UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D. C. 20460

OFFICE OF PREVENTION. PESTICIDES AND TOXIC **SUBSTANCES**

PC Code:

122101

DPBarcode: D301776

January 27, 2005

MEMORANDUM

SUBJECT:

Data Evaluation Report (DER) of

Terrestrial field dissipation of propiconazole (Banner MAXX) applied to turf and

bare ground in California (MRID: 45528701);

Propiconazole (Banner MAXX): Final report addendum. Terrestrial field dissipation of propiconazole (Banner MAXX) applied to turf and bare ground in California

(MRID: 45528702);

Terrestrial field dissipation of Tilt® on bare soil in California (MRID: 45528703); and Foliar washoff and field runoff monitoring of Tilt® fungicide applied to celery in

rolabel a 1/27/2005

California (MRID: 45528704)

FROM:

James Lin, Environmental Engineer

Environmental Risk Branch I

Environmental Fate and Effects Division (7507C)

THRU:

Sid Abel, Branch Chief

Environmental Risk Branch I

Environmental Fate and Effects Division (7507C)

TO:

Lisa Jones

Reregistration Division (7505C)

This memo provides the notification of the availability of the subject reviews. The two guideline field dissipation studies (164-1) are classified acceptable. The non-guideline study of foliar washoff and field runoff for celery plots does provide some useful information in quantifying the foliar washoff model parameter for EFED's PRZM (Pesticide Root Zone Model).

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Data Requirement:

PMRA Data Code:

EPA DP Barcode: NA OECD Data Point: EPA Guideline: 164-1

Test material: CGA-64250

End Use Product name: Banner Maxx

Concentration of a.i.: 14.3%

Formulation type: Microencapsulated (MEC)

Active ingredient

Common name: Propiconazole.

Chemical name

IUPAC:

cis-trans-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-

1,2,4-triazole.

CAS name:

1-[[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-

triazole.

CAS No:

60207-90-1. CGA-64250.

Synonyms: SMILES string:

Clc1cc(ccc1C1(Cn2cncn2)OC(CO1)CCC)Cl.

Primary Reviewer: Dan Hunt

Dynamac Corporation

Signature:

Date:

QC Reviewer: Joan Harlin

Dynamac Corporation

Signature:

Date:

Secondary Reviewer: James Lin

EPA

Company Code:

Active Code:

Use Site Category:

EPA PC Code: 122101

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CITATION:

MRID 45528701

Manuli, P.J. and R.S. Kludas. 1999. Terrestrial field dissipation of propiconazole (Banner MAXX) applied to turf and bare ground in California. Unpublished study performed by Grayson Research, LLC, Creedmoor, NC and ADPEN Laboratories, Inc., Jacksonville, FL, and sponsored and submitted by Novartis Crop Protection, Inc., Greensboro, NC. Grayson Research Study No.: GR97-283. Novartis –.: 296-97. Study initiation June 8, 1998, and completion July 8, 1999 (p. 7). Final report issued July 8, 1999.

MRID 45528702

Manuli, P.J. and R.S. Kludas. 2001. Propiconazole (Banner® MAXX™): Final report addendum. Terrestrial field dissipation of propiconazole (Banner MAXX) applied to turf and bare ground in California. Unpublished study performed by Grayson Research, LLC, Creedmoor, NC and ADPEN Laboratories, Inc., Jacksonville, FL, and submitted by Syngenta Crop Protection, Inc., Greensboro, NC. Grayson Research Study No.: GR97-283. Syngenta No.: 296-97. Study initiation June 8, 1998, and completion February 21, 2001 (p. 7). Final report issued February 21, 2001.

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Administrative Conclusions: This study is classified acceptable and partially satisfies the guideline requirement for a terrestrial field dissipation study.

EXECUTIVE SUMMARY:

Soil dissipation/accumulation of *cis-trans*-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (propiconazole; CGA-64250) under U.S. field conditions was conducted in a bare plot and a turf plot of sandy loam soil in California (ecoregion not reported). The experiment was carried out in accordance with USEPA Subdivision N Guideline §164-1 and in compliance with the USEPA GLP standards. Propiconazole was broadcast sprayed four times (at 21-day intervals) to both test plots at a target application rate of 1.98 kg a.i./ha/application (1.77 lb a.i./A/application) in separate bare ground and turf test plots measuring approximately 90 x 6 m that were each divided into three subplots for sampling. The test substance was applied at 100% of the proposed maximum label rate. Rainfall was supplemented with irrigation to reach 450% of the 10-year average rainfall during the study period. Separate bare ground and turf control plots were located 60 m away from the two treated plots.

The application rate was verified for each test application using filter papers placed in glass petri plate tops that were then placed in each of the three sections of the two test plots immediately prior to each test application (12 pads total per application). Mean recoveries of propiconazole from the application rate monitors placed in the bare plot represented 89% of the target application rate for the four applications. Mean recoveries of propiconazole from the application rate monitors placed in the turf plot represented 93% of the target application rate. Mean recoveries from field spikes (prepared at 500 ppb) were 89.8 \pm 9.6% for propiconazole, 87.0 \pm 3.5% for CGA-91305, 93.7 \pm 3.5% for CGA-217495, 71.5 \pm 4.2% for Hydroxy Isomers, and 95.9 \pm 8.5% for CGA-71019. The length of time that the samples were stored prior to analysis was not reported.

Soil samples were taken prior to and following each application and at 1, 3, 7, 14, 30, 60, 90, 120, 180, 270, 360, 450, and 540 days following the fourth application to a depth of 0-120 cm in both the bare ground and turf plots. Grass and thatch samples were also collected from the turf plot at each sampling interval. Soil samples were reflux extracted with 70% methanol:deionized water, passed through a SAX SPE column, and then applied to a ENV SPE column attached on top of a SCX SPE column. The SPE columns were disconnected and eluted separately for propiconazole, CGA-217495, CGA-91305, CGA-71019, and Hydroxy Isomers, CGA-118244, CGA-118245, and CGA-136735. Samples collected from the bare plot were analyzed following up to a maximum of 216 days of storage. Samples collected from the turf plot were analyzed following up to a maximum of 217 days of storage. The LOQ was 5.0 ppb for all analytes in soil. Grass samples were extracted by shaking with acetone and were analyzed for propiconazole using LC/MS/MS. The LOQ was 50 ppb.

In the <u>bare plot</u>, propiconazole was detected in the 0-15 cm soil depth at 463 ppb following the first application, 696 ppb following the second application, 1256 ppb following the third application, and a maximum of 1556 ppb at 3 days following the fourth application. Following

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the fourth application, propiconazole decreased to 687 ppb by 120 days and 313 ppb by 270 days, and was 75.4 ppb at 540 days posttreatment, the last sampling interval. Propiconazole was detected sporadically in the 15-30 cm soil depth, and was not detected below the 30-45 cm soil depth. The major transformation products detected were CGA-217495, CGA-91305, and CGA-71019. CGA-217495 was initially detected in the 0-15 cm soil depth at 20.6 ppb prior to the second application, increased to a maximum of 254 ppb at 90 days after the fourth application, and decreased to 60.3 ppb by 540 days. CGA-217495 was detected in the 15-30 cm, 30-45 cm, and 45-60 cm depths at maximum concentrations of 37.5 ppb (270 days), 16.8 ppb (270 days), and 10.1 ppb (120 days), respectively. CGA-91305 was initially detected in the 0-15 cm soil depth at 6.53 ppb prior to the second application, increased to a maximum of 48.0 ppb at 90 days after the fourth application, and decreased to 11.7 ppb by 540 days. CGA-91305 was detected in the 15-30 cm and 30-45 cm depths at maximum concentrations of 11.0 ppb (270 days) and 6.0 ppb (270 days), respectively. CGA-71019 was initially detected in the 0-15 cm soil depth at 5.13 ppb prior to the second application, increased to a maximum of 87.5 ppb at 90 days after the fourth application, and decreased to 21.5 ppb by 540 days. CGA-71019 was detected in the 15-30 cm, 30-45 cm, and 45-60 cm depths at maximum concentrations of 14.6 ppb (270 days), 12.2 ppb (360 days), and 11.9 ppb (360 days), respectively.

Under field conditions in the <u>bare plot</u>, propiconazole had a reviewer-calculated half-life value in the 0-15 cm soil depth of 124 days ($r^2 = 0.93$) after the fourth application, calculated using linear regression. A DT90 value was not calculated. The total carryover of residues of propiconazole and its transformation products was 4.8% and 8.3% of the maximum propiconazole detection in soil (1556 ppb), respectively, at the end of the study period, 540 days after the fourth application.

In the turf plot, propiconazole was detected below the thatch in the 7.5-15 cm soil depth twice, at 50.3 ppb at 1 day, and 11.4 ppb at 7 days after the last application, and was detected once in the 15-30 cm depth. Propiconazole was detected in the grass at 93542 ppb following the first application, 60717 ppb following the second application, 64492 ppb following the third application, and 70867 ppb following the fourth application. Following the fourth application, propiconazole decreased to 33533 ppb by 3 days, 7000 ppb by 30 days, and was last detected at 352.3 ppb at 120 days posttreatment. Propiconazole was detected in the 0-7.5 cm thatch layer at a maximum of 541 ppb at 7 days after the fourth application, decreased to 101-177 ppb by 14-90 days, and was detected at 11.9 ppb at 540 days posttreatment, the last sampling interval. The major transformation products detected in soil (defined as detection >10 ppb) were CGA-217495 and CGA-71019. CGA-217495 was detected sporadically in the 7.5-15 cm soil depth at concentrations up to 6.5 ppb (120 days), and was detected once each in the 15-30 cm and 30-45 cm soil depths at concentrations of 11.1 ppb and 5.5 ppb, respectively, at 180 days. CGA-71019 was detected in the 7.5-15 cm, 15-30 cm, 30-45 cm, and 45-60 cm soil depths at maximum concentrations of 22.4 ppb (90 days), 8.2 ppb (180 days), 6.0 ppb (180 days), and 9.9 ppb (360 days), respectively. The major transformation products detected in thatch were CGA-217495, CGA-91305, and CGA-71019. CGA-217495 was initially detected in the 0-7.5 cm thatch layer at 30.0 ppb prior to the second application, increased to a maximum of 155 ppb at 60 days after the fourth application, and was last detected at 7.7 ppb at 450 days. CGA-91305 was initially detected in the 0-7.5 cm thatch layer at 36.8 ppb prior to the second application, increased to a



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maximum of 122 ppb at 60 days after the fourth application, and decreased to 5.5 ppb by 540 days. **CGA-71019** was initially detected in the 0-7.5 cm thatch layer at 5.4 ppb following the second application, increased to a maximum of 200 ppb prior to the fourth application, and decreased to 18.3 ppb by 540 days.

