DATA EVALUATION RECORD

STUDY 5

CHEM 102001 Thiophanate-methyl §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41560902
Soeda, Y., and H. Shiotani. 1987. Thiophanate-methyl - Batch equilibrium (adsorption/desorption). Study No. NISSO EC-89. Unpublished study performed by Nippon Soda Co. LTD. Japan, and submitted by Atochem North America, Inc. Philadelphia, PA.

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study cannot be used to fulfill data requirements.

2. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of thiophanate-methyl and its degradates.

3. This study is unacceptable for the following reasons:

the soils were autoclaved prior to use, thereby altering soil physical and chemical properties; and

the soils were sieved through a 0.5 mm sieve, removing a significant portion of the soil sand fraction and possibly reducing the apparent mobility of thiophanate-methyl and thiophanate-methyl residues.

4. Since the soils were autoclaved and sieved to 0.5 mm, the problems with this study cannot be resolved with the submission of additional data. A new study must be conducted.

METHODOLOGY:

Unaged thiophanate-methyl

Based on preliminary experiments, an equilibration time of 4 hours and a soil:solution ratio of 10 g:20 mL were selected.

Japanese sand, silt loam, sandy loam, clay loam soils and a silt loam river sediment were sieved (0.5 mm) and autoclaved (Table 1). The soils were each mixed with sterile (filtered at 0.2 um) 0.01 M calcium nitrate solutions containing uniformly ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity >99%, specific activity 15 mCi/mmol, Amersham International) plus unlabeled thiophanate-methyl (purity not specified, Nippon Soda) at 0.2, 0.8, 3.2, and 12.8 ug/mL (10 g soil:20 mL solution). The soil:solution slurries were shaken at room temperature for 4 hours. After shaking, the soil:solution slurries were centrifuged and the supernatants were decanted.

In order to study desorption, each removed supernatant was replaced with an equal volume of pesticide-free 0.01 M calcium nitrate solution. The soil:solution slurries were shaken for 4 hours at room temperature, then centrifuged, and the supernatants were removed. The desorption procedure was repeated one time.

Aliquots of the supernatants that were removed following adsorption and each of the two desorption steps were analyzed for total radioactivity using LSC. Also, the supernatants removed immediately following adsorption were analyzed for thiophanate-methyl and its degradates. The supernatants were extracted twice with methylene chloride. The methylene chloride extracts were concentrated (method not reported), and the concentrate was spotted onto TLC plates developed with ethyl acetate:methylene chloride:acetone:acetic acid (50:50:2:1, v:v:v:v). Radioactive areas on the TLC plates were located using autoradiography, quantified by LSC, and identified by comparison to R_f values of reference standards that were chromatographed separately.

After the second desorption step, duplicate samples of the four different treatment concentrations of each soil were combined yielding an 80 g sample of each soil. The composited sample was extracted twice with methanol. Water was added to the methanol extracts to make a 50% aqueous solution prior to extraction with methylene chloride. The methylene chloride extract was analyzed by TLC as described above.

Aged thiophanate-methyl residues

Uniformly ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity >99%, specific activity 43.7 uCi/mg, Amersham International) was dissolved in 500 uL methanol and mixed with nonsterile sandy loam soil (Odawara). The soil moisture was adjusted to 75% of 0.33 bar moisture content, and the soil was incubated in the dark at 22 C for 2 days. After incubation, the soil was extracted with methanol. Water was added to the methanol extract to obtain a 50% aqueous solution, which was extracted with methylene chloride. The methylene chloride extract was evaporated, and the residue was analyzed by TLC as described above.

Solutions of 0.01 M calcium nitrate containing uniformly ring-labeled [^{14}C]thiophanate-methyl residues at 0.2, 0.8, 3.2, and 12.8 ug/mL were prepared from the methylene chloride extract of incubated soil. These solutions were filter-sterilized (0.2 um) and then mixed with sieved (0.5 mm), autoclaved samples of Odawara sandy loam soil (20 mL solution:10 g soil). The soil solution slurries were equilibrated and analyzed for both adsorption and desorption as described above.

