

Degradation of the Sulfonylurea Herbicide [¹⁴C]Amidosulfuron (HOE 075032) in Saskatchewan Soils under Laboratory Conditions

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The degradation of the herbicide [¹⁴C]amidosulfuron (HOE 075032) was studied in three Saskatchewan soils at 0.1 µg/g under controlled temperature and moisture conditions. At 85% of field capacity, degradation approximated to first-order kinetics at soil temperatures of 10, 20, and 30 °C, with half-life values ranging from 14 ± 2 days (mean and standard deviation) in a loamy sand incubated at 30 °C to 231 ± 41 days in a clay at 10 °C. In a clay at 20 °C, herbicide degradation followed first-order kinetics and was directly correlated with soil moisture, with half-life values varying from 246 ± 21 days at 50% of field capacity to 63 ± 7 days at 100%. There was negligible herbicide breakdown in air-dried soils incubated at 30 °C for 70 days. During the study period, solvent-extractable ¹⁴C degradation products accounted for up to 48% of the applied radioactivity. Solvent-nonextractable radioactivity associated with the soils incubated at 20 °C ranged from 4 to 11% of the initial treatment.

INTRODUCTION

The sulfonylurea herbicide amidosulfuron, also referred to as HOE 075032 [Figure 1, R = CH₃; 3-(4,6-dimethoxy-pyrimidin-2-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea] is currently being evaluated in Canada at rates up to 45 g/ha for the postemergence control of broadleaf weeds in cereal and other crops.

As with other sulfonylurea herbicides (Beyer et al., 1988), the water solubility is pH dependent. In aqueous media, at 20 °C, the solubility of amidosulfuron is 3.3, 9.0, and 13 500 mg/L at pH values of 3, 5.8, and 10, respectively (Technical Information HOE 075032 Experimental Herbicide, 1990). Amidosulfuron is relatively nonvolatile with a vapor pressure of 1.3 × 10⁻⁶ Pa at 20 °C (Technical Information HOE 075032 Experimental Herbicide, 1990). Amidosulfuron undergoes degradation in the soil, presumably by both microbiological and chemical mechanisms similar to those reported for other sulfonylurea herbicides (Joshi et al., 1985; Beyer et al., 1988; Brown, 1990; Cambon et al., 1992), for which the demethylated product [Figure 1, R = H; 3-(6-hydroxy-4-methoxypyrimidin-2-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea] has been identified as a breakdown product (Technical Information HOE 075032 Experimental Herbicide, 1990).

The objectives of the present laboratory studies were to determine the rates of breakdown and fate of [¹⁴C]-amidosulfuron in three Saskatchewan soils at 85% of field capacity and at 10, 20, and 30 °C. The rates of breakdown of [¹⁴C]amidosulfuron in a clay at 20 °C and at 50, 65, 85, and 100% of field capacity were also studied.

MATERIALS AND METHODS

Soils. Three soils were used in the laboratory persistence studies: a Udic Boroll clay from Indian Head, a Typic Boroll clay from Regina, and a Typic Boroll loamy sand from White City (all located in Saskatchewan). All soils were collected from the 0-5-cm soil horizon during September 1991. The soils were screened through a 2-mm sieve and stored in plastic sacks at 4 ± 1 °C until October 1991, when the studies were initiated. Physical characteristics of the soils were determined by the Saskatchewan Soil Testing Laboratory (Saskatoon, SK, Canada) and are summarized in Table I.

Chemicals. 3-(4,6-Dimethoxypyrimidin-[2-¹⁴C]-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea was obtained from

Hoechst Aktiengesellschaft (Frankfurt am Main, Germany) with a specific activity of 2.57 MBq/mg and a radiochemical purity >96% as determined by thin-layer chromatographic (TLC) and radiochemical analysis (see later). The [¹⁴C]amidosulfuron was dissolved in 95% ethanol to give a solution with 422 kBq/mL and containing 164 µg of amidosulfuron/mL. Analytical samples (>99% pure) of nonradioactive amidosulfuron and the soil degradation product (cf. Figure 1) were also provided by Hoechst Aktiengesellschaft. For TLC purposes, a solution of the former was prepared in acetone (2 mg/mL), while a solution of the latter (2 mg/mL) was prepared using a mixture of water and acetonitrile (3:1 v/v) as solvent.