Under field conditions in the <u>turf plot</u>, propiconazole had a reviewer-calculated half-life value in the grass of 16 days ($r^2 = 0.95$) after the fourth application, and in the thatch of 110 days ($r^2 = 0.85$) after the fourth application, calculated using linear regression. The reviewer did not calculate a half-life for propiconazole in soil due to the low level of detection in soil. A DT90 value was not calculated. The total carryover of residues of propiconazole and its transformation products from thatch was 2.2% and 5.5% of the maximum propiconazole detection in the 0-7.5 cm thatch layer (541 ppb), respectively, at the end of the study period, 540 days after the fourth application.

The major route of dissipation of propiconazole under terrestrial field conditions at the test site (bare and turf plots) was transformation.

RESULTS SYNOPSIS

Bare plot

Location/soil type: Porterville, California/Sandy loam (0-120 cm).

Half-life: 124 days (reviewer-calculated, based on residues in the 0-15 cm soil layer only).

DT90: Not determined.

Major transformation products detected: CGA-217495, CGA-91305, and CGA-71019.

Dissipation routes: Transformation.

Turf plot

Location/soil type: Porterville, California/Sandy loam-loam (0-120 cm).

Half-life (grass): 16 days (reviewer-calculated).

Half-life (thatch): 110 days (reviewer-calculated, following the maximum detection at 7 days).

Half-life (soil): Not calculated, due to too few detections in soil.

DT90: Not determined.

Major transformation products detected in soil: CGA-217495 and CGA-71019.

Major transformation products detected in thatch: CGA-217495, CGA-91305, and CGA-71019.

Dissipation routes: Transformation.



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The final report (MRID 45528701) covers all events from study initiation through collection and analysis of the 180-day posttreatment samples. The addendum to the final report (MRID 45528702) includes a summary of all remaining field events (270-, 360-, 450-, and 540-day posttreatment sampling events). Page numbers cited in this DER refer to the final report unless otherwise referenced to the final report addendum.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED:

The study was conducted according to USEPA Pesticide Assessment Guidelines Subdivision N, §164-1 (p. 1). Deviations from EPA Subdivision N, §164-1 are:

COMPLIANCE:

The study was conducted in compliance with USEPA FIFRA (40 CRF Part 160) Good Laboratory Practice standards (p. 3). Signed and dated GLP Compliance, Quality Assurance, Data Confidentiality, and Certification of Authenticity statements were provided (pp. 2, 3, 5, and 6).

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A. MATERIALS:

1. Test Material

cis-trans-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-

ylmethyl]-1H-1,2,4-triazole. (propiconazole; CGA-64250;

Table 1, p. 46).

Chemical Structure

of the active ingredient:

See DER Attachment 2.

Description:

Clear yellow-amber liquid (Appendix 1, p. 131).

Storage conditions of

test chemicals:

Propiconazole was stored at ambient temperature (-0.5°C to

32°C) and its transformation products were stored refrigerated

(p. 29; Appendix 3, Figure 4, p. 219).

Physico-chemical properties of propiconazole

Parameter	Values	Comments	
Water solubility	0.1 g/L	At 20°C.	
Vapour pressure/volatility	1.30 x 10 ⁻⁴ Pa	At 20°C.	
UV absorption	Not reported		
pKa	Not reported		
$K_{ow}/log K_{ow}$	Not reported		
Stability of Compound at room temperature	Stable		<u> </u>



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2. Test site: The test site was located approximately 3 miles southwest of Porterville, California, in Tulare County (p. 29; Figure 1, p. 94). The study site was representative of a geographic and climatic region for fescue turf (p. 14). The soil at the test site was classified as a Cajon fine sandy loam (p. 29). The soil in the bare ground test plot was characterized as sandy loam from 0 to 120 cm, and the soil in the turf plot was characterized as sandy loam from 0 to 30 cm and 90 to 120 cm and as loam from 30 to 90 cm (p. 29; Table 3, pp. 50-51). An agricultural chemical plot history indicated that Roundup Ultra and Terrazole 35W had been applied to both the treated bare ground and turf plots within the last three years and that Mancozeb had also been applied to the treated bare ground plot (Table 2, pp. 47-49).

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

Details		Test site	
Geographic	Latitude	Not reported	
coordinates	Longitude	Not reported	
	Province/State	California	
	Country	US	
Ecoregion		Not reported	
Slope Gradient		<1%	
Depth to ground water (m)		77.7 m	
Distance from weather station used for climatic measurements		Precipitation data were recorded on-site throughout the study period. Precipitation, air temperature, relative humidity, solar radiation and evapotranspiration data were supplied by the California Irrigation Management Information System in Visalia, located approximately 19.7 miles northwest from the field site.	
(Yes/No). If no, pro	arting or during the 0 year normal levels ovide details.	Yes. Total water input (precipitation plus irrigation) during the study period was 84.62 inches or 450% of the 10-year average rainfall during the study period.	

Data were obtained from pp. 29 and 30 and Tables 5-7, pp. 54-66 of the study report and from Tables 2-3, pp. 26-29 of MRID 45528702.



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

Use	Year	Treated bare ground plot	Treated turf plot
Crops grown	Previous year	Bare ground	Turf
	2 years previous	Bare ground	Turf
	3 years previous	Squash	Turf
Pesticides used	Previous year	Roundup Ultra	Roundup Ultra
	2 years previous	Roundup Ultra and Terrazole 35W.	Roundup Ultra and Terrazole 35W.
	3 years previous	Mancozeb	None
Fertilizers used	Previous year	Not reported	Not reported
	2 years previous	Not reported	Not reported
	3 years previous	Not reported	Not reported
Cultivation methods,	Previous year	Not reported	Not reported
if provided (eg., tillage)	2 years previous	Not reported	Not reported
	3 years previous	Not reported	Not reported

Data were obtained from Table 2, pp. 48-49 of the study report.

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3. Soils:

Table 3: Properties of the soil from the treated bare plot.

Property				Dept	h (cm)			
	0-15	15-30	30-45	45-60	60-75	75-90	90- 105	105- 120
Textural classification	SL	SL	SL	SL	SL	SL	SL	SL
% sand	52	54	56	56	52	56	58	64
% silt	42	40	36	38	42	40	36	30
% clay	6	6	8	6	6	4	6	6
pН	8.7	8.7	8.8	9.0	9.2	9.4	9.6	9.5
Total organic matter (%)	1.2	0.6	0.4	0.2	0.3	0.2	0.1	0.2
CEC (meq/100 g)	12.1	20.2	21.6	23.0	22.5	23.0	22.8	20.5
Bulk density (g/cm³)	1.12	1.09	1.07	1.07	1.06	1.13	1.13	1.14
Moisture at 1/3 atm (%)	15.9	18.4	18.5	18.7	18.7	18.4	16.9	14.5
Taxonomic classification (e.g., ferro-humic podzol)	Mixed, t	hermic Ty	pic Torrip	samments.				<u>I </u>
Soil mapping unit	Not repo	rted						

Data were obtained from Table 3, p. 50 of the study report. SL = Sandy loam.

The taxonomic classification was obtained from the NRCS for the Cajon soil series.

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Table 4: Properties of the soil from the treated turf plot.

Property				D	epth (cm	ı)		5400	
	0-7.5	7.5-15	15-30	30-45	45-60	60-75	75-90	90- 105	105- 120
Textural classification	SL	SL	SL	L	L	L	L	SL	SL
% sand	58	58	48	48	48	50	48	52	52
% silt	36	36	46	44	44	42	44	40	40
% clay	6	6	6	8	8	8	8	8	8
рН	7.5	7.8	8.4	8.9	9.1	9.1	9.3	9.3	9.3
Total organic matter (%)	2.2	1.4	0.9	0.7	0.4	0.9	0.3	0.3	0.1
CEC (meq/100 g)	10.5	11.2	15.2	21.6	22.3	24.1	23.4	23.9	22.7
Bulk density (g/cm³)	1.01	1.08	1.11	1.05	1.08	1.05	1.05	1.11	1.09
Moisture at 1/3 atm (%)	17.4	15.7	16.1	18.8	18.2	20.1	19.7	18.7	18.6
Taxonomic classification (e.g., ferro-humic podzol)	Mixed,	thermic T	ypic Torr	ipsamme	nts.				
Soil mapping unit	Not rep	orted		· · · · · ·					

Data were obtained from Table 3, p. 51 of the study report. SL = Sandy loam. L = Loam.

The taxonomic classification was obtained from the NRCS for the Cajon soil series.

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B. EXPERIMENTAL DESIGN:

1. Experimental design:

Table 5: Experimental design.

Details		Bare plot	Turfolot
Duration of study		603 days (540 days after the last application).	603 days (540 days after the last application)
Bare or turf		Bare	Turf
Control used (Yes/No)		Yes	Yes
No. of replications	Controls	One	One
	Treatments	Three	Three
Plot size	Control	28.9 x 6.1 m	28.9 x 6.1 m
(III II V 7)	Treatment	89.9 x 6.1 m	89.9 x 6.1 m
Distance between control plot and treated plot	nd treated plot	60.96 m	60.96 m
Distance between treated plots		1.5 m	1.5 m
Application rate(s) used (g a.i/ha)	a)	1980 g a.i./ha/application	1980 p a i /ha/ann lication
Was the maximum label rate per ha used in study? (Yes/No)	r ha used in study?	Yes	Yes
Number of applications		Four	Болг
Application Date(s) (dd mm	Application 1	16/06/1998	8661/90/91
	Application 2	07/07/1998	07/07/1998
	Application 3	28/07/1998	28/07/1998
	Application 4	18/08/1998	18/08/1998

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Details		Bare plot				Turf plot			
For multiple applications, application rate at Day 0 and at each application time (mg a.i./kg soil) ¹	lication rate at Day 0 and i./kg soil) ¹	1.18 mg a.i./kg	3)			2.62 mg a.i./kg	kg		
Application method (eg., spraying, broadcast etc.)	/ing, broadcast etc.)	Broadcast spray	ray		ļ -	Broadcast spray	rav		
Type of spray equipment, if used	ed	Tractor-mounted sprayer equipped with T-Jet 110-04 flat fan nozzles spaced 20 inches apart and at a height of 16 inches above the soil.	nted sprayer in nozzles s it of 16 inch	equipped was paced 20 inc.	th T-Jet hes apart soil	Tractor-mou 110-04 flat f	Tractor-mounted sprayer equipped with T-Jet 110-04 flat fan nozzles spaced 20 inches apart and at a height of 16 inches change the	equipped wi	h T-Jet es apart
Total volume of spray solution applied/plot OR total amount broadcasted/plot	applied/plot OR total	113-119 gal/A	4			113-118 gal/A	A	s acove me	init.
Identification and volume of carrier (e.g., water), if used	ırrier (e.g., water), if	Water				Water			
Name and concentration of co-solvents, adjuvants and/or surfactants, if used	solvents, adjuvants	None				None			
Indicate whether the following monthly reports were submitted:	monthly reports were								
Precipitation Average minimum and maximum air temperature Average minimum and maximum soil temperature Average annual frost-free periods		Yes Yes No No				Yes Yes No No			
Indicate whether the Pan evaporation data were submitted	ration data were	Yes				Yes			
Meteorological conditions			Application	ation			Application	tion	
nonward de Green		1	2	3	4	1	2	3	4
	Cloud cover) %0	%0	40%	%0	%0	%0	40%	%0
	Temperature (°C)	28.3	28.9	31.7	25.0	28.3	28.9	31.7	25.0
	Humidity	52%	28%	36%	43%	52%	28%	36%	43%

