

US EPA ARCHIVE DOCUMENT

CONCLUSIONS

Degradation - Photodegradation in Water

1. This study is scientifically valid and provides useful information on the photodegradation of glyphosate acid in pH 5 and pH 7 aqueous buffer solutions.
2. This study meets Subdivision N Guidelines for the fulfillment of EPA data requirements on photodegradation.
3. Phosphonomethylene-labeled [^{14}C]glyphosate acid, at a concentration of 9.8 ± 0.22 ppm, degraded with a registrant-calculated half-life of 45 days in sterile pH 5 aqueous buffer solution which was irradiated with natural sunlight while maintained at 25 ± 3 °C for up to 30 days; however, the registrant-calculated half-life was extrapolated beyond the scope of the observed data. In contrast, the parent compound was stable in the dark control solution. Data are means of two replicates with the exception of day 0 data; means for the degradates were reviewer-calculated. In the irradiated solution, the parent was initially 97.9% of the applied radioactivity, decreased to 82.9% by 12 days posttreatment, and was 61.8% at 30 days. The major degradate AMPA was a maximum of 27.6% of the applied at 30 days posttreatment. In the dark controls, the parent compound was 94.6-97.9% of the applied throughout the incubation period. The minor degradate AMPA was present at a maximum of 2.1% of the applied radioactivity at 30 days posttreatment.

Phosphonomethylene-labeled [^{14}C]glyphosate acid, at a concentration of 9.5 ± 0.15 ppm, was stable in sterile pH 7 aqueous buffer solution which was irradiated with natural sunlight while maintained at 25 ± 3 °C for up to 30 days. The parent was initially present at 97.7% of the applied radioactivity and was 89.3% at 30 days posttreatment. The minor degradate AMPA was present at a maximum of 6.6% of the applied radioactivity at 30 days posttreatment (reviewer-calculated mean). Dark controls were not prepared for the pH 7 system.

METHODOLOGY

Phosphonomethylene-labeled [^{14}C]glyphosate acid {N-(phosphonomethyl)glycine; radiochemical purity 97.5%, specific activity 42.7 mCi/mmol; p. 13}, was added at concentrations of 9.8 ± 0.22 and 9.5 ± 0.15 ppm to sterile 0.015 M pH 5 (acetate) and 0.005 M pH 7 (phosphate) aqueous buffer solutions, respectively (p. 19). Solutions were transferred to autoclaved, quartz (pH 5 and pH 7 irradiated samples) or borosilicate (pH 5 dark controls) glass vessels and irradiated with natural sunlight in October (Richmond, CA; latitude 38°N) at 25 ± 3 °C for up to 30 days; pH 5 dark control samples were wrapped in aluminum foil. Temperature was maintained with a circulating water bath (Table II, p. 32). To capture [^{14}C]volatiles, each test vessel was equipped with an outlet

port and each set of samples was connected to a series of traps containing ethylene glycol (one trap) and 10% aqueous NaOH (two traps); filter sterilized air was continuously drawn through the sets of vessels by means of a pump (Figure 4, p. 47). Sunlight intensity and cumulative energy (250-700 nm, integration range) were measured using a radiometer. Total sunlight energy was 249.5 W·min/cm²; average sunlight intensity was not reported (Table III, p. 33). Duplicate samples were removed for analysis at 2, 6, 12, 20, and 30 days posttreatment; a single sample was removed for analysis from each of the pH 5 and pH 7 systems at 0 days posttreatment (p. 20).

At each sampling interval, samples were transferred to scintillation vials, the test vessels were rinsed with water twice, the rinsates added to the sample solution, and the combined solutions were analyzed in triplicate for total radioactivity by LSC; the limit of quantitation was not reported (p. 21). Aliquots of each sample were analyzed by HPLC (Bio-Rad HRLC Glyphosate column) with an isocratic mobile phase of 5 mM KH₂PO₄ (pH 2.1):methanol (96:4, v:v; p. 22). Samples were co-chromatographed with non-radiolabeled reference standards that were visualized with UV light (unspecified wavelength). Eluent fractions were collected and analyzed for total radioactivity by LSC; the limit of detection was reported as twice the background (p. 24). Mean column recoveries were 97.6 ± 2.2% for the pH 5 samples and 97.8 ± 1.8% for the pH 7 samples (p. 23). Compound identities were confirmed using one-dimensional TLC on silica gel plates developed sequentially in methanol:aqueous ammonium hydroxide (29.9%):trichloroacetic acid:water (55:14:0.45:31, v:v:w:v). Test solutions were co-chromatographed with nonradiolabeled reference standards which were visualized using iodine vapors; areas of radioactivity were located by using radioimage scanning (p. 23).

Triplicate aliquots of the volatile trap solutions were analyzed for total radioactivity by LSC at each sampling interval; recovered radioactivity was divided among the contributing samples remaining (p. 21); radiolabeled ¹⁴CO₂ in the NaOH traps was confirmed in selected samples by precipitation with BaCl₂.

