# Dissipation of [$^{14}$C]Amidosulfuron (HOE 075032) in Prairie Soils

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The degradation of the herbicide [$^{14}$C]amidosulfuron (HOE 075032) was studied in two Saskatchewan (SK) and one Manitoba (MB) soil. The half-life of [$^{14}$C]amidosulfuron when applied at 97 g/ha ranged from 247 ± 9 days (mean ± standard deviation) in the fine-loamy soil from Minto, MB, to 13 ± 1 days in the fine-silty soil from Swift Current, SK. In the coarse-loamy soil from Bradwell, SK, the half-life of [$^{14}$C]amidosulfuron was 29 ± 1 days. Herbicide degradation followed first-order dissipation kinetics in all three soils. There was less movement of [$^{14}$C]amidosulfuron in the soil from Manitoba compared to both soils from Saskatchewan. The higher pH of the Minto, MB, soil, and the drier, cooler climatic conditions may account for the longer half-life of amidosulfuron in this soil.

**Keywords:** *Amidosulfuron; HOE 075032; sulfonylurea; herbicide; residue*

## INTRODUCTION

Amidosulfuron, also known as HOE 075032 (Figure 1, R = $CH_3$), is a sulfonylurea herbicide tested in Canada at doses up to 45 g/ha for postemergence control of broadleaf weeds in cereals and other crops (Smith and Aubin, 1992). The solubility of amidosulfuron is pH dependent. In aqueous media, at 20 °C, the solubility of amidosulfuron was found to be 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 nonvolatile (vapor pressure $1.3 \times 10^{-5}$ Pa at 20 °C), with a p$K_a$ of 3.58, and is 99% deprotonated at pH 5.6. It undergoes microbial and chemical degradation to the demethylated breakdown product known as HOE 101630 (Figure 1, R = H) (*Technical Information HOE 075032 Experimental Herbicide, 1990*).

In general, sulfonylurea herbicides have activity as low as 1 g/ha (Hay, 1990) and degrade slowly in cold, dry, heavy soils that have high pH (>7.5), thus causing potential injury problems in broadleaf crops planted the following season (Walker and Brown, 1982; Beyer et al., 1988). Carry-over is of particular concern in western Canada due to the long, cold winters and hot dry summers, which are not conducive to continuous, steady breakdown of herbicides. Under laboratory conditions half-lives of amidosulfuron ranged from 14 days in a sandy loam soil incubated at 30 °C to 231 days in a clay soil maintained at 10 °C (Smith and Aubin, 1992).

The objective of this study was to determine the dissipation rate of [$^{14}$C]amidosulfuron and its metabolites under field conditions in three western Canadian dryland soils with different pH values, textures, moistures, and temperatures that were cultivated under typical agronomic conditions for western Canada.

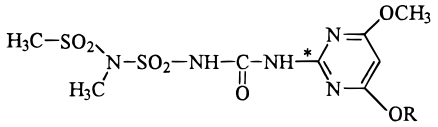


**Figure 1.** Structure of amidosulfuron, HOE 075032 (R = $CH_3$), and the demethylated soil degradation product HOE 101630 (R = H). The asterisk indicates the position of the $^{14}$C label.

## MATERIALS AND METHODS

**Chemicals.** 3-(4,6-Dimethoxypyrimidin-[2-$^{14}$C]-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea was obtained from Hoechst Aktiengesellschaft (Frankfurt am Main, Germany) with a specific activity of 2267 MBq/g and a radiochemical purity of >99%. Analytical samples of nonradioactive amidosulfuron (HOE 075032, 98.5% pure) and the soil degradation product 3-(6-hydroxy-4-methoxypyrimidin-2-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea (HOE 101630, 97.2% pure) were also provided by Hoechst Aktiengesellschaft. For HPLC analysis, a solution of nonradioactive amidosulfuron was prepared in acetonitrile (1 mg/mL), while HOE 101630 (1 mg/mL) was prepared using a mixture of water and acetonitrile (3:1, v/v).

**Soils.** Three types of soils were used in the study: a Bradwell soil (Typic Haploboroll, coarse-loamy, mixed) from Saskatchewan (SK), a Ryerson soil (Udic Haploboroll, fine-loamy, mixed) from Minto, Manitoba (MB), and a Swinton soil (Typic Haploboroll, fine-silty, mixed) from Swift Current (SK). Physical characteristics of each soil are summarized in Table 1.