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Details		Bare plot	Turf plot
	Wind speed and direction	1.7-4.3, E 0.7-3.1, 1.3-3.8, 0 NE NE	1.7-4.3, E 0.7-3.1, 1.3-3.8, 0 NE NE
	Sunlight (hr)	Not reported	Not reported
Pesticides used during study:			None
name of product/a.i concentration: amount applied: application method:	n:	Roundup 8 applications of 1% solution Broadcast	
Supplemental irrigation used (Yes/No)		Yes	Yes
If yes, provide the following details:	ails:		
No. of irrigation: Interval between irrigation: Amount of water added each time: Method of irrigation:		81 2-25 days 0.5-1.25 inches Sprinkler	81 2-25 days 0.5-1.25 inches Sprinkler
Indicate whether water received through rainfall + irrigation equals the 30 year average rainfall (Yes/No)	Č,	Yes	Yes
Were the application concentrations verified? (Bridescribe in Section 2*, if used)	efly	Yes	Yes
Were field spikes used? (Briefly describe in Section 31, if used)		Yes	Yes
Good agricultural practices followed (Yes or No)		Not reported	Not reported
Indicate if any abnormal climatic events occurred during the study (eg., drought, heavy rainfall, flooding, storm etc.)		Precipitation during the study period appeared to be typical for the region. Total rainfall during the study period was 16.95 inches or 90% of the 10-year historical average for the period.	typical for the region. Total rainfall during the r historical average for the period.

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Details	Bare plot	Turfulot
If turf plots are used, provide the following details:	N/A	
Plant - Common name/variety: Details of planting: Crop maintenance (eg., fertilizers used):		Variety of turf not reported Not reported The turf was periodically mowed to a height of 2 inches and clipnings were left on the whot
Volatilization included in the study (Yes/No) (if included, describe in Section 48)	No	No
Leaching included in the study (Yes/No) (if included, describe in Section 5 ¹)	Yes	Yes
Run off included in the study (Yes/No) (if included, describe in Section 6*)	No	No

Data were obtained from pp. 29-32, Tables 4-10, pp. 52-69, Figure 2, p. 95 and Appendix 1, Figure 3, p. 129 of the study report, and from Tables 1-3, pp. 25-29

of MRID 45528702. The bare ground plot was disked and floated five days prior to the first test application.

The application rate at day 0 for each application, reported as mg a.i./kg soil, was calculated by the reviewer and is based on the site-specific bulk density of the 0-15 cm soil depth (1.12 g/cm³) for the bare plot and the 0-7.5 cm soil depth (1.01 g/cm³) for the turf plot, and the target application rate of 1.77 lb a.i./A for each

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*2. Application Verification: The application rate was verified for each test application using four Whatman No. 3 filter papers (15-cm diameter) placed in glass petri plate tops that were then placed in each of the three sections of the two test plots immediately prior to each test application (12 pads total per application; p. 32). All plate tops were collected within 30 minutes of the test application, sealed with tape, and placed in a field cooler with dry ice. The filter papers were extracted by shaking for 30 minutes with acetone, and the extracts were diluted with acetone and 10% methanol:water prior to analysis by LC/MS/MS (p. 35; Appendix 3, p. 208). Filter papers were analyzed for propiconazole and not for transformation products of propiconazole.

In addition to the application verification procedure described above, duplicate tank mix samples were collected prior to and following each test application to verify the concentration of propiconazole in the spray solution (p. 32). Spray solution samples were diluted with 10% methanol:water and analyzed for propiconazole by LC/MS/MS (p. 36; Appendix 3, p. 208).

- ¹3. Field Spiking: Field spikes (transit stability monitors) were prepared in duplicate for propiconazole and its transformation products CGA-91305, CGA-217495, Hydroxy Isomers, and CGA-71019 by fortifying control soil in the field with each analyte at 500 ppb (Appendix 2, p. 53 in MRID 45528702). The field spikes were sent to the analytical laboratory under the same conditions as the test samples. The length of time that the samples were stored prior to analysis was not reported.
- § 4. Volatilization: Volatilization was not measured.
- 15. Leaching: Five cores were taken from the three treated subplots (15 cores total per treated plot) of the bare and turf plot prior to and following each application and at 1, 3, 7, 14, 30, 60, 90, 120, 180, 270, 360, 450, and 540 days following the fourth application to a depth of 0-120 cm to determine the mobility of the test substance in the soil profile (pp. 33-34).
- *6. Run off: Run off was not studied.
- 7. Supplementary Study: To determine the frozen storage stability of propiconazole and the transformation products CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 in grass and thatch/sod samples, separate grass, and thatch/sod samples were fortified in duplicate with each analyte at 1000 ppb and stored frozen for up to 24 months (p. 35). Samples were analyzed at day 0 and following 1, 3, 6, 9, 12, 18, and 24 months of storage.

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8. Sampling:

Table 6: Soil sampling - Bare ground plot.

Details	Bare ground plot
Method of sampling (random or systematic)	Random
Sampling intervals	Prior to and following each application and at 1, 3, 7, 14, 30, 60, 90, 120, 180, 270, 360, 450, and 540 days following the fourth application.
Method of soil collection (eg., cores)	Separate 0-15 cm and 15-120 cm cores were collected.
Sampling depth	120 cm
Number of cores collected per plot	15 (five from each subplot).
Number of segments per core	Eight
Length of soil segments	15 cm
Core diameter (Provide details if more than one width)	5.625 cm (2.25 inches) for the 0-15 cm depth samples and 4.375 cm (1.75 inch) for the 15-120 cm depth samples.
Method of sample processing, if any	Following sectioning of the soil cores, three sample composites were prepared for each sampling interval and depth by combining the cores from each of the three subplots. Soil samples from the 0-15, 15-30, 30-45, and 45-60 cm horizons were processed for analysis by grinding and mixing with dry ice using a Hobart food chopper.
Storage conditions	Frozen
Storage length (days)	Up to 216 days

Data were obtained from pp. 33-35 and Appendix 3, Tables 1.b-1.e, pp. 231-242 of the study report and from Appendix 2, Tables 1.b.-1.e., pp. 65-68 of MRID 45528702.

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Table 7: Grass, thatch and soil sampling - Turf plot.

Details	Turf plot
Method of sampling (random or systematic)	Random
Sampling intervals	Prior to and following each application and at 1, 3, 7, 14, 30, 60, 90, 120, 180, 270, 360, 450, and 540 days following the fourth application.
	Grass sampling
Method of grass collection	Grass samples were collected from one foot square quadrant frames using hand clippers.
Number of grass samples collected per plot	15 (five from each subplot).
Plant parts collected	Actively growing grass blades above the crown/stem zone.
Processing of plant samples (eg., drying, grinding)	Not reported
Storage conditions	Frozen
Storage length (days)	Up to 217 days.
So	il and thatch sampling
Method of soil collection (eg., cores)	Cores, collected from the quadrant areas after removal of the grass clippings.
Sampling depth	7.5 cm for thatch and 120 cm for soil.
Number of cores collected per plot	15 (five from each subplot).
Number of segments per core	Eight
Length of soil segments	7.5 cm (7.5-15 cm depth samples) or 15 cm (all other depths).
Core diameter (Provide details if more than one width)	5.625 cm (2.25 inches) for the thatch samples and 4.375 cm (1.75 inch) for the soil samples.
Method of sample processing, if any	Following sectioning of the soil cores, three sample composites were prepared for each sampling interval and depth by combining the cores from each of the three subplots. Soil/thatch samples from the 0-7.5, 7.5-15, 15-30, and 30-45 cm horizons were processed for analysis by grinding and mixing with dry ice using a Hobart food chopper.
Storage conditions	Frozen
Storage length (days)	Up to 217 days.

Data were obtained from pp. 33-35 and Appendix 3, Tables 2.b.-2.e. and Table 3, pp. 247-258 and 260-261 of the study report and from Appendix 2, Tables 2.b.-2.f. and Table 3, pp. 70-75 of MRID 45528702.

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9. Analytical Procedures: Soil and thatch samples were analyzed for propiconazole (purity of analytical standard: 97.2%) and the transformation products CGA-217495 (purity of analytical standard: 91.6%; 98.1%; 97.3%), CGA-91305 (purity of analytical standard: >99.9%; 99.8%), CGA-71019 (purity of analytical standard: >99.9%), and Hydroxy Isomers, CGA-118244 (purity of analytical standard: 98.4%; 97.5%), CGA-118245 (purity of analytical standard: >99.9%; 99.2%), and CGA-136735 (purity of analytical standard: 99.7%; 97.6%; Appendix 3, Figures 4-5, pp. 219-220 in MRID 45528701 and Appendix 2, Figures 4-5, pp. 59-60 in MRID 45528702) using analytical method AG-677 (p. 36). The chemical names of the transformation products were not reported.

Soil samples (20 g) were reflux extracted with 100 mL of 70% methanol:deionized water for 1 hour and filtered (GF/F vacuum filtration; Appendix 3, p. 209 and Figure 1, p. 214). After the addition of 100 µL of concentrated ammonium hydroxide, the sample was passed through a preconditioned SAX SPE column and concentrated using a rotovap. The sample was acidified with 100 µL of acetic or phosphoric acid, diluted with deionized water, and passed through a preconditioned ENV SPE column attached on top of a preconditioned SCX SPE column. The SPE columns were disconnected and eluted separately. ENV analytes (propiconazole, CGA-217495, CGA-91305, and Hydroxy Isomers) were eluted with acetonitrile, concentrated to 3 mL, diluted with acetonitrile, and deionized water prior to analysis by LC/MS. SCX analytes (CGA-71019) were eluted with 2.5% ammonium hydroxide in 70% (v/v) methanol:deionized water, concentrated to 3 mL, then diluted with methanol and deionized water prior to analysis by LC/MS. The LOQ was 5.0 ppb for all analytes in soil (p. 36; Appendix 3, p. 210).

LC/MS/MS operating parameters for soil and thatch samples

Parameters	Сотрои	nds analyzed
	Propiconazole, CGA-217495, CGA- 91305 and Hydroxy Isomers	CGA-71019
LC/MS/MS	PE Sciex API 365 with TurbolonSpray Inlet	PE Sciex API 365 with TurboIonSpray Inlet
Column	Intersil ODS-2, 5 µm particle size, 4.6 mm i.d., 15 cm length	Zorbax 300 SCX, 5 μm particle size, 4.6 mm i.d., 15 cm length
Mobile phase	A: 0.1% (v/v) Acetic acid in acetonitrile B: 0.1% (v/v) Acetic acid in purified water	A: 25% (v/v) Methanol/water, 0.1% acetic acid B: 25% (v/v) Methanol/water, 20 mM ammonium acetate
Flow rate	1.5 mL/min	1.0 mL/min
Gradient	A:B (v:v) 30:70 to 75:25 to 100:0	Isocratic, A:B (v:v), 95:5

Data were obtained from Appendix 3, pp. 215-216 of the study report.