The pH of the buffer solution was measured at each sampling interval; pH was 4.8-5.1 for the pH 5 system and 6.8-7.0 for the pH 7 system (Table I, p. 31). Temperature was measured continuously in the water bath using a thermocouple; temperature ranged from 22.2 °C to 26.7 °C throughout the study (Table II, p. 32). The sterility of the test solutions was confirmed by plating on selective media at 0 and 30 days posttreatment (pp. 21, 22).

DATA SUMMARY

Phosphonomethylene-labeled [¹⁴C]glyphosate acid (radiochemical purity 97.5%), at a concentration of 9.8 ± 0.22 ppm, degraded with a registrant-calculated half-life of 45 days (r² = 1.0) in sterile pH 5 aqueous buffer solution which was irradiated with natural sunlight while maintained at 25 ± 3 °C for up to 30 days (Table XI, p. 41; Figure 13, p.

56); however, the registrant-calculated half-life was extrapolated beyond the scope of the observed data (see Comment #1). In contrast, the parent compound was stable in the dark control solution (Table XII, p. 42). Data are means of two replicates with the exception of day 0 data; means for the degradates were reviewer-calculated. Based on HPLC analysis of the irradiated solution, the parent compound was initially present at 97.9% of the applied radioactivity, decreased to 82.9% of the applied by 12 days posttreatment, and was 61.8% of the applied at 30 days posttreatment (p. 26; Table XI, p. 41). The major degradate

aminomethylphosphonic acid (AMPA)

was initially present (day 0) at 1.4% of the applied radioactivity, increased to 10.3% of the applied by 12 days posttreatment, and was a maximum of 27.6% of the applied at 30 days posttreatment (Table IX, p. 39). An unidentified minor degradate (Degradate 1) was present at a maximum of 7.5% of the applied radioactivity at 30 days posttreatment. Uncharacterized [¹⁴C]residues were a maximum of 2.2% of the applied at 6 days posttreatment. [¹⁴C]Volatiles were negligible (Table VI, p. 36). In the dark controls, the parent compound was present at 94.6-97.9% of the applied radioactivity throughout the incubation period (Table XII, p. 42). The minor degradate AMPA was a maximum of 2.1% of the applied radioactivity at 30 days posttreatment (Table IX, p. 39). An unidentified minor degradate (Degradate 1) was a maximum of 0.4% of the applied radioactivity at 30 days posttreatment. Uncharacterized [¹⁴C]residues were a maximum of 1.1% of the applied radioactivity at 12 days posttreatment. [¹⁴C]Volatiles were negligible (Table VII, p. 37).

Phosphonomethylene-labeled [¹⁴C]glyphosate acid (radiochemical purity 97.5%), at a concentration of 9.5 ± 0.15 ppm, was stable in sterile pH 7 aqueous buffer solution which was irradiated with natural sunlight while maintained at 25 ± 3 °C for up to 30 days (Table XIII, p. 43; Figure 13, p. 56). Dark controls were not prepared for the pH 7 system. Data are means of two replicates with the exception of day 0 data; means for the degradates were reviewer-calculated. Based on HPLC analysis of the irradiated solution, the parent was initially present at 97.7% of the applied radioactivity and was 89.3% of the applied at 30 days posttreatment (Table XIII, p. 43). The minor degradate aminomethylphosphonic acid (AMPA) was a maximum of 6.6% of the applied radioactivity at 30 days posttreatment (Table X, p. 40). An unidentified minor degradate (Degradate 1) was a 2.9% of the applied radioactivity at 30 days posttreatment. Uncharacterized [¹⁴C]residues were a maximum of 2.9% of the applied at 12 days. [¹⁴C]Volatiles were negligible (Table VIII, p. 38).

Material balances (based on LSC analysis of individual replicates) were 98.7-102.9% of the applied radioactivity for the irradiated pH 5 buffer solution, 99.1-102.6% of the applied for the pH 5 dark control solution, and 102.2-105.7% of the applied for the irradiated pH 7 buffer solution (Tables VI-VIII; pp. 36-38).

COMMENTS

1. The registrant-calculated half-life of the parent (45 days) in the irradiated pH 5 system was estimated assuming the continuation of the degradation pattern beyond the scope of the observed data. However, data which appear linear may become curvilinear with time, and half-life estimations based on extrapolated data may be inaccurate.
2. The water bath temperature was not held at 25 ± 1 °C; rather, it ranged from 22.2 °C to 26.7 °C throughout the study (Table II, p. 32). The reviewer reported the temperature range as 25 ± 3 °C.
3. A phosphate buffer solution was used for the pH 7 test solution; it is recommended that borate or acetate buffers be utilized to minimize buffer effects.
4. Solution samples were placed at a 30° angle with respect to the horizon to maximize irradiation (p. 18).
5. The study was conducted with 0.015 M and 0.005 M concentration buffer solutions for the acetate and phosphate buffer, respectively, rather than the recommended 0.01 M concentration. Buffers should be used at the lowest concentration possible to prevent catalysis effects.
6. The test system solutions from Day 0 and Day 30 were plated on sterilized Trypticase Soy Agar plates and incubated (48 hours at 35 °C) to confirm sterility of the test systems; samples showed no growth.
7. The reported water solubility of the parent compound at 20 °C was 9100 mg/L (pH not specified; p. 13).

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