3-11-2002

Data Evaluation Report on the terrestrial field dissipation of Tetraconazole

PMRA Submission Number {} EPA MRID Number 44865404

Data Requirement: PMRA Data Code:
EPA DP Barcode: D266647
OECD Data Point:
EPA Guideline: 164-1

Test material: BPL 048

End Use Product name: Eminent 40EW **Concentration of a.i.:** 40 g/L
Formulation type: Emulsifiable Concentrate

Active ingredient:
Common name: Tetraconazole
Chemical name:
IUPAC: (RS)-2-(2,4-dichlorophenyl)-3-(1H-1,2,4-triazol-1-yl)propyl 1,1,2,2-tetrafluoroethyl ether
CAS name: 1-[2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)propyl]-1H-1,2,4-triazole
CAS No: 112281-77-3
Synonyms:
SMILES string:

Primary Reviewer: Allen Roberts
Dynamac Corporation
Signature: Allen Roberts
Date: 6/13/01

QC Reviewer: Joan Harlin
Dynamac Corporation
Signature: Joan L. Harlin
Date: 6/13/01

Secondary Reviewer: Iwona Maher
EPA
Date: 3/11/2002

Company Code:
Active Code:
Use Site Category:
EPA PC Code: 120603

CITATION: Zini, G. 1998. Analysis of tetraconazole residues in soil. Unpublished study performed by Isagro Ricerca, Novara, Italy, and sponsored by Isagro S.p.A., Segrate, Italy. Laboratory ID No. 2226. Study initiated January 14, 1998 and completed November 13, 1998.

EXECUTIVE SUMMARY:

Soil dissipation/accumulation of tetraconazole under field conditions was conducted in a bare plot at one site in Salerano sul Lambro, Italy. The experiment was carried out in accordance with the Subdivision N Guideline 164-1, and in compliance with the Italian GLP standard. Tetraconazole (Eminent 40EW; Emulsifiable Concentrate; 40 g a.i./L) was sprayed at 0.120 kg a.i./ha in one 20 X 3 m plot using single application. The proposed label rate was not provided. Rainfall was not supplemented with irrigation and the 30-year average rainfall was not reported.

The application rate was verified using application monitors. Ten petri dishes covered with filter paper were collected from the treated and control plot at day 0 and extracted with acetone. There was 89.8% recovery in the samples from these monitors based on the field application calculations. Field spiking was not performed.

Soil samples were taken at 5 hours and 7, 21, 56, 114, 161, 333, and 365 d post-application to a depth of 30 cm. The soil samples were sectioned into 0-10, 10-20, and 20-30 cm segments, extracted with a methyl alcohol:water mixture, followed by dichloromethane liquid/liquid partitioning, and analyzed for tetraconazole residues by GC using a flameless ionization detector, calibrated for nitrogen. Samples were not analyzed for degradates of tetraconazole. The LOD and LOQ for tetraconazole was 0.001 mg/kg and 0.007 mg/kg, respectively.

The measured zero-time concentration was 0.088 mg a.i./kg soil, which is 108% of the applied rate. Tetraconazole dissipated from 0.086-0.090 mg a.i./kg soil at Day 0 (0-10 cm depth) to 0.006 mg a.i./kg soil (both duplicates) by Day 365. Tetraconazole was not detected above the LOQ at depths below the 0-10 cm soil layer.

Under field conditions, tetraconazole had a non-linear half-life ($t_{1/2}$) of 41 d ($r^2 = 0.71$) and linear $t_{1/2}$ of 128 d ($r^2 = 0.86$). The initial tetraconazole dissipation was rapid in the first 7 days and after that progressed slowly. At the end of the 365-day period, the total carryover of residues of tetraconazole was 7% of the applied amount.

The major route of dissipation of tetraconazole under terrestrial field conditions at the site could not be determined.

