DATA EVALUATION RECORD

STUDY 2

CHEM 061601 Paraquat dichloride §162-1

FORMULATION--00--ACTIVE INGREDIENT

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Vickers, J.A., A.D. Hurt, and D.W. Bewick. 1989. Paraquat: degradation in aerobic soil. Laboratory Project No. 88JH386/Report No. RJ0788B. Unpublished study performed and submitted by ICI Americas Inc., Wilmington, DE.

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REVIEWED BY: Laura Parsons
ORG: EFGWB Review Section I

Laura Parsons
26 AUG 1993

APPROVED BY: Paul Mastradone
ORG: Chief, EFGWB Review Section I

Paul J Mastradone
26 AUG 1993

CONCLUSIONS:

Metabolism -- Aerobic Soil

1. This study can be used to fulfill data requirements.

2. Paraquat at 4.32 ppm did not degrade in sandy loam soil incubated under aerobic conditions at 20 ± 2 C for 180 days. Paraquat comprised 93% of the applied radioactivity at 180 days posttreatment. Most of the radioactivity was extracted with technical grade paraquat by isotopic exchange. There was no volatile radioactivity. No degradates were reported from TLC or HPLC analyses.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic soil degradation of [^{14}C]paraquat in sandy loam soil. No additional information on the aerobic soil metabolism of paraquat is required at this time.

METHODOLOGY:

Sandy loam soil (64% sand, 22% silt, 14% clay, pH 6.5, organic matter 2.7%, CEC 10.8 meq/100 g) was collected, air-dried, sieved to 2 mm, and moistened to 40% of the moisture holding capacity. These samples were stored at 20 ± 2 C for 20 days. Samples (25 g dry weight) were weighed into glass sample dishes (3 cm deep; 3.7 cm diameter) and a

mixture of [2,6-pyridyl-^{14}C]paraquat [1,1-dimethyl-4,4-bipyridinium dichloride; radiochemical purity >98%, specific activity 734 GBq/mMol, ICI) and unlabeled paraquat in water was added dropwise to the soil surface. The glass dishes were placed on coated wire racks which fit inside a glass column (Figure 3). Humidified, CO_2-free air was pumped into the glass column and then vented through a series of tubes containing 0.1 M HCl, 2-methoxyethanol, and ethanolamine as traps for volatile radioactivity. The glass columns were incubated in the dark at 20 $\pm$ 2 C; distilled water was added as necessary to maintain 40% moisture. Duplicate glass dishes of soil were removed for analysis after 0, 3, 7, 30, 61, 90, and 180 days posttreatment. Duplicate dishes were also removed at 1, 14, 120, 271, and 372 days posttreatment; these samples were frozen to be analyzed later if necessary.

The soil samples were extracted three times; after the extraction the phases were separated by filtration and the filtrates were analyzed by LSC. Soil samples were first shaken with 100-150 mL of methanol for 1 hour. The second extract was for 2-4 hours with 100 or 150 mL of aqueous technical grade paraquat solution (7440 ppm paraquat cation) in order to desorb radiolabeled [^{14}C]paraquat by isotopic exchange. The soil was further extracted by a 5-6 hour reflux with 6 M HCl and the extracted soil was freeze-dried, ground, and analyzed by LSC following combustion.

The methanol extract did not contain detectable radioactivity and was not further analyzed. The extracts from the technical grade paraquat step and the acid reflux step were analyzed by one-dimensional TLC on silica gel plates developed with toluene:butanol:methanol:1 M HCl (10:20:50:20, v:v:v:v) or methanol:6 M HCL (65:35, v:v); samples were cochromatographed with reference standard paraquat. To detect paraquat, the developed plates were sprayed with a solution of potassium iodoplatinate; paraquat appeared as black-brown spots on a red-brown background. Radioactive areas were located and quantified by linear scan; the location was checked by autoradiography. For a confirmatory method, aliquots of the extracts were also analyzed by HPLC on a Beckman Ultrasphere-IP column eluted with a mobile phase of water:methanol (75:25, v:v). The HPLC mobile phase also contained: 11.35 g of octane sulphonic acid (sodium salt), 10.3 mL o-phosphoric acid, and 12.7 mL diethylamine per liter of mobile phase. Detection was by UV at 310 nm; fractions of the HPLC flow were collected and analyzed by LSC.

Derivatization of paraquat in the extracts: Aliquots from the 0 and 180 day samples were treated with a mixture of 9 M NaOH and 1% potassium ferric cyanide to derivatize the paraquat in the samples to [^{14}C]1,1-dimethyl-4,4-bipyridyl-2,2-dione. These samples were analyzed by TLC on silica gel plates developed with chloroform:acetone:methanol (80:10:10, v:v:v); paraquat was located by fluorescence quenching. Radioactive areas were located and quantified by linear scan; the location was checked by autoradiography. HPLC was again used as a confirmatory technique

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using the same system described above except that the mobile phase contained only 2.27 g of octane sulphonic acid instead of 11.35 g.

Aliquots of the volatile trapping solutions were removed for LSC analysis at each sampling interval or at two weeks intervals

DATA SUMMARY:

[^{14}C]Paraquat at 4.32 ppm (0.90 lb ai/A) did not degrade when incubated in sandy loam soil under aerobic conditions at 20 $\pm$ 2 C for 180 days. [^{14}C]Paraquat comprised 88.8-99.5% of the applied radioactivity at all sampling intervals (Table IV). No radioactivity was recovered from the volatile traps; radioactivity which was not removed by the three extraction methods ranged from 0.5-4.1% of the applied dose. Material balances were 92.5-96.8% at all reported intervals.

COMMENTS AND DISCUSSION:

1. The amount of radioactivity that was recovered as "dione" from the derivatized soil was approximately equivalent to the amount of paraquat identified in the HPLC extracts, 90.6-98.2% of the extract as paraquat in the soil extracts compared to 94.7-96.6% of the radioactivity in the derivatized extract as dione (comparison of Tables V and VI). This confirms that the radioactivity in the soil extracts was due to [^{14}C]paraquat.

2. Subdivision N guidelines require that aerobic soil metabolism studies be conducted for 1 year or until the pattern of formation and decline of degradates is established. In this study the soil was sampled for up to 372 days posttreatment, but these samples were frozen "for later analyses if necessary". Since paraquat has to shown to be very persistent in the field dissipation studies, probably no significant information could be gained from the analysis of the later samples.

3. It has been reported that paraquat adsorbs to glass. In this study, the air was pumped through the glass column which enclosed the incubation dishes. There was no rinse of this glass column and the material balances were good confirming that paraquat is not volatile after soil application.

4. A justification of the method of isotopic exchange of paraquat with radiolabeled paraquat was found in a review of environmental behavior of paraquat in Herbicides: Chemistry, Degradation, and Mode of Action. 1976. Edited by P.C. Kearney and D.D. Kaufman, Marcel Dekker, Inc. New York. Chapter 10. Paraquat adsorbs to montmorillinite by fitting between the silicate layers and has been shown to freely exchange with other paraquat molecules (shown by radioactive tracer studies) and to exchange with NH_4^+ and Ba^{2+} when mixed with very high concentrations of salts.

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