

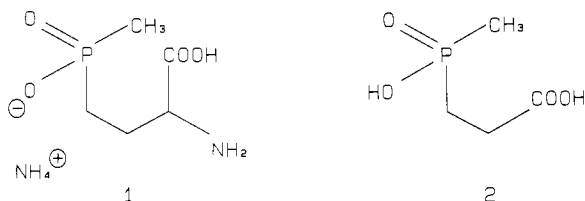
Persistence and Transformation of the Herbicide [¹⁴C]Glufosinate-Ammonium in Prairie Soils under Laboratory Conditions

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The degradation of the herbicide [¹⁴C]glufosinate-ammonium (the ammonium salt of DL-homoalanin-4-ylmethylphosphinic acid), at a rate of 2 ppm, was studied in three prairie soils at 85% of their field capacity moistures at both 20 and 10 °C. In all soils the herbicide was biologically transformed to degradation product(s) that underwent further slow degradation with release of [¹⁴C]carbon dioxide. At 20 °C, the soil half-life values for the [¹⁴C]herbicide were 3-7 days and, at 10 °C, 8-11 days. Over a 90-day incubation period at 20 °C, between 28 and 55% of the applied radioactivity was released from treated soils as [¹⁴C]carbon dioxide; solvent-extractable degradation product(s) accounted for 19-37% of the applied radioactivity; between 2.4 and 9.5% of the initial ¹⁴C was incorporated into soil microbial biomass and 7-13% into the fulvic, humic, and humin soil fractions.

The postemergence experimental herbicide HOE 39866, with the proposed common name of glufosinate-ammonium (1, the ammonium salt of DL-homoalanin-4-ylmethylphosphinic acid), is currently being evaluated on the Canadian prairies, at rates up to 1 kg/ha, for the nonselective control of annual and perennial broadleaf weeds and grasses in a variety of crop and noncrop situations.

Glufosinate-ammonium is the ammonium salt of an amino acid referred to here as glufosinate, although it is also known as phosphinothricin (Bayer et al., 1972). The ammonium salt 1 is nonvolatile, soluble in polar solvents such as water and methanol, and insoluble in nonpolar organic solvents (Anonymous, 1983). Glufosinate interferes with photosynthesis by inhibition of glutamine synthetase, the enzyme that catalyzes the combination of glutamic acid and ammonia (Leason et al., 1982; Fraser and Ridley, 1984). The herbicide undergoes breakdown in the soil with formation of 3-(hydroxymethylphosphinyl)propionic acid (2) as degradation product (H. Gildemeister, Hoechst Aktiengesellschaft, personal communication, 1986).



Currently nothing has been reported on the fate of glufosinate-ammonium in Canadian soils, and the studies to be described were undertaken to investigate the persistence and transformation of [¹⁴C]glufosinate-ammonium in three Saskatchewan soils under laboratory conditions. These experiments were designed to (a) measure the rate of breakdown of the [¹⁴C]herbicide in fortified soils incubated at 20 and 10 °C and (b) determine the release of [¹⁴C]carbon dioxide and, after a 90-day period, measure the incorporation of radioactivity into the soil biomass.

MATERIALS AND METHODS

Soils. The three soils used in these studies were a clay, a clay loam, and a sandy loam; the composition and physical characteristics of these soils are presented in Table I.

Table I. Composition and Physical Characteristics of Soils

| soil | composition, % | | | | field capacity, % | pH |
|------------|----------------|------|------|-----------------|-------------------|-----|
| | clay | silt | sand | organic content | | |
| clay | 70 | 25 | 5 | 4.2 | 40 | 7.7 |
| clay loam | 30 | 40 | 30 | 11.7 | 35 | 6.0 |
| sandy loam | 10 | 25 | 65 | 4.0 | 20 | 7.6 |

Soil samples were collected, during the spring of 1986, from the 0-10-cm soil horizons of fallow areas that had not been cropped for several years. The soil moisture at the time of collection was 10% of field capacity. After being screened through a 2-mm screen, the soils were stored at laboratory temperature, in wooden boxes, until use in the spring and winter of 1986.

