9-16-94

DATA EVALUATION RECORD

STUDY 5

CHEM 059101 Chlorpyrifos §164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 42924801
Racke, K.D., and C.K. Robb. 1993b. Dissipation of chlorpyrifos in warm-season turfgrass and fallow soil in Florida. Laboratory Study ID: ENV90125. Unpublished study performed by Weed Systems, Inc., Melrose, FL (field operations); and DowElanco, Indianapolis, IN (laboratory analysis). Submitted by DowElanco, Indianapolis, IN.

STUDY ID 40356608
McKellar, R.L., and W.C. Brown. 1984. Determination of triclopyr and 3,5,6-trichloro-2-pyridinol in soil by gas chromatography. Study ID # ACR 84.2. Unpublished method submitted by DowElanco, Indianapolis, IN.

STUDY ID No MRID
Dixon-White, H.E. 1994. Determination of 3,5,6-trichloro-2-pyridinol in soil by gas chromatography/mass spectrometry. Study ID # GRM 92.12.R2. Unpublished method of DowElanco, Indianapolis, IN.

STUDY ID No MRID
Wetters, J.H. 1988. Determination of residues of 2-methoxy-3,5,6-trichloropyridine in soil by gas chromatography. Study ID # ACR 86.4. Unpublished method of DowElanco, Indianapolis, IN.

DIRECT REVIEW TIME = 30

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FROM 8-14-95 CHLORPYRIFOS REG - EFED CHAPTER

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study can be used towards the fulfillment of data requirements.

2. Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) dissipated with an initial (days 0-28) half-life of 6.5-11.4 days and a secondary (days 28-120) half-life of 23.8-38.3 days in the 0- to 15-cm depth of bareground and turf-covered plots of sand soil located in Florida that were treated once at 4 lb ai/A with chlorpyrifos (Dursban Turf Insecticide, 45.4% EC) in June 1991. Two degradates, 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxypyridine (TMP), were isolated from the treated soils at average maximum concentrations of 0.14 ug/g at 7 days posttreatment and 0.02 ug/g at 28 days posttreatment, respectively. Neither chlorpyrifos nor its degradates were detected (<0.01 ug/g) below a soil depth of 15 cm.

3. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the dissipation of the EC formulation of chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) from bareground and turf-covered plots of sand soil treated at 4 lb ai/A.

4. This study may be used to support the registration of the EC formulation of chlorpyrifos at a maximum application of 4 lb ai/A on turf. Information on the dissipation of the EC formulation of chlorpyrifos at 4 lb ai/A on bareground and turf-covered field plots at a second site (Indiana) is provided in Study 2 of this submission (MRID 42924802).

METHODOLOGY:

Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate; Dursban Turf Insecticide, 45.4% EC, DowElanco) was applied once at 4 lb ai/A to three bareground and three turf-covered plots (each 25 x 50 feet, 0.03 acres) of Millhopper sand soil (96.7% sand, 0% silt, 5.6% clay, 1.0-1.2% organic matter, pH 6.3-6.4, CEC 1.5-2.7 meq/100 g) located in Putnam County, Florida (Figure 2). The broadcast applications were made on June 18, 1991, using a tractor-mounted boom sprayer; in the vegetated plots at the time of treatment, the height of the St. Augustinegrass was 3-4 inches, and the thickness of the thatch layer was 0.75 inches. Untreated bareground and turf-covered plots (each 25 x 25 feet, 0.01 acres) located 70 feet upslope from the treated plots were maintained as controls. During the study, all plots were sprinkler-irrigated to maintain >100% of the normal monthly rainfall, and the turfgrass plots were mowed, fertilized, and irrigated according to "typical turf maintenance practices." Five soil cores were randomly collected from each treated plot 1 day prior to and immediately after treatment, and at 7, 14, 28, 57, 120, 239, and 360 days posttreatment. Five soil cores were collected from each untreated plot prior to treatment of the test plots, and at 120 and 360 days.

