DATA EVALUATION RECORD

STUDY 3

CHEM 417300 Glyphosate Acid §161-3
CAS No. 1071-83-6
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 44320644
Esser, T. 1996. Glyphosate acid: [p-methylene-^{14}C]glyphosate acid: photodegradation in/on soil by natural sunlight. PTRL Project No.: 547W. Unpublished study performed by PTRL West, Inc., Richmond, CA; and submitted by Zeneca Ag Products, Wilmington, DE.

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CONCLUSIONS

Degradation - Photodegradation on Soil

1. This study is scientifically valid and provides useful information on the photodegradation of glyphosate acid on soil.

2. This study does not meet Subdivision N Guidelines for the fulfillment of EPA data requirements on photodegradation on soil for the following reason:

   (i) material balances were <90% of the applied radioactivity.

3. Radiolabeled [p-methylene-^{14}C]glyphosate acid, at a nominal application rate of 10.2 ppm, appeared to be photolytically stable on sandy loam soil that was irradiated with natural sunlight in Richmond, CA, for up to 30 days. Registrant-calculated half-lives for the parent compound on the irradiated and dark control soils were 6.5 days ($r^2 = 0.94$) and 6.6 days ($r^2 = 0.92$), respectively. For both the irradiated and dark control soils, however, the apparent first half-life occurred prior to 6 days (between 2 and 6 days). All data, designated as percentages of the applied radioactivity, represent percentages of the nominal application. Data are reported as means of two replicates unless otherwise noted. In irradiated soil samples, the parent compound was initially 89.2% of the applied radioactivity, decreased to 54.4% by 2 days and 26.5% by 6 days posttreatment, and was 3.2% at 30 days. The major degradate AMPA was a maximum of 28.4% of the applied radioactivity at 20 days posttreatment and was 19.8% at 30 days. Nonextractable [^{14}C]residues were a maximum of 33.6% of the applied radioactivity at 30 days posttreatment; 6.3%, 3.6%, and 23.7% of the applied radioactivity was associated with the fulvic acid, humic acid, and humin fractions, respectively, at day 30. Evolved $^{14}CO_2$ accounted for 15.0% of the applied radioactivity at day 2, was a maximum of 32.9% of at 12 days posttreatment, and was 29.5% at 30 days; [^{14}C]organic volatiles were a maximum of 1.9% of the applied radioactivity at 20 days posttreatment. In the dark control soil samples, the parent compound was initially 89.2% of the applied radioactivity, decreased to 59.1% by 2 days and 24.8% by 6 days, and was 3.6% at 30 days posttreatment. The major degradate AMPA was a maximum of 28.0% of the applied radioactivity at 20 days posttreatment and was 24.3% at 30 days. Evolved $^{14}CO_2$ accounted for 17.2% of the applied radioactivity at day 2, was a maximum of 36.7% at 12 days posttreatment and was 30.1% at 30 days; [^{14}C]organic volatiles were a maximum of 5.8% of the applied radioactivity at 30 days posttreatment.

METHODOLOGY

Subsamples (3.1 g) of sieved (2 mm) sandy loam soil (collected from Visalia, CA; 71.2% sand, 20.0% silt, 8.8% clay, 0.5% organic matter, pH 8.3, CEC 6.1 meq/100 g; Table V,

p. 40) were weighed into round quartz glass containers, moistened with deionized water to form a slurry, and then air dried to form a 1- to 2-mm thick layer (p. 22). The soil samples were adjusted to 75% of 0.33 bar moisture content; samples were weighed periodically, and water was added as necessary in order to maintain the soil moisture content at 75% of 0.33 bar (p. 23). Soil samples were treated with [p-methylene-^{14}C]glyphosate acid {PMG; -(phosphonomethyl)glycine; radiochemical purity 97.3%, specific activity 42.7 mCi/mmole; p. 15} at a nominal application rate of 10.2 ppm (p. 16). Sample containers were sealed and incubated at 24.9 ± 0.03 °C in a chamber equipped with a recirculating water bath (Table II, p. 37); temperature was monitored using thermocouples placed inside the water bath and two samples (one irradiated and one dark control; p. 21). Dark controls were prepared as above, except that the sample containers were borosilicate glass and wrapped with aluminum foil. Humidified air was drawn through the chamber and into an ethylene glycol trap and two 10% NaOH traps in series (Figure 5, p. 55). Samples were irradiated under natural sunlight for up to 30 days (October 18 to November 17, 1995 in Richmond, CA; latitude 38°N, longitude 122°W); daily weather conditions were provided (Table III, p. 38). The light intensity of the natural sunlight (measured at 250-700 nm) was a maximum of 2.4 x 10^4 μW/cm^2 over the incubation period (Table IV, p. 39); total light energy was 7.0 ± 2.0 W/min/cm^2. Duplicate samples were removed for analysis at 0, 2, 6, 12, 20, and 30 days posttreatment.

