DATA EVALUATION RECORD UNDATED

STUDY 4

CHEM 103601 Glyphosate §162-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41723601

Kesterson, A. and S.B. Jackson. 1990. Aerobic aquatic metabolism of [^{14}C]glyphosate. PTRL Report No. 1300. PTRL Study No. 366. 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 Aquatic

1. Study MRID #41723601 does not satisfy the aerobic aquatic metabolism (162-3) data requirement at this time for the following reason:

a) Two degradates that comprised up to 2.0% of the applied (0.08 ppm) and 2.8% (0.11 ppm) were not identified.

2. Glyphosate degraded with a half-life of approximately 7 days in flooded silty clay loam sediment that was incubated in the dark at 25°C. The major nonvolatile degradate was aminomethylphosphonic acid. At 30 days posttreatment, $^{14}CO_2$ totaled 22.8% of the applied.

METHODOLOGY:

Aliquots (92 mL) of pond water (pH 7.3, total alkalinity 84 mg/L $CaCO_3$, total suspended solids 6 mg/L) were placed in flasks, treated at 4.1 ppm with an aqueous solution of [^{14}C]glyphosate (radiochemical purity 98.8%, specific activity 3.98 mCi/mMole, Monsanto), then a portion (20 g dry weight) of silty clay loam sediment (12% sand, 59% silt, 29% clay, 0.9% organic matter, pH 6.6, CEC 16 meq/100 g), collected from the same pond, was added to each flask. The treatment rate was based on 20 g sediment and 100 mL water; water volume included 92 mL of pond water, 1 mL of test solution, and moisture in the sediment. Flasks were swirled to mix the contents, covered with aluminum foil, flushed with oxygen, sealed with ground-glass stoppers, and incubated in darkness at approximately 25 C. Duplicate flasks were sampled at 0, 1, 3, 7, 10, 15, 20, 24, and 30 days posttreatment. Volatiles were collected every 7 days during the study and when flasks were sampled; oxygen 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 samples were extracted two or three times with 0.5 N potassium hydroxide, then 3- to 30-day samples were further extracted one to three times with 0.03 M ethylenediaminetetraacetic acid. 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 was combined with 10% of the potassium hydroxide extract from the sediment and adjusted to pH 2-3. Aliquots of the pooled sample were analyzed using HPLC using a Partisil SAX column eluted with methanolic potassium phosphate buffer; fractions were collected at 1-minute 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.

DATA SUMMARY:

[^{14}C]Glyphosate (radiochemical purity 98.8%), at 4.1 ppm, degraded with an observed half-life of approximately 7 days in flooded silty clay loam sediment that was incubated in the dark at 24.6 $\pm$ 0.57 C for 30 days; the calculated half-life was 14.4 days ($r = 0.948$). Glyphosate decreased from 91.6-94.4% of the applied at day 0 to 46.1-54.4% at 7 days, and was 21.8-22.6% at 30 days (Table VIII). The major nonvolatile degradate was

aminomethylphosphonic acid (AMPA).

AMPA comprised 3.1-3.4% of the applied at day 0, then increased and remained relatively stable comprising 19.4-25.0% at 7-30 days. Two unidentified unknowns A and B were detected at maximums of 2.0% of

the applied (0.08 ppm) at day 20, and 2.8% (0.11 ppm) at day 24, respectively (Table VIII).

At 30 days posttreatment, evolved $^{14}CO_2$ totaled an average 22.8% of the applied radioactivity, organic volatiles accounted for 2.5%, and unextractable [^{14}C]residues accounted for 7.2% (Table VI). [^{14}C]Residues associated with the water fraction of the sediment:water systems comprised an average 1.2% of the applied at day 0, increased to 9.4% at 7 days, then decreased to 5.4% at 30 days. During the study, the pH of the sediment:water systems ranged from 5.9 to 7.0 and the dissolved oxygen content ranged from 5.0 to 19.5 mg/L (Table V). Material balances ranged from 77.3 to 104.8% (mean 92.7 $\pm$ 8.3%) of the applied.

COMMENTS:

1. Two degradates of [^{14}C]glyphosate (Unknowns A and B) were isolated and detected at up to 2.0% of the applied (0.08 ppm) and 2.8% (0.11 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 1.4% of the applied. Subdivision N guidelines specify that all degradates present at >0.01 ppm (approximately 0.3% of the applied) should be identified.

2. Material balances tended to be lower in the 10- to 30-day samples ranging from 77.3 to 95.1% of the applied. It was demonstrated in the anaerobic aquatic metabolism study (STUDY 3, MRID 41723701) that $^{14}CO_2$ losses could account for the low material balances.

3. 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 preferable 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.

Glyphosate Metabolism DER

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