UNDATED

DATA EVALUATION RECORD

STUDY 3

CHEM 103601 Glyphosate §162-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41723701
Kesterson, A. and S.B. Jackson. 1990. Anaerobic aquatic metabolism of [^{14}C]glyphosate. PTRL Report No. 1304. PTRL Study No. 367. Performed by Pharmacology and Toxicology Research Laboratory East, Inc., Richmond, KY, and submitted by Monsanto Agricultural Company, St. Louis, MO.

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CONCLUSIONS:

Metabolism - Anaerobic Aquatic

1. Study MRID #41723701 does not satisfy the anaerobic aquatic metabolism (162-3) data requirement for the following reasons:

a) An accurate assessment of the dissipation pattern of glyphosate and the formation and dissipation of its degradates could not be made because the concentrations of glyphosate and its degradate AMPA were too variable between 15 and 90 days posttreatment.

b) Freezer storage stability data were not provided.

c) Two degradates that comprised up to 1.4% of the applied (0.05 ppm) and 6.2% (0.24 ppm) were not identified.

2. A new anaerobic aquatic metabolism (162-3) study needs to be completed.

METHODOLOGY:

Definitive experiment

Silty clay loam sediment (12% sand, 59% silt, 29% clay, 0.9% organic matter, pH 6.6, CEC 16 meq/100 g) was collected from a pond bottom, flooded with water from the same pond (pH 7.3, total alkalinity 84 mg/L $CaCO_3$, total suspended solids 6 mg/L), and incubated at 4 C for 6 days. In the presence of a nitrogen atmosphere, aliquots (58 mL) of pond water were placed in flasks and treated at 3.87 ppm with an aqueous solution of [^{14}C]glyphosate (radiochemical purity 98.8%, specific activity 3.99 mCi/mMole, Monsanto); then a portion (20 g dry weight) of silty clay loam sediment was added to each flask. The treatment rate was based on 20 g sediment and 101.5 mL water; water volume included 58 mL of pond water, 1 mL of test solution, and moisture in the sediment. Flasks were swirled to mix the contents, purged with nitrogen, sealed with ground-glass stoppers, and incubated in darkness at approximately 25 C. Duplicate flasks were sampled at 0, 1, 4, 7, 15, 29, 60, 90, 180, 270, and 365 days posttreatment. Volatiles were collected every 1-2 weeks during the study and when flasks were sampled; nitrogen was flushed through each flask then sequentially through ethylene glycol and 10% sodium hydroxide trapping solutions (Figure 1). Following collection of volatiles, the pH and dissolved oxygen content of each sediment:water system were determined.

The sediment and water fractions were separated using centrifugation. Aliquots of each water sample were analyzed for total radioactivity using LSC, then the remaining sample was stored at 4 C until HPLC analysis. Sediment fractions were extracted as presented in Table III; the 0- to 90-day samples were extracted twice (once for 30 minutes, then overnight) with 0.5 N potassium hydroxide, 180-day samples were extracted three times (30 minutes each) with 0.5 N ammonium hydroxide followed by three times (twice for 1 hour, then overnight) with 0.5 N potassium hydroxide, and 270- and 365-day samples were extracted three times (twice for 30 minutes, then overnight) with 0.5 N potassium hydroxide. The 15- and 29-day samples were also extracted with 0.03 M ethylenediaminetetraacetic acid after the potassium hydroxide extractions. Extracts were analyzed for total radioactivity using LSC and stored at 4 C until HPLC analysis. Unextractable [^{14}C]residues remaining in the extracted sediment were quantified by LSC following combustion.

To analyze each sediment:water system for glyphosate and its degradates, 10% of the water fraction (if it contained >2% of the applied radioactivity) was combined with 10% of the potassium hydroxide extract from the sediment and 10% of the ammonium hydroxide extract (if available) and adjusted to pH 2-3. Aliquots of the pooled sample were analyzed using HPLC; fractions were collected at 60- to 90-second intervals and analyzed for radioactivity using LSC. Radioactive peaks were identified by comparison to retention times of reference standard [^{14}C]glyphosate and its degradate [^{14}C]aminomethylphosphonic acid.

Trapping solutions were analyzed for total radioactivity using LSC.

