DATA EVALUATION RECORD

STUDY 3

CHEM 069601 Pyrazon §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41507915

Patel, J.R. 1989. Degradation studies - Lab photodegradation on soil. ^{14}C-Pyrazon photolysis on soil surface. Report No. M8902. BASF Registration Document No. 89/5089. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC.

DIRECT REVIEW TIME = 16

REVIEWED BY: W. Martin TITLE: Staff Scientist

EDITED BY: K. Patten TITLE: Task Leader
T. Colvin-Snyder Staff Scientist

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: S. Termes
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-2243

SIGNATURE: Nov. 20, 1990

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study cannot be used to fulfill data requirements at the present time.

2. The reported results indicate that pyrazon degraded with a calculated (by extrapolation) half-life of 69 days on autoclaved sandy loam soil that was irradiated for 4 weeks using a xenon light source and a 12-hour photoperiod at 24.5 C.

3. This study may be acceptable to fulfill EPA Data Requirements for Registering Pesticides if the registrant submits adequate additional information.

4. The registrant must submit the following additional information:
a. Material balances for the dark controls (including identification of compounds in the different radioactive fractions).
b. Discuss why the soil was autoclaved (half-lives under aerobic conditions for a sandy loam soil was 90 days).

METHODOLOGY:

Dried, sieved (2 mm), autoclaved sandy loam soil from Dinuba, CA (54% sand, 32.0% silt, 14% clay, 0.5% organic matter, pH 7.7, CEC 14.4 meq/100 g) was placed into divided petri dishes to a depth of 2 mm and treated at 506 ppm with a methanol solution containing unlabeled pyrazon (purity >99.5%, source not specified) spiked (2463:4.2, w:w) with pyradiazinone ring-labeled [^{14}C]pyrazon (labeled in the 4- and 5-C positions; radiochemical purity 95.84%, specific activity 9.54 x 10^8 dpm/mg, BASF). The petri dishes were placed inside a water-jacketed photolysis chamber, which was covered with a quartz plate and sealed (Figure 8). The temperature in the chambers was maintained at 24.5 C by circulating cooling water through the water jacket. Humidified, filter-sterilized, CO_2-free air was drawn through the photolysis chamber, then vented through volatile traps consisting of a polyurethane plug, a tube of 2,4-dinitrophenylhydrazine solution, two tubes of scintillation cocktail (Harvey), and activated charcoal (Figure 9). The treated soil was irradiated for 12-hour intervals over a 4-week period (except weekends, when the samples were not irradiated) using a filtered xenon lamp (Hanau Suntest) that had an intensity of 1725 uE/m^2·sec (Table 2, Figures 2 and 3); the light intensity was measured daily at the top of the reaction chamber with a radiometer/photometer. Soil samples were collected at 1, 2, 3, and 4 weeks posttreatment (up to 340.68 hours of irradiation); the volatile traps were changed at each sampling interval. At the termination of the experiment, the photolysis chamber was purged with air for 24 hours before disassembly to insure collection of all volatiles. Treated soils that were incubated in the dark to serve as controls were sampled for analysis at 2 and 4 weeks posttreatment. All samples were stored in the dark at 4 C until analysis.

Soil samples were extracted three times with methanol using a vortex vibrating mixer followed by a shaker for 3 hours. The petri dishes that contained the treated soil were washed four times with methanol. The methanol extracts and the rinsate were combined, evaporated to dryness (method not reported), and redissolved in methanol; an aliquot was analyzed for total extractable radioactivity using LSC. The extracted soil was further extracted twice with 0.1 N HCl in methanol using a vortex mixer. The extracts were concentrated by evaporation; an aliquot was analyzed for total radioactivity using LSC. The methanol and methanolic HCl extracts were analyzed by one-dimensional TLC on silica gel plates developed in ethyl acetate:methanol:acetic acid (8:1:1). The radioactive areas were located and quantified by radioscanning, and were identified by comparison to a nonradiolabeled reference standard (method of

visualization not reported). Unextractable [^{14}C]residues in the extracted soil were quantified using LSC following combustion.

The polyurethane plugs, activated charcoal, and trapping solutions were analyzed for total radioactivity (analytical method not specified).

DATA SUMMARY:

Pyrazon (purity >99.5%) plus pyradiazinone ring-labeled [^{14}C]pyrazon (labeled in the 4- and 5-C positions; radiochemical purity 95.84%), at 506 ppm, photodegraded with a registrant-calculated half-life of 69 days on autoclaved sandy loam soil that was irradiated at 24.5 C using a xenon lamp that had an intensity of 1725 uE/m^2·sec and a 12-hour photoperiod. In contrast, pyrazon did not degrade in the dark control during the 4-week study.

In the irradiated samples, extractable [^{14}C]residues decreased from 99.6% of the total recovered radioactivity immediately posttreatment to 82.4% after 340.68 hours (Table IV). At 340.68 hours posttreatment, approximately 78% of the [^{14}C]residues recovered were pyrazon, 3.3% were "a complex mixture of non-distinguishable polar components", 8% were unextractable [^{14}C]residues, and volatile [^{14}C]residues trapped in the scintillation cocktail (assumed to be carbon dioxide) totaled 9.57% (Table IV). During the study, the material balances for the irradiated soil were 94.79-101.06% (Table V). Material balances for the dark controls were not reported.

COMMENTS:

1. Material balances for the dark control were not provided.

2. The reason as to why the soil was autoclaved is not clear, considering that the reported half-life for aerobic metabolic degradation in a sandy loam soil was 90 days.

3. Based on the methodology provided, the scintillation cocktail was analyzed only for total radioactivity and not for specific [^{14}C]compounds; the study authors appear to have assumed that all radioactivity absorbed by the cocktail was carbon dioxide.

4. The half-life of pyrazon appears to have been calculated based only on the concentration of pyrazon in the combined methanol extracts, rather than on the concentration of pyrazon in both the methanol and methanolic HCl extracts. After 340 hours of irradiation, the methanolic HCl extracts contained approximately 7% of the recovered radioactivity as pyrazon; the concentration of undegraded pyrazon in the system at 340 hours was 78% rather than 72% of the recovered.

5. The statistical estimation of the photodegradation half-life of pyrazon reported in this study is of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

6. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the R_f of reference standards.

   In this study, the sample extracts were analyzed using one-dimensional TLC with one solvent system. Radioactive areas on the TLC plates were identified only by comparison to the location of a reference standard.

PAGES 3.5 THROUGH 3.14 HAVE BEEN REMOVED FROM THIS DOCUMENT. THOSE PAGES CONSIST OF REGISTRANT-SUBMITTED DATA.