RESULTS SYNOPSIS

Location/soil type: Salerano sul Lambro, Italy/sandy loam
DT50: 128 days (Lotus Notes Program, linear first order), 41 days (Sigma Plot Software)
Major transformation products detected: Not determined
Dissipation routes: Could not be determined

Study Acceptability: This study is scientifically valid and considered supplemental but not acceptable for the purpose of tetraconazole risk assessment because different liquid formulation of the product, soil type, climate, and site variables contributed to high uncertainty of the study

(2)

results. Additionally, the study does not satisfy the guideline requirement for a terrestrial field dissipation study (164-1) because soil samples were not analyzed for degradates of tetraconazole and a storage stability study (using either spiked field or spiked lab samples) was not conducted to determine the stability of the test compound during storage.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The study was conducted according to U.S. EPA Pesticide Assessment Guidelines Subdivision N, 164-1. Deviations from EPA Subdivision N 164-1 are:

Patterns of formation/decline of degradates of tetraconazole were not determined. Soil samples were not analyzed for degradates of tetraconazole. This does not affect the validity of the study.

Rainfall and pan evaporation data were not provided. This affects the study data interpretation.

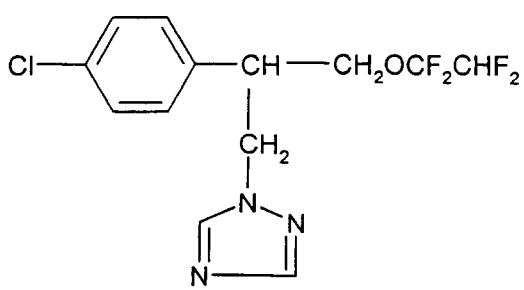
A storage stability study was not conducted using either spiked field or spiked lab samples. This does not affect the validity of the study.

COMPLIANCE: The study was conducted in compliance with the Italian Principles of Good Laboratory Practice. The GLP Compliance Statement was signed by the study director (November 1998) and sponsor (March 1999). Quality Assurance and Data Confidentiality Claims statements were also provided.

A. MATERIALS:

1. Test Material BPL 048

Chemical Structure of the active ingredient(s):



Description: Emulsifiable Concentrate (40 g/L)

Storage conditions of test chemicals: 4°C

Physico-chemical properties: Physico-chemical properties were not provided.

2. Test site: The test site was located in Salerano sul Lambro, Italy (Field phase report, pp. 8-9). The test plot had previously been treated with Glyphosate (Roundup).

Table 1: Geographic location, site description and climatic data at the study site.

Details		
Geographic coordinates	Latitude	Not provided
	Longitude	Not provided
	Province/State	Lombardia
	Country	Italy
	Ecoregion	N/A
Slope Gradient		0
Depth to ground water (m)		Not provided
Distance from weather station used for climatic measurements		Not provided
Indicate whether the meterological conditions before starting or during the study were within 30 year normal levels (Yes/No). If no, provide details.		30-year normal levels were not provided.
Other details, if any		N/A

Data from p. 11, Field phase report, pp. 8-9, 17; climatic data pp. 1-13.

Table 2: Site usage and management history for the previous three years.

Use	Year	
Crops grown	Previous year	Not provided
	2 years previous	Not provided
	3 years previous	Not provided
Pesticides used	Previous year	Glyphosate
	2 years previous	Glyphosate
	3 years previous	Glyphosate
Fertilizers used	Previous year	Not provided

Use	Year	
	2 years previous	Not provided
	3 years previous	Not provided
Cultivation methods, if provided (eg., Tillage)	Previous year	Not provided
	2 years previous	Not provided
	3 years previous	Not provided
Other details, if any	Previous year	Not provided
	2 years previous	Not provided
	3 years previous	Not provided

Data from Field phase report, pp. 8, 10

3. Soils:

Table 3: Properties of the soil

Property	Depth not reported
Textural classification	Sandy loam
% sand	62.2
% silt	28.4
% clay	9.4
pH (1:1 soil:water or other)	4.47
Total organic matter (%)	0.6%
CEC (meq/100 g)	Not provided
Bulk density (g/cm3)	Not provided
Moisture at 1/3 bar (%)	Not provided
Taxonomic classification (e.g., ferro-humic podzol)	Not provided
Soil mapping unit	Not provided
Others	N/A

Data from Field phase report, p. 11

B. EXPERIMENTAL DESIGN:

1. Experimental design:

Table 5: Experimental design.