Supplemental biometer flask experiment

Under a nitrogen atmosphere, pond water (88 mL) and silty clay loam sediment (20 g dry weight) were placed in six biometer flasks and treated with [^{14}C]glyphosate at 4.15 ppm, then sealed and incubated as described above. The side well of each biometer flask contained 1

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N sodium hydroxide to trap evolved CO_2, and a polyurethane foam plug was placed in the connecting arm to trap organic volatiles (Figure 2). Humidified nitrogen was drawn through the flasks to maintain a positive pressure. Sodium hydroxide solutions and polyurethane foam plugs were removed and replaced, if necessary, every 2 weeks. Duplicate flasks were sampled at 1, 3, and 6 months posttreatment. Sediment and water fractions were separated and analyzed as described above. Sodium hydroxide trapping solutions and polyurethane foam plugs were analyzed for total radioactivity using LSC.

DATA SUMMARY:

[^{14}C]Glyphosate (radiochemical purity 98.8%), at 3.87 ppm, degraded with an observed half-life of 4-7 days in anaerobic (flooded plus nitrogen atmosphere) silty clay loam sediment that was incubated in the dark at 25.4 ± 0.84 C for 1 year; the calculated half-life was 208 days (r = 0.749). Glyphosate decreased from 95.1-95.4% of the applied at day 0 to 47.0-47.6% at 7 days, then was variable ranging from 12.9 to 58.4% between 15 and 90 days, and was 17.8-22.8% at 180-365 days (Table XI). The major nonvolatile degradate was

aminomethylphosphonic acid (AMPA).

AMPA comprised 3.4-4.2% of the applied at day 0, increased to a maximum 31.6% at 15 days, then ranged from 13.9 to 23.7% up to 365 days. Two unidentified unknowns A and B were detected at maximums of 1.4% of the applied (0.05 ppm) at days 1 and 15, and 6.2% (0.24 ppm) at day 29, respectively (Table XI).

At 1 year posttreatment, evolved $^{14}CO_2$ was the major degradate totaling 35.0% of the applied radioactivity, organic volatiles accounted for 1.2%, and unextractable [^{14}C]residues accounted for 3.9% (Table VIII). [^{14}C]Residues associated with the water fraction of the sediment:water systems decreased from 7.6-8.3% of the applied at day 0 to 0.2% at day 365 (Table VIII). During the study, the pH of the sediment:water systems ranged from 5.7 to 6.5 and the dissolved oxygen content ranged from 1.2 to 3.7 mg/L (Table VI). Material balances ranged from 69.6 to 104.3% (mean 86.6 ± 10.4%) of the applied. In a related study using biometer flasks, it was determined that lost $^{14}CO_2$ could account for the low material balances in the definitive study.

COMMENTS:

1. An accurate assessment of the dissipation pattern of glyphosate and the formation and dissipation of its degradates could not be made because the concentrations of glyphosate and its degradate AMPA were too variable between 15 and 90 days posttreatment.

2. Apparently, water fractions and sediment extracts were stored at 4 C for up to 11 months prior to HPLC analysis. It was reported that parent glyphosate was stable during the 11-month storage period. To support this, the study authors reported that analysis of the day 0 potassium hydroxide sediment extract 7 days after sampling detected 91.7% of the recovered radioactivity as parent glyphosate (Figure 7) and when reanalyzed 11 months later detected 94.5% as glyphosate (Table X). The analysis of one sample does not establish that parent glyphosate was stable in all of the stored extracts and water samples. In the aerobic soil metabolism study (STUDY 2, MRID 41742901), a similar analysis of one soil extract detected that

glyphosate degraded by 10% during 14 months of storage at 4 C. A storage stability study should be provided for glyphosate and its degradate AMPA under the conditions that the sediment extracts and water samples were stored in this study.

3. Two degradates of [^{14}C]glyphosate (Unknowns A and B) were isolated and detected at up to 1.4% of the applied (0.05 ppm) and 6.2% (0.24 ppm), but were not identified. It was also reported that several other minor unknowns were detected, but that no single minor unknown exceeded 1% of the applied; the "others" combined were detected at up to 1.8% of the applied. Subdivision N guidelines specify that all degradates present at >0.01 ppm (approximately 0.3% of the applied) should be identified.

4. Apparently, neither UV absorbance nor radiometric detection was used in conjunction with the HPLC. The radiochromatograms that were provided were "reconstructed" following LSC analysis of eluate fractions collected during HPLC. Radioactive peaks were then identified by comparison to retention times of reference standard [^{14}C]glyphosate and [^{14}C]AMPA. It is preferred to use UV absorbance or radiometric detection during HPLC analysis to better monitor the separation of compounds especially when the compounds have a varying retention time, as the study authors reported was the case with glyphosate.

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