Chemicals. [¹⁴C]Glufosinate, labeled in the two -CH₂-carbon atoms, with a specific activity of 51.33 μCi/mg was provided by Hoechst Aktiengesellschaft, Frankfurt am Main, Germany, as was the formulated glufosinate-ammonium (200 g/L) and samples of analytically pure glufosinate-ammonium (1) and 3-(hydroxymethylphosphinyl)propionic acid (MPPA, 2). Radiochemical purity of the [¹⁴C]glufosinate-ammonium was 95%, as determined by thin-layer chromatography using two solvent systems selected for these studies (see later text). The nature of the 5% impurity in the [¹⁴C]herbicide was unknown. [¹⁴C]Glufosinate-ammonium was diluted with the nonradioactive formulated material and an aqueous solution prepared containing 24.8 μCi/mL and 5 mg of glufosinate-ammonium/mL.

Degradation Studies. Aliquots of all three soil types were weighed into 175-mL polystyrene foam cartons and moistened with sufficient distilled water to yield samples (50 g) at 85% of their respective field capacities. The cartons were capped with plastic lids and incubated in the dark at either 20 ± 1 or at 10 ± 1 °C. All cartons were weighed every second day, and if necessary, distilled water added to replace moisture lost by evaporation. After each addition, the soils were thoroughly stirred to maintain a uniform moisture content. Following a 7-day equilibration period, [¹⁴C]glufosinate-ammonium (20 μL, 1.1 × 10⁶ dpm, 100 μg of herbicide) was added to the soils to give treatments containing 2 ppm of glufosinate-ammonium, based on moist soil weight. This concentration is equal to a rate of 1 kg/ha, assuming that, in the field, the chemical is located in the top 5 cm of the soil. The soils were carefully mixed to ensure distribution of the herbicide; the cartons were lightly capped to permit exchange of air but reduce

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water evaporation and incubated in the dark at 20 ± 1 or 10 ± 1 °C. Distilled water was added every second day, with stirring, to replace moisture lost by evaporation.

Duplicate treatments incubated at 20 °C were extracted and radiochemically analyzed after 0.1, 3, 7, 14, 28, 56, and 84 days to determine the amounts of radioactivity recoverable and transformation products present. Two replicate treatments incubated at 10 °C were similarly extracted and analyzed after 7, 14, 21, and 35 days.

For comparative purposes, samples (50 g) of all three air-dried soils at 10% of their field capacities were treated as described above and fortified with 2 ppm of [¹⁴C]glufosinate-ammonium. Following incubation in the dark at 20 ± 1 °C, duplicate treatments were extracted and radiochemically analyzed after 35 and 70 days.

Extraction and Analysis. The soils from the cartons were placed in 250-mL glass-stoppered flasks, and water was added so that the total volume of water added, together with the water present in the soil, was equivalent to 100 mL. Calcium hydroxide was then added to each flask (300, 500, and 750 mg to the sandy loam, clay, and clay loam slurries, respectively), and the flasks were shaken on a wrist-action shaker for 1 h. The soils were allowed to remain in contact with the alkaline extractant for a further 20 h before being shaken for a second 1-h period. Following centrifugation at 3500 rpm for 10 min, extractable radioactivity was determined by radioassay of the clear extract (2 mL).

Further portions of the aqueous extract (5 mL) were placed in a 20-mL glass tube, and 2 drops of 12 N hydrochloric acid was added from a Pasteur pipet. The acidified solution was evaporated to dryness at 50 °C on a rotary evaporator and the residue dissolved in 3 drops of distilled water. The aqueous solution was then examined by thin-layer and radiochemical techniques for the presence of ¹⁴C-containing compounds.

