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DATA EVALUATION RECORD

STUDY 3

CHEM 057701 Malathion §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 41695501
Dykes, J., K. Kabler, and B. W. Allen. 1990. Determination of the photolysis rate on the surface of soil with malathion. Laboratory Report No. 37575. Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and submitted by the Malathion Reregistration Task Force.

DIRECT REVIEW TIME = 8

REVIEWED BY: C. Cooke TITLE: Staff Scientist

EDITED BY: K. Ferguson TITLE: Task Leader
W. Martin Staff Scientist

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

APPROVED BY: Richard J. Mahler
TITLE: Hydrologist
ORG: EFGWB/EFED/OPP
TEL: 703-305-7991

SIGNATURE: Richard J. Mahler DEC 15 1992

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. EFGWB concludes that this study is scientifically valid and provides supplemental information that shows malathion is stable to soil photolysis. After 30 days incubation, 85.4% of the applied radioactivity was still parent malathion. The study does not satisfy the data requirements because:

   1. The more rapid degradation of malathion in the dark control samples was not explained. A detailed explanation should be provided to explain the enhanced degradation of malathion in the dark control samples as compared to the irradiated soil (63 vs. 173 days, respectively). However, EFGWB notes that the R^2 values

(0.5116 and 0.2992) reported for the regression analysis were not significant; therefore, there may be too much variation in the data to reach any conclusion related to the differences between results of the dark and light experiments.

2. At least three degradates that were detected with TLC were not identified.

3. The soil that was used in this study was not the same soil as used in the aerobic soil metabolism study as suggested by the Subdivision N Guidelines. The use of the same soil for both studies may have assisted in explaining the more rapid degradation in the dark. Furthermore, an acceptable explanation is needed to justify using different soils.

If the registrant can satisfactorily resolve the above problems, this study probably can be upgraded to satisfying the photolysis on soil data requirements; however, resolution of the above discussion points probably will not change EFGWB's conclusion that malathion is stable to soil photolysis.

3. The section below listed as "REVIEWER'S COMMENTS", contain further details of the problems noted with the study.

METHODOLOGY:

Subsamples (1 g) of sieved (2-mm) sandy loam soil (54% sand, 36% silt, 10% clay, 0.8% organic matter, pH 6.5, CEC 4.7 meq/100 g) were weighed into vials, caked with water, and allowed to air dry. The soils were then treated at a nominal rate of 10 ug/g with [2,3-^{14}C]malathion (radiochemical purity 94.9%, specific activity 90.0 uCi/mg, Amersham) in methanol.

A portion of the open vials of soil was placed in a stainless steel chamber that was covered with a borosilicate glass plate; humidified, CO_2-free air was drawn through the chamber, then vented sequentially through a polyurethane foam plug, one tube of ethylene glycol, one tube of 1 N sulfuric acid, and two tubes of 1 N potassium hydroxide (Figures 2 and 3). The chamber was externally cooled with circulating water to maintain a temperature of 23.5 $\pm$ 3.7° C.

The treated soil samples were irradiated for 26 days on 12-hour light/dark cycles using a borosilicate glass-filtered xenon lamp. The intensity of the radiation from the lamp was measured prior to and after the irradiation period, and was stated to be approximately equal to that of natural sunlight between wavelengths of 290 and 750 nm measured at 40 degrees N at the autumnal equinox (Table II; Figure 5). The remaining vials of treated soil were placed in a sealed "metabolism vessel", which was wrapped in aluminum foil to exclude the light but was otherwise similar to the photolysis chamber. The chamber was externally cooled with circulating water to maintain a temperature of 25.0 $\pm$ 1° C.

Duplicate vials of irradiated and dark control soil were removed for analysis at 0, 1, 4, 7, 11, 14, 21, and 26 days posttreatment; the trapping solutions were changed at the same intervals.

Since the final sampling interval was 26 days rather than the 30 days specified by Subdivision N guidelines, the experiment was repeated with a limited number of samples. Samples were collected for analysis only at 1, 14.8 (15), and 30.8 (31) days posttreatment.

The soil samples were extracted three times by shaking with methanol; the extracts were centrifuged and the supernatant decanted after each extraction. The extracts were combined and aliquots were analyzed for total radioactivity using LSC. Additional aliquots were analyzed using one-dimensional TLC on silica gel plates developed with toluene:glacial acetic acid (4:1, v:v).

The samples were cochromatographed with the reference standards. [^{14}C]Malathion was located on the plates by linear scanning; standards were located by UV quenching. The plates were then autoradiographed to identify other areas of radioactivity. Radioactive zones were scraped from the plates, and the [^{14}C]compounds were desorbed from the silica gel with methanol and quantified using LSC. The extracts from the 30-day irradiated and dark control soils were also analyzed using HPLC with a mobile phase of acetonitrile:0.05 M phosphate buffer (step gradient) and with UV (220 nm) detection. Unextracted [^{14}C]residues in the methanol-extracted soil were quantified using LSC following combustion.