At three different sites an 8 m × 7 m area was cultivated and leveled using a rake. A 1.2-m-high plastic snow-fence was erected to surround the entire treatment area. A total of 30 microplots (five rows of six microplots) were positioned within the 8 m × 7 m area. Each microplot area was delineated with four flat, wooden stakes positioned in the ground forming a 10 cm × 10 cm area. These stakes were used as a guide when the treated soil was added as well as to identify the treated areas for subsequent sampling. Each microplot was located no closer than 1 m from any adjacent microplot or site perimeter. The entire fenced-in areas were kept weed-free during the monitoring period.

Soil from the 0−5-cm depth at all locations was collected several weeks prior to the application of [$^{14}$C]amidosulfuron. The soil was air-dried and screened through a 2-mm sieve. Thirty scintillation vials, containing 10 g of soil, were prepared

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S0021-8561(97)00550-5 CCC: $15.00 
Published on Web 02/12/1998

**Table 1. Composition and Physical Characteristics of Soils**

| soil depth (cm) | soil type | % composition | | | physical characteristics | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | sand | silt | clay | CEC[a] | pH[b] | EC[c] | OM[d] | IC[e] | FC[f] |
| | | | | Bradwell, SK | | | | | | |
| 0−10 | coarse-loamy | 53 | 26 | 21 | 17.2 | 6.4 | 0.1 | 3.3 | 0.06 | 18.6 |
| 10−20 | | 60 | 21 | 19 | 12.5 | 6.8 | 0.1 | 1.7 | 0.04 | 16.8 |
| 20−30 | | 58 | 22 | 20 | 12.3 | 7.1 | 0.1 | 1.2 | nd[g] | 14 |
| | | | | Minto, MB | | | | | | |
| 0−10 | fine-loamy | 28 | 39 | 33 | 31.5 | 7.9 | 0.6 | 6.6 | 0.18 | 34.8 |
| 10−20 | | 22 | 42 | 36 | 30.1 | 8.2 | 0.6 | 4.8 | 0.32 | 33.3 |
| 20−30 | | 22 | 42 | 36 | 24.6 | 8.1 | 1.9 | 3 | 0.77 | 39.9 |
| | | | | Swift Current, SK | | | | | | |
| 0−5 | fine-silty | 33 | 42 | 25 | 20.7 | 6.2 | 0.1 | 1.8 | 0.14 | 18.1 |
| 5−10 | | 31 | 44 | 25 | 21.2 | 6.4 | 0.1 | 1.8 | 0.02 | 20.0 |
| 10−15 | | 28 | 45 | 27 | 21.4 | 6.5 | 0.1 | 1.5 | 0.03 | 24.7 |
| 15−30 | | 25 | 47 | 28 | 22.7 | 7.2 | 0.1 | 1.4 | 0.02 | 24.9 |

[a] Cation exchange capacity (mequiv/100 g). [b] 1:2 soil to water. [c] Electrical conductivity (mS/cm). [d] Percent organic matter. [e] Percent inorganic carbon. [f] Field moisture capacity (0.33 bar). [g] Not determined.

for each site. A stock solution of [$^{14}$C]amidosulfuron was prepared in 1:1 (v/v) 95% ethanol/acetone. Liquid scintillation spectroscopy was used for quantitative detection of radiolabeled amidosulfuron. Analysis confirmed that the solution contained 1.46 MBq/mL.

Each vial was spiked with 0.22 MBq (97 $\mu$g of herbicide) of [$^{14}$C]amidosulfuron stock solution equivalent to 97 g/ha, assuming the herbicide is equally distributed in the 0−5-cm soil horizon (Smith et al., 1990). The solvent was allowed to evaporate, and the vials were shaken by hand for 15 s.

The Bradwell, Minto, and Swift Current sites were treated on July 3, 1992, July 8, 1992, and June 11, 1993, respectively. During the application, a wooden form (10 × 10 × 5 cm) was positioned around flat, wooden stakes to minimize wind interference. Spiked soil (described above) from a scintillation vial was carefully poured through a glass funnel onto the central area of each microplot. A small volume of acetone was used to rinse the vial, and the rinsate was added as part of the application. Immediately following each application, the surface area of each microplot was covered with fresh sieved soil and lightly tamped with a flat-bottom instrument.