Degradation Studies. Samples (50 g) of all three soils at 85% of their field capacities (FC) were weighed into 175-mL polystyrene foam cartons fitted with plastic lids and incubated in the dark at 10 ± 1, 20 ± 1, or 30 ± 1 °C for 7 days prior to addition of [¹⁴C]amidosulfuron. An additional series of samples of the Regina clay at 50, 65, and 100% FC were similarly prepared and incubated at 20 ± 1 °C. All incubations were carried out in laboratory incubators (Conviro Products Co., Winnipeg, MB, Canada). The cartons were weighed every 2 days, and distilled water was added as necessary, with stirring, to replace lost moisture. Following the preliminary incubation, [¹⁴C]amidosulfuron (30 µL, 12.7 kBq, 4.92 µg of herbicide) was added to each carton. This concentration of 0.1 µg/g, based on moist soil, is approximately equivalent to a field rate of 50 g/ha assuming that, under field conditions, the chemical is distributed in the top 5 cm of soil (Smith et al., 1990). The soils were thoroughly stirred with a spatula to distribute the herbicide, and the cartons were capped and reincubated at the required temperatures. Water was added, by weight with stirring, as necessary, to replace moisture lost by evaporation. For control purposes, to assess nonbiological degradation and soil extraction recoveries, air-dried (<10% of FC) samples of all soils (40 g) were fortified with [¹⁴C]-amidosulfuron (30 µL, 4.92 µg) and incubated in the dark at 30 ± 1 °C. Samples (40 g) of air-dry White City loamy sand were similarly treated and incubated in the dark at 20 ± 1 °C.

Extraction and Analysis of Soils Incubated at 20 °C and 85% FC. Aqueous acidic acetonitrile, in conjunction with an extended shaking, was used since such a procedure has proved reproducibly efficient for the recovery of a variety of herbicide residues from both laboratory and aged field soils (Smith, 1992). Excellent recoveries of the sulfonylurea herbicides chlorsulfuron and metsulfuron-methyl from treated Saskatchewan soils have been reported using such an extraction protocol, with the herbicides then being partitionable into methylene chloride (Smith and Hsiao, 1985; Smith, 1986). Thus, after 7, 14 (omitted for the Regina clay), 28, 56, and 84 days, triplicate soil samples were analyzed by transferring the soil from each carton to a 250-

Table I. Composition and Physical Characteristics of Soils

location	soil type	composition, %			organic content, %	pH	cec, mequiv/100 g	cond, ms/cm	field capacity, ^a %
		clay	sand	silt					
Indian Head	clay	48	22	30	3.7	7.6	36	0.6	38
Regina	clay	62	2	36	3.3	7.5	52	1.0	40
White City	loamy sand	11	80	9	1.6	7.3	10	0.4	15

^a Percent moisture (w/w) at 5 kPa suction.

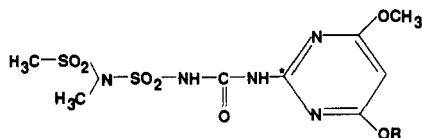


Figure 1. Structure of amidosulfuron (R = CH₃) and the demethylated soil degradation product (R = H). The position of the ¹⁴C label is indicated by the asterisk.

mL glass-stoppered flask and the cartons rinsed with sufficient extraction solvent (acetonitrile/water/glacial acetic acid 80:20:2.5 v/v/v) so that the total volume of solvent, together with the water present in the moist soils, was equal to 100 mL. The rinsing was added to the flask, and flask and contents were shaken on a mechanical shaker for 1 h. The soil was then allowed to remain in contact with the extraction solution overnight before being shaken for a further 1-h period. After settling, samples were centrifuged (3500 rpm for 5 min) and aliquots (4 mL) analyzed for radioactivity remaining. A portion of the clear extract (25 mL, equivalent to 10 g of moist soil) was evaporated to dryness at 40 °C using a rotary evaporator and the residue dissolved in methanol (25 mL), an aliquot of which (4 mL) was analyzed for radioactivity. The remaining methanol was transferred to a 50-mL tapered glass tube and evaporated at 40 °C to <0.5 mL using a stream of dry nitrogen. These extracts were then examined by TLC using two different solvent systems and any ¹⁴C products present quantified by radiochemical analysis.

