6	17	17	4
nonsterile/25 °C	0	57	23	4	2
	56	4	4	39	23
nonsterile/5 °C	0	57	23	4	1
	56	10	11	39	8

	probability > F			
test variable	chlorimuron	metabolites[a]	saccharin	unextracted
treatment (T)	NS[b]	NS	0.05	<0.01
days (D)	<0.01	<0.01	<0.01	<0.01
T × D	NS	<0.01	<0.01	NS

[a] Pyrimidine amine or ethyl benzoate sulfonamide. [b] NS, F statistic > 0.10.

Table 8. Slope, Intercept, R Square (R^2), F Statistic, and Half-Life ($t_{1/2}$) for First-Order Linear Regression of Chlorimuron Dissipation in Granby sl Incubated at 5 and 25 °C

variable	treatment	slope	intercept	R^2	$t_{1/2}$[a]	CI[b]
extracted	sterile/25 °C	−0.003 ± 0.002	100	0.40	231	87−347
	nonsterile/25 °C	−0.010 ± 0.001	98	0.97**[c]	69	58−99
	nonsterile/5 °C	−0.003 ± 0.002	99	0.28	231	87−231
chlorimuron	sterile/25 °C	−0.041 ± 0.008	85	0.86**	17	11−39
	nonsterile/25 °C	−0.052 ± 0.004	66	0.98**	13	11−17
	nonsterile/5 °C	−0.032 ± 0.008	87	0.80*	22	13−69

[a] $t_{1/2}$ (days) = −0.693/slope. [b] CI, 95% confidence interval (days). [c] *, **, significant at 0.05 and 0.01 probability, respectively.

chlorimuron as a result of hydrolysis of the sulfonylurea bridge in the extraction. Sabadie (1995) reported that chlorimuron is hydrolyzed in methanol to form the alcoholysis product, ethyl benzoate sulfonamide methyl carbamate. In soil, 100% of the radioactivity was extracted by the procedure but 57−63% of the radioactivity coeluted with chlorimuron at day 0 (Tables 6 and 7).

Chlorimuron Recovery from Soil. Statistical analysis of the data found no significant differences between the phenyl- and pyrimidine-^{14}C-labeled chlorimuron for extraction, proportion of radioactivity in the water or methanol eluate from the C_6 column, intact chlorimuron, or hydrolysis products. No measurable loss of extractable radioactivity was detected from the nonsterile treatment at 5 °C or the sterile treatment at 25 °C up to 56 days for either the phenyl- or pyrimidine-^{14}C-labeled chlorimuron (Figure 4; Table 8). A smaller proportion of radioacitivity (57 vs 85% of added radioactivity) was extracted from nonsterile soil at 25 °C than at 5 °C, respectively (Table 6). Thus, the rate of decrease in extractable radioactivity was greater at 25 °C than at 5 °C (Table 8). Fuesler and Hanafey (1990) reported that a decrease in temperature reduced the rate of degradation of chlorimuron in soil. More unextracted radioactivity (23%) was measured from nonsterile soil incubated at 25 °C than from the other treatments (Table 6). Three to 5% of the phenyl- or pyrimidine-^{14}C-labeled chlorimuron from the nonsterile soil treatment was recovered as CO_2. Radioactive carbon dioxide evolution was found in the nonsterile treatment which received chlorimuron labeled in the phenyl or pyrimidine group, indicating both hydrolysis products were susceptible to mineralization by microorganisms.

The cyclohexyl column retained 63−94% of the total radioactivity in the soil extracts (Figure 4). Only 6% of the radioactivity in the soil extracts was unretained by the cyclohexyl column at time of treatment. The proportion of radioactivity unretained by the cyclohexyl column increased with time of incubation of the treatments (Figure 4). The aqueous eluate of the extract from the nonsterile and sterile treatments incubated at 25 °C contained 37 and 36%, respectively, of the extracted radioactivity after 56 days. Lesser amounts (16%) were found in this fraction from the nonsterile treatment at 5 °C. No saccharin (R_f 0.36) or other identifiable metabolites were detected in the aqueous eluate by TLC using solvent mix 1 or 2.

TLC of the methanol eluate of the soil extracts at 56 days revealed a compound at R_f 0.51 for phenyl-labeled chlorimuron and R_f 0.87 for pyrimidine-labeled chlorimuron in addition to chlorimuron (R_f 0.61) using solvent mix 2. Chlorimuron is hydrolyzed in acid soil to ethyl benzoate sulfonamide and pyrimidine amine (Fuesler and Hanafey, 1990; Brown, 1990). Saccharin (39%) was detected in the nonsterile treatments at 5 and 25 °C and in the sterile treatment (17%) after 56 days (Table 7). Saccharin is formed quantitatively from the alkyl benzoate sulfonamide (Fuesler and Hanafey, 1990). Fuesler and Hanafey (1990) identified demethylchlorimuron and saccharin in nonsterile, moist soil treated with chlorimuron.