Recovery efficiencies from fortified samples treated with malathion at 5 to 15 ppm was >100% of the applied radioactivity (Table IV).

The polyurethane foam plugs were extracted three times with methanol, and the methanol extracts were analyzed for total radioactivity using LSC. Aliquots of the trapping solutions were analyzed for total radioactivity using LSC.

DATA SUMMARY:

[2,3-^{14}C]Malathion (radiochemical purity 94.9%), applied at a nominal rate of 10 ug/g to sandy loam soil, ranged from 96.0% to 104.8% of the applied radioactivity with no discernable pattern during 26 days of irradiation (12-hour light/dark cycle) with a xenon arc lamp at 23.5 $\pm$ 3.7° C; at 31 days posttreatment, [^{14}C]malathion was 85.4% (Table V). The intensity of the radiation from the lamp was approximately equal to that of natural sunlight between wavelengths of 290 and 750 nm measured at 40 degrees N at the autumnal equinox.

In the dark control, [^{14}C]malathion was $\geq$100% of the applied radioactivity at 0 and 1 day posttreatment, then ranged from 56.6% to 77.1% with no discernible pattern between 4 and 31 days (Table VI).

The registrant-calculated half-lives for the irradiated soil and the dark controls were 173 and 63.4 days, respectively (Tables V and VI, Figures 6

and 7). It was reported that no degradate was >5.5% of the applied radioactivity; HPLC analysis of the day 30 irradiated soil extract detected small amounts (quantitative data not provided) of malaoxon and the monoacid (Figure 9).

During the study, the material balances of the irradiated soil were ≥100% of the applied radioactivity; while the dark controls material balances were 85.7-107.1% with no discernible pattern (Tables VII and VIII).

In the irradiated soil at 31 days posttreatment, [^{14}C]malathion comprised 89.4-91.6% of the radioactivity recovered from the TLC plate; one unknown (R_f 0.26) was 3.0-3.7%, origin material was 0.9-2.2%, and the three zones located between discrete areas of [^{14}C]residues were each 0.2-3.4% (Tables IX and X). At 31 days posttreatment, an average 10.07 ug of [^{14}C]residues were recovered from the irradiated samples: 8.77 ug in the soil extracts; 0.78 ug as unextracted [^{14}C]residues; and 0.52 ug as volatiles (Table VII).

In the dark control soil at 31 days posttreatment, [^{14}C]malathion comprised 94.6-99.3% of the radioactivity applied to the TLC plate; two unknowns (R_fs 0.37 and 0.40) were each 0.5-1.2%, origin material was 0.2-2.2%, and the three zones located between discrete areas of [^{14}C]residues were each 0.2-0.5% (Tables XI and XII). At 31 days posttreatment, an average 9.58 ug of [^{14}C]residues were recovered from the dark control samples: 5.72 ug in the soil extracts; 3.29 ug as unextracted [^{14}C]residues; and 0.57 ug as volatiles (Table VIII).

REVIEWER'S COMMENTS:

1. Malathion appeared to degrade more rapidly in the dark controls than in the irradiated samples. The study authors stated that this was "possibly" due to a higher bacterial population in the dark soil than in the irradiated soil, but provided no explanation for the higher concentration of organisms in the dark control soil. Since changes in factors such as soil moisture and temperature can accompany irradiation and can in turn affect microbial populations, the study authors must more clearly identify the reasons for the enhanced degradation in the dark control.

2. If the same soil were used in this study that was used in the aerobic soil metabolism study, it would help in comparing if the aerobic metabolism study was faster in the dark control than in the light exposed samples. The same soil is needed in both studies so that direct comparisons can be made between microbial and photochemical pathways of degradation. Furthermore, Subdivision N Guidelines Section 161-3 (c) (2) (ii) states: "One of the soils (e.g., sandy loam, silt loam, or other soil appropriate to the application site) specified in Section 162-1 (aerobic soil metabolism study) should be used, if data from that study are also submitted."

3. At least three [^{14}C]degradates (R_f 0.26, 0.37, and 0.40) that were detected using one-dimensional TLC were not identified. Using HPLC,

malaoxon and the monoacid were identified in the soil extract but not quantified; it was uncertain if these were the same compounds identified using TLC.

4. Attempts were made to increase the extractability of the [^{14}C]residues from the soil. Both methanol:water (3:1, v:v) and methanol:water that had been adjusted to pH 3 with glacial acetic acid were tried, but no increase in extractability was observed.

5. There was a discrepancy in the reported temperatures for the photolysis chamber; 25.6° ± 1.7° C was reported in the "SUMMARY" section, 25° ± 1° C was reported in the "DEFINITIVE STUDY" section, and 23.5° ± 3.7° C was reported in the "RESULTS AND DISCUSSION" section.

MALATHION

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