After solvent extraction, the soil was collected by vacuum filtration and successively washed with extraction solvent (100 mL), methanol (50 mL), and acetone (50 mL). All washings were discarded since they contained negligible amounts of radioactivity. The soils were dried at 80 °C for 2 h, and triplicate samples (1 g) of each soil were assayed for radioactivity by combustion analysis.

Triplicate samples of the air-dry White City loamy sand incubated at 20 ± 1 °C with [¹⁴C]amidosulfuron were analyzed, as described above, after 84 days.

Solvent recoveries of radioactivity from triplicate samples (40 g) of all three air-dried soils (<10% FC), fortified 48 h previously with [¹⁴C]amidosulfuron at the 0.12 µg/g level, were 99 ± 1, 95 ± 0, and 100 ± 3% from the Indian Head clay, Regina clay, and White City loamy sand, respectively. Evaporation of the centrifuged soil extracts (25 mL) under reduced pressure at 40 °C, followed by thin-layer and radiochemical analysis (see later), indicated all of the radioactivity to be [¹⁴C]amidosulfuron. Similar fortification at the 0.012 µg/g level gave recoveries of 96 ± 2, 95 ± 2, and 93 ± 1%, respectively, from the three soils. Thus, in the persistence studies, zero-time recoveries of [¹⁴C]amidosulfuron were taken as 96 ± 3%, the mean recovery from all three soils at the two rates.

Extraction and Analysis of Soils Incubated at 10 and 30 °C and of Regina Clay Incubated at 20 °C at 50, 65, and 100% FC. Triplicate soil treatments incubated with [¹⁴C]amidosulfuron at 10 ± 1 °C were extracted and analyzed after 28, 63, and 84 days, respectively, while the treatments incubated at 30 ± 1 °C were similarly analyzed after 7, 14 (omitted for Indian Head clay), 21, 28, 42, and 70 days. In the case of the Regina clay, incubated at 20 ± 1 °C and at 50, 65, and 100% FC levels, extraction and analysis were carried out after 28, 56, and 84 days.

The soil from each carton was transferred to a 250-mL glass-stoppered flask and shaken with aqueous acidic acetonitrile exactly as described above. After settling, samples were centrifuged (3500 rpm for 5 min) and aliquots (4 mL) analyzed for radioactivity remaining. A portion of the clear extract (25 mL, equivalent to 10 g of moist soil) was added to 5% aqueous sodium chloride (100 mL) in a 250-mL separatory funnel and extracted

with two portions of methylene chloride (50 mL each). Radioactivity remaining in the aqueous phase was determined by direct assay of a portion (2 mL). Prior experiments indicated that [¹⁴C]-amidosulfuron is quantitatively recovered from extraction solvent/sodium chloride solution with methylene chloride. The organic extracts were combined and evaporated to dryness at 40 °C using a rotary evaporator, and the residue was dissolved in methanol (25 mL), an aliquot of which (4 mL) was analyzed for radioactivity. The remaining methanol was transferred to a 50-mL tapered glass tube and evaporated at 40 °C to <0.5 mL using a stream of dry nitrogen. These extracts were then examined by TLC using two different solvent systems and any ¹⁴C products present quantified by radiochemical analysis.

None of the solvent-extracted soil residues in these studies were examined for associated radioactivity by combustion analysis.

Triplicate analyses of all air-dried soils (<10% FC) incubated for 70 days at 30 ± 1 °C with [¹⁴C]amidosulfuron were conducted as described above.

Calculation and Presentation of Data. For the degradation studies in the three soils at 85% FC and incubated at 20 °C, the solvent-extractable radioactivity was obtained by direct assay of the acetonitrile extractant. Following evaporation of the acetonitrile extracts and the redissolving of the residues in methanol, losses in radioactivity ranged from 0 to 7% with a mean and standard deviation of 3 ± 3%. Such differences were attributed to losses of volatile products on evaporation and the possible inability of methanol to dissolve certain ¹⁴C degradation products from the residue adhering to the glass of the evaporation flask. All calculations of [¹⁴C]amidosulfuron and extractable ¹⁴C degradation products were based on the methanol-extractable radioactivity.

