DATA EVALUATION RECORD

STUDY 3

CHEM 102001 Thiophanate-methyl §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41482807
Soeda, Y., and H. Shiotani. 1987. Thiophanate-methyl - Photodegradation on soil. Laboratory Project ID NISSO EC-75. Unpublished study performed by Nippon Soda Co., Ltd., Kanagawa, Japan, and submitted by Pennwalt Corporation, Philadelphia, PA.

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Soeda, Y. 1990. Phase 3 summary of existing study MRID 41482807; thiophanate-methyl - Photodegradation on soil. Project EC-75. Prepared by Nippon Soda Co., Ltd., Kanagawa, Japan, and submitted by Pennwalt Corporation, Philadelphia, PA.

DIRECT REVIEW TIME = 16

REVIEWED BY: J. Harlin TITLE: Staff Scientist

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

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: 31st May 1991

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study cannot be used to fulfill data requirements at this time. The information in the study can be considered as partially fulfilling data requirements at this time.

2. Reported results indicated that thiophanate-methyl photodegraded with an observed half-life of 2.9-5.5 days in sterile sandy loam soil

irradiated with natural sunlight in Japan at air temperatures of -0.9 to 17.6 C. In the dark controls, the observed half-life was 10.3-19.3 days. The degradates methyl 2-benzimidazolylcarbamate (MBC) and methyl N-[2-(N'-methyoxycarbonyl-thioureido)phenylaminocarbonyl]carbamate (DX-105) were isolated from both the irradiated and dark control soils.

3. This study may be acceptable to fulfill EPA data requirements for photodegradation of phenyl ring-labeled [^{14}C]thiophanate-methyl on soil if the registrant provides the following additional information:

   a. Report the intensity of the natural sunlight (see Discussion).

   b. Provide a more thorough comparison between the Japanese soil used and American soils. This should include identification of the USDA soil series name(s) to which the Japanese may correspond (if any). Volcanic ash composition and clay mineralogy should also be reported, if available.

METHODOLOGY:

Samples (100 g) of air-dried, sieved (2-mm) sandy loam soil (53% sand, 29% silt, 18% clay, 1.7% organic matter content, pH 7.4, CEC 35.6 meq/100 g from Odawara) were each weighed into petri dishes, autoclaved at 120 C for 20 minutes, and adjusted to 75% of 0.33 bar moisture holding capacity. Uniformly phenyl ring-labeled thiophanate-methyl (radiochemical purity >99%, specific activity 15 mCi/mmol, Amersham International) plus unlabeled thiophanate-methyl (purity >99%, source not specified), dissolved in methanol, was filter-sterilized (0.2 um), then applied to the surface of the soil at 22 ug/cm^2 using a microsyringe; the application was reported to be equivalent to 2.8 lb/A of a 70% WP formulation. Each petri dish was then covered with a quartz plate and wrapped in aluminum foil. All petri dishes were placed outdoors in Kanagawa, Japan (35 16' N latitude, 139 11' E longitude), in an area described as being free of shade and reflections of sunlight (intensity of the sunlight was not reported). The aluminum foil was removed from half of the plates; the remainder remained wrapped to serve as dark controls. All plates were positioned on a black rubber sheet at a 30-degree angle with respect to the horizontal with the upper end pointing due north. Air temperatures, measured three times per day during the experiment, ranged from -0.9 to 17.6 C (Table 2). Two irradiated and two dark control samples were removed for analysis at 0, 1, 2.9, 5.5, 10.3, and 19.3 days posttreatment.

The soil samples were extracted twice with methanol:water (8:2, v:v) by shaking for 20 minutes and then centrifuged. The methanol:water extracts were mixed with distilled water and then partitioned twice with methylene chloride; the extraction efficiencies ranged from 53.9 to 85.2%. The methylene chloride extracts were concentrated to dryness. The residues were redissolved in methylene chloride and

analyzed by one-dimensional TLC on silica gel plates developed in ethyl acetate:methylene chloride:acetone:acetic acid (50:50:2:1, v:v:v:v). Radioactive areas were located using autoradiography and tentatively identified by comparison to reference standards. [^{14}C]Residues were scraped from the plates, eluted from the silica gel, and quantified by LSC. The method detection limit for TLC analysis was 0.004 ppm. Aliquots of the silica gel extracts were purified by HPLC using methanol:methylene chloride (4:96, v:v) and an unspecified method of detection. Following purification, the identities of the [^{14}C]compounds were analyzed by MS in the EI mode.

The soils were analyzed for unextracted [^{14}C]residues by LSC following combustion; the detection limit was 0.002 ppm. In order to determine the amount of unextracted residues in the humin, humic acid, and fulvic acid fractions of the soil organic matter, the soils were further extracted. The soil samples were extracted twice by shaking with 0.5 N sodium hydroxide solution for one hour and centrifuged. The supernatant (humic acid and fulvic acid fractions) was filtered under reduced pressure and adjusted to pH 1 with hydrochloric acid. The sediment (humic acid fraction) was filtered, and the filtrate (fulvic acid fraction) was adjusted to pH 6 and extracted two times with methylene chloride. The extract was concentrated under reduced pressure and analyzed by one-dimensional TLC as described previously.