Grass samples were analyzed for propiconazole only, using a modified version of analytical method AG-677 (p. 36; Appendix 3, p. 210). Grass samples (2 g) were extracted by shaking with acetone for 30 minutes and the extracts were concentrated, reconstituted with 30%



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acetonitrile/water, and analyzed by LC/MS/MS using the conditions reported for the soil/thatch samples. The LOQ was 50 ppb (p. 36).

II. RESULTS AND DISCUSSION

1. APPLICATION MONITORS: Mean recoveries of propiconazole from the application rate monitors placed in the bare plot were $18.3~\mu g/cm^2$, $17.9~\mu g/cm^2$, $18.2~\mu g/cm^2$, and $18.9~\mu g/cm^2$ for each of the four applications, respectively, which represents 89% of the target application rate (pp. 37-38; Table 13, pp. 72-75). Mean recoveries of propiconazole from the application rate monitors placed in the turf plot were $18.7~\mu g/cm^2$, $18.8~\mu g/cm^2$, $20.1~\mu g/cm^2$, and $18.8~\mu g/cm^2$ for each of the four applications, respectively, which represents 93% of the target application rate (pp. 37-38; Table 14, pp. 76-79).

The mean concentration of propiconazole in the tank mix samples was 1339 $\mu g/mL$ which represents approximately 78% of the expected concentration (p. 38; Table 12, p. 71). Propiconazole concentrations ranged from 1280-1520 $\mu g/mL$ for the first application, 980-1520 $\mu g/mL$ for the second application, 1300-1560 $\mu g/mL$ for the third application, and 960-1420 $\mu g/mL$ for the fourth application.

- **2. RECOVERY FROM FIELD SPIKES**: Mean recoveries from the field spikes were $89.8 \pm 9.6\%$ for propiconazole, $87.0 \pm 3.5\%$ for CGA-91305, $93.7 \pm 3.5\%$ for CGA-217495, $71.5 \pm 4.2\%$ for Hydroxy Isomers, and $95.9 \pm 8.5\%$ for CGA-71019 (Appendix 2, Table 12, p. 91 in MRID 45528702). The length of time that the samples were stored prior to analysis was not reported.
- 3. MASS ACCOUNTING: A mass balance was not determined.



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Table 8. Mean concentration of propiconazole residues expressed as ppb soil, in the bare plot.

Compound	Soil depth					ing the last ap	
	(cm)	App 1	20	App 2	20	App 3	20
Propiconazole	0-15	463	392	696	677	1256	990
	15-30	5.1	5.7	11.8	<5.0	15.7	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-217495	0-15	<5.0	20.6	24.4	42.8	75.2	76.9
	15-30	<5.0	5.1	<5.0	5.8	<5.0	5.1
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-91305	0-15	<5.0	6.53	6.00	15.2	13.5	21.5
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	5.4
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Hydroxy Isomers	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-71019	0-15	<5.0	5.13	<5.0	12.5	17.4	19.2
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

Data were obtained from Table 15, pp. 80-83 of the study report. The LOQ was 5.0 ppb. All values are means of three replicates. Total extractable and total non-extractable residues were not determined.



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Table 8 (cont.). Mean concentration of propiconazole residues expressed as ppb soil, in the bare plot.

Compound	Soil depth		S	Sampli	ng tim	es (apj	olicatio	on or d	lays fo	llowin	g the la	ast app	licatio	n)	
	(cm)	App 4	1	3	7	14	30	60	90	120	180	270	360	450	540
Propiconazole	0-15	1530	1466	1556	1379	1254	999	853	878	687	415	313	187	108	75,4
	15-30	7.1	10.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	9,9	40.3	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.2	<5.0	5.9	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-217495	0-15	63.8	129	109	176	148	178	182	254	168	226	101	77.2	77.2	60.3
·	15-30	6.1	<5.0	<5.0	<5.0	<5.0	8.7	<5.0	<5.0	26.8	9.2	37.5	5.9	<5.0	6.1
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	14.9	<5.0	16.8	6.4	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	10.1	<5.0	5.8	9.4	<5.0	<5.0
CGA-91305	0-15	26.4	27.4	25.9	26.3	33.2	45.6	41.5	48.0	41.3	27.8	43.3	22.1	17.2	11.7
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	6.6	<5.0	<5.0	7.4	<5.0	11.0	5.8	<5.0	5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	6.0	<5.0	<5.0	<5.0
·	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Hydroxy	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Isomers	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-71019	0-15	23.4	30.2	25.3	26.9	53.0	60.4	71.6	87.5	44.4	45.1	40.5	59.7	30.4	21.5
	15-30	5.8	<5.0	<5.0	<5.0	<5.0	10.3	9.5	<5.0	11.5	<5.0	14.6	13.5	10.6	7.3
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	5.4	<5.0	<5.0	11.1	6.0	9.7	12.2	8.4	7.5
	45-60	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	6.9	11.9	<5.0	8.1

Data were obtained from Table 15, pp. 80-83 in the study report and from Table 4, p. 30 of MRID 45528702. The LOQ was 5.0 ppb. All values are means of three replicates. Total extractable and total non-extractable residues were not determined.



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Table 9. Mean concentration of propiconazole residues expressed as ppb soil, in the turf plot.

Compound	Soil depth	Samp	ling times (a	application or	days follow	ing the last ap	plication)
	(cm)	App 1	20	App 2	20	App 3	20
Propiconazole	Thatch	104	322	408	188	369	350
	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-217495	Thatch	<5.0	30.0	37.1	49.1	42.8	85.0
	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-91305	Thatch	<5.0	36.8	44.9	63.1	69.8	78.6
	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Hydroxy Isomers	Thatch	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-71019	Thatch	<5.0	<5.0	5.4	14.1	17.9	200
	7.5-15	<5.0	<5.0	<5.0	5.6	6.3	5.8
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

Data were obtained from Table 16, pp. 84-87 of the study report. The LOQ was 5.0 ppb. All values are means of three replicates. Total extractable and total non-extractable residues were not determined.



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Table 9 (cont.). Mean concentration of propiconazole residues expressed as ppb soil, in the turf plot.

Compound	Soil			Sampli	ing tim	ies (ap	plicati	on or o	lays fo	llowin	g the la	ast app	olicatio	on)	<u> </u>
	depth (cm)	App 4	1	3	7	14	30	60	90	120	180	270	360	450	54
Propiconazole	Thatch	346	517	397	541	171	155	177	101	86.0	44.8	46.6	16.1	13.8	11.9
	7.5-15	<5.0	50.3	<5.0	11.4	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	5.4	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-217495	Thatch	88.8	105	115	63.3	88.1	104	155	64.8	74.1	28.6	20.3	5.8	7.7	<5.0
	7.5-15	<5.0	<5.0	6.0	5.1	<5.0	<5.0	<5.0	<5.0	6.5	5.0	5.6	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	11.1	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.5	<5.0	<5.0	<5.0	<5.0
CGA-91305	Thatch	79.9	76.7	79.3	76.6	88.9	113	122	58.8	88.8	43.8	29.5	12.9	13.4	5.5
	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
*	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
·	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Hydroxy	Thatch	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Isomers	7.5-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	< 5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-71019	Thatch	130	26.4	29.8	21.3	25.9	38.0	54.3	28.9	54.6	24.4	28.3	30.3	51.3	18.3
	7.5-15	<5.0	5.6	<5.0	7.3	5.4	17.5	12.5	22.4	12.9	9.1	8.3	<5.0	10.4	6.2
	15-30	<5.0	<5.0	<5.0	<5.0	5.8	6.1	<5.0	5.2	<5.0	8.2	5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	6.0	<5.0	<5.0	<5.0	<5.0

Data were obtained from Table 16, pp. 84-87 of the study report and from Table 5, pp. 31-32 of MRID 45528702. The LOQ was 5.0 ppb. All values are means of three replicates. Total extractable and total non-extractable residues were not determined.



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Table 10. Mean concentration of propiconazole residues expressed as ppb in grass samples.

Compound			-	Sam	Sampling times (application or days following the last application)	s (applica)	ion or da	ys follow	ing the la	st applicat	ion)			
	App 1	20	App 2	20	20 App 3 20	20								
Propiconazole	93542	93542 20867	60717	13733	64492 15833	15833								
	App 4	_	,	7	7	3.0	И	8						
					- T-	2	8	3	120	180	270	360	450 540	540
Propiconazole	70867	60200	33533	28933	28933 23233 7000	7000	4100	549.0	3523	<50.0	0.0\$>	4100 5490 3523 <50.0 <50.0 <50.0 <50.0	0.03/	0.03/
Data was a Late									7.7.7	2000	>20.0	2.50	7.00	0.00

Data were obtained from Table 17, p. 88 of the study report and from Table 6, p. 33 of MRID 45528702.

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4. PARENT COMPOUND: In the <u>bare</u> plot, propiconazole was detected in the 0-15 cm soil depth at 463 ppb following the first application, 696 ppb following the second application, 1256 ppb following the third application, and a maximum of 1556 at 3 days following the fourth application (Table 15, p. 80). Following the fourth application, propiconazole decreased to 687 ppb by 120 days and 313 ppb by 270 days, and was 75.4 ppb at 540 days posttreatment, the last sampling interval (Table 15, pp. 80-83 in MRID 45528701 and Table 4, p. 30 in MRID 45528702). Propiconazole was detected sporadically in the 15-30 cm soil depth (maximum of 40.3 ppb at 180 days), and was detected twice in the 30-45 cm soil depth (5.2-5.9 ppb, 90 and 180 days).

In the <u>turf</u> plot, propiconazole was detected twice in the **7.5-15 cm soil depth** (maximum of 50.3 ppb at 1 day posttreatment of the fourth application) and once in the **15-30 cm soil depth** (5.4 ppb, 7 days; Table 16, pp. 84-87 in MRID 45528701 and Table 5, p. 31 in MRID 45528702). Propiconazole was detected in the **grass** at 93542 ppb following the first application, 60717 ppb following the second application, 64492 ppb following the third application, and 70867 ppb following the fourth application (Table 17, p. 88). Following the fourth application, propiconazole decreased to 33533 ppb by 3 days, 7000 ppb by 30 days, and was last detected at 352.3 ppb at 120 days posttreatment. Propiconazole was detected in the 0-7.5 cm **thatch** layer at 104 ppb following the first application, 408 ppb following the second application, 369 ppb following the third application, and 346 ppb following the fourth application. Following the fourth application, propiconazole increased to a maximum of 541 ppb by 7 days, decreased to 101-177 ppb by 14-90 days and 46.6 ppb by 270 days, and was 11.9 ppb at 540 days posttreatment, the last sampling interval.

