[12-1-88]

DATA EVALUATION RECORD

STUDY 10

CHEM 059101 Chlorpyrifos §164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

FICHE/MASTER ID 40059001
Oliver, G., R. McKellar, K. Woodburn, et al. 1987. Field dissipation and leaching study for chlorpyrifos in Florida citrus. Laboratory Report No. GH-C 1870. Unpublished study prepared by Dow Chemical U.S.A., Ag Chemistry R&D Laboratories. 94 p.

DIRECT REVIEW TIME = 10

REVIEWED BY: L. Binari TITLE: Staff Scientist

EDITED BY: T. Colvin-Snyder T. Colvin-Snyder TITLE: Staff Scientist

APPROVED BY: W. Spangler W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: P. Datta
TITLE: Chemist
ORG: EFED/OPP
TEL: 557-9733

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

This study is scientifically sound and provides supplemental information towards the registration of chlorpyrifos. This study does not fulfill EPA Data Requirements for Registering Pesticides because freezer storage stability data were not provided.

Ancillary Study - Well Water Monitoring

This study is scientifically sound and provides supplemental information towards the registration of chlorpyrifos. This study does not fulfill EPA Data Requirements for Registering Pesticides because freezer storage stability data were not provided.

SUMMARY OF DATA BY REVIEWER:

Field Dissipation - Terrestrial

Chlorpyrifos dissipated with a half-life of 1-5 days in the upper 1 inch of sand soil beneath the tree canopy and in exposed row areas in an orange grove located in Highlands County, Florida, which had been treated with chlorpyrifos (Lorsban 4E, 4 lb/gal EC) at 1 lb ai/A on November 6, 1985. Following a second and third application of chlorpyrifos at 1 lb ai/A on November 20 and December 17, 1985, the dissipation half-lives of chlorpyrifos were 14-27 and 4-13 days, respectively. The registrant-calculated half-lives were 1.3-4, 7.3-<27, and 1.4-<32 days following the first, second, and third applications, respectively. In the 0- to 1-inch layer of soil, the maximum average concentrations of chlorpyrifos were 1.76-2.57 ppm (days 1-4 after the second treatment); chlorpyrifos declined to <0.1 ppm (detection limit) by day 27 following the second treatment and by day 32 following the third treatment. In the 0- to 6-inch soil layer, chlorpyrifos ranged from <0.1 to 0.19 ppm (average concentration) and was not detected at lower soil depths (up to 60 inches). In the 0- to 1-inch soil layer, the degradate . . .

3,5,6-trichloro-2-pyridinol

...reached maximum concentrations of 0.96-1.33 ppm on days 0-1 following the third treatment and declined to <0.05 ppm (detection limit) by day 295. In the 0- to 6- and 6- to 18-inch soil depths, 3,5,6-trichloro-2-pyridinol concentrations were ≤0.1 ppm and were not detected at lower soil depths. Except for one soil sample (0- to 1-inch depth, 5 days after first treatment, 0.12 ppm), concentrations of the degradate . . .

2-methoxy-3,5,6-trichloropyridine

...were ≤0.05 ppm in the 0- to 1-, 0- to 6-, and 6- to 18-inch soil depths and were not detected (<0.01 ppm) at lower soil depths.

Ancillary Study - Well Water Monitoring

Chlorpyrifos and its degradates . . .

3,5,6-trichloro-2-pyridinol and

2-methoxy-3,5,6-trichloropyridine

...were not detected (detection limits 250 ppt, 0.05 ppm, and 0.01 ppm, respectively) at any sampling interval (up to 295 days after third application) in the water from two wells located in an orange grove in Highlands County, Florida, that received three applications of chlorpyrifos (Lorsban 4E, 4 lb/gal EC) at 1 lb ai/A in November and December 1985; the soil type was a sand.

2

DISCUSSION:

General

1. The length of time samples were stored frozen prior to analysis was not reported and storage stability data were not provided.

2. During the study, rainfall plus irrigation totaled 62.5 inches and air temperatures ranged from 3 to 29.3°C. Soil temperatures (0- to 1-inch depth) beneath the tree canopy and in exposed row areas ranged from 7.8 to 28.9 and 8.0 to 30.6°C, respectively.

3. The depth to the water table was 29-35 feet.

Field Dissipation - Terrestrial

1. It was not described how soil samples were treated prior to analysis (such as thawing, sieving, and homogenizing techniques).

2. The registrant believes that soil samples taken immediately prior to and immediately after the second application were mislabeled making it appear that residue levels were higher before the second application rather than after.