At all sites, soil samples were collected from three microplots in a random fashion at 13 different times ranging from 0 to 66 weeks after treatment (WAT). Soil samples were excavated incrementally from the 0−5-, 5−10-, 10−15-, and 15−30-cm depths using a stainless steel form that was designed to sample a 100 cm$^2$ area 5 cm deep. Prior to the removal of the 0−5-cm depth, a Back-Saver soil probe (3.18-cm diameter) was used to collect soil from the buffer area outside the metal form. A single, solid core was removed to a 30-cm depth along all four sides of the metal form. Soil samples from the buffer area around each microplot were analyzed to determine if any radioactivity moved laterally. Each core was subdivided and composited. Soil from the buffer area and lower depths within the microplots was not collected 0 WAT.

Once buffer samples were collected, the treated area was excavated. Soil surrounding the stainless steel form was removed to a specified depth (e.g. 5 cm) to allow a hacksaw blade to cut across the bottom of the metal form. This technique minimized the amount of disturbance to the sampling profile and provided a uniform soil volume. The entire sample within the steel form was removed and transferred to a labeled, foil-lined bag. The metal form was then repositioned and pressed down another 5-cm depth. All excavated holes were repacked with untreated soil and leveled.

Untreated soil samples were collected at 0, 4, and 16 WAT. Triplicate sites were selected at random along the inside perimeter of the fence. Untreated soil was taken prior to collection of treated soil to avoid contamination of the metal form and hence the untreated soil samples.

All collected samples were transported in coolers packed with dry ice or in a portable freezer equipped with a gas-powered generator. Samples were stored frozen prior to analysis. The moisture content of the soil was determined by weighing duplicate subsamples before and after drying at 105 °C for 24 h.

**Recovery of Radioactivity.** Laboratory studies were conducted to assess the extractability of [$^{14}$C]amidosulfuron from the soils. Soil samples from all four depths (0−5, 5−10, 10−15, and 15−30 cm) were weighed and subsequently air-dried overnight. Soil (40 g) from each experimental site was spiked with 0.011 MBq of [$^{14}$C]amidosulfuron (0.12 $\mu$g of herbicide/g of soil) dissolved in ethanol. The samples were incubated for 36 h in sealed glass jars that were kept in the dark and extracted as described by Smith and Aubin (1992). The soil samples (40 g) were shaken with 100 mL of aqueous acetonitrile [acetonitrile/water/glacial acetic acid (80:20:2.5, v/v/v)] and centrifuged, and the radioactivity in an aliquot of the supernatant was determined. A 25-mL aliquot of the supernatant (equivalent to 10 g of moist soil) was evaporated to near dryness under reduced pressure at 40 °C using a rotary evaporator. The remaining residue was brought up to 2 mL in water/acetonitrile (1:1, v/v) and filtered through a 0.22-$\mu$m nylon filter before being injected into the HPLC. After solvent extraction, the soil (ca. 40 g) was collected by vacuum filtration, successively washed to remove all solvent-extractable radioactivity, and dried. Triplicate samples (1 g) of each soil were assayed for radioactivity by combustion analysis to determine bound radioactivity. Following extraction, [$^{14}$C]amidosulfuron was determined by HPLC to be the only radioactive species present in the spiked soil samples.

**Soil Extraction and Analysis.** Extraction of radioactive amidosulfuron from field samples was accomplished in two steps. First, frozen soil samples from the three [$^{14}$C]amidosulfuron-treated field sites were thawed at 20 °C and mixed using a rotary blender. Triplicate samples of 1 g were taken randomly throughout the mixture and combusted to quantitate radioactivity. Samples that contained high radioactivity (>25 Bq/1 g of soil) were taken through an extraction process. The extraction and analysis method was identical to that described in the radioactivity recovery study. Soil samples (50 g) were shaken with 100 mL of aqueous acetonitrile. The amount of solvent added was corrected to account for the moisture content of each soil sample. Soil particles were separated from the aqueous solution by centrifugation. Radioactivity remaining in the soil was determined by combustion. Radioactivity in the aqueous solutions was measured by liquid scintillation spectroscopy.