Thin-Layer Chromatography. TLC plates precoated with a 0.1-mm layer of cellulose, and without fluorescence indicator, were obtained from E. Merck, Darmstadt, Germany. After development to a height of 8 cm above the origin, the plates were dried in a current of warm air and examined for radioactive compounds on a Model 2832 Berthold Automatic TLC linear analyzer (Labserco Ltd., Oakville, Ontario). The R_f values of [¹⁴C]glufosinate-ammonium and the ¹⁴C degradation product(s), isolated from the various soil incubations, were compared in a variety of solvent systems, but for the present studies 2-propanol-acetone-hydrochloric acid (30:7.5:12.5) and butanol-acetone-hydrochloric acid (25:10:15) were used. With the former solvent mixture [¹⁴C]glufosinate had R_f 0.48, with the degradation product(s) appearing as a broader area with R_f 0.84. In the latter solvent system the R_f values of [¹⁴C]glufosinate and the degradation product(s) were 0.33 and 0.72, respectively. In the acidic solvents, the [¹⁴C]glufosinate-ammonium dissociates and is converted to [¹⁴C]glufosinate. The R_f value of MPPA could not be determined since the compound has no ultraviolet absorption and underwent no reaction with reagents normally sensitive to carboxylic acid and phosphorus groupings. By comparing peak areas from the various chromatogram scans, and knowing the amounts of radioactivity extracted from each soil, the concentrations of the radioactive compounds present in the soil extracts were calculated. All soil extracts were subjected to both chromatographic separation systems and the ¹⁴C data averaged for each sampling date.

[¹⁴C]Carbon Dioxide Evolution Studies. Duplicate samples (50 g) of the three soils at 85% of their field

capacities were weighed into polystyrene foam cartons and placed in 2-L Mason jars fitted with spring-clip lids. The jars were placed in a darkened incubator at 20 ± 1 °C for 7 days. No moisture losses occurred from the soils under these conditions. After this equilibration period, the soils were treated, exactly as described above, with [¹⁴C]glufosinate-ammonium solution (20 μL, 100 μg). In each jar was placed a 50-mL beaker containing a 20-mL glass vial filled with 0.2 N aqueous sodium hydroxide (15 mL) solution to absorb [¹⁴C]carbon dioxide evolved (Soulas et al., 1984). After treatment, the jars were reincubated under darkened conditions at 20 ± 1 °C. Samples (1.0 mL) of the sodium hydroxide solution were assayed for radioactivity at regular intervals, at which time the absorbing vials were replaced with others containing fresh sodium hydroxide. During the 90-day incubation period there were negligible moisture losses from the soils by evaporation. The cumulative amounts of [¹⁴C]carbon dioxide released were calculated as a percentage of the total radioactivity originally applied to the soils.

Determination of Radioactivity Incorporated into the Biomass. To measure the amount of ¹⁴C from the labeled herbicide that had been incorporated into soil microorganisms, the chloroform fumigation-incubation technique was used (Jenkinson and Powlson, 1976; Chaussod and Nicolardot, 1982; Soulas et al., 1984). For this, the soils that had been incubated in the Mason jars for 90 days at 20 °C were transferred to 250-mL glass beakers and placed in a desiccator together with a beaker containing chloroform (50 mL). The chloroform had previously been shaken with distilled water (4 × 100 mL portions) to remove the ethanol stabilizer and other water-soluble impurities and dried over sodium sulfate. The desiccator was evacuated for 10 min, by a water aspirator, and left under vacuum overnight. Next day, the vacuum was released and the beaker of chloroform removed. The desiccator was then evacuated five successive times to purge all traces of chloroform from the soils. Distilled water was added to the soils to remoisten them to 85% of their respective field capacities, and the soils were transferred to polystyrene foam cartons. Each carton was placed in a 2-L Mason jar, together with a beaker containing a vial filled with 0.2 N aqueous sodium hydroxide solution (15 mL) and, after sealing, the jars were placed in darkened incubator at 20 ± 1 °C. Cumulative release of [¹⁴C]carbon dioxide was determined at weekly intervals, for 21 days, by assaying the radioactivity in portions (1 mL) of the sodium hydroxide solution. The caustic solution in the vials was replaced following every sampling.

After a 21-day incubation, the soils were extracted with aqueous calcium hydroxide solution (see above), and solvent-extractable radioactivity was determined. No attempts were made to examine these extracts by thin-layer chromatography. The soil residues, following solvent extraction, were collected by vacuum filtration and washed with water (2 × 100 mL portions), which were discarded after it was shown that they contained negligible traces of radioactivity. Finally, each soil residue was dried overnight at 90 °C and any radioactivity remaining measured by soil combustion analysis.

For comparative purposes, four replicates (50 g) of each soil type at 85% of their field capacities were incubated in the dark at 20 ± 1 °C for 1 week and then treated with [¹⁴C]glufosinate-ammonium (20 μL, 100 μg). After 1 h, the fortified soils were fumigated with chloroform, as described above, and the cumulative release of [¹⁴C]carbon dioxide was determined, as before, over 21- and 90-day periods.