At each sampling interval, samples were extracted twice by shaking with acidified 1 M KH_2PO_4 (pH 2, H_3PO_4) and centrifuged, and the supernatants were decanted and combined (p. 24; Figure 6, p. 56). Aliquots of the combined extracts were analyzed for total radioactivity by LSC. An aliquot of the extract was filtered (0.45 μm) and analyzed by HPLC (Bio-Rad HRLC Glyphosate column) using an isocratic mobile phase of 5 mM KH_2PO_4 (pH 2.1, H_3PO_4) in 4% methanol (p. 26); the limit of detection was 0.03 ppm or 0.3% of the applied radioactivity (p. 27). Eluent fractions were collected at half-minute intervals for analysis by LSC. Samples were co-chromatographed with nonradiolabeled reference standards. To confirm compound identities, the extracts were also analyzed by one-dimensional TLC on silica gel plates developed in methanol:ammonium hydroxide (29.9%):trichloroacetic acid:water (55:14:0.45:31, v:v:v:v); areas of radioactivity on the TLC plates were quantified by radioimage scanning. Samples were co-chromatographed with nonradiolabeled reference standards visualized using iodine vapors. Triplicate samples of the post-extracted soil were analyzed by LSC following combustion.

To determine bound [^{14}C]residues, selected post-extracted soil samples (irradiated day 30) were extracted twice by shaking with 0.1 M NaOH for 24 hours under nitrogen gas and centrifuged, and the supernatants were decanted and combined (p. 24; Figure 6, p. 56). The combined extract was acidified to pH 1 (6 *N* HCl) and centrifuged, and the supernatant was analyzed by LSC to determine [^{14}C]residues associated with the fulvic acid fraction. The soil pellet was redissolved in 0.1 M NaOH and analyzed by LSC to determine [^{14}C]residues associated with the humic acid fraction. The remaining

[^{14}C]residues in the extracted soil were associated with the humin fraction.

At each sampling interval, an aliquot of each trapping solution was analyzed by LSC (p. 23). To confirm the presence of $^{14}CO_2$ in selected NaOH traps (day 6), aliquots of the NaOH solution were precipitated with $BaCl_2$ (p. 25). Due to high $^{14}CO_2$ evolution and low material recoveries, an acidic phosphate buffer (pH 2.0) was injected into sample containers (days 20 and 30); the containers were connected to the trapping system as described above and the soil:solution mixture was vortexed to release $^{14}CO_2$ adsorbed to the soil.

To determine soil viability prior to incubation, soil samples were serially diluted in buffer solutions, and aliquots of the diluted samples were added to selective-media plates and incubated at ambient temperature (p. 22). The plates were analyzed visually for microbial growth; a total count of colonies was performed. Total bacteria, actinomycetes, and fungi were 5.1×10^6, 2.1×10^6, and 0.009×10^6 CFU/g of soil, respectively (Table VI, p. 41).

DATA SUMMARY

Radiolabeled [p-methylene-^{14}C]glyphosate acid (radiochemical purity 97.3%), at a nominal application rate of 10.2 ppm, appeared to be photolytically stable on sandy loam soil that was irradiated with natural sunlight in Richmond, CA, for up to 30 days. Registrant-calculated half-lives for the parent compound on the irradiated and dark control soils were 6.5 days ($r^2 = 0.94$) and 6.6 days ($r^2 = 0.92$), respectively (Tables XII-XIII; pp. 49, 50). For both the irradiated and dark control soils, however, the apparent first half-life occurred prior to 6 days (between 2 and 6 days). All data, designated as percentages of the applied radioactivity, represent percentages of the nominal application. Data are reported as means of two replicates unless otherwise noted. In irradiated soil samples, the parent compound was initially present at 89.2% of the applied radioactivity, decreased to 54.4% by 2 days and 26.5% by 6 days posttreatment, and was 3.2% of the applied at 30 days posttreatment (Tables IXA, XI; pp. 44, 48). The major degradate

aminomethylphosphonic acid (AMPA)

was initially (day 0) present at 2.2% of the applied radioactivity, increased to a maximum of 28.4% of the applied by 20 days posttreatment, and was 19.8% of the applied at 30 days posttreatment. An unidentified minor degradate (Degradate 1) was present at a maximum of 3.4% of the applied radioactivity at 20 days posttreatment. Uncharacterized [^{14}C]residues were $\leq$0.71% (single replicate) of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were initially (day 0) 3.1% of the applied radioactivity, increased to 13.9% of the applied by 12 days, and were a maximum of 33.6% of the applied at 30 days posttreatment; 6.3%, 3.6%, and 23.7% of the applied radioactivity was associated with the fulvic acid, humic acid, and humin fractions,

respectively, at 30 days posttreatment (p. 31). Evolved $^{14}CO_2$ initially (day 2) accounted for 15.0% of the applied radioactivity, increased to a maximum of 32.9% by 12 days, and was 29.5% at 30 days posttreatment (Table XA, p. 46; see Comment #1); [^{14}C]organic volatiles were a maximum of 1.9% of the applied radioactivity at 20 days posttreatment.