**Measurement of Radioactivity.** Radioactivity in the various solutions was measured using a Beckman LS6K-SC scintillation counter (Beckman Instruments Inc., Fullerton, CA). Ecolite (+) (ICN Biomedicals Inc., Irvine, CA) scintillation cocktail was used. The unextracted radioactivity was quantified by oxidizing the extracted soil material in a model OX-300 biological oxidizer (R. J. Harvey Instrument Corp., Hillsdale, NJ). The resulting $^{14}CO_2$ was trapped in carbon-14

**Table 2. Radioactivity Recovered from Soils Treated with [$^{14}$C]Amidosulfuron**

| | % of applied radioactivity[a] (*X* days after application) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| soil depth (cm) | *X* = 7 | *X* = 14 | *X* = 28 | *X* = 56 | *X* = 105 | *X* = 112 | *X* = 308 | *X* = 364 | *X* = 371 | *X* = 420 | *X* = 448 | *X* = 462 |
| | | | | | | Bradwell, SK | | | | | | |
| 0−5 | 103 ± 5 | 92 ± 5 | 85 ± 2 | 101 ± 6 | | 57 ± 2 | 61 ± 7 | | 37 ± 1 | | | 35[b] |
| 5−10 | 1 ± 0 | 6 ± 0 | 4 ± 0 | 7 ± 0 | | 18 ± 2 | 15 ± 2 | | 14 ± 1 | | | 6 |
| 10−15 | nd[c] | nd | nd | nd | | 4 ± 0 | 4 ± 0 | | 4 ± 0 | | | 3 |
| 15−30 | nd | nd | nd | nd | | 3 ± 1 | 3 ± 0 | | 4 ± 1 | | | 1 |
| total | 104 ± 5 | 98 ± 3 | 89 ± 3 | 108 ±5 | | 82 ± 4 | 83 ± 6 | | 59 ± 3 | | | 45 |
| | | | | | | Minto, MB | | | | | | |
| 0−5 | 98 ± 9 | 88 ± 3 | 99 ± 4 | 107 ± 3 | 97 ± 4 | | 84 ± 2 | 58 ± 9 | | | 36 ± 2 | |
| 5−10 | nd | nd | nd | nd | nd | | 2 ± 1 | 5 ± 1 | | | 10 ± 3 | |
| total | 98 ± 9 | 88 ± 3 | 99 ± 4 | 107±3 | 97 ± 4 | | 86 ± 2 | 63 ± 7 | | | 46 ± 3 | |
| | | | | | | Swift Current, SK | | | | | | |
| 0−5 | 86 ± 3 | 69 ± 8 | 28 ± 2 | 28 ± 2 | | 18 ± 4 | | | 13 ± 7 | 10 ± 2 | | 13 ± 1 |
| 5−10 | 5 ± 0 | 38 ± 0 | 17 ± 1 | 13 ± 1 | | 9 ± 1 | | | 6 ± 1 | 5 ± 0 | | 7 ± 1 |
| 10−15 | nd | nd | 12 ± 1 | 7 ± 0 | | 7 ± 1 | | | 3 ± 1 | 4 ± 1 | | 4 ± 1 |
| 15−30 | nd | nd | 14 ± 2 | 9 ± 3 | | 6 ± 0 | | | 4 ± 0 | 3 ± 0 | | 3 ± 1 |
| total | 91 ± 3 | 107±6 | 71 ± 2 | 57 ± 3 | | 40 ± 3 | | | 26 ± 5 | 22 ± 2 | | 27 ± 1 |

[a] Data are expressed as a percent of radioactivity recovered at day 0. Mean and standard deviation from three replicates. [b] Determined from one replicate. [c] Not detectable.

cocktail (R. J. Harvey Instrument Corp.) and quantified by liquid scintillation counting as described above. The efficiency of $^{14}CO_2$ recovery, as determined by combusting [$^{14}$C]Spec Chec (Packard, Downers Grove, IL) calibration standards, was >95%.