Following the 21-day incubation period, duplicate samples of each soil type were extracted and radiochemically analyzed.

Amounts of ¹⁴C incorporated into the microbial biomass of soils incubated 90 days with [¹⁴C]glufosinate-ammonium were calculated by determining the cumulative flush of [¹⁴C]carbon dioxide, released over the 21-day period following chloroform fumigation, and subtracting from these data the cumulative amounts of [¹⁴C]carbon dioxide, released over a similar time, from the control soils treated with the [¹⁴C]herbicide for 1 h prior to chloroform exposure. The amount of ¹⁴C incorporated into the soil microbial biomass was estimated by dividing this difference by the mineralization rate factor (K_c) of 0.41 (Anderson and Domsch, 1978; Biederbeck et al., 1984; Soulas et al., 1984; Voroney and Paul, 1984).

Radioactivity Determination. The radioactivity in the various solutions was measured by adding aliquots to scintillation solution (15 mL) consisting of an equivolume mixture of toluene and 2-methoxymethanol containing 0.4% of PPO (2,5-diphenyloxazole) and 0.1% of POPOP [1,4-bis(5-phenyloxazol-2-yl)benzene]. Radioactivity was assayed on a Packard Tri-Carb 300C liquid scintillation spectrometer, with counting efficiencies being determined using an external ²²⁶Ra standard.

Radioactivity associated with the solvent-extracted soils was measured by combustion of the soils in a Packard Model 306 sample oxidizer as previously reported (Smith and Muir, 1984).

RESULTS AND DISCUSSION

Since glufosinate-ammonium is an ammonium salt (1), it must be assumed that in the near-neutral prairie soils (Table I) the compound undergoes dissociation to the anionic form with the ammonium cation being adsorbed to soil colloids. The glufosinate anion would then reassociate with inorganic cations present in the soil before undergoing breakdown. A similar dissociation of dimethylamine salts of the acidic herbicides 2,4-D and dicamba has already been reported for Saskatchewan soils (Grover and Smith, 1974).

Several solvent systems were compared to determine the most efficient for the recovery of radioactivity from air-dried soils fortified 7 days previously with 2 ppm of [¹⁴C]glufosinate-ammonium. Extraction solvents such as aqueous methanol and aqueous acetonitrile recovered <25% of the applied radioactivity. Water was found to extract over 60% of the initial ¹⁴C, but the solutions were highly colored. Aqueous calcium hydroxide solution gave recoveries of [¹⁴C]glufosinate from all soils of over 90%, presumably as the calcium salt, and yielded colorless extracts. It was also noted that the extended extraction procedure, involving the overnight contact of the treated soils with the alkaline solution, was necessary to give reproducible recoveries of radioactivity.

The degradation rates of [¹⁴C]glufosinate in Saskatchewan soils at 85% of field capacity and at 20 °C are compared in Table II. Extraction of the soils after incubation for 0.1 day indicated (Table II) that over 90% of the applied radioactivity was recoverable from the soils with the ratio of [¹⁴C]glufosinate to ¹⁴C products being the same as in the supplied [¹⁴C]herbicide. This confirmed that no degradation of the [¹⁴C]glufosinate had occurred as a result of the soil extraction procedure and subsequent workup.

With time, there was a loss of extractable radioactivity from the treated soils. By the end of the 84-day incubation period 29, 52, and 35% of the applied ¹⁴C was solvent recoverable from the clay, clay loam, and sandy loam

Table II. Radioactivity Recovered from Soils Treated with 2 ppm [¹⁴C]Glufosinate-Ammonium following Incubation at 20 ± 1 °C and 85% of Field Capacity