The reviewer-calculated half-life of propiconazole in soil under terrestrial field conditions was 124 days after the fourth application ($r^2 = 0.93$) for the bare ground plot. Reviewer-calculated half-lives of propiconazole in grass and thatch were 16 days after the fourth application ($r^2 = 0.95$) and 110 days after the fourth application ($r^2 = 0.85$), respectively, for the turf plot. However, the reviewer notes that the observed half-life in thatch occurred within 7 days of reaching a maximum concentration at 7 days following the fourth application. The half-lives were based on all data points and calculated using linear regression analysis performed on a plot of ln-transformed propiconazole concentrations vs. time and the equation $t_{1/2} = -\ln 2 / k$, where k is the rate constant. The reviewer did not calculate a half-life for propiconazole in soil due to the low level of detection in soil. A DT90 value was not determined.



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5. Transformation products: The major transformation products, defined as being detected in soil at >0.01 ppm (10 ppb), were CGA-217495, CGA-91305 (bare plot only), and CGA-71019 (chemical names were not reported; structures were reported in Appendix 3, Figure 5, p. 220).

Bare plot. CGA-217495 was initially detected in the 0-15 cm soil depth at 20.6 ppb prior to the second application, increased to a maximum of 254 ppb at 90 days after the fourth application, and decreased to 60.3 ppb by 540 days, the last sampling interval (Table 15, pp. 80-83 in MRID 45528701 and Table 4, p. 30 in MRID 45528702). CGA-217495 was detected in the 15-30 cm, 30-45 cm, and 45-60 cm depths at maximum concentrations of 37.5 ppb (270 days), 16.8 ppb (270 days), and 10.1 ppb (120 days), respectively. CGA-91305 was initially detected in the 0-15 cm soil depth at 6.53 ppb prior to the second application, increased to a maximum of 48.0 ppb at 90 days after the fourth application, and decreased to 11.7 ppb by 540 days, the last sampling interval. CGA-91305 was detected in the 15-30 cm and 30-45 cm depths at maximum concentrations of 11.0 ppb (270 days) and 6.0 ppb (270 days), respectively. CGA-71019 was initially detected in the 0-15 cm soil depth at 5.13 ppb prior to the second application, increased to a maximum of 87.5 ppb at 90 days after the fourth application, and decreased to 21.5 ppb by 540 days, the last sampling interval. CGA-71019 was detected in the 15-30 cm, 30-45 cm, and 45-60 cm depths at maximum concentrations of 14.6 ppb (270 days), 12.2 ppb (360 days), and 11.9 ppb (360 days), respectively.

Turf plot. CGA-217495 was detected sporadically in the 7.5-15 cm soil depth at concentrations up to 6.5 ppb (120 days), and was detected once each in the 15-30 cm and 30-45 cm soil depths at concentrations of 11.1 ppb and 5.5 ppb, respectively, at 180 days (Table 16, pp. 84-87 in MRID 45528701 and Table 5, pp. 31-32 in MRID 45528702). CGA-217495 was initially detected in the 0-7.5 cm thatch layer at 30.0 ppb prior to the second application, increased to a maximum of 155 ppb at 60 days after the fourth application, and was last detected above the LOQ at 7.7 ppb at 450 days. CGA-71019 was detected in the 7.5-15 cm, 15-30 cm, 30-45 cm, and 45-60 cm soil layers at maximum concentrations of 22.4 ppb (90 days), 8.2 ppb (180 days), 6.0 ppb (180 days), and 9.9 ppb (360 days), respectively. CGA-71019 was initially detected in the 0-7.5 cm thatch layer at 5.4 ppb following the second application, increased to a maximum of 200 ppb prior to the fourth application, and decreased to 18.3 ppb by 540 days, the last sampling interval. CGA-91305 was not detected in soil above the LOQ, but was a major transformation product in thatch, defined as being detected at >10 ppb. CGA-91305 was initially detected in the 0-7.5 cm thatch layer at 36.8 ppb prior to the second application, increased to a maximum of 122 ppb at 60 days after the fourth application, and decreased to 5.5 ppb by 540 days, the last sampling interval.



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Table 11: Chemical names and CAS numbers for the transformation products of propiconazole.

Applicant's Code Name	CAS Number	CAS and/or IUPAC Chemical Name(s)	Chemical formula	Molecular weight	SMILES string
CGA-217495					
CGA-91305					
CGA-118244					
CGA-118245					
CGA-136735					
CGA-71019					

Structures are presented in Appendix 3, Figure 5, p. 220 of the study report. Chemical names were not reported.

6. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES: Non-extractable residues were not measured.

Table 12: Dissipation routes of propiconazole under field conditions.

Route of dissipation		% of applied amount (at	the end of study period)
		Bare plot	Turf plot
Accumulation (residues over) in soil/carry	4.8%	2.2%
Transformation ²	CGA-217495	4.3%	0%
	CGA-91305	1.1%	1.0%
	CGA-71019	2.9%	4.5%
	Total	8.3%	5.5%
Leaching, if measured	Propiconazole	Not below 30-45 cm	Not below 15-30 cm
	CGA-217495	Could not be determined ³	Could not be determined ³
	CGA-91305	Not below 30-45 cm	Not below 0-7.5 cm
	CGA-71019	Could not be determined ³	Could not be determined ³
Volatilization, if measur	ed	Not measured	Not measured
Plant uptake, if measure	d	N/A	Not measured
Run off, if measured		Not measured	Not measured
Total	•		

Data were obtained from Tables 15-17, pp. 80-88 of MRID 45528701 and Tables 4-6, pp. 30-33 of MRID 45528702.

¹ Calculated by the reviewer from the residue detected at the end of the study period and the maximum detection in soil (1556 ppb from the 0-15 cm depth, bare plot) or thatch (541 ppb from the 0-7.5 cm thatch layer, turf plot).

² Calculated by the reviewer after adding transformation product concentrations in each soil depth detected at the end of the study period and then dividing by the maximum propiconazole detection in soil. The sum is not intended to express a concentration by depth, but rather approximate a concentration if all residues measured were confined to a single layer. Transformation product concentrations were not converted to parent equivalents prior to determining transformation.

³ Residues were detected in the maximum soil depth analyzed, 45-60 cm for the bare ground plot, and 30-45 cm for the turf plot. The reviewer notes that the 45-60 cm soil depth was also analyzed for the turf plot at the 360-day sampling interval only, and that CGA-71019 was detected above the LOQ at that interval.

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- 7. **VOLATILIZATION:** The concentration of applied propiconazole lost through volatilization was not determined.
- **8. PLANT UPTAKE:** Plant uptake was not measured.
- 9. LEACHING: In the <u>bare ground plot</u>, propiconazole and CGA-91305 were not detected below the 30-45 cm soil depth, and the transformation products CGA-217495 and CGA-71019 were both detected in the lowest soil depth analyzed, the 45-60 cm soil depth (Table 15, pp. 80-83 in the study report and Table 4, p. 30 in MRID 45528702). In the <u>turf plot</u>, CGA-91305 was not detected below the thatch layer, propiconazole was not detected below the 15-30 cm soil depth, and CGA-217495 and CGA-71019 were both detected in the 30-45 cm soil layer (Table 16, pp. 84-87 in the study report and Table 5, pp. 31-32 in MRID 45528702). Soil samples collected from the turf plot were also analyzed to a depth of 45-60 cm at the 360-day sampling interval only; CGA-71019 was the only analyte detected above the LOQ.
- 10. RUN OFF: Run off was not studied.
- 11. RESIDUE CARRYOVER: In the <u>bare ground plot</u>, the total carryover of the parent and transformation products was 4.8% and 8.3% of the maximum propiconazole detection in soil (1556 ppb), respectively, at the end of the study period, 540 days after the fourth application (Table 15, pp. 80-83 in the study report and Table 4, p. 30 in MRID 45528702). A DT90 value was not determined for propiconazole. In the <u>turf plot</u>, the total carryover of the parent and transformation products was 2.2% and 5.5% of the maximum propiconazole detection in thatch (541 ppb), respectively, at the end of the study period, 540 days after the fourth application (Table 16, pp. 84-87 in the study report and Table 5, pp. 31-32 in MRID 45528702). A DT90 value was not determined for propiconazole.
- 12. SUPPLEMENTARY STUDY RESULTS: Results from the laboratory storage stability study conducted using thatch samples indicated that recoveries of all analytes studied decreased slightly during the 12-month storage interval; however, all mean recoveries were >70% by the end of the storage period (Appendix 2, Table 9, pp. 87-88 in MRID 45528702). Mean recoveries of propiconazole from grass samples ranged from 82.9-101.1% during the 12-month storage interval, with no pattern of decline (Appendix 2, Table 10, p. 89 in MRID 45528702). Recoveries from thatch and grass are reported in the table below.

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Mean recoveries from thatch samples.

Storage Interval					Recovery (%)	(%) A				
(months)	,		(,			
	Fropiconazole	azole	CGA-217495	7495	CGA-91305	1305	Hydroxy Isomers	somers	CGA-71019	1019
	Replicates	Mean	Replicates	Mean	Replicates	Mean	Replicates	Mean	Replicates	Mean
3	102.2	6'96	113.4	114.1	99.4	99.4	92.5	6.68	84.4	92.3
	91.5		114.7		99.3		87.2		100.1	
9	0.96	96.3	92.0	89.2	93.0	92.1	82.7	81.2	73.9	75.7
	96.5		86.3		91.2	·	1.61	Ÿ	. 77.5	
6.	8.06	8.98	6.68	84.0	84.4	82.6	82.5	79.9	72.9	72.6
:	82.7		78.0		80.7		77.2		72.2	
12	89.5	88.4	108.9	101.5	81.0	85.4	7.77	75.1	77.3	71.9
	87.2		94.1		89.7		72.4		66.4	

Data were obtained from Appendix 2, Table 9, pp. 87-88 of MRID 45528702. Percent recoveries were corrected for average procedural recoveries <100%. Means are reviewer-calculated based on replicate values.

Mean recoveries from grass samples.

			Sampling interval (months)	rval (months)		
	0	1	3	9	6	12
Replicates	95.4	85.1	104.7	87.4	6.86	85.6
	94.2	83	93.9	96.2	103.3	80.1
Mean	94.8	84.1	99.3	91.8	101.1	82.9

Data were obtained from Appendix 2, Table 10, p. 89 of MRID 45528702. Percent recoveries were corrected for average procedural recoveries <100%. Means are reviewer-calculated based on replicate values.