**HPLC Chromatography.** The filtered extracts were analyzed on a Shimadzu model LC-6A liquid chromatography system (Shimadzu Scientific Instruments Inc., Columbia, MD), equipped with a Spherex column [10 × 250 mm, 5-$\mu$m particle size; reversed phase ($C_{18}$); Phenomenex, Torrance, CA] and a Shimadzu SPD-M6A detector set at 238 nm wavelength. Elution was effected at 22 °C using a mobile phase of two solvents, A [$H_2O$ + (0.1% v/v) sulfuric acid (pH 2.5)] and B (acetonitrile), starting with pure A and continuing with a linear gradient to 90% B over 70 min at a flow rate of 2.0 mL/min. For Bradwell samples from day 308 onward the same chromatographic parameters were used but with a concave (no. 2) gradient to separate the parent from the metabolites. For all Swift Current and Minto soils (308−448 days), a linear gradient described above and a flow rate of 1.0 mL/min were used to improve the resolution of the chromatograms. The radiolabeled residues were detected and quantified by a Radiomatic FL-ONE\Beta A-200 radioactivity flow detector (Radiomatic Instruments and Chemical Co. Inc., Tampa, FL). The column eluant was automatically augmented with 4 mL/min of Ecolite liquid scintillation solution before reaching the detector. The retention time of amidosulfuron was compared to that of the authentic radiolabeled standard. The retention time of HOE 101630 was compared to a nonlabeled standard.

## RESULTS

The mean recovery of radioactivity from the three air-dried soil types (40 g) from each soil depth, spiked with [$^{14}$C]amidosulfuron (0.12 $\mu$g) 36 h prior to extraction, was 94 ± 4% of the applied radioactivity. All of the radioactivity was [$^{14}$C]amidosulfuron as determined by HPLC, indicating that the conditions used for extraction and chromatography did not cause degradation of the parent compound.

As time after application of amidosulfuron increased, there was a gradual loss of applied radioactivity from all three soils. Losses amounted to 55% after 462 days in the Bradwell, SK, soil, 73% after 462 days in the Swift Current, SK, soil, and 54% after 448 days in the Minto, MB, soil (Table 2). These losses can be attributed to unrecovered $^{14}CO_2$ being produced by degradation of [$^{14}$C]amidosulfuron and its $^{14}$C metabolites (Smith and Aubin, 1992), nonextractable or "bound" $^{14}$C originating from [$^{14}$C]amidosulfuron, and/or leaching of $^{14}$C compounds through the soil profile.

Amidosulfuron was more mobile in soils from the Bradwell and Swift Current sites (Table 2). Seven days after application of [$^{14}$C]amidosulfuron, these soils had detectable radioactivity in the 5−10-cm soil horizon. From day 28 to day 462, detectable radioactivity was found in all soil depths of the Swift Current soil. In the Bradwell soil, radioactivity was found at all depths from day 112 onward. In contrast, there was little movement of radioactivity in the Minto soil. For example, 308 days after herbicide application, there was only 2% of the applied radioactivity found in the 5−10-cm soil profile (Table 2). No radioactivity was detected below the 5−10-cm profile at the Minto site. Regardless of the soil type, there was little (3.34 Bq/g of soil) or no radioactivity detected in soil from the buffer strips, indicating that there was little lateral movement of the herbicide.

Breakdown of amidosulfuron was found to be greater in the 0−5-cm depth of the Bradwell and Swift Current soils than in the Minto soil (Table 3). Half-lives were calculated by assuming first-order kinetics and were 13 ± 1, 29 ± 1, and 247 ± 9 days for the Swift Current, Bradwell, and Minto soils, respectively (Table 5). A metabolite, hereafter known as metabolite B, comigrated with the authentic standard of HOE 101630 as determined by HPLC. This metabolite was found in the Bradwell soil from days 7 to 56 (0−5 cm) with a maximum amount of 11% (of applied radioactivity) occurring at day 28. Three other metabolites were found in the Bradwell soil, hereafter known as metabolites A, C, and D. Metabolite A was found from days 14 to 56, metabolite C from days 7 to 56, and metabolite D from days 28 to 56 (Table 3). In the Minto soil (0−5 cm), metabolite B was found from days 7 to 448 and metabolite C from days 28 to 448 (Table 3). In the Swift Current soil, metabolites B and C were found from days 7 to 56 (0−5 cm) (Table 3). Most of the $^{14}$C metabolites were polar, but no attempts were made to identify these degradation products. Regardless of the soil type or depth, <25% of the recovered radioactivity was bound (not extractable with solvent).

