UNDATED

DATA EVALUATION RECORD

STUDY 2

CHEM 103601 Glyphosate §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41742901
Kesterson, A.L. and R.H. Atkins. 1991. Aerobic metabolism of [^{14}C]glyphosate in sandy loam and silt loam soils with biometer flask. PTRL Report No. 1301. PTRL Study No. 368. R.D. No. 1031. 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 - Aerobic Soil

1. Study MRID #41742901 can be used for supplemental information but does not satisfy the Photodegradation in Water (161-2) data requirement for glyphosate for the following reasons.

a) In the day 0 soil extracts, parent glyphosate comprised only 44.5-50.6% of the applied radiocarbon in the sandy loam soil and 64.3-82.2% in the silt loam soil.

b) Freezer storage stability data were not provided.

c) Three degradates that comprised up to 3.5% of the applied (0.140 ppm), 3.6% (0.144 ppm), and 0.6% (0.024 ppm) were not identified.

2. A new aerobic soil metabolism study (162-1) needs to be completed.

3. Glyphosate degraded rapidly with half-lives of < 1 day in sandy loam soil and 1-3 days in silt loam soil that were incubated in the dark at 25°C and 75% of the 0.33 bar moisture. The major nonvolatile degradate was aminomethylphosphonic acid and reached a maximum conc. of 26.3-28.7% at 14 days. At 12 months postreatment, $^{14}CO_2$ was the major degradate and totaled ≥ 70.5% of the applied.

METHODOLOGY:

Samples (50 g) of air-dried, sieved (2 mm) sandy loam (68% sand, 22% silt, 10% clay, 2.8% organic matter, pH 7.3, CEC 9.0 meq/100 g) and silt loam (24% sand, 68% silt, 8% clay, 1.0% organic matter, pH 7.5, CEC 10.7 meq/100 g) soils were placed in biometer flasks, treated at 4.0 ppm with an aqueous solution of [^{14}C]glyphosate (radiochemical purity 98.8%, specific activity 3.98 mCi/mmole, Monsanto), and adjusted to 75% of 0.33 bar moisture. The side well of each biometer flask was filled with 1 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). The flasks were sealed and incubated at 25.0 $\pm$ 0.1 C in darkness. Humidified oxygen was drawn through the flasks to maintain a positive pressure. To maintain the soil moisture content, flasks were weighed at 3, 7, and 14 days posttreatment and monthly thereafter; water was added, as needed, to adjust the flasks to the original weight. Duplicate flasks of each soil were sampled at 0, 1, 3, 7, and 14 days and 1, 2, 3, 4, 6, 9, and 12 months posttreatment. Sodium hydroxide solutions and polyurethane foam plugs were removed and replaced, if necessary, at each sampling interval up to 4 months posttreatment; thereafter, the solutions were replaced monthly, and the foam plugs were removed at each sampling interval.

An aliquot (5 or 10 g) of each soil sample was extracted three times with 0.5 N potassium hydroxide followed by one extraction with 1 N potassium hydroxide. Following each extraction, the soil was separated from the solution using centrifugation. Extracts were combined, analyzed for total radioactivity using LSC, then stored at 4 C for up to 14 months prior to clean-up and further analysis. For clean-up, an aliquot of extract was applied to an AG-50W-X8 resin column (converted to ammonium form) and eluted with 0.1 N ammonium hydroxide. The eluate was concentrated and analyzed using HPLC using a Partisil SAX column eluted with methanolic potassium phosphate buffer; 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. Total radioactivity in the soil was quantified prior to and after extraction by LSC following combustion.

Sodium hydroxide trapping solutions were analyzed for total radioactivity using LSC. Polyurethane foam plugs were extracted with methanol and total radioactivity was quantified using LSC.

Six additional flasks of each soil type were autoclaved twice at 15 psi and 121 C for 1 hour prior to treatment and incubation as described above. Duplicate flasks of the sterile soils were sampled at 1, 3, and 6 months posttreatment and analyzed as previously described.