DATA SUMMARY:

Phenyl ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity >99%), at 22 ug/cm^2, degraded with an observed half-life of 2.9-5.5 days on sterile sandy loam soil that was irradiated with sunlight outdoors in Japan for 19.3 days in December 1986. During the study, air temperatures ranged from -0.9 to 17.6 C. Thiophanate-methyl decreased from 78.7% of the applied at "0 days" posttreatment to 43.8% at 2.9 days, 37.8% at 5.5 days, and 23.6% at 19.3 days (Table 4). In the dark controls, the observed half-life of thiophanate-methyl was 10.3-19.3 days; thiophanate-methyl decreased from 78.7% of the applied at "0 days" to 41.8% at 10.3 days and 30.4% at 19.3 days. In the irradiated and dark control samples, the degradates

methyl 2-benzimidazolylcarbamate (MBC) and

methyl N-[2-(N'-methyoxycarbonylthioureido)phenyl-aminocarbonyl]carbamate (DX-105)

reached maximum concentrations of 20.8-21.7% and 1.8-2.6% of the applied, respectively, at 19.3 days posttreatment. Unidentified degradates ("others") were ≤4.3% of the applied. Unextracted [^{14}C]residues in the irradiated and dark control soils were 36.4-41.2% of the applied at 19.3 days posttreatment: 18.6-19.4% of the applied was in the humin, 14.1-20.4% was in the fulvic acid, and 2.2-

2.9% was in the humic acid fractions. Material balances ranged from 93.7 to 101.7% of the applied during the study.

COMMENTS:

1. The registrant-calculated half-life for the photodegradation of thiophanate-methyl (1.6 days) does not agree with the observed data; therefore, the calculated half-life was not reported in the data summary of this review. At "0 days" posttreatment, 21.3% of the applied radioactivity was not thiophanate-methyl. "0 Days" was not defined by the study author; it was uncertain if the soils were extracted immediately posttreatment, or if the study authors treated the soils, set up the remaining samples, and then extracted the "0 days" sample. As a result, it could not be determined if the degradation of thiophanate-methyl occurred prior to or after application of the pesticide to the soil. Therefore, rather than assume that the initial application was 100% of the applied, the half-lives should correspond to the times at which the concentration of thiophanate-methyl is approximately 39% of the applied--between 2.9 and 5.5 days for the irradiated soil and between 10.3 and 19.3 days for the dark controls. The calculated half-lives were further distorted by the lack of frequent sampling during the early stages of the experiment when the majority of the degradation occurred, and by the fact that the degradation appears to follow a curvilinear rather than a linear pattern.

2. The intensity of the natural sunlight was not reported. The study authors stated that the relative sunlight intensity was determined for the first two weeks of the experiment using a chemical actinometer of p-nitroacetophenone and pyridine; however, relative sunlight intensity data were not provided.

3. The study authors stated that the soils were autoclaved to prevent the formation of degradates during the test, since, in aerobic soil metabolism experiments, the parent compound had a very short half-life (<1 day) in three unsterilized soils. In addition, the authors believed that the difference between photodegradation of thiophanate-methyl in the sterilized sunlight-irradiated and dark control soils would be clearer as compared to unsterilized irradiated and control soils.

4. The test soil was Japanese. Japanese soils often contain volcanic ash and are usually atypical of soils in the continental United States. The registrant stated that this soil is similar to a soil obtained from Pennsylvania; however, insufficient information concerning the composition of the Japanese soil, such as volcanic ash content and types of clay present, was provided to support this claim (Table 1). Studies conducted using Japanese soils generally cannot be used to fulfill EPA guidelines. However, since in a photodegradation on soil study the soil acts as a surface for photolysis and limited interaction between the soil and pesticide is

involved, the use of the Japanese soil, although not preferred, is not unacceptable. The registrant must provide better characterization and comparison of the soils, which must include identifying which USDA soil series name(s) the Japanese soil may correspond (if any). Volcanic ash composition and clay mineralogy should also be reported, if available.

5. The temperature was not maintained constant between 18 and 30 C during the study. The study authors stated that the temperature was not controlled in order to determine the photodegradation of thiophanate-methyl under "practical conditions".

6. The soil samples were adjusted to 75% of 0.33 bar moisture holding capacity prior to the initiation of the study. It was stated that although the soil moisture was not subsequently measured during the course of the experiment, soil moisture was expected to remain at an adequate level throughout the short duration of the study.

7. Complete descriptions of the analytical methodology were not provided. For HPLC analysis, the method of detection that was used was not stated. For TLC analysis, it was not stated whether the [^{14}C]compounds were identified by comparison to the R_f values of reference standards that were chromatographed separately or to standards chromatographed on the same plates as the methylene chloride extracts. The R_f values of thiophanate-methyl and three degradates were provided in Table 1 of the original document.

8. EFGWB prefers that [^{14}C]residues in samples be separated by chromatography 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 a single solvent system. Identities of thiophanate-methyl and degradates were confirmed by MS.

9. Recovery efficiencies from fortified soil samples were not provided.

10. The schedule of irradiation of the soil samples is presented in Table 3.