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DATA EVALUATION RECORD

STUDY 5

CHEM 417300	Glyphosate Acid	§163-1

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FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 44320646
Thomas, P. K. and M. C. G. Lane. 1996. Glyphosate acid: adsorption and desorption properties of properties of in (sic) 5 soils. Laboratory Project ID: 95JH222. Unpublished study performed by ZENECA Agrochemicals, Berkshire, UK; and submitted by ZENECA Ag Products, Wilmington, DE.

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CONCLUSIONS

Mobility - Leaching and Adsorption/Desorption

1. This study is not scientifically valid and does not provide useful information on the soil mobility (batch equilibrium) of glyphosate acid in two U.S. and three British soils. The parent compound was unstable in the test systems and degraded during the equilibration period; therefore, reported conclusions concerning compound mobility in soil were questionable.

2. This study does not meet Subdivision N Guidelines for the partial fulfillment of EPA data requirements on soil mobility (batch equilibrium) for the following reasons:

   (i) the parent compound was not stable throughout the definitive study;

   (ii) the material balances were not reported across all application levels for four of the five soils;

   (iii) sterilized soils were used, but mobility data from reference chemicals of known mobility were not submitted; and

   (iv) K_{des} values were not reported.

3. Phosphonomethyl-labeled [^{14}C]glyphosate acid, at nominal concentrations of 0.05, 0.1, 0.2, 1.0 and 2.0 µg/mL, was studied in sandy loam (Visalia), British sand, British sandy loam (18 Acres), British silty clay loam (Wisborough Green) and silty clay loam (Champaign) soil:solution slurries that were equilibrated for 4 hours at 20 ± 2 °C. However, results were questionable due to the instability of the parent compound in the test systems. Freundlich K_{ads} values were 64 for the sand soil (0.5% o.m.), 9.4 for the sandy loam soil (Visalia), 470 for the silty clay loam soil (3.9% o.m.; Wisborough Green), 700 for the silty clay loam soil (Champaign) and 90 for the sandy loam soil (18 Acres); corresponding K_{oc} values were 22000, 1600, 21000, 33000 and 5000 mL/g. Respective 1/N values were 0.75, 0.72, 0.93, 0.94 and 0.76 for adsorption. Freundlich K_{des} values were not reported. The reviewer-calculated coefficient of determination (r^2) values for the relationships K_{ads} *vs*. organic matter, K_{ads} *vs*. pH and K_{ads} *vs*. clay content were 0.60, 0.59 and 0.82, respectively.

METHODOLOGY

Based on the results of a preliminary study of the adsorption of phosphonomethyl-labeled [^{14}C]glyphosate acid {carboxymethyl aminomethylphosphonic acid; radiochemical purity 95%, specific activity 1.67 GBq/mmol; p. 14} to sandy loam soil (Visalia), a 4-hour

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equilibration period was chosen for the adsorption phase of the definitive study (p. 15; Appendix 1, Table 8, p. 32). A preliminary study to determine the desorption equilibration period was not performed. In a preliminary study, adsorption of the test compound to the Teflon centrifuge tubes was reportedly not observed (p. 32); 94% of the applied radioactivity was recovered following a 48-hour equilibration period.

For the adsorption phase of the definitive study, aliquots (19 mL) of 0.01 M $CaCl_2$ solution were added to Teflon centrifuge tubes containing subsamples (1 g) of air-dried, sieved (2 mm) British sand (Lilly Field), sandy loam (Visalia), British silty clay loam (Wisborough Green), silty clay loam (Champaign) and British sandy loam (18 Acres) soils (Table 2, p. 13) and the samples were pre-equilibrated overnight on a shaker (pp. 11, 15). The centrifuge tubes containing the soil subsamples were treated with phosphonomethyl-labeled [^{14}C]glyphosate acid, dissolved in 0.01 M $CaCl_2$ solution (1 mL), at nominal concentrations of 0.05, 0.1, 0.2, 1.0 and 2.0 µg/mL (Table 4, p. 16); duplicate tubes were prepared for each soil type/treatment rate combination. The tubes containing the soil:solution slurries (1:20, w:v) were equilibrated by shaking for 4 hours at 20 ± 2 °C. Following the adsorption equilibration period, soil:solution slurries were centrifuged; the supernatants were decanted and, if necessary, filtered (p. 17). Aliquots of supernatant from each sample were analyzed for total radioactivity by LSC; the limit of detection was not reported. Supernatants were placed in frozen storage (-20 ± 5 °C) prior to TLC analysis. Supernatants were concentrated and an aliquot of each was analyzed using TLC on cellulose plates developed with 0.1 M HCl (pp. 18, 20); the limit of detection was not reported. Radioactive residues on the TLC plates were detected by radioimage scanning. Samples were co-chromatographed with radiolabeled reference standards which were visualized by a phosphorimager.

