

DATA EVALUATION RECORD

STUDY 5

CHEM 128997 Tebuconazole §164-1

CAS No. 107534-96-3

FORMULATION-06-WETTABLE POWDER

STUDY ID 44108313

McKelvey, S. B., G. C. Mattern, C. V. Lam, D. L. Green, and B. A. Dehart. 1996. Terrestrial field dissipation of tebuconazole (ELITE) on Fresno, California soil, 1992. Bayer Study No.: FR022110. Bayer Report No.: 106956. Unpublished study performed by Bayer Research Farm, Fresno, California (in-life phase); Bayer Environmental Fate Analytical Laboratories, Stilwell, KS (processing and compositing); and QC, Inc., Southampton, PA and Writers, Inc., Wilmington, DE (analytical phase); and submitted by Bayer Corporation, Kansas City, MO.

DIRECT REVIEW TIME =

REVIEWED BY: Andrew Glucksman

SIGNATURE:

TITLE: Staff Scientist

DATE:

EDITED BY: Dan Hunt

SIGNATURE:

TITLE: Staff Scientist

DATE:

EDITED BY: Kathleen Ferguson

SIGNATURE:

TITLE: Senior Staff Scientist

DATE:

ORG: Dynamac Corporation
Rockville, MD

TEL: 301-417-9800

APPROVED BY: Amer Al-Mudallal

TITLE: Chemist

ORG: ERB 1/EFED/OPP

TEL: 703-605-0566

SIGNATURE:


 3/13/2000
ABSTRACT

Tebuconazole (ELITE 45 DF), broadcast applied eight times (7-day intervals) at a nominal application rate of 0.113-0.206 lb a.i./A/application (total application rate of 1.28 lb a.i./A) onto a plot of sandy loam soil (planted with grape seedlings) near Fresno, CA, dissipated with a registrant-calculated half-life of 177 days ($r^2 = 0.86$) following the eighth application. However, greater than 50% of the parent dissipated prior to 1 day posttreatment. The parent was present in the 0- to 6-inch depth at 0.05, 0.12, 0.19, 0.22,



0.25, 0.31, and 0.39 $\mu\text{g/g}$ immediately following each of the seven applications, respectively, and was not detected above 0.02 $\mu\text{g/g}$ in any replicate below the 0- to 6-inch depth. Following the eighth application, the parent was initially (time 0) present in the 0- to 6-inch depth at 0.34-1.64 $\mu\text{g/g}$ (mean 0.83 $\mu\text{g/g}$), was 0.31-0.43 $\mu\text{g/g}$ from 1 to 28 days posttreatment, was 0.23 $\mu\text{g/g}$ at 91 days, was 0.10-0.14 $\mu\text{g/g}$ from 182 to 273 days, and was 0.04-0.07 $\mu\text{g/g}$ from 365 to 548 days. The parent not detected in the 6- to 12-inch depth above 0.04 $\mu\text{g/g}$ (single replicate), was not detected above 0.06 $\mu\text{g/g}$ (single replicate) in the 12- to 24-inch depth, and was not detected below that depth. No degradates were identified from the soil. Grape seedlings were not analyzed for the parent or degradates.

MATERIALS AND METHODS

Tebuconazole { α -[2-(4-chlorophenyl)ethyl]- α -(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol; ELITE 45 DF, 45.9% a.i.; p. 18; Figure 1, p. 87} was broadcast applied eight times (7-day intervals; June 15-August 3, 1992) at nominal application rates of 0.113-0.206 lb a.i./A/application (total application rate of 1.28 lb a.i./A) onto a plot (75 x 173.3 ft divided into five equal subplots; slope 2%; Figures 3, 4, pp. 89, 90) of sandy loam soil (53.2% sand, 37.6% silt, 9.2% clay, 0.27% organic matter, pH 7.8, CEC 4.5 meq/100 g; Table 3, p. 39) near Fresno, CA; grape seedlings were planted on May 23, 1992. Applications were made using a tractor-mounted boom sprayer with twelve Tee Jet 8003 flat-fan nozzles and a delivery height of 18 inches. A control plot (dimensions not specified) was located 15-100 feet from the test plot. Round-Up[®] (glyphosate, 1% solution) was applied to selected areas of the plot on August 26 and September 22, 1992 (Table 4, pp. 40-41). A three-year plot history indicated use of Dual 8[®] (metolachlor), Treflan 5 (trifluralin), FOE 5043 60 WP, and Cotoran 4 (fluometuron; Table 2, p. 38). The depth to the water table was approximately 75 feet. Environmental data were collected off-site; however, precipitation data were collected on-site (p. 20). Precipitation was supplemented with irrigation (above-ground sprinkler); total water input (76.72 inches) was 472% of the 10-year mean annual precipitation (Tables 5-7, pp. 42-66). Pan evaporation data were not reported.