In the dark control soil samples, the parent compound was initially present at 89.2% of the applied radioactivity, decreased to 59.1% by 2 days and 24.8% by 6 days posttreatment, and was 3.6% of the applied at 30 days posttreatment (Table IXB, p. 45). The major degradate

AMPA

was initially (day 0) present at 2.2% of the applied radioactivity, increased to a maximum of 28.0% of the applied by 20 days posttreatment, and was 24.3% of the applied at 30 days posttreatment. An unidentified minor degradate (Degradate 1) was present at a maximum of 1.5% of the applied radioactivity at 20 days posttreatment. Uncharacterized [^{14}C]residues were ≤0.49% (one replicate) of the applied radioactivity throughout the incubation period. Nonextractable [^{14}C]residues were initially (day 0) 3.1% of the applied radioactivity and were a maximum of 7.3% of the applied at 30 days posttreatment. Evolved $^{14}CO_2$ initially (day 2) accounted for 17.2% of the applied radioactivity, increased to a maximum of 36.7% of the applied by 12 days posttreatment, and was 30.1% of the applied at 30 days posttreatment (Table XB, p. 47; see Comment #1); [^{14}C]organic volatiles were a maximum of 5.8% of the applied radioactivity at 30 days posttreatment.

Material balances (based on LSC analysis of individual replicates) were variable for both the irradiated and dark control soil samples, at 81.8-95.6% and 80.0-97.6% (with the exceptions of 64.4% and 66.8% for single replicates) of the applied radioactivity, respectively (Table VII, VIII; pp. 42, 43; see Comment #1). A pattern of loss was observed for the dark control samples.

COMMENTS

1. The material balances were 81.8-95.6% (8 of 12 samples <90%) and 64.4-97.6% (7 of 12 samples <90%) for the irradiated and dark control samples, respectively (Tables VII, VIII; pp. 42, 43). A pattern of loss was observed for the dark control samples. Subdivision N Guidelines require that material balances be in the reasonable range of 90-110% of the applied radioactivity. The study author state that the material losses experienced after 2 days posttreatment were due to the rapid and steady formation of $^{14}CO_2$ (p. 30; Table VIII, p. 43); the reviewer noted that the maximum $^{14}CO_2$ concentrations were observed at 12 days posttreatment rather than 30 days posttreatment. The study author reported corrected $^{14}CO_2$ data values in an attempt to account for the lost

radioactivity (Tables XA, XB; pp. 46, 47). No data were provided to support the conclusion that the unrecovered radioactivity was $^{14}CO_2$.

2. Nonextractable [^{14}C]residues were unacceptably high in the irradiated soil, accounting for 33.6% of the applied radioactivity at 30 days posttreatment (Table XI, p. 48). Additional extractions may have been useful in removing the nonextractable [^{14}C]residues. However, it was determined that 6.3%, 3.6%, and 23.7% of the radioactivity was associated with the fulvic acid, humic acid, and humin fractions, respectively, at 30 days posttreatment (p. 31). In the dark control soil, nonextractable [^{14}C]residues were much lower, accounting for 7.3% of the applied radioactivity at 30 days posttreatment.

3. The application of the parent corresponded to 10 lb/A, which is 25% greater than the maximum application rate (8 lb/acre; p. 23).

4. A three-year plot history indicated that the sandy loam soil utilized in the study was previously treated with Gramoxone Extra® (paraquat) in 1992, and diazinon and malathion in 1993 (p. 21).

5. The study author stated that the sandy loam soil was the same type of soil used in an aerobic soil metabolism study of glyphosate acid (p. 22; MRID 44320645).

6. The proposed metabolic pathway for the degradation of glyphosate acid was presented in Figure 16 (p. 66).

7. Characteristics of a loam soil were also reported in Table V (p. 40). The reviewer notes that this soil was not used in the study.

8. The reviewer notes that the apparent first half-life occurred prior to 6 days in both the irradiated and dark control soils. The half-life of the parent in each soil occurred between 2 and 6 days (the next sampling interval). Because the half-lives were so short, to determine if the compound is truly photolytically stable on soil, it may be necessary to conduct the study using sterilized soils in order to remove the effects of microbial degradation from the overall degradation.

9. The method detection limits were not reported for LSC or TLC analyses. It is necessary that both limits of detection and quantitation be reported to allow the reviewer to evaluate the adequacy of the method for the determination of the test compound and its degradates.

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