Evaluation of an amidosulfuron recropping trial was conducted at the Manitoba site. Several rotational crops were evaluated after emergence for plant number, plant height, and injury (Table 6). Amidosulfuron had no

**Table 3. Quantification of $^{14}C$ Degradation Products Found at the 0−5-cm Depth in Soils Treated with [$^{14}C$]Amidosulfuron**

| $^{14}C$ extracted from soil | % of applied radioactivity[a] ($X$ days after application) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $X = 7$ | $X = 14$ | $X = 28$ | $X = 56$ | $X = 105$ | $X = 112$ | $X = 308$ | $X = 364$ | $X = 371$ | $X = 420$ | $X = 448$ | $X = 462$ |
| | | | | | | Bradwell, SK | | | | | | |
| solvent extractable | 95 ± 8 | 80 ± 6 | 68 ± 2 | 76 ± 8 | | 38 ± 7 | 37 ± 7 | | 22 ± 2 | | | 15[b] |
| amidosulfuron | 87 ± 8 | 62 ± 4 | 42 ± 1 | 31 ± 3 | | 13 ± 1 | 8 ± 1 | | 4 ± 1 | | | 2 |
| metabolite A | nd[c] | 3 ± 0 | 8 ± 2 | 20 ± 3 | | nd | nd | | nd | | | nd |
| metabolite B | 4 ± 0 | 9 ± 1 | 11 ± 0 | 10 ± 2 | | nd | nd | | nd | | | nd |
| metabolite C | 3 ± 0 | 5 ± 1 | 5 ± 0 | 11 ± 1 | | nd | nd | | nd | | | nd |
| metabolite D | nd | nd | 1 ± 1 | 3 ± 1 | | nd | nd | | nd | | | nd |
| other | 1 ± 0 | 1 ± 0 | 1 ± 0 | 1 ± 1 | | 25 ± 1 | 29 ± 6 | | 18 ± 1 | | | 13 |
| soil associated[d] | 8 ± 1 | 12 ± 1 | 17 ± 0 | 25 ± 2 | | 19 ± 1 | 24 ± 5 | | 15 ± 3 | | | 20 |
| total recovered $^{14}C$ | 103 ± 5 | 92 ± 5 | 85 ± 2 | 101 ± 6 | | 57 ± 2 | 61 ± 7 | | 37 ± 1 | | | 35 |
| | | | | | | Minto, MB | | | | | | |
| solvent extractable | 89 ± 7 | 80 ± 5 | 84 ± 8 | 94 ± 4 | 84 ± 6 | | 67 ± 1 | 44 ± 14 | | | 24 ± 2 | |
| amidosulfuron | 85 ± 7 | 78 ± 5 | 81 ± 9 | 90 ± 4 | 79 ± 6 | | 60 ± 1 | 37 ± 12 | | | 13 ± 2 | |
| metabolite B | 2 ± 2 | 1 ± 0 | 1 ± 1 | 2 ± 1 | 2 ± 0 | | 3 ± 0 | 3 ± 1 | | | 2 ± 1 | |
| metabolite C | nd | nd | 1 ± 1 | 1 ± 1 | 2 ± 1 | | 2 ± 1 | 1 ± 1 | | | 1 ± 1 | |
| other | 2 ± 1 | 1 ± 1 | 1 ± 0 | 1 ± 0 | 1 ± 1 | | 2 ± 0 | 3 ± 1 | | | 8 ± 1 | |
| soil associated | 9 ± 3 | 8 ± 2 | 15 ± 3 | 13 ± 1 | 13 ± 1 | | 17 ± 0 | 14 ± 4 | | | 12 ± 2 | |
| total $^{14}C$ recovered | 98 ± 9 | 88 ± 3 | 99 ± 4 | 107 ± 3 | 97 ± 4 | | 84 ± 2 | 58 ± 9 | | | 36 ± 2 | |
| | | | | | | Swift Current, SK | | | | | | |
| solvent extractable | 81 ± 6 | 59 ± 8 | 22 ± 2 | 21 ± 2 | 11 ± 4 | | | | | | | |
| amidosulfuron | 74 ± 6 | 49 ± 7 | 16 ± 2 | 11 ± 1 | 4 ± 2 | | | | | | | |
| metabolite B | 2 ± 1 | 3 ± 1 | 1 ± 0 | 1 ± 0 | nd | | | | | | | |
| metabolite C | 2 ± 1 | 4 ± 1 | 2 ± 1 | 2 ± 0 | nd | | | | | | | |
| other | 3 ± 1 | 3 ± 1 | 3 ± 1 | 7 ± 1 | 7 ± 2 | | | | | | | |
| soil associated | 5 ± 0 | 10 ± 2 | 6 ± 2 | 7 ± 1 | 7 ± 3 | | | | | | | |
| total $^{14}C$ recovered | 86 ± 3 | 69 ± 8 | 28 ± 2 | 28 ± 2 | 18 ± 4 | | | | | | | |

[a] Data are expressed as a percent of radioactivity recovered at day 0; mean and standard error from three replicates. [b] Determined from one replicate. [c] Not detectable. [d] Determined by combustion of the solvent-extracted soils.