The application rate was confirmed using six application pads placed in each subplot immediately prior to each application (p. 19). Immediately following each application, the pads were composited by subplot and extracted by shaking with acetonitrile. Samples were shipped frozen to the analytical laboratory and analyzed by HPLC (Microsorb C18 column) using an isocratic mobile phase of acetonitrile:water (4:1, v:v) and equipped with a UV (220 nm) detector (p. 26). Mean recoveries of the parent from the application monitoring pads were 60-87% of the expected (p. 30). Mean recoveries of the parent from the soil (all depths) were 52-117% of the expected (p. 31).

Soil samples were collected 4 days prior to the first application, immediately each application, and at 1, 3, 5, 10, 14, 28, 56, 91, 182, 273, 365, 465, and 548 days posttreatment (relative to the eighth application; Table 4, pp. 40-41). At each sampling interval, three soil samples (2.38-inch diameter for samples collected following the first application; 1.68-inch diameter for all other samples) were randomly collected from each treated subplot (15 cores total; p. 17). Samples were collected using a Giddings sampler device equipped with an acetate liner. Soil cores were collected to a depth of 6 inches immediately following the first application, and to a minimum depth of 48 inches at all other sampling intervals. Samples were stored frozen at the field facility until being shipped frozen to the processing laboratory. At the processing laboratory, 1/8th inch of the outer soil cores was shaved and discarded; samples were sectioned into six inch increments and composited by depth. The composited samples were shipped frozen to the analytical laboratory. Samples were stored frozen for up to 365 days and 1057 days prior to analysis for tebuconazole and 1,2,4-triazole, respectively (p. 27). Grape seedlings were not incorporated into the soil or removed from the plot during the study period (p. 17).

Samples were analyzed for the parent compound. Soil samples were extracted by refluxing for four hours with methanol:water (7:3, v:v; p. 21); the samples were cooled and vacuum-filtered through Celite. The filtrate was concentrated by rotary evaporation and partitioned three times with methylene chloride. The organic phase was filtered through sodium sulfate, which was rinsed three times with methylene chloride. The organic phase was concentrated by rotary evaporation and evaporated to dryness under nitrogen. The residue was reconstituted with ethyl acetate and the solution was filtered (0.45 μm); aliquots were analyzed by capillary GC with nitrogen-phosphorous detection. The limit of detection was 0.01 $\mu\text{g/g}$ (p. 27). Instrument operating conditions were as follows:

Analytical Column: HP-1; 50 m x 0.32 mm

Injection Port: 250°C isothermal

Nitrogen-Phosphorous Detector: 300°C isothermal

Column Oven Temperature Program: 180°C for 1 minute, 180°C to 230°C at 10°C per minute, hold at 230°C for 20 minutes

Flow Rates: Carrier gas - 2 mL/minute helium; Combustion make-up gas - 26 mL/minute nitrogen, 4.5 mL/min hydrogen, and 170 mL/min air.