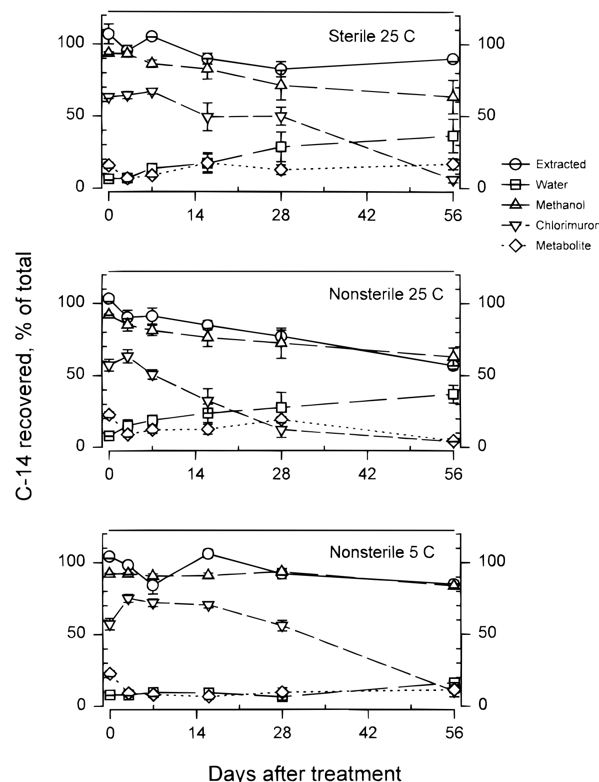

Figure 4. Total radioactivity recovered from sterile and nonsterile Granby sl soil incubated at 5 and 25 °C: proportion of carbon-14 in the extract as intact chlorimuron and its hydrolysis metabolites (pyrimidine amine or ethyl benzoate sulfonamide) in the methanol eluate from a cyclohexyl column and proportion of total carbon-14 in the water and methanol eluate from a cyclohexyl column. Vertical lines represent standard error of the mean (n = 2).

The time for loss of half of the radioactivity (half-life) from the soil was determined by regression of radioactivity or chlorimuron in the soil extracts with time. Chlorimuron dissipation in soil was best described by first-order reaction kinetics, although little improvement in R^2 was found between the zero- and first-order kinetics models. Half-life was calculated as the ratio of −0.693 and the coefficient of regression (slope). No significant change in extractable radioactivity was detected at 5 °C or in the sterile treatment (Table 8). The half-life for extractable radioactivity was 69 days at 25 °C in nonsterile soil.

The half-life for chlorimuron was estimated to be 13 and 17 days, respectively, in nonsterile and sterile soil at 25 °C and 22 days in nonsterile soil at 5 °C (Table

8). These estimates for loss of chlorimuron in soil agree with previously reported results for chlorimuron in field and laboratory studies (Schroeder, 1994; Vencill and Banks, 1994). Reddy et al. (1995) reported a half-life for chlorimuron in soil of >2 months.

CONCLUSION

Chlorimuron appears to be fairly stable to microbial mineralization at the alkaline pH of this water as evidenced by the quantitative recoveries of radioactivity and absence of $^{14}CO_2$ evolution. The main mode of dissipation appears to be chemical hydrolysis of the sulfonylurea bridge followed by slow microbial degradation of the hydrolysis products. Pyrimidine amine appears to be less stable than the ethyl benzoate sulfonamide hydrolysis product, which cyclizes to saccharin. The estimated degradation rate of chlorimuron in the water at 25 °C was calculated to be 0.095%/day with little or no dissipation at 5 °C (<7% loss in 112 days). At this rate of dissipation it is estimated that chlorimuron in water at 25 °C and pH >7 would have a half-life of 526 days. Venkatesh et al. (1993) reported a half-life of 107 days for chlorimuron dissipation at 30 °C in a photolysis tube without photosensitizers. Sabadie (1995) found faster dissipation of chlorimuron at pH <8 than at greater pH. Harvey et al. (1985) reported that sulfometuron methyl was stable in water at pH 7 or 9 (87−91% intact herbicide recovered after 30 days) but rapidly degraded at pH 5 (22% recovered after 30 days). The water used in this study had pH >7 after treatment with chlorimuron; thus, dissipation of chlorimuron would be expected to be slow. The loss of radioactivity identifiable as chlorimuron in the methanol eluate suggests this compound undergoes alteration, but the degradation products were nonpolar since little radioactivity was found in the aqueous eluate from the cyclohexyl column.

In sterile and nonsterile soil, chlorimuron was rapidly altered to polar and nonpolar products. The time for chlorimuron to be reduced to 50% of its initial concentration was 13 days in nonsterile soil and 17 days in sterile soil at 25 °C. A slower rate of dissipation was measured at 5 °C, which conforms to previously reported studies (Fuesler and Hanafey, 1990). The metabolites from chlorimuron are mineralized to CO_2, and extractability decreases with time as reported for this and other sulfonylurea herbicides (Reddy et al., 1995; Brown, 1990).

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