DATA EVALUATION RECORD

STUDY 4

CHEM 102001	Thiophanate-methyl	§162-3 and 162-2
FORMULATION--00--ACTIVE INGREDIENT		

STUDY ID 40061501
Dykeman, R. 1986. Thiophanate-methyl--anaerobic aquatic metabolism. Laboratory Project ID. WT-1-82. Unpublished study performed and submitted by Agchem Division, Pennwalt Corp., Tacoma, WA.

STUDY ID 92186019
Wright, J. 1990. Phase 3 summary of MRID 40061501: Thiophanate-methyl anaerobic aquatic metabolism. Project WT-1-82. Prepared by Atochem Northamerica, Philadelphia, PA.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Metabolism - Anaerobic Aquatic

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

2. [^{14}C]Thiophanate-methyl degraded with a half-life of <1 day in a silt loam soil:water system incubated under anaerobic conditions at 21 C in the dark. The degradates methyl 2-benzimidazolylcarbamate (MBC), 1-(3-methoxycarbonyl-2-thioureido)-2-(3-methoxycarbonylureido)benzene

(DX-105), dimethyl-4,4'-o-phenylenebis(allophanate) (FH-432), and methyl N-[2-(thioureido)phenylaminocarbonothioyl]carbamate (AV-1951) were isolated.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the anaerobic aquatic metabolism of uniformly ring labeled-[^{14}C]thiophanate-methyl.

4. No additional information on the anaerobic aquatic metabolism of thiophanate-methyl is required at this time.

METHODOLOGY:

Silt loam soil (23.3% sand, 63.9% silt, 12.7% clay, 1.35% organic matter, pH 6.2, CEC 10 meq/100 g) was mixed with water (pH 6.3) in 250 mL Erlenmeyer flasks (41.5 g soil:100 mL water). The soil and water had been obtained from a rice field in Arkansas. The flasks were sealed and maintained at 21 ± 1 C in the dark. After 41 days, uniformly ring labeled-[^{14}C]thiophanate-methyl (radiochemical purity 99%, specific activity 4.66 mCi/mmol, Pathfinder Laboratories, Inc.), dissolved in methanol, was added at 6 ug/g to the flasks. Each flask was sealed with a glass absorption tower containing a polyurethane foam plug to trap organic volatiles, a layer of Ascarite to trap $^{14}CO_2$, and layers of glass wool and Drierite to keep the Ascarite from being saturated with moisture (Figure 2). The flasks were incubated in the dark at 21 ± 1 C. The soil, water, foam plugs, and ascarite volatile traps from duplicate flasks were analyzed at 0, 1, 7, 14, 28 days and at 2, 3, 6, 9, and 12 months posttreatment. In addition, foam plugs and ascarite from all flasks remaining at 2 months posttreatment were sampled at the 2-month interval, as well as when the flask was removed from incubation for analysis.

The water was decanted from the soil, and aliquots of the water were analyzed by LSC. The water was extracted three times with chloroform. The combined chloroform extracts were concentrated on a rotary evaporator, then evaporated to near dryness using a steam bath with a stream of air. The sample was dissolved in chloroform and spotted onto silica gel TLC plates developed in one dimension using ethyl acetate:chloroform:methanol (60:40:1, v:v:v). Nonradiolabeled standards of parent thiophanate-methyl and degradates were cochromatographed with the samples; Rf values of standards were obtained by fluorescent quenching. Radioactive areas were located by radioscanning, and radioactive zones were scraped and analyzed by LSC for quantification.

The soil was extracted with acetone:chloroform (9:1, v:v) by sonication for one minute and then centrifuged. The acetone:chloroform supernatant was decanted. The extracted soil was further extracted with methanol:0.2 N HCl (15:1, v:v). The acetone:chloroform and methanol:HCl extracts were analyzed by LSC. The solvents were removed from each extract by rotary evaporation, and the pH of the

remaining aqueous portion was adjusted to pH 6.5-7. Each aqueous extract was partitioned three times with chloroform; the combined chloroform extracts were concentrated and analyzed by TLC as described above. The extracted soil was air-dried and stored frozen (or refrigerated if sample was analyzed within 24 hours) until analysis for unextracted [^{14}C]residues using LSC following combustion.

Foam plugs were placed in vials containing scintillation cocktail, and the contents of the vials were analyzed by LSC. The ascarite samples were extracted with water by stirring for one minute, and the water was analyzed by LSC.

DATA SUMMARY:

Uniformly ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity 99%), at 0.6 ug/g, degraded with a half-life of <1 day (calculated half-life 0.02 days) in a silt loam soil:water system (41.5 g soil:-100 mL water) that was incubated under anaerobic conditions in the dark at 21 ± 1 C. In the water, parent thiophanate-methyl declined from 73.11% of the applied immediately posttreatment to 17.17% at 1 day; thiophanate-methyl was not detected (detection limit not reported) after 3 months (Table 4). In the soil, thiophanate-methyl was 0.75% of the applied at day 0, 4.26% at 7 days posttreatment (maximum concentration), and 0.60% at 12 months (Table 5). Four degradates were isolated and identified:

methyl 2-benzimidazolylcarbamate (MBC), at maximum concentrations of 60.58% of the applied in water at 1 day posttreatment and 42.95% in soil at 28 days posttreatment;

1-(3-methoxycarbonyl-2-thioureido)-2-(3-methoxycarbonylureido)benzene (DX-105), at maximum concentrations of 6.45% in water immediately posttreatment and 0.88% in the soil at 7 days posttreatment;

dimethyl-4,4'-o-phenylenebis(allophanate) (FH-432), at maximum concentrations of 4.26% in water at 1 day posttreatment and 2.01% in soil at 9 months; and

methyl N-[2-(thioureido)phenylaminocarbonothioyl]carbamate (AV-1951), at maximum concentrations of 3.93% in the water at 1 day posttreatment and 0.72% in the soil at 7 days posttreatment.

At 12 months posttreatment, unextracted residues in the soil totaled 83.68%, and $^{14}CO_2$ totaled 4.07% (Table 1). Organic volatiles were not detected (detection limit not reported). Material balances during the study ranged from 80.85 to 105.27%.

COMMENTS:

1. More than 50% of the applied thiophanate-methyl degraded between the first two sampling intervals of 0 and 1 days posttreatment. Therefore, the accuracy of the calculated half-life of 0.02 days is questionable, although the half-life was clearly <1 day.

2. Only the samples taken at 14 days and the 9 months posttreatment had material balances of <90%.

3. Values reported for the concentrations of thiophanate-methyl and its degradates are the means of values obtained from duplicate samples.

4. The study author stated that a second TLC system was used to confirm the identification of FH-432 in replicate A of the 9 month samples. This second TLC system was not further described.

5. Method detection limits and recoveries from fortified samples were not reported.

6. The test water had a conductivity of 230 umhos/cm^2 and a total soluble salts content of 109.7 ppm.

7. The distribution of radioactivity in the soil and water fractions is presented in Figure 3.

8. The submitted study contains a response to an EPA data audit carried out on 8/6-7/87.

9. EFGWB would have preferred that the dissolved oxygen content and/or redox potential (Eh) of the aqueous phase had been monitored throughout the duration of the study and reported. EFGWB strongly recommends that in future studies conducted under anaerobic conditions these parameters be measured and reported.