5-7-1998

DATA EVALUATION RECORD
DER 2

SHAUGHNESSY No. 417300
COMMON NAME: Glyphosate
CHEMICAL NAME: N-(phosphono-methyl) glycine
FORMULATION: Active Ingredient
DATA REQUIREMENT: (162-1)

MRID No:44125717
John Mao, July 3, 1996, Glyphosate Acid-Determination of Soil Metabolism under aerobic conditions. Sponsored by Industria Prodotti Chimici S.P.A. Via F. Beltrami 11-20026 Novate Milan, Italy. Performed by Springborn Laboratories, Inc. Health and Environmental Sciences, 790 Main Street, Wareham, Massachusetts 02571-1075. SLI Study # 13582.0795.6100.760; #96-5-6508.

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CONCLUSIONS:

1. Study MRID #44125717 is acceptable and completely satisfies the aerobic soil metabolism (162-1) data requirement for glyphosate acid.

2. [^{14}C]Glyphosate at 5.55 ppm, degraded with a registrant calculated first order half-life of 7.5 days (r^2= 0.9875) in a Washington sandy loam soil that was incubated in the dark at approximately 25 C and 75% of the FMC for up to 120 days. The major non-volatile degradate was aminomethylphosphonic acid (AMPA) which comprised a maximum of 32.9% by day 30, then decreased to 18 to 27% of the applied by days 60 and 90 respectively. Extensive mineralization took place as the major degradate was $^{14}CO_2$ at 53% by day 120. Soil bound residues were generally <10 to 11% of the applied with the exception of day 90 and 120.

MATERIALS AND METHODS:

Samples of moist (75% of field capacity), sieved (2 mm) Washington sandy loam soil (52% sand, 44% silt, 4% clay, 1.2% OM, pH 8.2, CEC 20.9 meq/100 g) were weighed (50 g) into flasks, treated at 5.55 ppm (9 lbs ai/A) with [^{14}C] N-(phosphono-methyl) glycine (radiochemical purity 95.9%, specific activity 54 mCi/mmol, Amersham) dissolved in water/acetonitrile 95:5. Each 250 ml flask was attached to a flow through system passing through one empty backflow trap, ethylene glycol, a second backflow trap, two potassium hydroxide traps and a final front flow (figure 1). The treated soil was maintained in the dark at approximately 25 C with a soil moisture content of 75 $\pm$ 10% OF FMC. Duplicate flasks of soil, ethylene glycol and potassium hydroxide solutions were sampled on days 0,1,3,7,14,30,60,90, and 120.

Soil samples were extracted twice with ammonium hydroxide by centrifugation then shaking. An aliquot was taken for LSC analysis as well as for centrifugation with a membrane filter with a molecular weight cutoff of 3000 daltons. The filtrate was then neutralized to pH 7 with phosphoric acid. The neutralized filtrate was then analyzed with LSC and HPLC. To determine non-extractable residues aliquots were taken and combusted followed by LSC measurements. To reduce the amount of non-extractables samples were extracted twice with 0.5N NaOH. An aliquot was then analyzed by LSC. Another aliquot was centrifuged, then again with a membrane filter (3000 dalton cutoff). The filtrate was adjusted to pH 7 with phosphoric acid and analyzed by LSC and HPLC. To determine bound residues the remaining soil was combusted followed by LSC measurements. LSC counting efficiencies of all experimental samples were determined using an external standard and a factory prepared calibration curve. The HPLC instrumentation consisted of a Waters Model 510 solvent pump, a Waters Model 710B autosampler, an Eppendorf column heater Model CH 30, a Beckman Model 171 radiometric detector, a Radiomatic Model A-280 radiometric detector, an Applied Biosystems Model 759A detector, a Hewlett-Packard Model 1047A refractive index detector, a Hewlett-Packard 3396B integrator, and a Gilson Model FC204 fraction collector.

