

DATA EVALUATION RECORD

STUDY 6

CHEM 128997 Tebuconazole §164-1

CAS No. 107534-96-3

FORMULATION-06-WETTABLE POWDER

STUDY ID 44108314

McKelvey, S. B., G. C. Mattern, and D. L. Green. 1996. Terrestrial field dissipation of tebuconazole (ELITE) on Watsonville, California soil, 1992. Bayer Study No.: FR022111. Bayer Report No.: 106957. Unpublished study performed by Plant Sciences, Inc., Watsonville, California (in-life phase); Bayer Environmental Fate Analytical Laboratories, Stilwell, KS (processing, compositing, and analytical phase); QC, Inc., Southampton, PA (analytical phase); and Writers, Inc., Wilmington, DE (report preparation); and submitted by Bayer Corporation, Kansas City, MO.

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ABSTRACT

Tebuconazole (ELITE 45 DF), broadcast applied eight times (6- to 8-day intervals) at a nominal application rate of 0.124 lb a.i./A/application (total application rate of 0.992 lb a.i./A) onto a plot of sandy loam soil (planted with grape seedlings) near Watsonville, CA, dissipated with a registrant-calculated half-life of 857 days ($r^2 = 0.49$). However, the half-life may be of questionable validity because it was determined beyond the scope of



the observed data. The parent compound was present in the 0- to 6-inch depth at 0.08-0.18 $\mu\text{g/g}$ immediately following each of the seven applications and was not detected above 0.07 $\mu\text{g/g}$ in any replicate below the 0- to 6-inch depth. Following the eighth application, the parent was present in the 0- to 6-inch depth at 0.27-0.31 $\mu\text{g/g}$ at 0-1 day posttreatment, was 0.17-0.28 $\mu\text{g/g}$ from 3 to 365 days posttreatment, and was 0.15-0.17 $\mu\text{g/g}$ from 461 to 554 days. The parent was $\leq 0.06 \mu\text{g/g}$ (single replicate) below the 6-inch depth. No degradates were identified from the soil. Grape seedlings or weeds 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. 92} was broadcast applied eight times (6- to 7-day intervals; June 30-August 18, 1992) at a nominal application rate of 0.124 lb a.i./A/application (total application rate of 0.992 lb a.i./A) onto a plot (43.3 x 262.5 ft divided into five equal subplots; slope $\leq 2\%$; Figure 4, p. 95) of sandy loam soil (71.2% sand, 17.2% silt, 11.6% clay, 1.16% organic matter, pH 6.0, CEC 11.56 meq/100 g; Table 3, p. 44) near Watsonville, CA; grape seedlings were planted on June 25, 1992. Applications were made using a tractor-mounted boom sprayer with eight Tee Jet 8003 flat-fan nozzles and a delivery height of 18 inches. A control plot (43.3 x 45 ft) was located approximately 35 feet from the test plot. Weeds were removed periodically by hand. A three-year plot history indicated that the parent or related compounds were not applied to the test plot (Table 2, pp. 42-43). The depth to the water table was >6 feet. Environmental data were collected off-site (p. 21); however, precipitation data were collected on-site. Precipitation was supplemented with irrigation (above-ground sprinkler); total water input (81.53 inches) was 238% of the 10-year mean annual precipitation (Tables 5-7, pp. 46-71). 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 (80:20, v:v) and equipped with a UV (220 nm) detector (p. 26). Mean recoveries of the parent from the application monitoring pads were 71-100% of the expected (p. 30). Mean recoveries of the parent from the soil (all depths) were 71-100% (mean 81%) of the expected (p. 31; Table 8, pp. 72-74).

Soil samples were collected prior (days not specified) to the first application, immediately following each application, and at 1, 3, 5, 10, 14, 28, 56, 92, 183, 274, 365, 461, and 554 days posttreatment (relative to the eighth application; Table 4, pp. 45-46). At each sampling interval, three soil samples (2.25-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. 20). 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 6-inch increments and composited by depth. The composited samples were shipped frozen to the analytical laboratory. Samples were stored frozen for up to 1274 and 1062 days prior to analysis for tebuconazole and 1,2,4-triazole, respectively (p. 28). Grape seedlings were not incorporated into the soil or removed from the plot during the study period; however, prunings were chipped, shredded, and applied to the plot on January 21, 1994 (p. 18).

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 evaporated, 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). Instrument 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 $86 \pm 32\%$ for the 0.01 ppm fortification (1 of 5 samples >120%), $95 \pm 9\%$ for the 0.02 ppm fortification, and $111 \pm 6\%$ for the 0.05 ppm fortification (p. 29; Appendix 1, pp. 159-161). Mean recoveries of 1,2,4-triazole were $86 \pm 6\%$ for the 0.01 ppm fortification, 94% for the 0.02 ppm fortification (single replicate), and 86% for the 0.05 ppm fortification (single replicate; p. 28).