For the 10 and 30 °C data and the data for the Regina clay at different moistures at 20 °C, differences in the amounts of radioactivity extracted by the acetonitrile and that observed in the methanolic solutions ranged from 0 to 5% with a mean and standard deviation of 2 ± 2% in the soils incubated at 10 °C and from 0 to 6% with a mean and standard deviation of 1 ± 2% in the soils incubated at 30 °C. These differences were considered to result from losses of ¹⁴C volatile products on evaporation and the possible inability of methanol to dissolve certain ¹⁴C degradation products from the residue adhering to the glass of the evaporation flask. Total amounts of ¹⁴C degradation products were calculated as that radioactivity not identified as [¹⁴C]-amidosulfuron (from TLC analysis) together with the radioactivity in the aqueous phase following methylene chloride extraction.

Thin-Layer Chromatography. For analysis of the evaporated methanol extracts, TLC plates coated with 0.25 mm of silica gel 60F-254 (E. Merck, Darmstadt, Germany) were used and developed to a height of 10 cm above the origin. After air-drying, the chromatograms were examined using a Berthold automatic TLC linear analyzer (Labserco Ltd., Oakville, ON, Canada). Nonradioactive amidosulfuron and the demethylated degradation product, run for comparative purposes, were identified by viewing the developed chromatograms under a shortwave ultraviolet lamp. The R_f values of the amidosulfuron and the degradation product in a mixture of ethyl acetate/toluene/glacial acetic acid (10:10:1 v/v/v) were 0.68 and 0.13 and in a mixture of acetone/hexane/glacial acetic acid (10:10:1 v/v/v) 0.85 and 0.38, respectively. By comparing the radioactive peak areas from the various chromatogram scans, and knowing the amounts of radioactivity extracted from each soil, one can calculate the amounts of radioactive compounds present in the soil extracts.

Measurement of Radioactivity. Radioactivity in the various solutions was measured using a Packard Tri-Carb 1900 TR liquid

Table II. Radioactivity Recovered with Time from Soils at 85% Field Capacity Treated with 0.10 $\mu\text{g/g}$ [^{14}C]Amidosulfuron following Incubation at 20 $^{\circ}\text{C}$

^{14}C extracted from soil	% of applied radioactivity ^a				
	7 days	14 days	28 days	56 days	84 days
Regina Clay					
solvent extractable	95 \pm 8	nd ^b	89 \pm 1	80 \pm 3	76 \pm 1
methanol soluble	89 \pm 6	nd	84 \pm 1	73 \pm 1	75 \pm 2
amidosulfuron	75 \pm 8	nd	68 \pm 2	54 \pm 1	52 \pm 1
degradation products	14 \pm 2	nd	15 \pm 2	18 \pm 1	18 \pm 2
soil associated	5 \pm 1	nd	8 \pm 0	11 \pm 3	11 \pm 1
total ^{14}C recovered	100 \pm 8	nd	97 \pm 1	91 \pm 3	87 \pm 1
Indian Head Clay					
solvent extractable	97 \pm 1	87 \pm 4	83 \pm 1	73 \pm 0	67 \pm 1
methanol soluble	91 \pm 1	82 \pm 4	81 \pm 4	69 \pm 1	67 \pm 2
amidosulfuron	71 \pm 2	59 \pm 4	50 \pm 2	43 \pm 6	37 \pm 6
degradation products	21 \pm 1	24 \pm 5	30 \pm 2	25 \pm 2	24 \pm 5
soil associated ^c	6 \pm 0	7 \pm 1	9 \pm 0	10 \pm 0	8 \pm 1
total ^{14}C recovered	103 \pm 1	94 \pm 4	92 \pm 1	83 \pm 0	75 \pm 0
White City Loamy Sand					
solvent extractable	93 \pm 4	87 \pm 2	80 \pm 0	68 \pm 2	60 \pm 0 (99 \pm 1) ^d
methanol soluble	93 \pm 3	89 \pm 2	78 \pm 1	62 \pm 2	60 \pm 1 (96 \pm 1)
amidosulfuron	74 \pm 5	54 \pm 5	39 \pm 1	24 \pm 1	23 \pm 2 (86 \pm 1)
degradation products	19 \pm 2	32 \pm 2	40 \pm 3	37 \pm 2	36 \pm 3 (10 \pm 1)
soil associated	4 \pm 1	4 \pm 1	9 \pm 1	10 \pm 1	7 \pm 5 nd
total ^{14}C recovered	97 \pm 4	91 \pm 2	89 \pm 1	78 \pm 2	67 \pm 2 (99 \pm 1)