RESULTS:

[^{14}C]Glyphosate (radiochemical purity 95.5%, specific activity 54 miCi/mmol), at 5.55 ppm, degraded with a registrant calculated first order half-life of 7.5 days (r^2= 0.9875) in a Washington sandy loam soil that was incubated in the dark at approximately 25 C and 75% of the FMC for up to 120 days. In the sandy loam soil, glyphosate comprised a mean (2 replicates) of 96.8% of the applied radioactivity at day 0, 80.1% at day 1, 68.2% at day 3, 48.6% at day 7, 19.4% at day 14, 6.1% at day 30, 3.8% at day 60, 5.2% at day 90, and 2.0% at day 120 (Table 6).

The major nonvolatile degradate in the extracts was aminomethylphosphonic acid (AMPA). AMPA comprised 6.5% of applied

at day 1, was 11.4% at day 3, 22.7% at day 7, 28.7% at day 14, then decreased to 27.5% at day 30, and further decreased to 26.4% at day 60, 17.9% at day 90, 21.5% at day 120 (Table 6). A HPLC radiochromatogram of test samples indicated an impurity was present in the dosing stock solution that was at a maximum of 6.1% of applied (0.34 ppm) at day 60 (Table 6). At 120 days posttreatment, evolved $^{14}CO_2$ was the major degradate totaling an average 53.2% of the applied radioactivity (Table 6). Organic volatiles were apparently not detected. Unextractable or bound [^{14}C]residues comprised up to a maximum of 16.2% by day 90. Day 90 and 120 soil samples were fractionated to isolate humin, fulvic and humic portions (Table 7). Material balances ranged from 90.8% to 132% (mean 102 $\pm$ 9.3%) of the applied (Table 5).

DISCUSSION:

1. Air-flow rates through the apparatus were not discussed.

2. The time from sampling to analysis was not discussed. It is assumed that it was immediate.

3. Extraction efficiency was determined at each sampling interval by fortification of 10 g of soil with 0.050 ml of radiolabeled stock solution (5.55 mg/kg of ^{14}C glyphosate), in addition a blank soil sample was prepared and extracted as well.

4. Since bound residues were present at >10% of applied a fulvic acid/humin fraction was performed at day 90 and 120. The extracted soil was placed in a centrifuged tube with 0.1 N $NaOH/CaCl_2$, then shaken overnight, centrifuged and decanted. The remaining soil was dried and weighed and adjusted to pH 1 with con HCL. The contents were then centrifuged and the precipitate representing the humic acid fraction was filtered out. The supernatant representing the fulvic acid portion was also collected. LSC analysis was performed on the fulvic acid, humic acid and the remaining soil, humin portions.

5. Microbial counts of soil samples were completed two days prior to study initiation and monthly thereafter. 99.0 ml of sterile water was added to 1.0 g of soil and placed on a Gyrotory shaker at 250 rpm for 15 to 30 minutes. One milliliter (1:100 dilution) was serially diluted to a range of 10^{-3} to 10^{-7}. 0.1 ml aliquots were plated in triplicate, and incubated at 24 or 25 C for 24 hours.

6. The degradation half-life of glyphosate was calculated from the ln glyphosate = kt, which assumes first-order kinetics.

7. For the fraction collection method, the method quantitation limit was defined as twice the detection limit and was calculated to be 0.016 mg/kg in soil which represented 0.15% and 0.29% of the applied 5.5 mg/kg respectively. For the radioHPLC analysis the method detection limit was defined as 1.5 times the detector background at approximately 120 dpm. At an injection volume of

0.1 ml and a specific activity of 142,529 dpm/ug, the method detection limit was calculated to be approximately 0.008 mg/L in soil extract and 0.032 mg/L in soil. The method quantitation limit was defined as twice the detection limit and was calculated as 0.064 mg/kg in soil. At an applied dose of 5.5 mg/kg the method detection and quantitation limits represents 0.58% and 1.2% of applied respectively.

Glyphosate-metabolism review

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