

12/15/92

DATA EVALUATION RECORD

STUDY 12

CHEM 057701

Malathion

\$163-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 42015201

Spare, W.C. and W.D. Cutchin. 1991. The volatilization of malathion from soil (A laboratory study). Laboratory Report No. Agrisearch Project No. 2901. Unpublished study performed by Agrisearch Incorporated, Frederick, MD and submitted by the Malathion Reregistration Task Force.

DIRECT REVIEW TIME = 5

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CONCLUSIONS:

Mobility-Laboratory Volatility

1. EFGWB concludes that the study is acceptable and provides information indicating that malathion does not volatilize rapidly from soil, since $\leq 5.1\%$ of the applied radioactivity volatilized during the 16 days of the study.
2. After 16 days the material balance averaged 88.1, 90.7 and 114.2%, respectively, for the ULV, EC and RTU formulations.
3. The data showed, with one exception, little or no residues recovered as CO_2 . The exception was with the EC formulation maintained at 50% soil moisture and at a air flow rate of 100 ml/min, which indicated 26.5% of the applied was recovered as CO_2 after 16 days of incubation.
4. There was no noticeable pattern of volatility between soil moisture regimes or air flow rates. Maximum air concentrations varied from 5.4 to 17.2, 1.8 to 5.4 and 18.4 to 74.5 $\mu\text{g}/\text{m}^3$ for the RTU, ULV and EC

formulations, respectively; while maximum air volatility varied from 0.4 to $17.0 \times 10^{-3} \text{ ug/cm}^2/\text{hour}$; all occurring with the 1st 2 days and indicating a low volatility.

5. Vapor pressure of the active ingredient at 25 °C was reported to be $3.4 \times 10^{-6} \text{ mm Hg}$.

METHODOLOGY:

Three formulations of malathion , Ready To Use (RTU, 46.2% a.i.), Ultra Low Volume (ULV, 91% a.i.) or Emulsifiable Concentrate (EC, 57% a.i.) were applied separately with ^{14}C -malathion (radiopurity = >99% and specific activity = 312 $\mu\text{Ci/mg}$) to a Blackoar silt loam soil from Clarence, MO that had been sieved through a 2 mm mesh screen. The soil had the following properties: sand, 26.0%; silt, 58.0%; clay, 16.0%; organic matter, 2.2%; cation exchange capacity, 11.1 meq/100 g; soil pH, 6.5; bulk density, 1.21 g/cm^3 and field moisture at 1/3 bar, 24%.

The effects of two soil moisture (50 and 75% moisture at 1/3 bar) and two air flow (100 and 300 ml/min. determined with a flow meter) regimes on malathion volatilization were studied by weighing fifty grams of air dried soil (56.69 g wet soil) into the volatilization flasks (Figure 2). Sufficient amounts of the appropriate stock solutions were then thoroughly mixed with the soil to yield the following maximum field rates, EC = 8 lb a.i./A, ULV = 16 fl. oz./A and RTU = 36 fl. oz./ A.

The soil contained in the flask had a surface area of 78.54 cm^2 . Humidity within each flask was measured with a thermocouple thermometer with a psychrometer probe, while temperature was determined with a continuous temperature recorder. The study was conducted inside an incubator with temperature maintained at $25 \pm 1 \text{ }^\circ\text{C}$ and in the dark, except for short periods when incandescent lighting was used for measurements. Each flask was attached to traps containing polyurethane plugs and 1N KOH to trap, respectively, volatile compounds and CO_2 . Samples were collected at 0, 1, 2, 3, 4, 5, 7, 9, 12, 14 and 16 days.

All measurements of ^{14}C -radioactivity were determined using a Liquid Scintillation Counter (LSC). Soil samples were oxidized in duplicate in a Biological Materials Oxidizer (BMO) and the $^{14}\text{CO}_2$ collected in trapping cocktail and counted using LSC. Volatile material was quantified in duplicate using Scint-A Cocktail and LSC.

The polyurethane foam plugs used as traps for volatile organic compounds were extracted with 10 ml acetonitrile/0.5N HCl (90:10, v:v) by shaking for 30 minutes and sonicating for 15 minutes prior to analyzing by LSC and concentrating prior to analysis with HPLC for confirmation.

To verify that the radioactivity found in the KOH traps was $^{14}\text{CO}_2$, selected samples were treated with BaCl_2 to remove CO_2 , and reanalyzed by LSC to confirm that loss of radioactivity had occurred (Table IX).