**Table 4. Quantification of $^{14}C$ Degradation Products Found at the 5−10-cm Depth in Soils Treated with [$^{14}C$]Amidosulfuron**

| $^{14}C$ extracted from soil | % of applied radioactivity[a] ($X$ days after application) | | | | |
|---|---|---|---|---|---|
| | $X = 14$ | $X = 28$ | $X = 56$ | $X = 112$ | $X = 308$ |
| | | Bradwell, SK | | | |
| solvent extractable | | | | 16 ± 4 | 11 ± 2 |
| amidosulfuron | | | | 5 ± 2 | 2 ± 1 |
| other | | | | 11 ± 2 | 9 ± 2 |
| soil associated[b] | | | | 2 ± 2 | 4 ± 1 |
| total $^{14}C$ recovered | | | | 18 ± 2 | 15 ± 2 |
| | | Swift Current, SK | | | |
| solvent extractable | 35 ± 2 | 15 ± 2 | 11 ± 1 | | |
| amidosulfuron | 30 ± 1 | 8 ± 1 | 3 ± 1 | | |
| metabolite B | 1 ± 1 | nd[c] | nd | | |
| other | 4 ± 2 | 7 ± 1 | 8 ± 1 | | |
| soil associated | 3 ± 0 | 2 ± 0 | 2 ± 0 | | |
| total $^{14}C$ receovered | 38 ± 1 | 17 ± 1 | 13 ± 1 | | |

[a] Data are expressed as a percent of radioactivity recovered at day 0; mean and standard error from three replicates. [b] Determined by combustion of the solvent extracted soils. [c] Not detectable.

**Table 5. Half-Life Values for the Breakdown of [$^{14}C$]Amidosulfuron at the 0−5-cm Soil Depth**

| soil type | half-life[a] (days) |
|---|---|
| Bradwell sandy loam | 29 ± 1 |
| Minto clay loam | 247 ± 9 |
| Swift Current loam | 13 ± 1 |

[a] Mean and standard deviation from three replicates.

effect on emergence of the crops. However, lentils, sugar beets, and sunflowers were severely injured by the herbicide 1 year after application. There was no injury to canola, peas, flax, and oats (Table 6). There were no significant differences in plant height or numbers for any of the crops tested (data not shown).

**Table 6. Effect of Amidosulfuron on Rotation Crops 1 Year after Application to the Minto, MB, Site**

| | weed/crop | | | | | | |
|---|---|---|---|---|---|---|---|
| | canola | lentils | peas | sun-flowers | flax | oats | sugar beets |
| rating unit (ECW)[a] | 0−9 | 0−9 | 0−9 | 0−9 | 0−9 | 0−9 | 0−9 |
| untreated | 9.0a | 9.0a | 9.0a | 9.0a | 9.0a | 9.0a | 9.0a |
| treated | 9.0a | 5.7b | 8.3a | 5.3b | 8.7a | 9.0a | 5.3b |

[a] Means followed by the same letter are not significantly different ($P \leq 0.5$) as determined by Duncan's multiple range test. Means are based on a 0−9 visual damage evaluation system recommended by the Expert Committee on Weed (ECW), Canada.

## DISCUSSION

Mobility of the sulfonylurea herbicides is reduced as organic matter content increases (Beyer et al., 1988; Smith, 1982). Therefore, the high organic matter content in the Minto soil may explain why amidosulfuron did not move beyond the 0−5-cm horizon until 308 days after application (Table 2). Conversely, increased mobility in the two Saskatchewan soils, especially the Swift Current site, may be attributed to more rainfall, as well as lower soil organic matter and clay content.