| days | % of applied radioactivity recovered ^a | | |
|------------|---|-------------------------------|--|
| | ¹⁴ C solvent extractable | [¹⁴ C]glufosinate | ¹⁴ C degradation product(s) |
| Clay | | | |
| 0.1 | 102 | 97 | 5 |
| 3 | 90 | 55 | 35 |
| 7 | 77 | 31 | 46 |
| 14 | 74 | 15 | 59 |
| 28 | 48 | 8 | 40 |
| 56 | 42 | 3 | 39 |
| 84 | 29 | 4 | 25 |
| Clay Loam | | | |
| 0.1 | 90 | 85 | 5 |
| 3 | 90 | 55 | 35 |
| 7 | 83 | 32 | 51 |
| 14 | 84 | 22 | 62 |
| 28 | 77 | 23 | 54 |
| 56 | 59 | 4 | 55 |
| 84 | 52 | 3 | 49 |
| Sandy Loam | | | |
| 0.1 | 97 | 92 | 5 |
| 3 | 94 | 47 | 47 |
| 7 | 80 | 24 | 56 |
| 14 | 78 | 9 | 69 |
| 28 | 56 | 6 | 50 |
| 56 | 42 | 2 | 40 |
| 84 | 35 | 2 | 33 |

^a Average of duplicate samples.

(Table II). Thin-layer chromatographic and radiochemical analysis indicated that there was a very rapid conversion of [¹⁴C]glufosinate to a product, or products, possessing a higher R_f value than the parent herbicide (Table II). Although this material appeared as a single broad spot on the cellulose plates with both chromatographic solvent systems, it is possible that more than one ¹⁴C compound was present.

Thus, it would appear that [¹⁴C]glufosinate underwent rapid transformation in the moist nonsterile soils to ¹⁴C product(s) which, in all soils, reached a concentration maximum after 14 days (Table II) and then slowly declined. After 28 days in soils incubated at 20 °C, <10% of the applied herbicide remained in the clay and sandy loam while 23% was present in the clay loam (Table II). After 84 days, breakdown of [¹⁴C]glufosinate was over 95% complete in all soils with between 25 and 49% of the applied radioactivity remaining in the form of ¹⁴C degradation product(s) (Table II). In all soils, the time for 50% of the herbicide to be degraded was between 3 and 7 days (Table II). The regression mean square values obtained from the first-order regression equations for the degradation of [¹⁴C]glufosinate were 0.77, 0.92, and 0.81 for the clay, clay loam, and sandy loam, respectively, indicating that, with the possible exception of the clay loam, the loss of [¹⁴C]glufosinate from the soils was not highly correlated with a first-order degradation mechanism.

In air-dried soils at 20 °C and at 10% of their respective field capacities, [¹⁴C]glufosinate underwent no detectable breakdown or transformation. Thus, after 35 and 70 days, almost quantitative recovery of the originally applied [¹⁴C]glufosinate was noted. There was a similar lack of breakdown of [¹⁴C]glufosinate in the moist soils, incubated at 20 °C in the Mason jars, that had been subjected to chloroform fumigation following treatment, 1 h previously, with the [¹⁴C]herbicide. After 21 days, 84, 85, and 82% of the applied radioactivity was recovered from the clay, clay loam, and sandy loam as [¹⁴C]glufosinate and 14, 5,

Table III. Radioactivity Recovered from Soils Treated with 2 ppm [¹⁴C]Glufosinate-Ammonium following Incubation at 10 ± 1 °C and 85% of Field Capacity

| days | % of applied radioactivity recovered ^a | | |
|------|---|-------------------------------|--|
| | ¹⁴ C solvent extractable | [¹⁴ C]glufosinate | ¹⁴ C degradation product(s) |
| | Clay | | |
| 7 | 96 | 53 | 43 |
| 14 | 90 | 36 | 54 |
| 21 | 82 | 23 | 59 |
| 35 | 69 | 13 | 56 |
| | Clay Loam | | |
| 7 | 90 | 61 | 29 |
| 14 | 88 | 43 | 45 |
| 21 | 87 | 30 | 57 |
| 35 | 84 | 20 | 64 |
| | Sandy Loam | | |
| 7 | 99 | 54 | 45 |
| 14 | 88 | 28 | 60 |
| 21 | 88 | 18 | 70 |
| 35 | 82 | 8 | 74 |

^a Average of duplicate samples.

and 12% of the ¹⁴C as degradation products. The fact that the [¹⁴C]herbicide is not significantly degraded in dry or sterilized soils indicated that glufosinate is degraded by soil microbial processes.