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III. STUDY DEFICIENCIES:

- 1. A storage stability study was not conducted using soil collected from the test site. However, the study authors stated that a storage CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 decreased slightly over time and exhibited questionable stability stability study of propiconazole and its transformation products, CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 Results from the stability study indicated that propiconazole was stable in soil for the duration of the 12-month storage interval, with recoveries ranging from 77.7% to 110.0% with no pattern of decline. However, recoveries of the transformation products was conducted under freezer conditions for up to 12 months (9 months for CGA-71019) in a separate study, MRID 45528703. for the duration of storage (see Table 19, pp. 63-64 of MRID 45528703).
- detected at levels above the LOQ in the lowest soil depth analyzed in the bare ground plot (the 45-60 cm depth) and in the turf plot notes that soil samples were collected to a depth of 120 cm; however, samples were not processed and analyzed below the 45-60 cm depth for the bare ground plot (p. 34). Soil samples collected from the turf plot below the 30-45 cm depth were not analyzed (the 30-45 cm depth; Tables 15-16, pp. 80-87 in MRID 45528701 and Tables 4-5, pp. 30-32 in MRID 45528702). The reviewer The depth of leaching was not determined for the transformation products CGA-217495 and CGA-71019, both of which were with the exception of samples collected at the 360-day sampling interval, which were analyzed to a depth of 45-60 cm 7



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IV. REVIEWER'S COMMENTS:

The study authors calculated half-lives for propiconazole using linear regression, non-linear regression, and ModelMaker (Figures 4, 6 and 8, pp. 97, 99 and 101, respectively, and Appendix 4, pp. 370-380). Linear regression methods gave the highest half-lives in all cases. The table below provides a summary of registrant-calculated half-lives.

	Time frame	Half-life (days)	K (days¹)	R ²
Bare ground plot (0-15 cm soil)	cm soil)			
Linear regression	0-180 days after last application	103.2	2900'0	0.95
Nonlinear regression	0-180 days after last application	2.79	0.0071	0.94
ModelMaker	All (0-568 days after first application)	85	0.0082	6.0
Turf plot (grass)				
Linear regression	0-180 days after last application	17.5	0.0396	0.97
Nonlinear regression	0-180 days after last application	6.5	0.1058	0.94
ModelMaker	All (0-568 days after first application)	9.3	0.0746	0.72
Turf plot (thatch, 0-7.5 cm)	5 cm)			
Linear regression	0-180 days after last application	56.6	0.0123	0.84
Nonlinear regression	0-180 days after last application	34.8	0.0199	0.73
ModelMaker	All (0-568 days after first application)	24	0.0289	69:0

- The chemical names and molecular weights of the transformation products of propiconazole were not reported.
- Transformation products CGA-217495, CGA-91305, CGA-118244, CGA-118245, CGA-136735, and CGA-71019 by using High The study authors stated that the soil method was previously validated and described in a previous study report (Novartis Analytical Method AG-677 titled "Analytical Method for the Determination of Propiconazole (CGA-64250) and its



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Performance Liquid Chromatography with Mass Spectrometric Detection Including Method Validation Data). The results from the method validation report were not reproduced in the terrestrial field dissipation study report.

- application, mean recoveries of propiconazole, CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 from soil were 92.7 $89.8 \pm 7.2\%$, $97.2 \pm 12.5\%$, $96.0 \pm 10.5\%$, and $96.4 \pm 22.6\%$, respectively, and corresponding recoveries from thatch were $93.1 \pm$ 78.3 ± 11.0% (Appendix 3, Tables 10-12, pp. 283-285). For samples analyzed following 180 days following the last application, were $80.6 \pm 15\%$, $90.8 \pm 10.4\%$, $95.3 \pm 11.6\%$, $94.4 \pm 10.9\%$, and $82.7 \pm 13\%$. Mean recovery of propiconazole from grass was mean recoveries of propiconazole, CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 from soil were 89.9 ± 8.0%, \pm 10.2%, 86.1 \pm 11.3%, 106 \pm 15.2%, 100 \pm 11.5%, and 84.6 \pm 18.4%, respectively, and corresponding recoveries from thatch 11.1%, 91.2 \pm 10.3%, 101.7 \pm 11.2%, 95.1 \pm 8.6%, and 98.3 \pm 25.9%. Mean recovery of propiconazole from grass was 84.3 \pm Concurrent recoveries were determined for propiconazole and its transformation products in soil, thatch, and grass samples at concentrations of 5, 50, 100, 250, 500, 1000, and 2000 ppb (p. 39). For samples analyzed through 180 days following the last 8.4% (Appendix 2, Tables 6-8, pp. 84-86 in MRID 45528702). 4.
- 5. The reviewer notes that an additional field dissipation study was conducted on a bare plot in California (MRID 45528703).

V. REFERENCES:

- Section 164-1, Terrestrial Field Dissipation Studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate,
- U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010. 5.
- U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078. 3



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Data Requirement:

PMRA Data Code:

EPA DP Barcode: NA OECD Data Point: EPA Guideline: 164-1

Test material: CGA-64250

End Use Product name: Tilt 3.6E

Concentration of a.i.: 42.2%

Formulation type: Emulsifiable concentrate

Active ingredient

Common name: Propiconazole.

Chemical name

IUPAC:

cis-trans-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-

1,2,4-triazole.

CAS name:

1-[[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-

triazole.

CAS No:

60207-90-1. CGA-64250.

Synonyms: SMILES string:

Clc1cc(ccc1C1(Cn2cncn2)OC(CO1)CCC)Cl.

Primary Reviewer: Dan Hunt

Dynamac Corporation

Signature:

Date:

QC Reviewer: Joan Harlin

Dynamac Corporation

Signature:

Date:

Secondary Reviewer: James Lin

EPA

Signature:

Date:

Company Code:

Active Code:

Use Site Category:

EPA PC Code: 122101

CITATION: Manuli, P.J. and B. Jacobson. 1999. Terrestrial field dissipation of Tilt® on bare soil in California. Unpublished study performed by Waterborne Environmental, Inc., Leesburg, VA, Plant Sciences, Inc., Watsonville, CA, and Adpen Laboratories, Jacksonville, FL, and sponsored and submitted by Novartis Crop Protection, Inc., Greensboro, NC. WEI Study No.: 242-28. Novartis Study No.: 115-97. Study initiation July 29, 1997, and completion June 4, 1999 (p. 7). Final report issued June 4, 1999.



Administrative Conclusions: This study is classified acceptable and partially satisfies the guideline requirement for a terrestrial field dissipation study.

EXECUTIVE SUMMARY:

Soil dissipation/accumulation of *cis-trans*-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (propiconazole; CGA-64250) under U.S. field conditions was conducted in a bare plot of sandy loam soil in California (ecoregion not reported). The experiment was carried out in accordance with USEPA Subdivision N Guideline §164-1 and in compliance with the USEPA GLP standards. Propiconazole was broadcast sprayed four times (at 7-day intervals) at a target application rate of 0.137 kg a.i./ha/application (0.122 lb a.i./A/application) in a test plot measuring approximately 43 x 24 m that was divided into five sampling zones. The test substance was applied at 110% of the maximum use rate according to the product label. Rainfall was supplemented with irrigation to reach 114% of the target moisture input during the study period. The treated plot was located 37 m away from the control plot.

The application rate was verified for each test application using fifteen Whatman No. 3 filter papers (15-cm diameter) that were placed in petri dish tops that were then placed randomly on the soil surface of the treated plot immediately prior to each test application. Mean recoveries of propiconazole from the application rate monitors were 70%, 72%, 75%, and 72% of the target application rate for each of the four applications, respectively. Field spikes were prepared for propiconazole and its transformation products but the samples were not analyzed in this study.

Soil samples were taken prior to and following each application and at 1, 3, 7, 14, 28, 61, 89, 118, 183, 278, 364, 479, and 567 days following the fourth application to a depth of 0-120 cm. Soil samples were reflux extracted with 70% methanol:deionized water, passed through a SAX SPE column, then applied to a ENV SPE column attached on top of a SCX SPE column. The SPE columns were disconnected and eluted separately for **propiconazole**, **CGA-217495**, **CGA-91305**, **CGA-71019** and Hydroxy Isomers, **CGA-118244**, **CGA-118245**, and **CGA-136735**. Samples were analyzed following up to 221 days for propiconazole, CGA-217495, CGA-91305, and Hydroxy Isomers, and up to 357 days for CGA-71019. The LOQ was 5.0 ppb for all analytes in soil.

The measured zero-time concentration of **propiconazole** in the 0-15 cm soil depth was 54.7 ppb, which is 90% of the applied rate. Propiconazole was detected in the 0-15 cm soil depth at 75.6 ppb following the second application, 90.7 ppb following the third application, and a maximum of 192.0 ppb following the fourth application. Following the fourth application, propiconazole decreased to 77.2 ppb by 89 days and 51.5 ppb by 118 days, and ranged from 58.3-97.7 ppb from 183-479 days posttreatment. Propiconazole was not detected below the 0-15 cm soil depth. The major transformation products detected were CGA-217495 and CGA-91305. **CGA-217495** was initially detected in the 0-15 cm soil depth at 5.2 ppb following the fourth application, increased to 10.0-11.1 ppb (4.1-4.5% of the total applied propiconazole) from 28-118 days, and decreased to 5.9 ppb by 479 days, the last sampling interval. **CGA-91305** was initially detected in the 0-15

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cm soil depth at 5.3 ppb following the fourth application and increased to a maximum of 10.6 ppb (4.3% of the total applied propiconazole) by 479 days. No transformation products were detected below the 0-15 cm soil depth.

Under field conditions at the test site, propiconazole had a reviewer-calculated half-life value in the 0-15 cm soil depth of 462 days ($r^2 = 0.24$) after the fourth application, calculated using linear regression. However, the reviewer notes that the dissipation pattern was bi-phasic, with a decline phase through approximately 118 days posttreatment followed by a stationary phase through the end of the study period. The DT50 was less than 89 days. A DT90 value was not determined. The total carryover of residues of propiconazole and its transformation products was 39.6% and 6.7% of the theoretical amount (determined based on a theoretical concentration of 61.0 ppb per application for the 0-15 cm soil depth and four test applications), respectively, at 479 days after the fourth application, the last sampling interval that samples were analyzed.

The major route of dissipation of propiconazole under terrestrial field conditions at the test site was transformation.

RESULTS SYNOPSIS

Location/soil type: Watsonville, California/Sandy loam (0-120 cm).

Half-life: 462 days (reviewer-calculated, based on residues in the 0-15 cm soil layer only).

DT90: Not determined.

Major transformation products detected: CGA-217495 and CGA-91305.

Dissipation routes: Transformation.

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I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The study was conducted according to USEPA Pesticide

Assessment Guidelines Subdivision N, §164-1 (p. 1). No deviations from EPA Subdivision N, §164-1 were noted.

COMPLIANCE: The study was conducted in compliance with USEPA FIFRA

(40 CRF Part 160) Good Laboratory Practice standards (p. 3). Signed and dated GLP Compliance, Quality Assurance, Data Confidentiality, and Certification of Authenticity statements

were provided (pp. 2, 3 5, and 6).

A. MATERIALS:

1. Test Material cis-trans-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-

ylmethyl]-1H-1,2,4-triazole (propiconazole; CGA-64250; Table

1, p. 42).

Chemical Structure

of the active ingredient:

See DER Attachment 2.

Description:

Emulsifiable concentrate formulation (p. 21).

Storage conditions of

test chemicals:

Propiconazole was stored at room temperature (0 to 38°C; p.