Details		
Duration of study		365 days
Uncropped (bare) or cropped		Bare
Control used (Yes/No)		Yes
No. of replications	Controls	1
	Treatments	1
Plot size (L x W m)	Controls	20 x 3
	Treatments	20 x 3
Distance between control plot and treated plot		18 m
Distance between treated plots		N/A
Application rate(s) used (g a.i/ha)		120
Was the maximum label rate per ha used in study? (Yes/No)		Not reported
Number of applications		One
Application Date(s) (dd mm yyyy)		4/8/97
For multiple applications, application rate at Day 0 and at each application time (mg a.i./kg soil)		N/A
Application method (eg., spraying, broadcast etc.)		Spraying
Type of spray equipment, if used		PULVAL sprayer
Total volume of spray solution applied/plot **OR** total amount broadcasted/plot		500 l/ha
Identification and volume of carrier (e.g., water), if used		Water
Name and concentration of co-solvents, adjuvants and/or surfactants, if used		Not provided

Details		
Indicate whether the following monthly reports were submitted: Average minimum and maximum precipitation Average minimum and maximum air temperature Average minimum and maximum soil temperature Average annual frost-free periods		 No Yes No No
Indicate whether the Pan evaporation data were submitted		No
Meteorological conditions during application	Cloud cover	Not provided
	Temperature (°C)	Not provided
	Humidity	Not provided
	Sunlight (hr)	Not provided
Pesticides used during study: name of product/a.i concentration: amount applied: application method:		Glyphosate Not provided Not provided Not provided
Supplemental irrigation used (Yes/No) If yes, provide the following details: No. of irrigation: Interval between irrigation: Amount of water added each time: Method of irrigation:		No
Indicate whether water received through rainfall + irrigation equals the 30 year average rainfall (Yes/No)		Could not be determined
Were the application concentrations verified? (Briefly describe in Section 2*, if used)		Yes
Were field spikes used? (Briefly describe in Section 3¶, if used)		No
Good agricultural practices followed (Yes or No)		Not reported
Indicate if any abnormal climatic events occurred during the study (eg., drought, heavy rainfall, flooding, storm etc.)		None reported
Plant - Common name/variety: Details of planting: Crop maintenance (eg., fertilizers used):		N/A

Details	
Volatilization included in the study (Yes/No) (if included, describe in Section 4[§])	No
Leaching included in the study (Yes/No) (if included, describe in Section 5[§])	Yes
Run off included in the study (Yes/No) (if included, describe in Section 6[§])	No

Data from Table 3, pp. 28-29; Field phase report, pp. 8-10, 12-14; (climatic data, pp. 1-13).

2. Application Verification: Ten petri dishes (10 cm) covered with filter paper (9 cm) were obtained from the treated and control plot on day 0 (p. 18). The filters were cut into small pieces and extracted with acetone. The dishes were washed with acetone and the washings were combined with the extracts. After solvent evaporation, the residues were redissolved in dichloromethane and the solvent extract was dried by filtering through anhydrous Na_2SO_4. After purification, the residues were redissolved in ethyl acetate and analyzed by GC using a nitrogen-phosphorus detector set for nitrogen.

3. Field Spiking: Not performed

4. Volatilization: Not studied

5. Leaching: Sampled cores were taken from the treated plot at 0, (5-hours), 7, 21, 56, 114, 161, 333, and 365 days after the application to a depth of 30 cm to determine soil residue mobility of the test substance through the soil profile (p. 18, Tables 3-4, pp. 28-31).

6. Run off: Not studied

7. Supplementary Study: A storage stability study was not conducted for this study.

8. Sampling:

Table 6: Soil sampling.

Details	
Method of sampling (random or systematic)	Not provided
Sampling intervals	0 (5-hours), 7, 21, 56, 114, 161, 333, and 365 days posttreatment
Method of soil collection (eg., cores)	Cores
Sampling depth	30-cm
Number of cores collected per plot	Not provided
Number of segments per core	1

Details	
Length of soil segments	30-cm
Core diameter	5-cm
Method of sample processing, if any	The 0-30 cm core segments were sectioned into 0-10 cm, 10-20 cm, and 20-30 cm segments and the 0-10 cm and 10-20 cm segments were homogeneously mixed and sieved through a 2-mm diameter hole stainless steel sieve.
Storage conditions	Frozen in the dark
Storage length (days)	Up to 7 months

Data from p. 18, Tables 3-5, pp. 28-33.