Soil samples were analyzed for the degradate 1,2,4-triazole (p. 22). Samples were extracted with 0.01 M potassium phosphate buffered-water (pH 7.0), centrifuged, and the supernatants were decanted through glass wool. The extracts were purified by passing through a column containing copper-activated Chelex 100. The extracts were derivatized with 2,4-dinitrofluorobenzene and partitioned into methylene chloride:water (ratio not specified). Organic phase extracts were concentrated, reconstituted in toluene, and passed through a glass column plugged with glass wool, packed with activated silicic

acid, and topped with anhydrous granular sodium sulfate. The extracts were evaporated to dryness, reconstituted in acetone:toluene (1:1, v:v), and analyzed by gas-liquid chromatography. The limit of detection was 0.01 $\mu\text{g/g}$ (p. 27). Column operating conditions were as follows:

Analytical Column: Restek Rtx-5; 30 m x 0.53 mm

Injection Port: 210°C isothermal

Detector: 300°C isothermal

Column Oven Temperature Program: 150°C for 5 minutes, 150°C to 230°C at 25°C per minute, hold at 230°C for 13 minutes

Flow Rates: Carrier gas - 4 mL/minute helium; Combustion make-up gas - 4.0 mL/min hydrogen and 175 mL/min air.

In a method validation study, soil samples collected from the control plot were fortified separately with tebuconazole and 1,2,4-triazole at 0.01, 0.02, and 0.05 ppm (p. 26). Mean recoveries of the parent were $99 \pm 28\%$ for the 0.01 ppm fortification (1 of 5 samples >120%), $98 \pm 18\%$ for the 0.02 ppm fortification, and $78 \pm 3\%$ for the 0.05 ppm fortification (p. 28; Appendix 1, pp. 154-156). Mean recoveries of 1,2,4-triazole were $86 \pm 10\%$ for the 0.01 ppm fortification, 83% for the 0.02 ppm fortification (single replicate), and 96% for the 0.05 ppm fortification (single replicate; p. 28).

To determine concurrent recoveries, soil samples were fortified separately with tebuconazole and 1,2,4-triazole at 0.05 and 0.1 $\mu\text{g/g}$ (p. 29). Mean recoveries of tebuconazole and 1,2,4-triazole (across both fortifications) were $100 \pm 11\%$ (range of 79 to 119%) and $90 \pm 16\%$ (range of 66 to 129%), respectively.

In a transit stability study of fortified field spikes, triplicate soil samples were fortified separately with tebuconazole and 1,2,4-triazole at 1.0 ppm at each sampling interval (p. 19). Samples were transported and stored (up to 397 days for tebuconazole and up to 654 days for 1,2,4-triazole; p. 27) in the same manner as the test samples. Data indicated that the parent was stable for up to 397 days; mean recoveries (across all sampling intervals) of the parent were 1.02-1.22 $\mu\text{g/g}$, with the exception of 0.75 $\mu\text{g/g}$ at time 0, 1.44 $\mu\text{g/g}$ at 273 days posttreatment, and 1.62 $\mu\text{g/g}$ at 365 days (Tables 9, 11, pp. 70, 72). Data indicated that the degradate 1,2,4-triazole was stable for up to 654 days; mean recoveries were 0.64-0.98 $\mu\text{g/g}$ with the exception of 1.7 $\mu\text{g/g}$ at 456 days posttreatment (Tables 10, 12, pp. 71, 73).

RESULTS/DISCUSSION

Tebuconazole (ELITE 45 DF), broadcast applied eight times (7-day intervals) at a nominal application rate of 0.113-0.206 lb a.i./A/application (total application rate of 1.28 lb a.i./A) onto a plot of sandy loam soil (planted with grape seedlings) near Fresno, CA, dissipated with a registrant-calculated half-life of 177 days ($r^2 = 0.86$; p. 32; Figure 66, p. 152) following the eight application. However, greater than 50% of the parent dissipated prior to 1 day posttreatment. The parent was present in the 0- to 6-inch depth at 0.05, 0.12, 0.19, 0.22, 0.25, 0.31, and 0.39 $\mu\text{g/g}$ immediately following each of the seven applications, respectively, and was not detected above 0.02 $\mu\text{g/g}$ in any replicate below the 0- to 6-inch depth (Tables 13, 14, pp. 74, 75). Following the eighth application, the parent was initially (time 0) present in the 0- to 6-inch depth at 0.34-1.64 $\mu\text{g/g}$ (mean 0.83 $\mu\text{g/g}$), was 0.31-0.43 $\mu\text{g/g}$ from 1 to 28 days posttreatment, was 0.23 $\mu\text{g/g}$ at 91 days, was 0.10-0.14 $\mu\text{g/g}$ from 182 to 273 days, and was 0.04-0.07 $\mu\text{g/g}$ from 365 to 548 days (Tables 15-17, pp. 76-78). The parent not detected in the 6- to 12-inch depth above 0.04 $\mu\text{g/g}$ (single replicate), was not detected above 0.06 $\mu\text{g/g}$ (single replicate) in the 12- to 24-inch depth, and was not detected below that depth. No degradates were identified from the soil (Tables 18-21, pp. 79-82). Grape seedlings were not analyzed for the parent or degradates.