For the desorption phase of the definitive study, a volume of pesticide-free 0.01 M $CaCl_2$ equal to the volume of supernatant that was decanted following the adsorption phase was added to soil pellets (see Comment #5; p. 18). Tubes containing soil:solution slurries were equilibrated by shaking for 21 hours at 20 ± 5 °C. Following equilibration, soil:solution slurries were centrifuged; the supernatants were decanted and, if necessary, filtered. Aliquots of supernatant from each sample were analyzed for total radioactivity by LSC. Supernatants were placed in frozen storage (-20 ± 5 °C) prior to TLC analysis, and analyzed as previously described.

To determine compound stability in the test systems, soil samples from the adsorption and desorption phases were extracted by shaking with potassium dihydrogen phosphate buffer (pH 2.1; p. 17; Figure 2, p. 19). Samples were centrifuged and the supernatants were decanted. The extracted soil was rinsed with acetone and the rinsate was decanted. The acetone rinsate and the buffer supernatant from each sample were combined, brought up to volume with distilled water and, if necessary, filtered. The combined extracts were analyzed by LSC and TLC as previously described (p. 18).

Following extraction, air-dried soil samples were analyzed for total radioactivity by LSC following combustion (pp. 18, 20); values were corrected for oxidation efficiency.

DATA SUMMARY

Phosphonomethyl-labeled [^{14}C]glyphosate acid (radiochemical purity 95%), at nominal concentrations of 0.05, 0.1, 0.2, 1.0 and 2.0 µg/mL, was studied in sandy loam (Visalia), British sand, British sandy loam (18 Acres), British silty clay loam (Wisborough Green) and silty clay loam (Champaign) soil:solution slurries that were equilibrated for 4 hours at 20 ± 2 °C. However, results were questionable due to the instabilty of the parent compound in the test systems. Freundlich K_{ads} values were 64 for the sand soil (0.5% o.m.), 9.4 for the sandy loam soil (Visalia), 470 for the silty clay loam soil (3.9% o.m.; Wisborough Green), 700 for the silty clay loam soil (Champaign) and 90 for the sandy loam soil (18 Acres; Table 6, p. 25); corresponding K_{oc} values were 22000, 1600, 21000, 33000 and 5000 mL/g. Respective 1/N values were 0.75, 0.72, 0.93, 0.94 and 0.76 for adsorption (Table 5, p. 24). The reviewer-calculated coefficient of determination (r^2) values for the relationships K_{ads} *vs*. organic matter, K_{ads} *vs*. pH and K_{ads} *vs*. clay content were 0.60, 0.59 and 0.82, respectively. Freundlich K_{des} values were not reported.

During the 4-hour equilibration period, 78-93% of the applied radioactivity was adsorbed to the sand soil (across all application levels), 31-54% of the applied was adsorbed to the sandy loam soil (Visalia), 97-98% of the applied was adsorbed to the silty clay loam soil (Wisborough Green), 97-98% of the applied was adsorbed to the silty clay loam soil (Champaign) and 84-95% of the applied was adsorbed to the sandy loam soil (18 Acres; Table 6, p. 25). Data indicating the percentages of the applied radioactivity desorbed from the five soils (across all application rates) were not reported; however, raw data were reported in Appendix 4 (Table 12, p. 45).

TLC stability data were reported as percentages of radioactivity in the supernatant or soil extract across all application rates only for the sandy loam (Visalia) soil and for the remaining soil samples treated at 0.2 µg/mL (Appendix 5, Table 13, p. 47). Recoveries of the parent compound in the supernatants following desorption were 72-88% for the sandy loam (Visalia) soil, 79% for the silty clay loam (Champaign) soil, 74% for the silty clay loam (Wisborough Green) soil, 78% for the sandy loam (18 Acres) soil and 90% for the sand soil. Recoveries of the parent compound in the soil extracts following desorption were 71-75% for the sandy loam (Visalia) soil, 77% for the silty clay loam (Champaign) soil, 64% for the silty clay loam (Wisborough Green) soil, 78% for the sandy loam (18 Acres) soil and 60% for the sand soil.

Material balances (across all application rates, based on LSC) were 84-105% for the sandy loam (Visalia) soil (Appendix 2, Table 9, p. 35). Material balances (for individual replicates treated at 0.2 µg/mL) were 97-98% for the silty clay loam (Champaign) soil,

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87-95% for the silty clay loam (Wisborough Green) soil, 96-97% for the sandy loam (18 Acres) soil and 88-93% for the sand soil (Appendix 2, Table 10, p. 36).

COMMENTS

1. Based on TLC analysis, the parent compound was not stable (<90%) in soil:solution slurries throughout the definitive study. TLC data were reported as percentages of radioactivity in the supernatant or soil extract across all application rates only for the sandy loam (Visalia) soil and for the remaining soil samples treated at 0.2 µg/mL (Appendix 5, Table 13, p. 47). Recoveries of the parent compound in the supernatnants following desorption were 72-88% for the sandy loam (Visalia) soil, 79% for the silty clay loam (Champaign) soil, 74% for the silty clay loam (Wisborough Green) soil, 78% for the sandy loam (18 Acres) soil and 90% for the sand soil. Recoveries of the parent compound in the soil extracts following desorption were 71-75% for the sandy loam (Visalia) soil, 77% for the silty clay loam (Champaign) soil, 64% for the silty clay loam (Wisborough Green) soil, 78% for the sandy loam (18 Acres) soil and 60% for the sand soil. However, adsorption coefficients were calculated assuming that all radioactivity was present as parent (p. 22).