^a Mean and standard deviation from three replicates. ^b Not determined. ^c Determined by combustion of the solvent-extracted soils. ^d Figures in parentheses represent data obtained from air-dry soils (<10% FC) incubated for 84 days with [^{14}C]amidosulfuron.

scintillation analyzer. Scinti-Verse II (15 mL, Fisher Scientific Co., Fairlawn, NJ) was the scintillation solution, and counting efficiencies were determined using a ^{139}Ba external standard. Radioactivity associated with the solvent-extracted soils was measured by combustion of samples (1 g) in a Harvey biological oxidizer, Model OX500 (R. J. Harvey Instrument Corp., Hillsdale, NJ). Recoveries of ^{14}C as [^{14}C]carbon dioxide from soils fortified with ^{14}C standards, immediately before combustion, were greater than 98%.

RESULTS AND DISCUSSION

As noted, the recoveries of radioactivity from air-dried soils treated with [^{14}C]amidosulfuron (0.12 or 0.012 μg) 48 h prior to extraction ranged from 93 to 100% with a mean of 96 \pm 3%. After 84 days in air-dry White City loamy sand at 20 \pm 1 $^{\circ}\text{C}$, there was quantitative recovery of the applied radioactivity (Table II), with 86 \pm 1% of the applied ^{14}C being identified as [^{14}C]amidosulfuron. Thus, over the 12-week incubation there appeared to be some chemical or possibly biological degradation of the ^{14}C -labeled herbicide in the dry soil. In the air-dried soils incubated for 70 days at 30 \pm 1 $^{\circ}\text{C}$, there was again quantitative recovery of the applied radioactivity (Table IV). Over 90% of the ^{14}C extracted from the two clays, and 82 \pm 3% in the case of the loamy sand, was identified as [^{14}C]amidosulfuron. From these data it was, thus, assumed that the analytical methodology was satisfactory for the recovery of the herbicide from soils.

Breakdown data of [^{14}C]amidosulfuron in the three soils at 85% of FC and at 10, 20, and 30 $^{\circ}\text{C}$ are summarized in Tables II, III, and IV). The studies conducted in the Regina clay at the different moisture levels and at 20 $^{\circ}\text{C}$ are summarized in Table VI. Although it was assumed that herbicide degradation was the result of both chemical and biochemical mechanisms, loss of [^{14}C]amidosulfuron approximated to first-order kinetics with 8 of the 12 R^2 values being >0.89. All others were >0.82, except for the case of the Regina clay incubated at 10 $^{\circ}\text{C}$ for which the R^2 value was 0.70. From the data presented in Tables II–IV and VI, the half-life values (time for 50% of the applied herbicide to be degraded assuming first-order breakdown) were calculated (Tables V and VI).

Table III. Radioactivity Recovered with Time from Soils at 85% Field Capacity Treated with 0.1 $\mu\text{g/g}$ [^{14}C]Amidosulfuron following Incubation at 10 $^{\circ}\text{C}$

^{14}C extracted from soil	% of applied radioactivity ^a		
	28 days	63 days	84 days
Regina Clay			
solvent extractable	98 \pm 3	96 \pm 2	95 \pm 2
amidosulfuron	79 \pm 4	74 \pm 5	77 \pm 4
degradation products	15 \pm 1	17 \pm 0	18 \pm 2
Indian Head Clay			
solvent extractable	98 \pm 1	90 \pm 1	87 \pm 1
amidosulfuron	63 \pm 1	46 \pm 1	45 \pm 3
degradation products	31 \pm 3	43 \pm 1	42 \pm 2
White City Loamy Sand			
solvent extractable	92 \pm 2	84 \pm 2	82 \pm 1
amidosulfuron	50 \pm 4	37 \pm 2	35 \pm 1
degradation products	41 \pm 2	47 \pm 2	48 \pm 0

^a Mean and standard deviation from three replicates.