The breakdown of [¹⁴C]glufosinate was slower in moist soils at 10 °C (Table III) than at 20 °C (Table II). At 10 °C the loss of [¹⁴C]glufosinate was highly correlated with first-order kinetics, with regression mean square values of 0.99 for the sandy loam and 0.98 for the other two soils. The times for 50% of the glufosinate to be degraded were 9, 11, and 8 days in the clay, clay loam, and sandy loam, respectively. In addition to [¹⁴C]glufosinate there appeared on the chromatographic plates, with both solvent systems, a second area of radioactivity with a higher *R_f* value than that of the herbicide. However, it was not possible to conclude whether this radioactivity was due to a single product, or several.

After 5 weeks of incubation at 10 °C, between 69 and 84% of the applied radioactivity was solvent recoverable from the soils and less than 20% of the applied ¹⁴C was in the form of [¹⁴C]glufosinate (Table III). At 10 °C the breakdown of the ¹⁴C degradation product(s) was considerably slower than at 20 °C, and after 5 weeks at the lower temperature, between 56 and 74% of the applied ¹⁴C herbicide was identifiable as transformation product(s) in the three soils (Table III).

From the present studies little can be said about the degradation product(s) of glufosinate, but, being an amino acid, it can perhaps be assumed that the herbicide is biologically transformed by such mechanisms as deamination, decarboxylation, oxidative deamination, and reductive deamination that are known to occur with the other amino acids (Alexander, 1977).

In the [¹⁴C] carbon dioxide evolution studies there was, with time, a gradual release of [¹⁴C]carbon dioxide from the moist nonsterile soils at 20 °C (Figure 1). At the end of the 90-day incubation period 55, 44, and 28% of the applied [¹⁴C]glufosinate-ammonium had been thus released from the sandy loam, clay, and clay loam. In contrast, the cumulative release of [¹⁴C]carbon dioxide from moist soils incubated for 90 days, after treatment with [¹⁴C]glufosinate-ammonium 1 h prior to fumigation with chloroform, was 2.5%, 1.7%, and 2.9% from the clay, clay loam, and sandy loam, respectively. These results indicate that in the moist nonsterile soils [¹⁴C]glufosinate is converted to

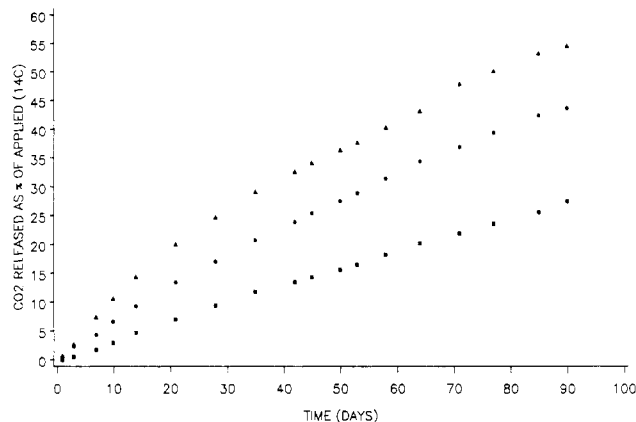


Figure 1. Cumulative release of [¹⁴C]carbon dioxide from clay (●), clay loam (■), and sandy loam (▲) treated with 2 ppm of [¹⁴C]glufosinate-ammonium following incubation at 20 ± 1 °C and 85% of field capacity. Average of duplicate samples. After 90 days the cumulative release of [¹⁴C]carbon dioxide from soils treated for 1 h with [¹⁴C]glufosinate-ammonium, prior to fumigation with chloroform and similar incubation, was 2.5%, 1.7%, and 2.9% of the applied ¹⁴C from the clay, clay loam, and sandy loam, respectively.

¹⁴C product(s) which themselves undergo further transformation to [¹⁴C]carbon dioxide.

A portion of the [¹⁴C]carbon dioxide emanating from the [¹⁴C]glufosinate and/or ¹⁴C degradation product(s) or small [¹⁴C]carbon-containing fragments formed by breakdown of these compounds will be incorporated into the soil microbial biomass. With time, these microorganisms will themselves be degraded and the ¹⁴C originally incorporated into the microbial cellular components released as [¹⁴C]-carbon dioxide and other ¹⁴C products that can eventually be incorporated into the fulvic, humic, and humin fractions of soil organic matter.