At the time of sampling, the turf, thatch, and upper 15 cm of soil were collected using a probe (2.25-inch id) equipped with an acetate liner. The soil core was removed intact with the liner, then immediately capped and placed in a cooler, and the stainless steel core sleeve was left in the ground. At the 7- through 360-day posttreatment sampling intervals, a second probe (1.5-inch id) equipped with an acetate liner was inserted through the sample hole to a depth of 90 cm using an electric hammer. The soil core was removed intact with the liner, capped, and placed in a cooler; the resulting hole was filled with untreated soil and marked to prevent resampling. The soil samples were frozen within 4 hours of collection, and shipped on dry ice to the analytical laboratory. Samples were stored frozen for <4 months prior to analysis for chlorpyrifos, and for <26 months for 3,5,6-trichloro-2-pyridinol [pages 22-23].

At the analytical laboratory, the deeper soil cores were divided into 15- to 30-, 30- to 50-, 50- to 70-, and 70- to 90-cm segments. The soil core segments were ground with dry ice in a Wiley mill "to a uniform consistency"; samples containing turfgrass and thatch were ground so that the plant material was "uniformly mixed" with the soil. With the exception of the immediate posttreatment 0- to 15-cm soil segments, which were analyzed individually [pages 24-25], the soil segments were composited by plot, sampling interval, and soil depth; composited samples were stored frozen in glass jars until analysis (storage conditions not further described).

The soil was analyzed for chlorpyrifos, 3,5,6-trichloro-2-pyridinol (TCP), and 3,5,6-trichloro-2-methoxypyridine (TMP) using analytical methods ACR 91.5, GRM 92.12.R2, and ACR 86.4, respectively. The limit of quantification for all methods was 0.01 ug/g. To isolate chlorpyrifos, soil samples were extracted by shaking with acetone for 1 hour; the mixtures were then centrifuged, and the supernatants removed. Aliquots of the acetone extract were acidified and partitioned with hexane; the hexane solution was analyzed by capillary GC using flame-photometric detection in the phosphorus mode. Recovery efficiencies from soil samples fortified with chlorpyrifos at 0.01-4.0 ug/g ranged from 67-108% of the applied, and averaged 88 $\pm$ 10%. To isolate TCP, soil samples were initially extracted with acidified acetone (acetone:0.1 N HCl; 90:10, v:v) by sonicating for 15 minutes, followed by shaking for 2 hours; the mixtures were then centrifuged, and the supernatants removed. Aliquots of the acidified acetone extract were concentrated by evaporation to remove the acetone, mixed with an acidified aqueous saturated solution of NaCl, and filtered through a C-18 reverse-phase column. The sorbed TCP was eluted from the column with methanol; the methanol eluate was then diluted with acidified saturated NaCl solution, and the mixture was partitioned with toluene. Residues in the toluene solution were derivatized to TCP-TMS (TCP-trimethylsilyl) with N,O-bis(trimethylsilyl)acetamide [BSA], and the derivatized solutions were analyzed by GC/MS. Recovery efficiencies from soil samples fortified with TCP at 0.01-0.20 ug/g ranged from 60-124% of the applied, and averaged 98 $\pm$ 14%. To isolate TMP, soil samples were extracted by shaking with acidified hexane (hexane:7.3 M

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phosphoric acid:water; 40:1:10, v:v:v) for 1 hour. The mixtures were centrifuged, and the hexane layer was removed by pipette. Aliquots of the hexane extract were analyzed by GC with electron-capture detection. Recovery efficiencies from soil samples fortified with TMP at 0.01-0.10 ug/g ranged from 75-121% of the applied, and averaged 94 ± 12%.