2. Adequate material balances were not reported for all soils. Material balances were reported across all application rates only for the sandy loam (Visalia) soil (Table 9, p. 35). Material balances of the remaining four soils were reported only for the samples treated at 0.2 µg/mL (Table 10, p. 36). Material balances for all soils across all application rates must be reported to allow the reviewer to account for all radioactivity throughout the study.

3. The study authors stated that all soils were sterilized by gamma irradiation prior to use to inhibit microbial degradation of the parent compound (pp. 10-11). If the registrant chooses to use sterilized soil to study compound mobility, the batch equilibrium studies must include reference chemicals of known mobility. Batch equilibrium data for reference chemicals of known mobility were not submitted. The reviewer notes, however, that degradation still occurred in the test systems. It is also noted that the parent compound is hydrolytically stable at pH 5-9, indicating that the observed degradation was likely microbially mediated.

4. Freundlich K_{des} values were not reported as required by Subdivision N Guidelines. However, Freundlich K_{oc} values for desorption were reported in Table 7 (p. 27).

5. The text of the study report did not adequately describe the methods. It appeared that the desorption phase was not performed on the same soil as the adsorption phase. The study authors stated that glyphosate acid was extracted from the soil remaining after decanting the adsorption phase supernatant (p. 17). In order for the desorption phase to be

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conducted on the same soil, the soil can not be extracted following adsorption unless additional sacrifice samples were prepared. Figure 2 (p. 19) illustrated that four replicates were utilized in the adsorption phase and that two replicates were utilized for the desorption phase. In this case, it would be possible to extract two replicates and still equilibrate the remaining two replicates during the desorption phase. However, the study authors stated in the methods for the adsorption phase that only duplicate soil:solution slurries were prepared for each treatment rate (p. 15). The desorption phase of the study must be conducted with the soil remaining following the adsorption phase. Clarification by the registrant is necessary.

6. The limits of detection and quantitation were not reported. It is necessary that both limits of detection and quantitation be reported to allow the reviewer to assure the adequacy of the method.

7. A 4-hour equilibration period was chosen for the adsorption phase of the definitive study. The study authors stated that the preliminary study showed that the distribution of phosphonomethyl-labeled [^{14}C]glyphosate acid between the soil and aqueous phases had reached an approximate equilibrium by 4 hours (p. 15). However, data from the preliminary study indicated that the equilibration period may not have been long enough for equilibrium to be established in the sandy loam (Visalia) soil system; the test compound appeared to continue to adsorb to the sandy loam soil following 4 hours of equilibration (Appendix 1, Table 8, p. 32). The percentage of the applied radioactivity adsorbed to the soil gradually increased from 53% at 4 hours to 63% at 48 hours. Based on the results of the preliminary stability and definitive studies (see Comment #1), the increased adsorption may have been due to the adsorption of an accumulating degradate (AMPA) of the test compound. Due to the instability of the test compound, an additional study with a longer equilibration period may not be possible.

8. The reviewer noted that four of the five soils were between pH 4 and 8 (Table 2, p.13); however, the sandy loam (Visalia) soil had a pH of 8.4. Subdivision N guidelines require data from four soils with pH's between 4 and 8.

9. The sandy loam soil from Visalia, California, was the same type of soil used in an aerobic soil metabolism study (MRID 44320645) of phosphonomethyl-labeled [^{14}C]glyphosate acid.

10. Three of the five soils utilized in the study were foreign (British) soils (Table 1, p. 12). In the U.S. EPA Rejection Rate Analysis (EPA 738-R-93-010, September 1993), EPA stated that the use of domestic soils is strongly preferred in mobility studies. However, the Agency will accept non-domestic/European soil for two of the four soils required if and only if the soils are characterized according to the USDA system. All soils were characterized according to the USDA system (Table 2, p. 13).

11. The series names of the soils were not reported. Instead, the soils were referred to by their geographic locations or descriptions of their geographic location (Table 1, p. 12).

12. The reviewer noted two apparent typographical errors. The concentration (0.156 µg/mL) of parent compound adsorbed to the sandy loam (18 Acres) soil treated at 0.2 µg/mL appeared to be missing a zero (Appendix 4, Table 11, p. 44); a concentration of 0.0153 µg/mL would correspond to a percentage of 92.2. The concentration (0.535 µg/mL) of parent compound desorbed from the sand soil treated at 1.0 µg/mL appeared to be missing a zero (Appendix 4, Table 12, p. 45); a concentration of 0.0535 µg/mL would correspond to a percentage of 5.4.

13. The 1/N values were 0.75, 0.72, 0.93, 0.94 and 0.76 for adsorption. Values outside the range of 0.90-1.10 indicate that the Freundlich model may not accurately describe the adsorption of the test compound across all concentrations.

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