The chloroform fumigation technique of Jenkinson and Powlson (1976) has been used to determine the incorporation of various ¹⁴C compounds, including herbicides, into the soil microbial biomass by measuring the [¹⁴C]carbon dioxide evolved from soil samples following fumigation with chloroform and subsequent incubation (Anderson and Domsch, 1978; Nicolardot et al., 1984; Soulas et al., 1984; Voroney and Paul, 1984). The chloroform treatment disrupts the microbial cell membranes, releasing the internal ¹⁴C constituents to microorganisms surviving the chloroform fumigation (Voroney and Paul, 1984), and a portion of the radioactivity from these ¹⁴C constituents is liberated as [¹⁴C]carbon dioxide. Thus, radioactivity incorporated into the microbial biomass can be assessed by measuring the flush of [¹⁴C]carbon dioxide evolved after the chloroform treatments. It must be confirmed that insignificant amounts of the pesticide are degraded to [¹⁴C]carbon dioxide in chloroform-treated soils after similar incubation, and a correction is made for any such releases (Soulas et al., 1984). In the present studies less than 2% of the applied radioactivity was evolved as [¹⁴C]carbon dioxide from moist soils treated with the [¹⁴C]herbicide 1 h prior to chloroform fumigation and subsequent incubation for 21 days.

The amount of radioactivity incorporated into the soil microbial biomass was calculated (as a percentage of the applied ¹⁴C) by dividing the flush of [¹⁴C]carbon dioxide released from the fumigated soils (expressed as percent of the original ¹⁴C treatment) by the mineralization rate constant (*K_c*).

The results from these fumigation experiments indicate that, after 90 days of incubation at 20 ± 1 °C and 85% of

Table IV. Radioactivity Recovered after 90 Days from Soils Treated with 2 ppm [¹⁴C]Glufosinate-Ammonium following Incubation at 20 ± 1 °C and 85% Field Capacity

| | % of applied ¹⁴ C ^a | | |
|--|---|-----------|------------|
| | clay | clay loam | sandy loam |
| radioact released as CO ₂ | 44 | 28 | 55 |
| aq extr radioact | 22 | 37 | 19 |
| radioact in biomass | 8 | 2 | 10 |
| radioact in fulvic, humic, and humin soil fractions ^b | 7 | 13 | 7 |
| total radioact | 81 | 80 | 91 |

^a Average of duplicate samples. ^b Obtained by combustion of soils after completion of biomass determinations and solvent extraction. Corrections were made to account for radioactive biomass carbon not released as [¹⁴C]carbon dioxide after chloroform fumigation.

field capacity, 9.5, 8.0, and 2.4% of the radioactivity from the applied [¹⁴C]glufosinate-ammonium had been incorporated into the microbial biomass of the sandy loam, clay, and clay loam.

Following the chloroform fumigation studies, solvent extraction of the 90-day-incubated soils recovered between 19 and 37% of the applied radioactivity. Combustion analysis of the solvent-extracted soils, after corrections to account for radioactive ¹⁴C biomass not released as [¹⁴C]carbon dioxide in the above fumigation experiments, indicated (Table IV) that between 7 and 13% of radioactivity from the [¹⁴C]glufosinate-ammonium treatments was associated with the fulvic, humic, and humin soil fractions.

From the studies conducted in the sealed Mason jars, between 80 and 91% of the originally applied radioactivity could be accounted for (Table IV). Some of the unaccounted for radioactivity can perhaps be attributed to [¹⁴C]carbon dioxide losses that occurred at weekly intervals while the vials containing the aqueous sodium hydroxide adsorbent were being replaced. It is interesting to note that the amounts of solvent-extractable radioactivity recovered from the soils in the [¹⁴C]carbon dioxide evolution studies after 90 days (Table IV) were about 25–45% lower than those recovered in the persistence studies after an 84-day incubation period (Table II). A possible explanation for this difference could be due to the fact that the [¹⁴C]carbon dioxide evolution studies were carried out during April, May, and June 1986, while the soil persistence studies were conducted during October, November, and December 1986. Thus, in the fresher soils, a larger microbial population could perhaps have resulted in a slightly increased breakdown of the various ¹⁴C degradation products.