The soil in each flask was thoroughly mixed and transferred into a 250 ml Nalgene bottle. The soil samples were extracted with 150 ml acetonitrile/0.5N HCl (90:10, v:v) by shaking for 30 minutes, centrifuged for 20 minutes and the supernatant recovered and the process repeated with 100 ml acetonitrile/0.5N HCl (90:10, v:v). Two 1 ml samples were removed from the combined supernatant for analysis by LSC and two 25 μ l aliquots were removed for TLC analysis. Soil extracts were also analyzed by HPLC for confirmation. Duplicate samples of soil were oxidized in the BMO to quantify the bound radioactivity. The soil with ULV and EC formulations were reextracted by Soxhlet for 18 hours with 300 ml of methanol. Two 1 ml aliquots were analyzed by LSC and duplicate samples of each residual soil were combusted with BMO to determine residual radioactivity.

Single dimension TLC was performed with plates coated 0.250 mm thick with silica gel or ethyl reversed phase KC2F and scanned by a Radioanalytical Imaging System. Silica gel plates were developed in 40 toluene/40 hexane/10 acetic acid (v:v:v) and 75 hexane/ 15 acetic acid/10 ethyl ether (v:v:v); reversed phase plates were developed in 4 methanol/1 water (v:v).

Products were confirmed on selected volatile and soil extract samples with HPLC (with radioactivity monitor) by comparing the retention time of the concentrated extracts to the retention time of analytical standards (Figures 3-7).

Material balance was determined by summation of radioactivity collected from volatiles, soil extracts and residual soil and dividing by the applied radioactivity times 100.

REPORTED RESULTS:

Average material balance in samples at time zero as a percent of the applied radioactivity ranged from 91.3 to 112.3 (Table VI).

After 16 days, the data showed, with one exception, between 0 and 5.1 % of the applied was recovered either as malathion or CO₂ (Table VII). The exception was the EC formulation maintained at 50% soil moisture and at a air flow rate of 100 ml/min, that showed 26.5% of the applied recovered as CO₂ after 16 days of incubation.

There was no noticeable pattern of volatility between soil moisture regimes or air flow rates. Maximum air concentrations varied from 5.4 to 17.2, 1.8 to 5.4 and 18.4 to 74.5 μ g/m³ for the RTU, ULV and EC formulations, respectively; while maximum air volatility varied from 0.4 to 17.0 x 10⁻³ μ g/cm²/hour Tables X-XXI).

Total radiocarbon material balance for the study was 114, 88 and 91% for the RTU, ULV and EC, respectively, at the end of the 16-day study (TABLE VII).

Thin-layer chromatography showed that 74.8 to 99.2% of the applied malathion remained as parent in the RTU treatment; conversely, 15.7-41.5 and 2.4-10.3% remained as parent from the ULV and EC test formulation, respectively (Table VIII). The average extractable percent of applied malathion from the soil was

RTU-96.9%, ULV-61.7% and EC-37.3%. The TLC analysis of the soil extracts showed the following percentages of the applied radioactivity remaining as malathion, RTU-83.8, ULV-26.8 and EC-6.2. Furthermore, combustion of the extracted soils resulted in the following average % of applied recovered as bound radioactivity, RTU-15.2, ULV-25.2 and EC-42.2.

The amount of malathion and CO₂ volatilized and plotted against time is illustrated in Figures 8-13. The data show that the greatest amount of volatilization generally occurred during the first two days of incubation and then steadily declined.

REVIEWER'S COMMENTS:

1. This study generally follows Subdivision N Guidelines and satisfies the Laboratory Volatility (163-2) data requirement.
2. Although EFGWB prefers that a sandy loam soil with low organic matter (<1%) be used in the laboratory volatility study, the soil used (Blackoak silt loam) has a K_d and K_{oc} , respectively of 1.63 and 163, which indicate low binding capacity of the soil. Therefore, EFGWB concludes that the use of the silt loam soil probably had a minimal effect on volatility.

MALATHION

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Pages 5 through 39 are not included.

The material not included contains the following type of information:

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 - ☐ Identity of product impurities.
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 - ☐ Description of quality control procedures.
 - ☐ Identity of the source of product ingredients.
 - ☐ Sales or other commercial/financial information.
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