At each specific temperature, breakdown was fastest in the White City loamy sand and slowest in the Regina clay. In all soils, degradation was temperature dependent, slowest at 10 $^{\circ}\text{C}$ and fastest at 30 $^{\circ}\text{C}$. From the kinetic data of breakdown at the three soil temperatures, the activation energies (Table VII) were calculated (Walker and Brown, 1983; Walker et al., 1983; Nash, 1988; Smith and Walker, 1989) from the Arrhenius equation. These activation energy values of 23–58 kJ/mol (Table VII) are similar to those listed for a variety of other herbicides (Nash, 1988).

The breakdown of [^{14}C]amidosulfuron in the Regina clay at 20 $^{\circ}\text{C}$ and at 50, 65, 85, and 100% of FC is summarized in Table VI. The herbicide breakdown at all four soil moistures followed first-order kinetics that were moisture dependent. The half-life values ranged from 246 days in clay at 50% FC (20% soil moisture) to 63 days in clay at 100% FC (40% moisture). As noted, breakdown in air-dried soil (<10% FC) was minimal (Tables II and IV). It has been shown (Walker and Barnes, 1981; Walker and Brown, 1983; Walker et al., 1983; Smith and Walker, 1989) that the effect of soil moisture on herbicide persistence can be empirically derived from

Table IV. Radioactivity Recovered with Time from Soils at 85% Field Capacity Treated with 0.1 μg/g [¹⁴C]Amidosulfuron following Incubation at 30 °C

¹⁴ C extracted from soil	% of applied radioactivity ^a					
	7 days	14 days	21 days	28 days	42 days	70 days
	Regina Clay					
solvent extractable amidosulfuron	100 ± 3	92 ± 1	91 ± 1	82 ± 2	78 ± 1	69 ± 0 (105 ± 1) ^b
degradation products	75 ± 1	73 ± 1	62 ± 3	57 ± 1	51 ± 7	41 ± 2 (92 ± 2)
	24 ± 4	19 ± 2	28 ± 3	22 ± 2	24 ± 1	29 ± 2 (12 ± 2)
	Indian Head Clay					
solvent extractable amidosulfuron	96 ± 1	nd ^c	85 ± 0	80 ± 1	72 ± 0	66 ± 1 (103 ± 1)
degradation products	67 ± 3	nd	51 ± 3	48 ± 2	43 ± 1	34 ± 1 (90 ± 2)
	29 ± 2	nd	34 ± 3	26 ± 0	29 ± 1	32 ± 0 (12 ± 2)
	White City Loamy Sand					
solvent extractable amidosulfuron	94 ± 2	88 ± 1	81 ± 1	74 ± 1	67 ± 1	60 ± 2 (105 ± 1)
degradation products	59 ± 2	46 ± 3	36 ± 3	32 ± 3	22 ± 1	12 ± 2 (82 ± 3)
	36 ± 0	42 ± 4	46 ± 2	43 ± 3	44 ± 1	47 ± 1 (19 ± 2)

^a Mean and standard deviation from three replicates. ^b Figures in parentheses represent data obtained from air-dry soils (<10% FC) incubated for 70 days with [¹⁴C]amidosulfuron. ^c Not determined.

Table V. Half-Life Values for the Breakdown of [¹⁴C]Amidosulfuron at 0.10 μg/g in Indian Head and Regina Clays and a White City Loamy Sand at 85% Field Capacity at 10, 20, and 30 °C

soil	half-life, ^a days		
	10 °C	20 °C	30 °C
Indian Head clay	63 ± 5	45 ± 11	33 ± 3
Regina clay	231 ± 41	79 ± 2	46 ± 5
White City loamy sand	44 ± 5	26 ± 3	14 ± 2

^a Mean and standard deviation from three replicates.

Table VI. Loss of [¹⁴C]Amidosulfuron from a Regina Clay (0.10 μg/g) and Half-Life Values at Different Moisture Levels following Incubation at 20 °C

soil moisture, % FC	[¹⁴ C]amidosulfuron, ^a % of applied			half-life, days
	28 days	56 days	84 days	
50	89 ± 3	85 ± 3	76 ± 3	246 ± 21
65	85 ± 1	76 ± 5	71 ± 3	177 ± 22
85 ^b	68 ± 2	54 ± 1	52 ± 1	78 ± 3
100	66 ± 2	56 ± 1	40 ± 5	63 ± 7

^a Mean and standard deviation from three replicates. ^b Data obtained from Table II.