9. Analytical Procedures: Soil samples were analyzed only for residues of tetraconazole (p. 12-16). Soil samples were extracted three times by shaking for 30 minutes with methyl alcohol:water mixture (9:1, v:v), followed by dichloromethane liquid/liquid partitioning. The final extracts were purified by column chromatography on alumina. Tetraconazole was analyzed by GC using a flameless ionization detector, calibrated for nitrogen. The limit of qualitative detection (LDC) and the limit of qualitative determination (LDM) for tetraconazole was 0.001 mg/kg and 0.007 mg/kg, respectively (p. 21).

II. RESULTS AND DISCUSSION

1. APPLICATION MONITORS: The recovery in the field application petri dishes at the treated plot was 89.8% of the nominal value (Table 3, p. 29).

2. RECOVERY FROM FIELD SPIKES: N/A

3. MASS ACCOUNTING: N/A

Table 7. Concentration of tetraconazole residues expressed as mg/kg

Compound	Soil depth (cm)	Sampling times (days)							
		5 hrs	7	21	56	114	161	333	365
Tetraconazole	0-10	0.090	0.043	0.032	0.025	0.020	0.019	0.009	0.006
	0-10	0.086	0.040	0.031	0.023	0.019	0.019	0.009	0.006
	10-20	<0.007	ND	ND	ND	ND	ND	ND	ND
	10-20	<0.007	ND	ND	ND	ND	ND	ND	ND

Data from Tables 3-4, pp. 28-31.

4. PARENT COMPOUND: The measured zero-time concentration was 0.088 mg a.i./kg soil, which is 108% of the applied rate (p. 22). Tetraconazole residues decreased from a maximum of

0.086-0.090 mg a.i./kg soil at Day 0 to 0.040-0.043 mg a.i./kg soil by 7 days, ranged from 0.019-0.025 mg a.i./kg soil from 56-161 days, and was 0.006 mg a.i./kg soil at 365 days posttreatment in the 0-10 cm soil layer (Table 3, pp. 28-29). The concentration of tetraconazole below the 10-cm depth was negligible at all sampling times (Table 4, pp. 30-31).

The 50% dissipation time (DT50) of tetraconazole in soil under terrestrial field conditions using the PC evaluation program (version 2.3) and the Sigma Plot® Scientific graphing software (version 4; pp. 19, 23; Figures 3-4, pp. 60-61) were:

BBA Program:	DT50 = 10 days	DT90 = 286 days
Sigma Plot:	DT50 = 5 days	DT90 = 320 days

The dissipation pattern of tetraconazole at the Italian field site was biphasic. Dissipation was most rapid during the initial 7 days of the study.

5. TRANSFORMATION PRODUCTS: Samples were not analyzed for transformation products of tetraconazole.

6. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES: N/A

Table 13: Dissipation routes of tetraconazole under field conditions.

Route of dissipation	% of applied amount (at the end of study period)
Accumulation (residues) in soil/ carry over	7%
Transformation (% of transformation products)	Samples were not analyzed for transformation products of tetraconazole
Leaching, if measured	The test compound did not leach below the 10-cm soil layer
Volatilization, if measured	Volatilization was not measured
Plant uptake, if measured	Plant uptake was not measured
Run off, if measured	Run off was not measured
Total	

7. VOLATILIZATION: Volatilization was not measured.

8. PLANT UPTAKE: Plant uptake was not measured.

9. LEACHING: Tetraconazole was not detected below the 10-cm soil layer (p. 22).

10. RUN OFF: Run off was not measured.

11. RESIDUE CARRYOVER: The DT90 value was 286 days (BBA Program) and 320 days (Sigma Plot Software). After 365 days, 7% of the applied parent compound were detected at the

field site, and has the potential to carryover into the following season. Samples were not analyzed for transformation products of tetraconazole.