Degradation of amidosulfuron in soil results from both biological and chemical mechanisms, which are themselves influenced by temperature, pH, and moisture content. Chemical hydrolysis of sulfonylurea herbicides (Figure 2) is a predominant means of degradation in acidic soils (Joshi et al., 1985; Beyer et al., 1988; Blair and Martin, 1988; Walker et al., 1989; Hay, 1990). At pH values above the p$K_a$ the sulfonylurea bridge exists as an anion and is not subject to hydrolysis, while at pH values near or below the p$K_a$ the bridge is protonated and readily undergoes hydrolysis. As an example, half-lives of triasulfuron ranged from 33 days at pH 5.8 to

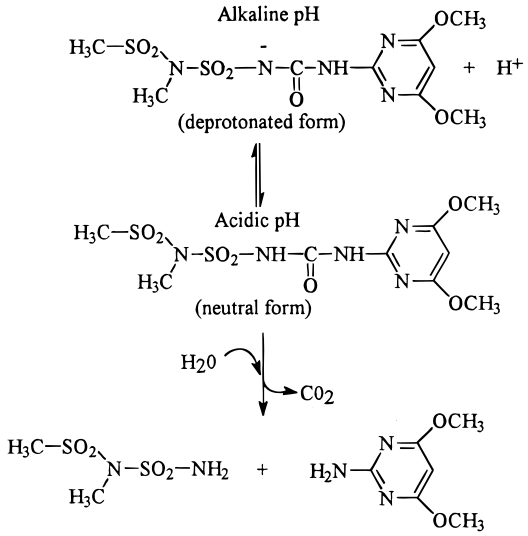


**Figure 2.** Hydrolysis of amidosulfuron [modified from Beyer et al. (1988)].

120 days at pH 7.4 (Walker and Welch, 1989). Microbial breakdown also contributes to the degradation of sulfonylureas in soils, although it is usually less significant than chemical hydrolysis. For example, degradation of chlorsulfuron was faster in nonsterilized soil than in sterilized soil (Joshi et al., 1985). Furthermore, higher soil temperatures and moisture content promoted both faster microbial degradation and chemical hydrolysis of sulfonylurea herbicides (Thirunarayanan et al., 1985; Beyer et al., 1988). Thus, the slower degradation of amidosulfuron in the Manitoba soil may be attributed mainly to the higher pH of the soil and, to a lesser extent, the cooler, drier environmental conditions that may result in slower microbial degradation. The soil persistence of amidosulfuron in the Minto soil is supported by the damage to sensitive rotational crops 1 year after application (Table 6). There was no damage to rotational crops at the two Saskatchewan sites (data not shown).

Degradation of amidosulfuron under field and laboratory conditions was also correlated in our studies. The half-lives of [$^{14}$C]amidosulfuron calculated from our field data for the fine-silty and coarse-loamy soils from Saskatchewan were 13 and 29 days (Table 5), respectively. These were similar to the laboratory result of 26 days calculated by Smith and Aubin (1992) using a loamy sand with pH 7.3. In a clay soil with pH 7.5 at 10 °C the half-life of [$^{14}$C]amidosulfuron calculated by Smith and Aubin (1992) was 231 days. This is comparable to our field results of 247 days in the Minto clay loam soil. The lower temperature used by Smith and Aubin (1992) was similar to the average temperatures at the Minto site.

In conclusion, our data indicate that the mobility and breakdown of amidosulfuron in prairie soils are highly dependent on soil pH, organic matter content, and temperature conditions. The movement and degradation of [$^{14}$C]amidosulfuron was greater in low pH, low organic matter content soils such as those in Saskatchewan. Conversely, heavy, cool, alkaline (>pH 7.5) soils such as the Minto clay loam result in carry-over of amidosulfuron, which led to damage of sensitive broadleaf crops planted the year after application.

## ABBREVIATIONS USED

HOE 075032 or amidosulfuron, 3-(4,6-dimethoxypyrimidin-2-yl)-1-(*N*-methyl-*N*-methylsulfonyl)aminosulfonylurea (R = $CH_3$); HOE 101630, 3-(6-hydroxy-4-methoxypyrimidin-2-yl)-1-(*N*-methyl-*N*-methylsulfonyl)-aminosulfonylurea (R = H).

## ACKNOWLEDGMENT

We thank AgrEvo Canada for providing radiolabeled [$^{14}$C]amidosulfuron and technical standards. We also thank Ms. Linda Veldhuis for technical assistance.

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Received for review June 25, 1997. Revised manuscript received December 1, 1997. Accepted December 11, 1997. This research was supported by funding from AgrEvo Canada and the Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA).

JF970550P