DATA EVALUATION RECORD

STUDY 4

CHEM 069008 Pyrethrin 1 §163-1

FORMULATION--00--ACTIVE INGREDIENT

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Reynolds, J.L., and R.A. Robinson. 1994. Adsorption and Desorption of [^{14}C]Pyrethrin 1 in Four Soils. XBL Study No. 93064; XBL Report No. RTP00156. Unpublished study performed by XenoBiotic Laboratories, Inc., Plainsboro, NJ; and submitted by Pyrethrin Joint Venture/Chemical Specialties Manufacturers Association, Washington, DC.

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study can be used towards the fulfillment of data requirements.

2. Pyrethrin [Pyrethrin 1; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester] was immobile in sand, sandy loam, silt loam, and silty clay loam soils, with Freundlich K_{ads} values were 198 for the Wakulla sand soil (1/n = 1.098), 268 for the North Dakota sandy loam soil (1/n = 0.9069), 430 for the Dundee silt loam soil (1/n = 1.047), and 310 for the Mahaska silty clay loam soil (1/n = 0.9222); corresponding K_{oc} values were 37847, 12472, 74175, and 16190, respectively. Pyrethrin comprised >93.6% of the applied in the supernatants and soil extracts; minor amounts of chrysanthemic acid were detected in the adsorption supernatant.

3. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (batch equilibrium) of unaged cyclopropane-labeled [1-^{14}C]pyrethrin [Pyrethrin 1; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane-carboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester] in sand, sandy loam, silt loam, and silty clay loam soils.

4. No additional information on the mobility of unaged pyrethrin in soil is required at this time. Information is needed on the mobility of aged residues originating from both the cyclopropane and cyclopentene portions of the molecule.

METHODOLOGY:

Sand, sandy loam, silt loam, and silty clay loam soils (Table III) were sieved (2 mm) for use in preliminary and definitive experiments. Based on the results of preliminary experiments, a soil:solution ratio of 1:100 (w:v) and an equilibration period of 3 hours were selected for use in the definitive experiment. It was also determined that pyrethrin readily bound to the walls of both glass and Teflon [page 14]; therefore, to minimize binding, the glass centrifuge tubes used during the study were coated with unlabeled pyrethrin prior to use.

For the definitive study, portions (0.3 g dry weight) of the four soils were weighed into precoated 50-mL glass centrifuge tubes, mixed with 30 mL of a 0.01 M calcium chloride solution, and treated with cyclopropane-labeled [1-^{14}C]pyrethrin [Pyrethrin 1; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester; radiochemical purity >97.8%, specific activity 54 mCi/mMol, Amersham International] at concentrations of 0, 0.05, 0.09, 0.50, or 0.81 ppm (soil basis) dissolved in acetonitrile; the concentration of cosolvent was <1% by volume. Two tubes were prepared for each treatment combination. Two additional tubes of each concentration of solution were prepared without soil, to serve as controls. All tubes were capped and wrapped in aluminum foil, and the soil:solution slurries (1:100, w:v) were equilibrated for 3 hours on a wrist-action shaker at ambient temperatures. After equilibration, the samples were centrifuged and the supernatants decanted; duplicate aliquots of the supernatants were analyzed by LSC.

To study desorption, the supernatants were replaced with 30 mL of pesticide-free 0.01 M calcium chloride solution, and the soil:solution slurries were equilibrated for 3 hours as previously described. Following equilibration, the samples were centrifuged and the supernatants decanted; duplicate aliquots of the supernatants were analyzed by LSC. After desorption, the soil samples were extracted twice with acetonitrile:acidified water (4:1, v:v) by sonicating for 10 minutes per extraction; after each extraction, the mixture was centrifuged and the supernatant decanted. The extracts

were combined, and aliquots were analyzed using LSC; the extracted soils were air-dried, and subsamples were analyzed using LSC following combustion.