12. SUPPLEMENTARY STUDY RESULTS: The registrant conducted seven other terrestrial field dissipation studies out of which two were conducted on the bare ground plots in GA and CA (MRID 44865405) and three were conducted on the bareground plots of loamy sand (Bad Oldesloe/ Pölitz), silty sand (Klein-Offenseth), strongly loamy sand (Hamburg-Moorfleet), and loamy silt (Uslar/Verliehausen) soils in Germany (MRID 44865406). Tetraconazole linear half-lives for loamy sand soil in Sunsweet, GA and sandy loam soil in Tulare County, CA were 91 ($r^2 = 0.62$; nonlinear $t_{1/2} = 90$ weeks and $r^2 = 0.59$) and 222 ($r^2 = 0.18$; nonlinear $t_{1/2} = 198$ weeks and $r^2 = 0.22$) weeks, respectively. At three of the German sites tetraconazole initially dissipated rapidly (Bad Oldesloe/ Pölitz, Klein-Offenseth, and Hamburg-Moorfleet, see Attachment) with initial half-lives of 18.6 days (0-27 days) and 31.8 days (0-29 days) in loamy sand soil and strongly loamy sand soil, respectively. The first order overall linear half-lives in all the German sites ranged from 182 to 800 days (an extrapolated value).

The domestic field dissipation data indicate that tetraconazole is persistant and will accumulate in the soil environment under field conditions. Although the German field dissipation study initially showed rapid tetraconazole dissipation in the first 8 to 30 days, after that it persisted in the soil unchanged indicating seasonal caryover of at least 30 to 40 µg/kg of tetraconazole. The U.S., German, and Italian studies were conducted on different tetraconazole liquid formulations (the Italian study: Eminent 40EW (40 g a.i./L); German study: M 14360 10 EC (10.86% a.i.); the U.S. study: Eminent 125 SL (124.4 g ai/L)).

III. STUDY DEFICIENCIES: The objective of this study was to establish dissipation rates of tetraconazole in soil under field conditions for the registration of tetraconazole as required by the United States Environmental Protection Agency. In this study European liquid formulation (Eminent 40EW) was tested instead of a formulation being registered for uses in the U.S. (Eminent 125 SL (124.4 g ai/L)). Additionally, the soil was analyzed only for tetraconazole; there was no attempt to identify transformation products. None of the study deficiencies are of sufficient concern to cause the study to be judged scientifically invalid. Additionally, a storage stability study (using either spiked field or spiked lab samples) was not conducted to determine the stability of the test compound during storage.

IV. REVIEWER'S COMMENTS:

1. Although the study is scientifically valid and considered supplemental, it may not be accepted for the purpose of tetraconazole risk assessment as a part of Eminent 125SL registration process because different liquid formulation of the product (Eminent 125 SL (124.4 g ai/L) versus Eminent 40EW (40 g a.i./L)), different soil types, different climate, and site variables contributed to high uncertainty of the studies' results.

2. The registrant-calculated DT50 values for tetraconazole are 5 days and 10 days. The EFED-calculated non-linear half-life ($t_{1/2}$) is 41 days ($r^2 = 0.71$) and the linear half-life is 128 days ($r^2 = 0.86$). The initial tetraconazole dissipation was rapid in the first 7 days and after that progressed slowly. No residues were detected below 10 cm depth. The rate of dissipation of tetraconazole may be affected by different liquid formulation of the product (Eminent 40EW - European formulation versus Eminent 125SL - formulation for US registration). The study meterological and field data were not sufficient to determine if other variables could influence the dissipation rate.

3. The maximum proposed application rate of the test substance was not reported in this study. The use of exaggerated dose rates may affect the degradation rate of the test chemical.

4. 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.

5. The soil texture was reported as a sandy loam in the field phase report and as a loamy sandy in the text of the study. The reviewer was unable to determine the textural classification based on the USDA classification system because the particle sizes used to determine the sand, silt, and clay fractions were not reported.

6. The treated plot was not replicated. The test plot consisted of a single 3 x 20 m plot.

7. The depth of the water table was not reported.

V. REFERENCES: No references were cited.

13