DATA SUMMARY:

[^{14}C]Glyphosate (radiochemical purity 98.8%), at 4.0 ppm, degraded with half-lives of <1 day in sandy loam soil and 1-3 days in silt loam soil that were incubated in the dark at 25.0 $\pm$ 0.1 C and 75% of 0.33 bar moisture for up to 12 months. In the sandy loam soil, glyphosate comprised 47.6% of the applied radioactivity at day 0, 32.4% at 1 day, 17.4% at 3 days, 2.8% at 1 month, and 0.5% at 12 months (Table XI). In the silt loam soil, glyphosate comprised 73.3% of the applied at day 0, 55.6% at 1 day, 25.6% at 3 days, 3.0% at 1

month, and 0.6% at 12 months (Table XII). The major nonvolatile degradate in the extracts of both soils was

aminomethylphosphonic acid (AMPA).

AMPA comprised 16.0-16.5% of the applied at day 0, was 26.3-28.7% at 14 days, decreased to 11.0-14.8% by 2 months, and was 1.5-2.2% at 9-12 months (Tables XI and XII). Three unidentified unknowns A, B, and C were detected at maximums of 3.5% of the applied (0.140 ppm), 3.6% (0.144 ppm), and 0.6% (0.024 ppm), respectively (Table XI).

At 12 months posttreatment, evolved $^{14}CO_2$ was the major degradate totaling an average 70.8% of the applied radioactivity in the sandy loam soil and 78.3% in the silt loam soil (Tables VII and VIII); organic volatiles accounted for <0.1% of the applied in both soils. Unextractable [^{14}C]residues comprised 3.2-11.9% of the applied in the sandy loam soil and 2.7-7.8% in the silt loam soil. Material balances ranged from 71.3 to 94.8% (mean 86.5 $\pm$ 5.3%) of the applied in the sandy loam soil and 81.4 to 103.2% (mean 91.4 $\pm$ 5.6%) in the silt loam soil (Tables VII and VIII).

In extracts of sterilized silt loam and sandy loam soil, glyphosate comprised 44.6-46.3% of the applied, respectively, at 6 months posttreatment; AMPA plus unknowns A and B were also detected. $^{14}CO_2$ was the major degradate (Tables XI and XII).

COMMENTS:

1. The study authors did not adequately define the "day 0" sample. In the day 0 soil extracts, parent glyphosate comprised only 44.5-50.6% of the applied in the sandy loam soil and 64.3-82.2% in the silt loam soil. Since glyphosate degrades rapidly, the time interval that occurred between treatment and extraction of the day 0 samples should be specified. It was reported that the glyphosate treatment solution was prepared with sterile, deionized water which would indicate that the glyphosate probably did not degrade prior to its application to the soil.

2. Soil extracts were stored at 4 C for up to 14 months prior to clean-up and further analysis. It was reported that extracts were analyzed for total radioactivity after storage to demonstrate that no losses of radiocarbon occurred during storage; however, those data were not provided. It was also reported that only minimal degradation of parent glyphosate occurred during the 14-month storage period. To support this, the study authors reported that analysis of the 1-day silt loam soil extract two days after sampling detected 82.9% of the recovered radioactivity as parent glyphosate (Figure 7) and when reanalyzed 14 months later, detected 73.0% as glyphosate (Table X). The analysis of one sample does not establish that parent glyphosate in all of the stored extracts degraded by only 10%. A storage stability study should be provided for glyphosate and its degradate AMPA under the conditions that the extracts were stored in this study.

3. Three degradates of [^{14}C]glyphosate (Unknowns A, B, and C) were isolated and detected at up to 3.5% of the applied (0.140 ppm), 3.6% (0.144 ppm), and 0.6% (0.024 ppm), but were not identified. It was also reported that several other minor unknowns were detected, but that no single minor unknown exceeded 2% of the applied; the "others" combined were detected at up to 4.6% 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.

5. Material balances for the day 0 sandy loam soil were low (71.3-74.3% of the applied), but appeared to be an isolated incident and did not significantly affect the outcome of the study.

glyphosate Metabolism DER

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