42) and its transformation products were stored refrigerated

(Appendix V, p. 203).

Physico-chemical properties of propiconazole

Parameter	Values	Comments
Water solubility	Not reported	
Vapour pressure/volatility	Not reported	
UV absorption	Not reported	
pKa	Not reported	
K _{ow} /log K _{ow}	Not reported	
Stability of Compound at room temperature	Not reported	

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2. Test site: The test site was located approximately 1 mile south of Watsonville, California, in Santa Cruz County (p. 22; Figures 1-2, pp. 68-69). The study site was representative of a geographic and climatic region for celery production in California (p. 15). The soil at the test site was classified as an Elder sandy loam and was characterized as sandy loam from 0 to 120 cm (p. 22; Table 3, p. 45). An agricultural chemical plot history indicated that Diazinon, Bravo 500, Kocide, Orthene, DPX-KN128, Malathion, Rally, and Thiolux had been applied to the treated plot within the last three years (Table 2, p. 43).

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

Details		Test site
Geographic	Latitude	Not reported
coordinates	Longitude	Not reported
	Province/State	California
	Country	US
	Ecoregion	Not reported
Slope Gradient		1%
Depth to ground water (m)		>3 m
Distance from weather station used for climatic measurements		Precipitation, daily air and soil temperature (6-inch depth), and pan evaporation data were recorded on-site throughout the study period.
	starting or during the 30 year normal levels	Yes. Total water input (precipitation plus irrigation) during the study period was 122.31 inches or 114% of the target moisture input during the study period. The target moisture input was determined by taking 120% of the 30-year average or 150% of the theoretical crop requirement for celery, whichever was greater.

Data were obtained from pp. 22 and 24 and Table 4, pp. 46-47 of the study report.

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

Use	Year	Treated plot	Control plot
Crops grown	Previous year	Strawberry	Celery
	2 years previous	Celery	Fallow
	3 years previous	Head and leaf lettuce.	Head and leaf lettuce.
Pesticides used	Previous year	DPX-KN128, Malathion, Rally and Thiolux.	Bravo
	2 years previous	Diazinon, Bravo 500, Kocide and Orthene.	None
	3 years previous	Diazinon	Diazinon
Fertilizers used	Previous year	Not reported	Not reported
	2 years previous	Not reported	Not reported
	3 years previous	Not reported	Not reported
Cultivation methods, if	Previous year	Not reported	Not reported
provided (eg., tillage)	2 years previous	Not reported	Not reported
	3 years previous	Not reported	Not reported

Data were obtained from Table 2, p. 43 of the study report.

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3. Soils:

Table 3: Properties of the soil from the test site.

Property				Deptl	h (cm)			
	0-15	15-30	30-45	45-60	60-75	75-90	90- 105	105- 120
Textural classification	SL	SL	SL	SL	SL	SL	SL	SL
% sand	72	70	70	66	58	52	64	70
% silt	18	20	22	24	32	38	26	22
% clay	. 10	10	8	10	10	10	10	8
pН	6.0	6.1	5.9	6.1	6.2	6.4	6.5	6.6
Total organic matter (%)	1.4	1.5	1.3	1.1	1.2	1.1	0.9	0.1
CEC (meq/100 g)	14.7	14.7	13.4	14.4	16.1	17.7	15.2	14.0
Bulk density (g/cm³)	1.36	1.35	1.34	1.29	1.24	1.23	1.28	1.30
Moisture at 1/3 atm (%)	12.0	12.5	12.8	13.8	17.8	19.0	14.9	12.5
Taxonomic classification (e.g., ferro-humic podzol)	Coarse	loamy, mi	xed, super	active, the	rmic, Cun	ulic Haple	oxerolls.	
Soil mapping unit	Not rep	orted						

Data were obtained from Table 3, p. 45 of the study report. SL = Sandy loam.

The taxonomic classification was obtained from the NRCS for the Elder soil series.

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B. EXPERIMENTAL DESIGN:

1. Experimental design:

Table 4: Experimental design.

Details		Test plot	
Duration of study		586 days (567 days after the last application)	
Bare or turf		Bare	
Control used (Yes/No)		Yes	
No. of replications	Controls	One	
	Treatments	One, divided into five sampling zones.	
Plot size	Control	18.2 x 10.0 m	
(L x W m)	Treatment	42.6 x 24.3 m	
Distance between control pl	ot and treated plot	37.4 m	
Distance between treated pl	ots	N/A	
Application rate(s) used (g	a.i/ha)	137 g a.i./ha/application	
Was the maximum label rat (Yes/No)		The application rate was 110% of the maximum label rate.	
Number of applications		Four	
Application Date(s) (dd	Application 1	06/08/1997	
mm yyyy)	Application 2	13/08/1997	
	Application 3	20/08/1997	
	Application 4	27/08/1997	
For multiple applications, application rate at Day 0 and at each application time (mg a.i./kg soil) ¹		0.061 mg a.i./kg	
Application method (eg., sp	oraying, broadcast etc.)	Broadcast spray	
Type of spray equipment, i	f used	Tractor-mounted sprayer equipped with eight TeeJet 8005 nozzles spaced 20 inches apart and at a height of 18-19 inches.	
Total volume of spray solutotal amount broadcasted/p		40 gal/A	
Identification and volume of used	of carrier (e.g., water), if	Water	
Name and concentration of and/or surfactants, if used	co-solvents, adjuvants	None	

Details		Test plot				
Indicate whether the following were submitted:	ng monthly reports					
Precipitation Average minimum and maxi Average minimum and maxi Average annual frost-free pe	mum soil temperature	Yes Yes No, averag No	ge only (6-inch d	lepth).		
Indicate whether the Pan eva submitted	poration data were	Yes	· · · · · · · · · · · · · · · · · · ·			
Meteorological conditions			A	plication		
during application		1	2	3	4	
	Cloud cover	100%	100%	100%	10%	
	Temperature (°C)	13.9	16.7	18.3	22.2	
	Humidity	94%	84%	95%	69%	
	Wind speed (mph)	0	0	0-1	0	
	Sunlight (hr)	Not report	ed			
Pesticides used during study			-			
name of product/a.i concent amount applied: application method:	ration:	Roundup Seven app Not report	lications at 1.52	lb a.i./A.		
name of product/a.i concent amount applied: application method:	ration:	Gramoxone One application at 3 pt/A. Not reported				
Supplemental irrigation use	d (Yes/No)	Yes				
If yes, provide the following	g details:	1	* .			
No. of irrigation: Interval between irrigation: Amount of water added each Method of irrigation:	h time:	42 2-200 day 0.37-2.32 Overhead	inches			
Indicate whether water rece irrigation equals the 30 year (Yes/No)	ived through rainfall + average rainfall	Yes				
Were the application concer (Briefly describe in Section	ntrations verified? 2*, if used)	Yes				
Were field spikes used? (Br 31, if used)	iefly describe in Section	Yes				
Good agricultural practices	followed (Yes or No)	Not report	ted	·		

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Details	Test plot
Indicate if any abnormal climatic events occurred during the study (eg., drought, heavy rainfall, flooding, storm etc.)	Total precipitation in January and February 1998 was 27.65 inches, compared to a historical average of 7.58 inches.
If turf plots are used, provide the following details:	N/A
Plant - Common name/variety: Details of planting: Crop maintenance (eg., fertilizers used):	
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 ¹)	Yes
Run off included in the study (Yes/No) (if included, describe in Section 6*)	No

Data were obtained from pp. 21-26; Table 2, p. 44; Tables 4-6, pp. 46-49; Figure 3, p. 70 and Appendix IV, pp. 163-182 of the study report. The plot areas were conventionally prepared by disking, preirrigating, rototilling, and then rolling with a ringroller prior to the first application.

*2. Application Verification: The application rate was verified for each test application using fifteen Whatman No. 3 filter papers (15-cm diameter) that were placed in petri dish tops that were then placed randomly on the soil surface of the treated plot immediately prior to each test application (p. 26). All plate tops were collected, sealed, and placed in freezers at the field facility within 2 hours of the test applications. The filter papers were extracted with methanol and the extracts were diluted with methanol and water prior to analysis by LC/MS/MS (p. 31; Appendix V, p. 193). Filter papers were analyzed for propiconazole and not for transformation products of propiconazole.

In addition to the application verification procedure described above, a set of six 10-mL spray solution samples was collected from the spray tank at each application (three samples were collected prior to and three samples were collected following each test application) to verify the concentration of propiconazole in the spray solution (p. 26). Spray solution samples were diluted with 10% methanol:water and analyzed for propiconazole by LC/MS/MS (p. 31; Appendix V, p. 193).

- ¹ 3. Field Spiking: Field spikes (transit stability samples) were prepared in duplicate for propiconazole and its transformation products CGA-91305, CGA-217495, Hydroxy Isomers, and CGA-71019 by fortifying control soil at the field site with each analyte at 0.50 ppm (pp. 29-30). The field spikes were placed into frozen storage at the field facility until sent to the analytical laboratory under the same conditions as the test samples.
- § 4. Volatilization: Volatilization was not measured.



¹ Registrant-calculated value (p. 33). The reviewer-calculated value was 0.067 mg a.i./kg, based on the site-specific bulk density of the 0-15 cm soil depth (1.36 g/cm³) and the target application rate of 0.122 lb a.i./A for each application.

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5. Leaching: Fifteen cores were taken from the treated plot prior to (either one day before or immediately before) and following each application and at 1, 3, 7, 14, 28, 61, 89, 118, 183, 278, 364, 479, and 567 days following the fourth application to a depth of 0-120 cm to determine the mobility of the test substance in the soil profile (pp. 26-27; Table 7, p. 50).

7. Supplementary Study: To determine the frozen storage stability of propiconazole and the transformation products CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 in soil, samples were fortified in duplicate with each analyte at 1000 ppb and stored frozen until analysis (p. 31 and Appendix V, p. 195). Samples were analyzed at day 0 and following 1, 3, 6, 9, and 12 months of storage, with the exception of CGA-71019 which was not analyzed at 12 months. The study authors stated that additional analyses of samples will be conducted at a later date (Appendix V, p. 197).

8. Sampling:

Table 5: Soil sampling.

Details	Treated plot
Method of sampling (random or systematic)	Random
Sampling intervals	Prior to and following each application and at 1, 3, 7, 14, 28, 61, 89, 118, 183, 278, 364, 479, and 567 days following the fourth application.
Method of soil collection (eg., cores)	Separate 0-15 cm and 15-120 cm cores were collected.
Sampling depth	120 cm, with the exception of cores collected immediately following the first application which were collected to a depth of 15 cm.
Number of cores collected per plot	15 (three from each sampling area)
Number of segments per core	Five
Length of soil segments	15 cm (0-15, 15-30, 30-45 and 45-60 cm sections) or 60 cm (60-120 cm section).
Core diameter (Provide details if more than one width)	5.325 cm (2.13 inches) for the 0-15 cm depth samples and 4.075 cm (1.63 inch) for the 15-120 cm depth samples.
Method of sample processing, if any	Following sectioning of the soil cores, three sample composites were prepared for each sampling interval and depth by combining one core from each of the five sampling zones. The method of soil processing was not reported.
Storage conditions	Frozen
Storage length (days)	Up to 221 days for propiconazole, CGA-217495, CGA-91305, and Hydroxy Isomers, and up to 357 days for CGA-71019.