DATA SUMMARY:

Chlorpyrifos (0,0-diethyl 0-3,5,6-trichloro-2-pyridyl phosphorothioate) dissipated with an initial (days 0-28) half-life of 6.5-11.4 days and a secondary (days 28-120) half-life of 23.8-38.3 days in the 0- to 15-cm depth of bareground and turf-covered plots of sand soil located in Florida that were treated once at 4 lb ai/A with chlorpyrifos (Dursban Turf Insecticide, 45.4% EC) in June 1991 (Tables XI and XII). Two degradates,

3,5,6-trichloro-2-pyridinol (TCP) and

3,5,6-trichloro-2-methoxypyridine (TMP),

were isolated from the treated soils at average maximum concentrations of 0.14 and 0.02 ug/g, respectively. Neither chlorpyrifos nor its degradates were detected (<0.01 ug/g) below a soil depth of 15 cm. Chlorpyrifos and its degradates were not detected in the control plots at any sampling interval.

In the upper 15 cm of the bareground plots, chlorpyrifos was 0.81-2.36 ug/g immediately posttreatment (average 1.67 ug/g), 0.33-0.69 ug/g at 7 and 14 days, 0.19-0.26 ug/g at 28 days, and ≤0.05 ug/g at 57 and 120 days (Table XII and Appendix K). TCP increased to a maximum average of 0.14 ug/g at 7 days posttreatment, and averaged 0.02 ug/g at 120 days; TMP was a maximum average of 0.02 ug/g at 28 days.

In the upper 15 cm of the vegetated plots, chlorpyrifos was 1.21-3.61 ug/g immediately posttreatment (average 2.46 ug/g), 0.58-0.72 ug/g at 7 days, 0.10-0.11 ug/g at 28 days, and ≤0.03 ug/g at 57 and 120 days (Table XI and Appendix H). TCP increased to a maximum average of 0.10 ug/g at 7 and 14 days posttreatment, and averaged ≤0.01 ug/g at 57 and 120 days; TMP averaged <0.01 ug/g at all sampling intervals. In the vegetated plots at the time of treatment, the height of the St. Augustinegrass was 3-4 inches, and the thickness of the thatch layer was 0.75 inches.

Between June and October 1991, average monthly air temperatures ranged from 20.7-26.1°C; average monthly soil temperatures ranged from 23.7-29.5, 24.0-29.4, and 24.7-28.7°C at the 1-, 4-, and 20-inch depths, respectively. The test plots received 0.4 inches of rain at 2 days posttreatment, and were irrigated with 0.5 inches of water at 4 and 6 days posttreatment; rainfall plus irrigation totaled 39.15 inches between June and October 1991, which was equivalent to 132.1% of the 30-year average rainfall. The slope of the test plots was

1-2%, and the depth to the water table was a minimum of 5 feet and an average of 15 feet [page 15].

COMMENTS:

1. Between 0 and 7 days posttreatment (first and second samplings), 73-76% of the chlorpyrifos applied to the bareground and turf-covered plots had degraded. The half-lives calculated by the study author using the data for 0 through 28 days posttreatment (6.3-6.8 days in the turf-covered plots and 10.2-12.4 days in the bareground plots) reflect the biphasic nature of the degradation of chlorpyrifos; the rate of chlorpyrifos degradation between later sampling intervals slowed considerably. Although in order to accurately establish the half-life of the test substance, it is preferred that the soil be sampled frequently enough that <50% of the applied residues dissipate between any two sampling intervals, the information on the pattern of dissipation of chlorpyrifos and the formation and decline of its degradates provided by this field study is adequate at this time.

2. Immediately posttreatment, the concentrations of chlorpyrifos in the treated bareground and turf-covered plots averaged 73.3 and 68.0%, respectively, of the nominal application rate of 4 lb ai/A (Table X). Analysis of samples of the tank mix used to make the application yielded an actual chlorpyrifos concentration of 0.48%; the theoretical concentration was calculated to be 0.44%.

3. The soil was analyzed only for chlorpyrifos, TCP, and TMP. In previously reviewed aerobic soil metabolism studies (MRIDs 00154723, 00155636, 00155637, 00025619, 40050401, and 42144911), TCP was the only significant nonvolatile degradate of chlorpyrifos. On infrequent occasions, minor amounts of TMP were isolated from the soils during incubation.