Table VII. Temperature and Moisture Dependence of [¹⁴C]Amidosulfuron Degradation in Saskatchewan Soils

soil	activation energy, kJ/mol	moisture dependence constants	
		A × 10 ⁻⁴	B
Indian Head clay	23 ± 1	nd ^a	nd
Regina clay	58 ± 3	14.5 ± 1.7	2.1 ± 0.0
White City loamy sand	41 ± 1	nd	nd

^a Not determined.

$$H = AM^{-B}$$

where H is the half-life in days at moisture content M (% w/w) and A and B are constants. The values for the two constants calculated from the data (Table VI) are summarized in Table VII. Knowing A and B and the activation energies (Table VII), as well as rainfall data and air temperature, one can predict the persistence of a herbicide in soil under field conditions (Walker, 1978; Walker and Zimdahl, 1981; Walker and Barnes, 1981; Walker and Brown, 1983; Walker et al., 1983; Smith and Walker, 1989).

After 84 days in moist soils incubated at 10 °C, amounts of ¹⁴C degradation products ranged from 18% of the applied radioactivity in the Regina clay to 48% in the White City loamy sand (Table III). In the moist soils incubated at 20 °C, amounts of degradation products ranged from 18 to 36% of the applied radioactivity (Table

II), while after 70 days at 30 °C, the figures were between 29 and 47% (Table IV). It was also noted that for each soil at each temperature there was a tendency for the amounts of ¹⁴C degradation products formed to reach a plateau after about 28 days. This would suggest that, after a month, the metabolites are being degraded at a similar rate to that of their formation.

From the TLC analyses, no ¹⁴C products could be identified. Most of the radioactivity was in the form of seemingly very polar products. If the demethylated degradation product (Figure 1, R = H) was formed in the soils, amounts were below the detection limit (<1% of the applied radioactivity). Other possible degradation products containing the radioactive carbon atom of [¹⁴C]-amidosulfuron could be based on pyrimidine structures formed from amidosulfuron by hydrolytic and demethylation mechanisms. In the present study, no special attempts were made to identify any degradation products.

All soils at 85% FC and incubated at 20 °C were combusted following solvent extraction. The residual radioactivity ranged from 4 to 11% over the 84-day incubation period (Table II), thus confirming that the majority of the radioactivity associated with the soils was being removed by the extraction procedure. Radioactivity remaining in the soils in a solvent nonextractable form can be attributed to several sources: ¹⁴C degradation products that are not recovered by the extraction procedure; ¹⁴C material incorporated into the soil microbial biomass as a result of [¹⁴C]carbon dioxide emanating from the [¹⁴C]amidosulfuron and/or ¹⁴C degradation products; or small ¹⁴C-containing fragments formed by breakdown of these compounds, which are utilized by degrading organisms. With time, the microorganisms themselves will be metabolized, and the radioactivity originally incorporated into the microbial cellular components will be released as [¹⁴C]carbon dioxide and other labeled products to become part of the fulvic, humic, and humin soil components (Soulas et al., 1984; Smith and Aubin, 1990).

In the moist soils incubated at 20 °C there was a gradual loss of radioactivity with time ranging from 13%, after 84 days, in the Regina clay to 33% in the White City loamy sand (Table II). This was attributed to possible losses of radioactivity from the ¹⁴C-labeled herbicide and/or ¹⁴C degradation products as [¹⁴C]carbon dioxide, by biological or chemical degradative mechanisms.

The present data indicate that the soil persistence of amidosulfuron is both moisture and temperature dependent and is thus similar in behavior to other sulfonylurea herbicides (Walker and Brown, 1983; Anderson and Dulka,

1985; Thirunarayanan et al., 1985; Beyer et al., 1988). The half-life values for amidosulfuron in the high-pH soils used in this study are also in agreement with persistence data reported for chlorsulfuron, metsulfuron-methyl, and sulfometuron-methyl (Walker and Barnes, 1983; Anderson and Dulka, 1985; Thirunarayanan et al., 1985; Smith, 1986; Walker and Welch, 1989; Walker et al., 1989). This would indicate a carry-over of amidosulfuron residues to a second crop year, under Canadian prairie weather conditions, following spring applications.

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