DEFICIENCIES/DEVIATIONS

1. The pattern of formation and decline of the degradates was not addressed; however, samples were analyzed for 1,2,4-triazole. One of the primary purposes of a terrestrial field dissipation study is the determination of the pattern of formation and decline of major degradates of the parent. The reviewer did not have access to an aerobic soil metabolism study to determine if degradates were observed during aerobic soil metabolism.
2. Storage stability data for the degradate 1,2,4-triazole were inadequate. Test samples were stored frozen for 1047 days prior to analysis, and storage stability data were only reported through 654 days posttreatment (Tables 10, 12; pp. 71, 73).
2. Pan evaporation data were not reported. Such data are necessary to determine water balances and to assess whether sufficient moisture was present to facilitate leaching of the test substance.
3. Grape seedling samples were not analyzed for the parent or 1,2,4-triazole. It is necessary that total residues in the crop be monitored in order to accurately determine the routes of dissipation of the test compound. The study authors stated that no fruits were produced during the study period (p. 17).

4. The observed and registrant-calculated half-lives were not similar. Greater than 50% of the parent dissipated prior to 1 day posttreatment (Tables 15-17, pp. 76-78). However, the registrant-calculated half-life was 177 days ($r^2 = 0.86$; Figure 66, p. 152). The half-life may be of questionable validity because the study authors stated that it was determined by summing the residues from the 0- to 24-inch depth at each sampling interval (p. 32). The half-life should be based on the 0- to 6-inch depth, rather than the entire soil core. The reviewer noted that the parent was not observed to leach.
5. The study authors stated that the rate of applications (0.99 lb a.i./A/crop season) was 1.1 times the maximum label rate to ensure that adequate test substance was reaching the soil (p. 17). However, the reviewer noted that the total application rate (1.28 lb a.i./A) was 1.4 times the maximum label rate. The reported maximum label rate for ELITE 45 DF is 0.90 lb a.i./A/crop season. Clarification from the study authors may be required.
6. The formulation of the test compound was reported as "ELITE 45 DF." However, because no formulation code exists for the dry flowable formulation, the reviewer designated the material as a wettable powder (formulation code 06).
7. The reviewer could not determine whether subplots were true replicate plots (separated by buffer zones; Figure 4, p. 93).
8. The reviewer noted that additional terrestrial field dissipation studies were also submitted.

ATTACHMENT 1
Tables cited in DER

THE FOLLOWING ATTACHMENT IS NOT AVAILABLE ELECTRONICALLY
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ATTACHMENT 2
Excel Workbook

0-6 inch depth

Sampling interval (days)	Parent [ug/g]			Average [ug/g]	ln average
	Rep 1	Rep 2	Rep 3		
0	1.64	0.52	0.34	0.83	-0.18232
1	0.31	0.44	0.33	0.36	-1.02165
3	0.35	0.49	0.46	0.43	-0.83625
5	0.52	0.39	0.9	0.60	-0.50529
10	0.3	0.29	0.33	0.31	-1.18199
14	0.34	0.34	0.41	0.36	-1.01243
28	0.29	0.34	0.31	0.31	-1.16049
56	0.22	0.08	0.22	0.17	-1.75254
91	0.25	0.27	0.16	0.23	-1.48427
182	0.18	0.1	0.15	0.14	-1.94258
273	0.12	0.1	0.08	0.10	-2.30259
365	0.07	0.05	0.05	0.06	-2.87057
456	0.1	0.09	0.03	0.07	-2.61274
548	0.04	0.05	0.03	0.04	-3.2189

Half-life (days) = 154.0