To determine concurrent recoveries, soil samples were fortified separately with tebuconazole at 0.05 and 0.1 $\mu\text{g/g}$, and 1,2,4-triazole at 0.02 $\mu\text{g/g}$ (p. 29). Mean recoveries of tebuconazole and 1,2,4-triazole (across both fortifications) were $97.6 \pm 9.3\%$ (range of 78 to 112%) and $88.7 \pm 14.2\%$ (range of 64 to 114%), 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, with the exception of 461 and 554 days posttreatment (1,2,4-triazole only; p. 20). Samples were transported and stored (up to 350 days for tebuconazole and up to 951 days for 1,2,4-triazole; p. 28) in the same manner as the test samples. Data indicated that the parent was stable for up to 350 days; mean recoveries (across all sampling intervals) of the parent were 0.96-1.23 $\mu\text{g/g}$, with the exception of 1.46 $\mu\text{g/g}$ at 183 days posttreatment, 1.81 $\mu\text{g/g}$ at 247 days, and 3.10 $\mu\text{g/g}$ at 365 days (Tables 9, 11, pp. 75, 77). Data indicated that the degradate 1,2,4-triazole was not stable during transport and storage; mean recoveries were 0.85-3.46 $\mu\text{g/g}$ for samples stored for 168-743 days, 0.36-1.05 $\mu\text{g/g}$ for samples stored for 797-847 days, and 0.51-0.79 $\mu\text{g/g}$ for samples stored for 895-951 days posttreatment (Tables 10, 12, pp. 76, 78).

RESULTS/DISCUSSION

Tebuconazole (ELITE 45 DF), broadcast applied eight times (6- to 8-day intervals) at a nominal application rate of 0.124 lb a.i./A/application (total application rate of 0.992 lb a.i./A) onto a plot of sandy loam soil (planted with grape seedlings) near Watsonville, CA, dissipated with a registrant-calculated half-life of 857 days ($r^2 = 0.49$; p. 33; Figure 66, p. 152). However, the half-life may be of questionable validity because it was calculated beyond the scope of the observed data. The parent compound was present in the 0- to 6-inch depth at 0.08, 0.09, 0.07, 0.07, 0.14, 0.13, and 0.18 $\mu\text{g/g}$ immediately following each of the first seven applications, respectively, and was not detected above 0.07 $\mu\text{g/g}$ in any replicate below the 0- to 6-inch depth (Tables 13, 14, pp. 79-80). Following the eighth application, the parent was initially (time 0) present in the 0- to 6-inch depth at 0.27 $\mu\text{g/g}$, increased to 0.31 $\mu\text{g/g}$ by 1 day posttreatment, was 0.17-0.28 $\mu\text{g/g}$ from 3 to 365 days posttreatment, and was 0.15-0.17 $\mu\text{g/g}$ from 461 to 554 days (Tables 15-17, pp. 76-78). The parent was 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 42-inch depth. No degradates were identified from the soil (Tables 20-22, pp. 86-88). Grape seedlings or weeds 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. Mean recoveries from field fortified spikes (Tables 10, 12; pp. 76, 78) indicated that 1,2,4-triazole was not stable during frozen storage over the time period for which test samples were stored. Additionally, soil samples analyzed for the parent compound were stored frozen for up to 1274 days; however, storage stability data were only reported through 350 days.
3. 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.
4. Grape seedling samples and weeds 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. 18).

5. The registrant-calculated half-life was 857 days ($r^2 = 0.49$; Figure 66, p. 157). However, the half-life may be of questionable validity because it was determined beyond the scope of the observed data. Data which appear linear may become curvilinear over time. Additionally, the study authors stated that the half-life was determined by summing the residues from the 0- to 24-inch depth at each sampling interval (p. 33). 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.
6. 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. 18). The reported maximum label rate for ELITE 45 DF is 0.90 lb a.i./A/crop season.
7. 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).
8. The reviewer could not determine whether subplots were true replicate plots (separated by buffer zones; Figure 4, p. 95).
9. The soil series name was not reported.
10. 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

Parent [ug/g]			Average [ug/g]	ln average
Rep 1	Rep 2	Rep 3		
0.22	0.42	0.18	0.27	-1.29706
0.51	0.2	0.26	0.32	-1.12907
0.18	0.22	0.24	0.21	-1.54490
0.28	0.22	0.35	0.28	-1.26113
0.35	0.17	0.3	0.27	-1.29706
0.24	0.14	0.22	0.20	-1.60944
0.26	0.3	0.22	0.26	-1.34707
0.29	0.14	0.25	0.23	-1.48427
0.2	0.19	0.3	0.23	-1.46968
0.16	0.19	0.17	0.17	-1.75254
0.16	0.33	0.2	0.23	-1.46968
0.29	0.2	0.15	0.21	-1.54490
0.23	0.1	0.11	0.15	-1.91959
0.17	0.2	0.15	0.17	-1.7525

Half-life (days) = 866.4