The present investigations indicate that glufosinate undergoes rapid microbial transformation in moist nonsterile soils. In dry soils, or in soils that have been sterilized by fumigation with chloroform, loss of radioactivity from the soils and transformation to other ¹⁴C product(s) was minimal. The ¹⁴C breakdown product(s) are considerably more stable in the soils than glufosinate but are nevertheless slowly degraded. The persistence of the glufosinate is greater in the clay loam than in the clay and sandy loam. As expected, breakdown of glufosinate

was faster in soils at 20 than at 10 °C.

It can therefore be concluded that, under field conditions, carryover of residues in the soil to the next crop year would not be expected following spring treatments of glufosinate-ammonium.

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LITERATURE CITED

- Alexander, M. "Mineralization and Immobilization of Nitrogen". In *Introduction to Soil Microbiology*, 2nd ed.; Wiley: New York, 1977.
- Anderson, J. P. E.; Domsch, K. H. "Mineralization of Bacteria and Fungi in Chloroform Fumigated Soils". *Soil Biol. Biochem.* 1978, 10, 207–213.
- Anonymous "Product Information HOE 39 866". Hoechst Aktiengesellschaft, Frankfurt, FRG, 1983.
- Bayer, E.; Gugel, K. H.; Hägele, K.; Hagenmaier, H.; Jessipow, S.; König, W. A.; Zähler, H. "Phosphinothricin und Phosphinothricyl-Alanyl-Alanin". *Helv. Chim. Acta* 1972, 55, 224–239.
- Biederbeck, V. O.; Campbell, C. A.; Zentner, R. P. "Effect of Crop Rotation and Fertilization on some Biological Properties of a Loam in Southwestern Saskatchewan". *Can. J. Soil Sci.* 1984, 64, 355–367.
- Chaussod, R.; Nicolardot, B. "Mesure de la Biomasse Microbienne dans les Sols Cultivés. I. Approche Cinétique et Estimation Simplifiée du Carbone Facilement Minéralisable". *Rev. Ecol. Biol. Sol.* 1982, 19, 501–512.
- Fraser, A. R.; Ridley, S. M. "Kinetics for Glutamine-Synthetase Inhibition by Phosphinothricin and Measurement of Other Enzyme Activities *In Situ* in Isolated Asparagus Cells Using a Freeze-Thaw Technique". *Planta* 1984, 161, 470–474.
- Grover, R.; Smith, A. E. "Adsorption Studies with the Acid and Dimethylamine Forms of 2,4-D and Dicamba". *Can. J. Soil Sci.* 1974, 54, 179–186.
- Jenkinson, D. S.; Powlson, D. S. "The Effects of Biocidal Treatments on Metabolism in Soil. I. Fumigation with Chloroform". *Soil Biol. Biochem.* 1976, 8, 167–177.
- Leason, M.; Cunliffe, D.; Parkin, D.; Lea, P. J.; Mifflin, B. J. "Inhibition of Pea Leaf Glutamine Synthetase by Methionine Sulphoxime, Phosphinothricin and Other Glutamine Analogues". *Phytochemistry* 1984, 21, 855–857.
- Nicolardot, B.; Chaussod, R.; Catroux, G. "Decomposition de Corps Microbiens dans des Sols Fumigés au Chloroforme: Effets du Type de Sol et de Microorganisme". *Soil Biol. Biochem.* 1984, 16, 453–458.
- Smith, A. E.; Muir, D. C. G. "Determination of Extractable and Nonextractable Radioactivity from Small Field Plots 45 and 95 Weeks after Treatment with [¹⁴C]Dicamba, (2,4-Dichloro-¹⁴C]phenoxy)acetic Acid, [¹⁴C]Triallate, and [¹⁴C]Trifluralin". *J. Agric. Food Chem.* 1984, 32, 588–593.
- Soulas, G.; Chaussod, R.; Verguet, A. "Chloroform Fumigation Technique as a Means of Determining the Size of Specialized Soil Microbial Populations: Application to Pesticide-Degrading Microorganisms". *Soil Biol. Biochem.* 1984, 16, 497–501.
- Voroney, R. P.; Paul, E. A. "Determination of *k_c* and *k_n* *In Situ* for Calibration of the Chloroform Fumigation-Incubation Method". *Soil Biol. Biochem.* 1984, 16, 9–14.

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