3. In a related study designed to determine the dissipation rate of chlorpyrifos in the soil surface layer, 1-foot square pieces of cheese-cloth were placed beneath the tree canopy and covered with soil to a depth of 0.25 inch. Soil samples were taken at 0, 1, 5, and 14 days after the first application of chlorpyrifos and analyzed. Chlorpyrifos dissipated with a half-life of 5-14 days. Chlorpyrifos declined from 6.4 ppm (immediately posttreatment) to 1.4 ppm by day 14. 3,5,6-Trichloro-2-pyridinol concentrations increased to 0.23 ppm by day 14 posttreatment and 2-methoxy-3,5,6-trichloropyridine declined from 0.24 ppm (day 1 posttreatment) to <0.01 ppm by day 14.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Field Dissipation - Terrestrial

Chlorpyrifos (Lorsban 4E, 4 lb/gal EC, Dow Chemical USA) was applied by boom sprayer three times at 1 lb ai/A to three plots in a commercial orange grove located in Highlands County, Florida, between November 6 and December 17, 1985. Each plot contained nine orange trees within a single row or adjacent rows (Figure 2, actual area not provided); the slopes of the plots were 0-2%, 0-3%, and ≈5%. The soil was a sand (upper 6 inches; 97-98% sand, 1-2% silt, 1% clay, 0.16-0.37% organic matter, pH 6.4-7.0, CEC 1.0-2.2 meq/100 g). The plots were also treated with dolomite (1200 lb/A) and 18-6-18 fertilizer (500 lb/A) in January 1986 and Temik 15 G (5 lb ai/A) and Ridomil 2E (0.6 lb ai/A) in March 1986. Soil samples were taken beneath the tree canopy and between the trees ("exposed" row area) immediately prior to each treatment and at intervals between 0 and 14 days following the first application, 0 and 27 days following the second application, and 0 and 295 days following the third application. Shallow soil samples (0- to 1-inch depth) were taken with a metal surface scraper (1-inch deep x 4-inches wide x 4-inches long), and all other soil samples (up to 60-inches deep) were taken with a hand auger equipped with a sand head. Soil samples were stored frozen until analysis.

For the determination of chlorpyrifos, soil samples were analyzed using Dow Chemical Method ACR 77.7. Each sample was extracted with acetone, and the extract was analyzed by GC with flame-photometric detection. For the determination of the degradate 3,5,6-trichloro-2-pyridinol, soil samples were analyzed using Dow Chemical Method ACR 84.4. Soil samples were heated at 130°C in methanolic sodium hydroxide for 30 minutes; this step yields total pyridinol as all "free" 3,5,6-trichloro-2-pyridinol and pyridinol resulting from the hydrolysis of chlorpyrifos is converted to the sodium salt. The extract was filtered, diluted, and the methanol was evaporated off. The sample was acidified (agent not described) and applied to a Sep-Pak C-18 column. The sample was eluted with methanol into benzene, then partitioned with sodium bicarbonate; the benzene phase was discarded. The sodium bicarbonate phase was acidified and partitioned with benzene. The benzene phase was derivatized with N,O-bis(trimethylsilyl)acetamide (BSA) to form the pyridinol trimethylsilyl derivative which was quantified by GC with electron-capture detection. Actual 3,5,6-trichloro-2-pyridinol was determined by the difference between the total pyridinol (as the pyridinol trimethylsilyl derivative) found and the pyridinol equivalents from chlorpyrifos found. For the determination of the degradate 2-methoxy-3,5,6-trichloropyridine, soil samples were analyzed using Dow Chemical Method ACR 86.4. Water was added to each soil sample which was then acidified (agent not described) and extracted with hexane. Hexane extracts were analyzed by GC with electron-capture detection. The detection limits for chlorpyrifos, 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine in soil were 0.1, 0.05, and 0.01 ppm, respectively. Recovery from fortified soil samples ranged

from 84 to 122% of the applied for chlorpyrifos, 60 to 122% for 3,5,6-trichloro-2-pyridinol, and 91 to 110% for 2-methoxy-3,5,6-trichloropyridine.

Ancillary Study - Well Water Monitoring

Two monitoring wells (2-inch diameter, 42- to 43-feet deep) were installed in the orange grove (Figure 2) prior to the first application of chlorpyrifos. Chlorpyrifos was applied as described above; however, an 8- to 10-foot diameter zone surrounding each well was not sprayed to prevent direct contamination. Each well contained a stainless steel pump (standard flow rate 1-1.25 gal/minute) with a Teflon bladder. The bottom intake of the pump was located 6-8 feet below the water table. Water samples were taken immediately prior to the first application of chlorpyrifos, 5 days after the first application, 4 and 14 days following the second application, and 4, 13, 32, 92, 211, and 295 days following the third application. Prior to sampling, each well was pumped to remove 2-4 well volumes of water. Water samples were stored frozen until analysis.

For the determination of chlorpyrifos, water samples were analyzed using Dow Chemical Method ACR 86.5. Each sample was applied to a Sep-Pak C-18 column. The sample was eluted with acetone into water, then partitioned with hexane. The hexane phase was analyzed by GC with flame photometric detection. For the determination of 3,5,6-trichloro-2-pyridinol, water samples were analyzed using Dow Chemical Method ACR 84.4 as described above for soil samples. For the determination of 2-methoxy-3,5,6-trichloropyridine, water samples were analyzed using Dow Chemical Method ACR 86.5. Each sample was extracted with hexane, and the extract was analyzed by GC with electron-capture detection. The detection limits for chlorpyrifos, 3,5,6-trichloro-2-pyridinol, and 2-methoxy-3,5,6-trichloropyridine in water were 250 ppt, 0.05 ppm, and 0.01 ppm, respectively. Recovery from fortified water samples ranged from 76 to 115% of the applied for chlorpyrifos, 110 to 122% for 3,5,6-trichloro-2-pyridinol, and 97 to 99% for 2-methoxy-3,5,6-trichlorpyridine.

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