DATA EVALUATION RECORD

STUDY 4

CHEM 069601 Pyrazon §162-1

FORMULATION--00--ACTIVE INGREDIENT

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is acceptable and may be used to partially fulfill data requirements.

2. Pyradiazinone ring-labeled [^{14}C]pyrazon degraded with half-lives of 90 and 152 days in aerobic sandy loam and sandy clay loam soils, respectively, at 25 C. The only nonvolatile degradate identified in the soils was dephenylated pyrazon, which comprised 46-56% of the applied at 373 days posttreatment. The proposed degradative pathway involves rapid dephenylation followed by slow mineralization of the degradate and/or parent. After 373 days, the amount of $^{14}CO_2$ formed in the treated sandy loam soil was ca. 19% of the applied; in the sandy clay loam, it was ca. 4% after 367 days. Non extractable

residues increased with time (after one year, up to 19% for the sandy clay loam soil and 13% for the sandy loam soil).

3. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of pyrazon in aerobic sandy loam and sandy clay loam soils.

4. The registrant must provide supporting evidence for the fate of the phenyl moiety resulting from dephenylation of parent pyrazon.

METHODOLOGY:

Sieved (2 mm) sandy loam from Dinuba, CA (54% sand, 32% silt, 14% clay, 0.50% organic matter, pH 7.7, CEC 14.40 meq/100 g) and sandy clay loam soils from Fuquay-Varina, NC (66.8% sand, 9.2% silt, 24.0% clay, 2.20% organic matter, pH 5.9, CEC 8.15 meq/100 g) were weighed (25 g) into glass dishes and treated at 3.95 ppm with an aqueous solution of pyradiazinone ring-labeled [^{14}C]pyrazon (radiochemical purity >99%, specific activity 96.559 mCi/mM, BASF). The soil was moistened to 75% of 0.33 bar, and the dishes were placed in a glass "reactor" (Figure 3). The reactor was sealed, covered with aluminum foil, placed in a dark growth chamber, and incubated at 25 ± 1 C. At 1-3 week intervals, the reactor was purged with humidified air for 1.5 hours; the air was vented through a polyurethane plug and a tube of scintillation cocktail (Harvey) to capture volatiles. The soil moisture was also adjusted at this time. Duplicate soil samples were removed for analysis immediately posttreatment, at 17 days posttreatment, and at 1, 2, 4, 8 and 12 months posttreatment.

The soil samples were immediately extracted three times with methanol; the soils from later sampling intervals were further extracted three times with 0.1 N HCl in methanol after the methanol extractions (Figure 4). The methanol and methanolic HCl extracts were analyzed by one-dimensional TLC on silica gel plates developed in toluene:-ethanol (75:25). The samples were cochromatographed with pyrazon and dephenylated pyrazon reference standards. The radioactive areas were located and quantified by radioscanning and identified by comparison to the R_f of the standards. The unextracted [^{14}C]residues in the soils were quantified by LSC following combustion.

In an attempt to classify the unextractable soil residues as humic acid, fulvic acid, or humin, soil samples collected at 1 year posttreatment were extracted with methanol and HCl in methanol, then further extracted with sodium hydroxide. The extract was acidified to pH 1; [^{14}C]residues remaining in solution were considered fulvic acids, those which precipitated from solution were considered humic acids, and those which were not extracted from the soil with sodium hydroxide were classified as humin.

The polyurethane plugs were extracted twice with methanol; the extracts were combined and analyzed using LSC. The scintillation cocktail was assayed directly using LSC.

DATA SUMMARY:

Pyradiazinone ring-labeled [^{14}C]pyrazon (radiochemical purity >99%), at 3.95 ppm, degraded with registrant-calculated half-lives of 90 days in sandy loam soil and 152 days in sandy clay loam soil that were incubated in the dark at 25 $\pm$ 1 C and 75% of 0.33 bar for approximately 1 year. Dephenylated pyrazon was the only nonvolatile degradate identified in the soils during the study. During the study, the material balances were $\geq$91.5% of the applied (Tables I-IV).

In the sandy loam soil, [^{14}C]pyrazon decreased from approximately 100% of the applied radioactivity in duplicate samples immediately posttreatment to 74.1-74.5% at 120 days, 14.9-23.5% at 240 days, and 6.1-8.1% at 373 days (Table X).

Dephenylated pyrazon,

the only degradate identified in the soil extracts, was a maximum of 55.8-55.9% of the applied at 373 days posttreatment. Extractable polar [^{14}C]residues were isolated at 1.6-2.3% of the applied (days 240 and 373 only). At 373 days posttreatment, $^{14}CO_2$ totaled 18.6% of the applied and unextractable [^{14}C]residues in the soil were 12.2-13.1% (Table IV). The unextractable [^{14}C]residues in the soil at 373 days posttreatment were found to be 9.1-9.8% humin, 4.8-5.8% fulvic acid, and 0.7-1.1% humic acid (Table XIII).

In the sandy clay loam soil, [^{14}C]pyrazon decreased from 95.0-96.3% of the applied radioactivity immediately posttreatment to 68.7-71.6% at 124 days, 22.8-35.8 at 244 days, and 17.6-23.8 at 367 days (Table IX). Dephenylated pyrazon, the only degradate identified in the soil extracts, was a maximum of 45.6-50.7% of the applied at 367 days posttreatment. Extractable polar [^{14}C]residues were isolated at 2.1% of the applied (day 244 only). At 367 days posttreatment, $^{14}CO_2$ totaled 3.9% of the applied and unextractable [^{14}C]residues in the soil were 18.0-20.0% (Table III). The unextractable [^{14}C]residues in the soil at 367 days posttreatment were found to be 7.3% humin, 13.6-14.5% fulvic acid, and 0.9% humic acid (Table XIII).

COMMENTS:

1. Although it is clear that pyrazon degraded from both soils with half-lives of between 4 and 8 months, sampling intervals during this period were too infrequent to accurately assess more precise degradation half-lives of pyrazon. The concentration of pyrazon declined by >40% between the 4 and 8 month sampling intervals. In

the sandy clay loam soil, pyrazon declined from 74.3% to 19.2% (Table XII); in the sandy loam soil, pyrazon declined from 70.2 to 29.3% (Table XI).

2. The study authors suggested that the disparity in half-lives (90 and 152 days) for the aerobic metabolism of pyrazon in the two soils is due to the difference in soil pH (7 and 5.9), with metabolism occuring more slowly in the more acidic soils. However, differences in microorangism population may also account for the different half-lives.

3. The polyurethane trap was reported to be an efficient trap for volatile organic compounds. The Harvey scintillation cocktail solution contained phenylethylamine to trap carbon dioxide.

4. Additional information is being requested on the fate of the phenyl moiety resulting from dephenylation of parent pyrazon.

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