The adsorption and desorption supernatants from one of the two 0.81 ppm samples from each soil, and the post-desorption acetonitrile:water extract from the same soils were partitioned twice against methylene chloride. Like extracts were combined, and aliquots of the organic and aqueous solutions were analyzed using LSC. The adsorption, desorption, and soil methylene chloride extracts were concentrated by rotoevaporation and/or under nitrogen, then analyzed for total radioactivity using LSC, and for specific compounds by reverse-phase HPLC using a Zorbax C-8 column coupled with an RP-18 guard column, and eluted with an acetonitrile:acidified (pH 4) 25 mM KH_2PO_4 gradient (20:80 to 100:0 to 20:80, v:v); the column was equipped with radioactive flow detection. [^{14}C]Compounds were identified by comparison to an unlabeled reference standard of pyrethrin. To confirm the identification of pyrethrin, "selected" methylene chloride extracts were also analyzed by GC/MS and GC/RAM.

DATA SUMMARY:

Based on batch equilibrium experiments, [^{14}C]pyrethrin was determined to be immobile in sand, sandy loam, silt loam, and silty clay loam soil:calcium chloride solution slurries (1:100, w:v) containing cyclopropane-labeled [1-^{14}C]pyrethrin [Pyrethrin 1; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester; radiochemical purity >97.8%] at 0.05, 0.09, 0.50, or 0.81 ppm (soil basis). The slurries were equilibrated in the dark for 3 hours at ambient temperatures. Freundlich K_{ads} values were 198 for the sand soil, 268 for the sandy loam soil, 430 for the silt loam soil, and 310 for the silty clay loam soil; corresponding K_{oc} values were 37847, 12472, 74175, and 16190, respectively, and n values were 0.91-1.10 (Tables VI-X). K_{des} values were 965 for the sand soil, 2332 for the sandy loam soil, 2600 for the silt loam soil, and 1151 for the silty clay loam soil; corresponding K_{oc} valued were 184767, 108679, 448257, and 60133, respectively, and n values were 0.61-0.86.

Pyrethrin was relatively stable throughout the study, comprising >93.6% of the applied in the supernatants and soil extracts. Minor amounts (4-5% of the applied) of chrysanthemic acid were recovered in the adsorption supernatant (Table XVI). Material balances following desorption were 90.50-111.86% of the applied (Table XI).

COMMENTS:

1. Because pyrethrin adsorbs readily to a variety of surfaces, a 2-mL solution of methylene chloride containing 20 ug of unlabeled pyrethrin was transferred into each 50-mL glass centrifuge tubes used

in the definitive experiment. The tubes were sealed with Teflon-lined caps, then inverted to cover the inner surface (including the caps). The caps were removed, and the solvent in the tubes and on the caps was allowed to evaporate. This procedure minimized the binding of pyrethrin to the sample container in lieu of the soil. Reported radioactivity recoveries ranged from 90.50-111.86% of the applied, suggesting that binding to test tubes was minimal.

2. The 1:100 soil:solution ratio was selected so that 20-80% of the pyrethrin in solution would be sorbed to the soil.

3. It has been reported that the pyrethrins are relatively insoluble in water (The Agrochemical Handbook, 3rd Edition). The use of a co-solvent in this experiment (acetonitrile, <1% by volume) allowed the concentration of pyrethrin in water to exceed expected solubilities, and the observed partitioning may have been between acetonitrile:soil rather than water:soil. However, the extremely high adsorption constants observed in this study, as well as confirmation of the theoretical likelihood that pyrethrin would partition to the soil organic matter rather than water confirm that pyrethrin I is immobile and will tend to attach itself to solid surfaces. Offsite exposure to pyrethrin I appears to be restricted to offsite spray drift and runoff events severe enough to induce soil erosion.

4. The desorption phase coefficients (n values) for the North Dakota sandy loam, the Dundee silt loam and the Wakulla sand ar all < 0.7. At n values significantly different from 1, the Freundlich isotherm may not be an accurate model of adsorption/desorption. However, it is possible to draw the broad conclusion that little pyrethrin can be desorbed by water, even where a cosolvent (acetonitrile) is used.

Pyrethrins review

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