DATA SUMMARY:

Unaged thiophanate-methyl

Based on batch equilibrium experiments, uniformly ring-labeled [^{14}C]thiophanate-methyl (radiochemical purity >99%), at 0.2-12.8 ug/mL, was mobile to very mobile in Japanese sand, silt loam, sandy loam, and clay loam soils and a silt loam river sediment; Freundlich K_{eds} values were 0.31 for the sand, 0.60 for the silt loam, 3.02 for the sandy loam, 5.69 for the clay loam, and 1.48 for the silt loam river sediment (Table 5). Reported Freundlich K_{des} values were 0.072-1.854 for the sand, 0.099-3.495 for the silt loam, 0.266-11.424 for the sandy loam, 0.173-7.4671 for the clay loam, and 0.173-7.467 for the silt loam river sediment (Table 6). Data for TLC analysis of the solution following the adsorption step and of the soil following the second desorption step indicated that significant degradation occurred during the study (Attachment 7).

Aged thiophanate-methyl residues

Based on batch equilibrium experiments, aged (2 days) [^{14}C]thiophanate-methyl residues, at 0.2-12.8 ug/mL, were mobile in Japanese sandy loam soil with a Freundlich K_{ads} of 4.94 (Table 5). The reported Freundlich K_{des} values were 0.293-15.294 (Table 6). After aging and prior to initiation of the batch equilibrium experiment, thiophanate-methyl comprised 37.8% of the extracted radioactivity,

1-(3-methoxycarbonyl-2-thioureido)-2-(3-methoxycarbonylureido)benzene (DX-105) comprised 4.7%,

dimethyl-4,4'-o-phenylenebis(allophanate) (FH-432) comprised 3.3%,

methyl 2-benzimidazolylcarbamate (MBC) comprised 47.1%,

and unidentified degradates comprised 7.1% (Table 2).

COMMENTS:

1. Autoclaving of soils may significantly change the physical and chemical properties of the soils. Autoclaving soils may affect the soil CEC by breaking down organic matter and/or expanding the crystalline structure of clay particles; the effect this has on soil properties is influenced by the types and amounts of organic matter and clay in the soil. The breakdown of organic matter could either increase or decrease the soil CEC depending on the amount of negative charges lost from the organic matter versus the amount of negative charges gained by exposing new soil surfaces. The expansion of clay particles would tend to increase the soil CEC by exposing new soil surfaces, thereby decreasing the mobility of pesticides in the soil. Autoclaving soils has also been shown to make soils more hydrophobic; the mechanism for this is not fully understood. Increasing the hydrophobic character of the soil may tend to increase the mobility of pesticides when applied to the soil as a solution, as it is done in the batch equilibrium method.

   Since several processes occur during autoclaving, changes in soil behavior after autoclaving cannot be predicted; mobility of pesticides in some soils is drastically altered while mobility remains unaffected in other soils. Due to the changes in soil properties that may be caused by autoclaving, most soil scientists hesitate to use autoclaved soils in experiments involving the investigation of soil physical and chemical properties.

2. The soils were sieved through a 0.5 mm sieve rather than the standard 2 mm soil sieve, removing a significant portion of the soil sand fraction. Decreasing the relative percentage of sand in a soil would tend to decrease the apparent mobility of the test substance. Note

also that smaller particle size fractions (as it is obtained when a 0.5 mm sieve is used) result in higher total surface area and increase the probability of adsorption.

3. The soils used in this study were Japanese soils, which often contain volcanic ash and are usually atypical of soils in the continental United States. Studies conducted using Japanese soils cannot be used to fulfill EPA guidelines. The new studies must be conducted with USA soils.

4. The reported Freundlich K_{des} values apparently were not calculated correctly, since a different K_{des} value was calculated for each solution concentration. For each soil, one Freundlich K_{des} value should result from linear regression using data from several solution concentrations.

5. Since data for the TLC analysis of thiophanate-methyl and its degradates following the initiation of batch equilibrium experiments were only presented in terms of percent recovered from the TLC plate rather than percent of the applied, and either soil or test solutions but not both were analyzed at any given point of the experiment, the amount of degradation of thiophanate-methyl or thiophanate-methyl residues that occurred during the experiments cannot be determined.

6. For TLC analyses, the R_f values of thiophanate-methyl and degradates DX-105, FH-432, and MBC were 0.57, 0.43, 0.25, and 0.32, respectively.

7. Simetryne was used as a reference pesticide for this study. Simetryne was very mobile to mobile in four soils and a river sediment, with Freundlich K_{ads} of 0.64 for the sand, 0.77 for the silt loam, 2.97 for the sandy loam, and 4.48 for the clay loam soils and 2.10 for the river sediment (Table 5).