DATA EVALUATION RECORD UNDATED

DER 4

SHAUGHNESSY No. 041402
COMMON NAME: Molinate
CHEMICAL NAME: S-Ethyl hexahydro-1H-azepine-1-carbothioate
FORMULATION: Not formulated, pure active ingredient, ^{14}C-labeled.
DATA REQUIREMENT: Aerobic aquatic metabolism (162-4)

MRID No: 41421802
Lay, M.M. 1990. Aerobic aquatic metabolism of molinate with Stockton adobe clay. Report No.PMS-268/RR 89-034B. Unpublished study performed and submitted by ICI Americas, Inc., Richmond, CA.

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CONCLUSIONS:

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

2. [^{14}C]Molinate degraded with an observed half-life of >30 days in flooded clay loam soil that was incubated in the dark at 30 C under aerobic conditions. The degradates identified were molinate sulfoxide, hexamethyleneimine (HMI), 3-keto molinate, S-ethyl-5-carboxypentyl thiocarbamate, 4-keto molinate, and carboxy methyl molinate. Carbamyl chloride was also identified, but it was considered to be an artifact.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of ring-labeled [^{14}C]molinate in clay loam soil under aerobic aquatic conditions.

4. No additional information is needed on the metabolism of molinate under aerobic aquatic conditions.

METHODOLOGY:

Portions of sieved (2 mm) clay loam soil (20.2% sand, 27.8% silt, 52.0% clay, 1.60% organic matter, pH 6.0, CEC 30.2 meq/100 g) were weighed (250 g) into 1-L sidearm biometer flasks, flooded with tap water (300 mL), and treated at 4.2 ug/g soil (1050 ug/flask) with ring-labeled [^{14}C]molinate (radiochemical purity 95-98%, specific activity 27.3 uCi/mmole, Wizard Laboratories) dissolved in acetone. After mixing the contents by swirling, the flasks were connected to a humidified oxygen source. Oxygen was forced through the flasks and vented through polyurethane foam plugs between the flask and side arm, and a 1 N sodium hydroxide trapping solution in the side arm (Appendix 2). The flasks were incubated in the dark at 30 C. Duplicate flasks were removed for analysis at 0, 1, 3, 7, 14, and 30 days posttreatment; control flasks containing sterilized (autoclaved plus sodium azide) molinate-treated soil were sampled at 14 and 30 days. The trapping solutions were changed at each sampling interval.

The soil and water were separated by centrifugation. The soil layer was Soxhlet-extracted with acetone:methanol (22:3) and then with methanol:hydrochloric acid (60:1). The acetone:methanol extracts were concentrated (method not reported), and aliquots were analyzed by LSC and one- and two-dimensional TLC on silica gel plates developed in one or more of the following solvent systems: 2,2,4-trimethylpentane:p-dioxane (2:1); toluene:ether (2:3); hexane:ethyl acetate:formic acid (30:30:1); toluene:acetone:acetic acid (19:1:2); 2-propanol:acetic acid:water (4:1:1); and 1-butanol:ethanol:acetic acid:water:formic acid (30:10:5:10:4). The extracts were cochromatographed with unlabeled reference standards. Radioactive areas on the plates were visualized by autoradiography and quantified by radioisotope scanning; the standards were located by UV fluorescence quenching. The [^{14}C]compounds were eluted from the silica gel with chloroform or methanol and the TLC identification was confirmed using GC/MS. The concentrated acetone:methanol extracts were partitioned three times with chloroform. The chloroform extracts were concentrated (method not reported) and aliquots were analyzed by LSC and TLC as previously described. The extracted soil was analyzed by LSC following combustion.

The water layer was extracted three times with methylene chloride (1:1). Both the water and methylene chloride extracts were analyzed by LSC, TLC, and GC/MS as previously described. The sodium hydroxide trapping solutions were precipitated with barium chloride to confirm the presence of CO_2; [^{14}C]residues in the precipitate were quantified by LSC. The polyurethane foam plugs were extracted three times with chloroform; the chloroform extracts were analyzed by TLC and LSC. The extracted plugs were placed in scintillation fluid, and unextracted radioactivity was measured directly by LSC.

DATA SUMMARY:

Ring-labeled [^{14}C]molinate (radiochemical purity 95-98%), at 4.2 ug/g soil, degraded with an observed half-life >30 days in flooded clay loam soil that was incubated in the dark at 30 C for 30 days. [^{14}C]Molinate was 86.84% of the applied radioactivity immediately posttreatment and declined to 65.52% of the applied radioactivity by 30 days (Table VIII). During the study, [^{14}C]residues associated with the soil layer increased from 44 to 62% of the applied radioactivity, and [^{14}C]residues associated with the floodwater decreased from 51 to 24% (Table III). Four degradates were identified in both the soil and floodwater:

molinate sulfoxide (maximum 8.872% of the applied radioactivity at 14 days posttreatment);

hexamethyleneimine (HMI) (maximum of 9.559% at 7 days posttreatment);

carbamyl chloride (maximum of 1.632% at 7 days posttreatment); and

3-keto molinate (maximum of 0.842% at 1 day posttreatment; Tables IV-VII).

Three degradates were identified only in the floodwater,

S-ethyl-5-carboxypentyl thiocarbamate,

4-keto molinate, and

carboxy methyl molinate;

each was present at ≤0.798% (Tables VI and VII). One unidentified [^{14}C]compound was present in the organic extract of the floodwater at a maximum of 0.249% of the applied at 14 days posttreatment (Table VI). Three other unidentified [^{14}C]residues were present in the aqueous extract of the floodwater at 0.112% of the applied at all sampling intervals (Table VII). $^{14}CO_2$ comprised 0.958% of the applied radioactivity by 30 days posttreatment; volatile molinate comprised 7.18% at 30 days (Table III). Unextracted radioactivity increased from 0.77% of the applied immediately posttreatment to 1.23-2.39% at 1-30 days posttreatment (Table III). Except for carbamyl chloride, the identical degradates were isolated from the sterile soil. During the study, material balances ranged from 84.57-95.27% (Table III).

COMMENTS:

1. The study author calculated a half-life of 27.7 days for molinate in this system. However, the concentration of molinate varied with a downward trend. The molinate recovery (Table VIII, Figure 8) makes degradation patterns unclear. The study author does not offer an explanation of the apparently anomalous data from the final sampling interval.

2. There is an apparent discrepancy between the data presented in terms of "% of the applied" (Tables IV-VII) and the data presented in terms of ppm (Tables IX and X-1). For example, molinate sulfoxide, present at 8.872% of the applied was 1.37 ppm while HMI, at 9.559% was 0.47 ppm. In this study the reviewer summed the percentages in Tables IV-VII for the data summary.

3. The study author stated that the degradate, carbamyl chloride, was an artifact. The study author provided two possible explanations: (1) carbamyl chloride was an artifact of hydrochloric acid extraction and (2) carbamyl chloride was derived from the reaction of HMI with phosgene (a contaminant in the methylene chloride used for extractions).

4. Table III has a column heading of "Volatile"; the study author stated that 7.73% of the total applied radioactivity was collected in the foam plugs and that TLC analysis showed that "...molinate was the only radioactive species in the chloroform extracts of the plugs."

5. The study author stated that the soil was Soxhlet-extracted with acetone:methanol (22:3) and then with methanol:hydrochloric acid (60:1). Although data are presented for the

methanol:hydrochloric acid extract, any manipulations of the extract and the methods of analysis were not described.

6. The description in the text of the oxygenation set-up and the system illustrated in the Appendix 2 do not agree.