4. The study authors stated in the report that chlorpyrifos, TCP, and TMP were stable during frozen storage and presented data to this effect (Table IX). The chlorpyrifos and TMP storage stability data are reviewed in this report (Studies RES91031 and RES91032, respectively; Study 3) and show that chlorpyrifos and TMP are stable during frozen storage in glass jars. However, the information on TCP was derived from a summary report (Gardner and Schotts, 1993: Frozen storage stability of triclopyr, 3,5,6-trichloro-2-pyridinol, and 3,5,6-trichloro-2-methoxypyridine [MRID 42630101]) which included information from only one soil. No details about the storage conditions, such as type of sample container, temperature of the freezer, and the moisture content of the soil were provided.

5. The sand, silt, and clay fractions sum to 102.3%, rather than 100%, in the 10- to 15-cm soil layer. The mineral fractions of all deeper segments also summed to >100%. Insufficient raw data were provided with the study to establish the cause of this error.

6. To determine the stability of chlorpyrifos and its degradates during shipping and handling, separate soil samples from the control plots

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were treated in the analytical laboratory with chlorpyrifos at 1.0 ug/g, TCP at 1.0 ug/g, or TMP at 0.1 ug/g. Fortified samples were analyzed for initial concentration of chlorpyrifos and TMP using the methods previously described; samples fortified with TCP were analyzed using method ACR 84.2 (described below). Portions were either stored frozen or shipped to the field site; shipped samples were then reshipped to the analytical laboratory under the same conditions expected for the test samples and analyzed within one day of return shipment receipt. Recoveries from the samples that were not shipped were 98% of the applied for chlorpyrifos, 102% for TCP, and 80% for TMP; recoveries of the samples that were shipped were 95-97% for chlorpyrifos, 100-108% for TCP, and 78-80% for TMP.

7. The analytical method used to determine the concentration of TCP in the shipped stability study was different from that used for the field samples. Using method ACR 84.2 (MRID 40356608), TCP was extracted from the soil by heating with methanolic sodium hydroxide (methanol:10% sodium hydroxide; 8:1, v:v). Aliquots of the extracts were diluted with acidified aqueous saturated NaCl solution and then extracted by shaking with toluene. (Note: Document describing method ACR 84.2 states that organic phase was benzene). The toluene phase was removed and extracted by shaking with 0.25 M sodium bicarbonate for 5 minutes; after centrifugation, the toluene phase was discarded. The aqueous phase was acidified with a small amount of concentrated HCl and filtered through a C-18 Sep-Pak cartridge. The sorbed TCP was eluted from the cartridge with methanol; the methanol eluate was then diluted with acidified water and the mixture was partitioned with toluene. Residues in the toluene phase were derivatized to TCP-TMS (TCP-trimethylsilyl) with N,O-bis(trimethylsilyl)acetamide [BSA], and the derivatized solutions were analyzed by capillary GC with electron capture detection. Reported recovery efficiencies during method validation from soil samples fortified with TCP at 0.05-1.0 ug/g ranged from 76-116% of the applied, and averaged 94 $\pm$ 7%.

8. The analytical method for chlorpyrifos (ACR 91.5) had been previously reviewed by EFGWB (review of MRID 42874702 dated 8/30/93; attached); copies of the analytical methods for TCP (GRM 92.12.R2) and TMP (ACR 86.4) are included in this report as Appendix A and B, respectively.

9. Soil samples collected at 239 and 360 days posttreatment were not analyzed because chlorpyrifos residues had reached <0.01 ug/g in the turf-covered plots and $\leq$0.03 ug/g (2% of the applied) in the bareground plots by 120 days [pages 25-26].

10. The test plots had not been cropped or treated with pesticides during the 3 years prior to treatment with chlorpyrifos. The plots were covered with bahiagrass and weeds prior to preparation of the site for planting and treatment.

MRID# 42924801

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