^{*6.} Run off: Run off was not studied.

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Data were obtained from pp. 26-29 and 31 and Table 7, p. 50 and Appendix V, Tables 1.a-1.c, pp. 212-220 of the study report.

9. Analytical Procedures: Soil samples were analyzed for propiconazole (purity of analytical standard: 97.2%) and the transformation products CGA-217495 (purity of analytical standard: 91.6%; 98.1%), CGA-91305 (purity of analytical standard: >99.9%), CGA-71019 (purity of analytical standard: >99.9%) and Hydroxy Isomers, CGA-118244 (purity of analytical standard: 98.4%), CGA-118245 (purity of analytical standard: >99.9%) and CGA-136735 (purity of analytical standard: 99.7%; Appendix V, Figures 4-5, pp. 203-204) using analytical method AG-677 (pp. 31-32; Appendix V, p. 194). The chemical names of the transformation products were not reported.

Soil samples (20 g) were reflux extracted with 100 mL of 70% methanol:deionized water for 1 hour and filtered (GF/F vacuum filtration; Appendix V, p. 194 and Figure 1, p. 198). After the addition of 100 μ L of concentrated ammonium hydroxide, the sample was passed through a preconditioned SAX SPE column and concentrated using a rotovap. The sample was acidified with 100 μ L of acetic or phosphoric acid, diluted with deionized water and passed through a preconditioned ENV SPE column attached on top of a preconditioned SCX SPE column. The SPE columns were disconnected and eluted separately. ENV analytes (propiconazole, CGA-217495, CGA-91305 and Hydroxy Isomers) were eluted with acetonitrile, concentrated to 3 mL, and then diluted with acetonitrile and deionized water prior to analysis by LC/MS. SCX analytes (CGA-71019) were eluted with 2.5% ammonium hydroxide in 70% (v/v) methanol:deionized water, concentrated to 3 mL, then diluted with methanol and deionized water prior to analysis by LC/MS. The LOQ was 5.0 ppb for all analytes in soil (pp. 31-32; Appendix V, p. 195).

LC/MS/MS operating parameters

Parameters	Compou	nds analyzed
	Propiconazole, CGA-217495, CGA- 91305 and Hydroxy Isomers	CGA-71019
LC/MS/MS	PE Sciex API 365 with TurbolonSpray Inlet	PE Sciex API 365 with TurboIonSpray Inlet
Column	Intersil ODS-2, 5 µm particle size, 4.6 mm i.d., 15 cm length	Zorbax 300 SCX, 5 µm particle size, 4.6 mm i.d., 15 cm length
Mobile phase	A: 0.1% (v/v) Acetic acid in acetonitrile B: 0.1% (v/v) Acetic acid in purified water	A: 25% (v/v) Methanol/water, 0.1% acetic acid B: 25% (v/v) Methanol/water, 20 mM ammonium acetate
Flow rate	1.5 mL/min	1.0 mL/min
Gradient	A:B (v:v) 30:70 to 75:25 to 100:0	Isocratic, A:B (v:v), 95:5

Data were obtained from Appendix V, pp. 199-200 of the study report.

II. RESULTS AND DISCUSSION

1. APPLICATION MONITORS: Mean recoveries of propiconazole from the application rate monitors placed in the treated plot were $0.96 \pm 0.13~\mu g/cm^2$, $0.99 \pm 0.14~\mu g/cm^2$, $1.02 \pm 0.11~\mu g/cm^2$, and $0.98 \pm 0.10~\mu g/cm^2$ for each of the four applications, respectively, which represents 70%, 72%, 75%, and 72% of the target application rate (p. 33; Table 12, p. 56).

The mean concentrations of propiconazole in the tank mix samples were $319 \pm 8 \mu g/mL$, $318 \pm 16 \mu g/mL$, $293 \pm 23 \mu g/mL$, and $306 \pm 38 \mu g/mL$ for each of the four applications, respectively, which represents 87%, 87%, 80%, and 83% of the expected concentration (p. 33; Table 11, p. 55).

- 2. RECOVERY FROM FIELD SPIKES: Field spikes were prepared for propiconazole and its transformation products but the samples were not analyzed for this report (pp. 29-30).
- 3. MASS ACCOUNTING: A mass balance was not determined.

Table 6. Mean concentration of propiconazole residues expressed as ppb soil.

Compound	Soil	Sampling	times (app	lication or d	lays follow	ing the last a	pplication)
	depth (cm)	App 1	7	App 2	6	App 3	6
Propiconazole	0-15	54.7	28.9	75.6	46.2	90.7	93.8
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-217495	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-91305	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Hydroxy Isomers	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
CGA-71019	0-15	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

Data were obtained from Tables 14-18, pp. 58-62 of the study report. The LOQ was 5.0 ppb. All values are means of three replicates. Total extractable and total non-extractable residues were not determined.

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Table 6 (cont.). Mean concentration of propiconazole residues expressed as ppb soil.

Compound	Soil depth				Samplir	Sampling times (application or days following the last application)	applicat	ion or da	rys follor	ving the	last app	lication)			
	(cm)	App 4	1	3	7	14	28	61	68	118	183	278	364	479	267
Pròpiconazole	0-15	192.0	170.7	144.5	124.3	133.0	156.3	102.8	77.2	51.5	71.8	7.76	58.3	9.96	ļ
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
CGA-217495	0-15	5.2	6.4	5.6	6.4	7.7	11.1	10.3	10.0	11.0	6.1	6.9	<5.0	5.9	
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
CGA-91305	0-15	5.3	<5.0	<5.0	<5.0	6.1	8.2	7.6	6.0	5.5	5.3	7.0	6.9	10.6	
	15-30	<5.0	0.2>	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	į
CGA-71019	0-15	<5.0	5.3	5.3	<5.0	<5.0	6.4	5.1	5.1	<5.0	<5.0	<5.0	<5.0	<5.0	
	15-30	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	
	30-45	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.1	<5.0	<5.0	<5.0	

Data were obtained from Tables 14-18, pp. 58-62 of the study report. The LOQ was 5.0 ppb. All values are means of three replicates. Hydroxy Isomers were not detected above the LOQ at any sampling interval. Total extractable and total non-extractable residues were not determined. PMRA Submission Number {.....}

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4. PARENT COMPOUND: The measured zero-time concentration of propiconazole in the 0-15 cm soil depth was 54.7 ppb, which is 90% of the applied rate (registrant-calculated; p. 33). Propiconazole was detected in the 0-15 cm soil depth at 75.6 ppb following the second application, 90.7 ppb following the third application, and was a maximum of 192.0 ppb following the fourth application (Table 14, p. 58). Following the fourth application, propiconazole decreased to 77.2 ppb by 89 days and 51.5 ppb by 118 days, and ranged from 58.3-97.7 ppb from 183-479 days posttreatment. Propiconazole was not detected below the 0-15 cm soil depth.

The reviewer-calculated half-life of propiconazole in soil under terrestrial field conditions was 462 days after the fourth application ($r^2 = 0.24$), based on all replicate data points and calculated using linear regression analysis performed on a plot of ln-transformed propiconazole concentrations vs. time and the equation $t_{1/2} = -\ln 2 / k$, where k is the rate constant. However, the reviewer notes that the dissipation pattern was bi-phasic, with a decline phase through approximately 118 days posttreatment followed by a stationary phase through the end of the study period. The study authors stated that this indicates that degradation of the test substance was limited by the relatively strong binding mechanism in the soil matrices. The DT50 was less than 89 days. A DT90 value was not determined.

5. TRANSFORMATION PRODUCTS: The major transformation products were CGA-217495 and CGA-91305 (chemical names were not reported; structures were reported in Appendix V, Figure 5, p. 204). A transformation product was considered a major transformation product if its maximum concentration exceeded 10% of the total applied propiconazole or 0.01 ppm.

CGA-217495 was initially detected in the 0-15 cm soil depth at 5.2 ppb following the fourth application, increased to 10.0-11.1 ppb (4.1-4.5% of the total applied propiconazole) from 28-118 days, and decreased to 5.9 ppb by 479 days, the last sampling interval (Table 15, p. 59). CGA-91305 was initially detected in the 0-15 cm soil depth at 5.3 ppb following the fourth application and increased to a maximum of 10.6 ppb (4.3% of the total applied propiconazole) by 479 days (Table 16, p. 60). The minor transformation product CGA-71019 was initially detected in the 0-15 cm soil depth at 5.3 ppb at 1 day following the fourth application, increased to a maximum of 6.4 ppb by 28 days, and was last detected at 5.1 ppb at 89 days posttreatment. No transformation products were detected below the 0-15 cm soil depth. The percentage of each transformation product, in terms of percent of the total applied propiconazole, was determined using actual transformation product concentrations instead of using parent equivalent values because the reviewer could not convert transformation product concentrations to parent equivalents since the molecular weights of the transformation products were not reported.

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Table 7: Chemical names and CAS numbers for the transformation products of propiconazole.

Applicant's Code Name	CAS Number	CAS and/or IUPAC Chemical Name(s)	Chemical formula	Molecular weight	SMILES string
CGA-217495					
CGA-91305					
CGA-118244					
CGA-118245					
CGA-136735					
CGA-71019					

Structures are presented in Appendix V, Figure 5, p. 204 in the study report. Chemical names were not reported.

6. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES: Non-extractable residues were not measured.

Table 8: Dissipation routes of propiconazole under field conditions.

Route of dissipation		% of applied amount (at the end of study period)		
		Test plot		
Accumulation (residue	s) in soil/carry over	39.6%		
Transformation ²	CGA-217495	2.4%		
	CGA-91305	4.3%		
	CGA-71019	0%		
Total		6.7%		
Leaching, if measured		No analytes were detected below 0-15 cm with one exception (CGA-71019 was detected in one replicate sample in the 30-45 cm soil depth).		
Volatilization, if measu	red	Not measured		
Plant uptake, if measured		N/A		
Run off, if measured		Not measured		
Total				

Data were obtained from Tables 14-18, pp. 58-62 of the study report.

¹ Calculated by the reviewer from the residue detected at the end of the study period and the total theoretical application of 244 ppb for the 0-15 cm soil depth, based on four test applications (calculated from the registrant-calculated theoretical concentration of 61.0 ppb per application for the 0-15 cm soil depth).

² Calculated by the reviewer by dividing the transformation product concentrations in the 0-15 cm soil depth at the end of the study period by the total theoretical application of propiconazole of 244 ppb for the 0-15 cm soil depth, based on four test applications. Transformation product concentrations were not converted to parent equivalents prior to determining transformation.

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- 7. VOLATILIZATION: The concentration of applied propiconazole lost through volatilization was not determined.
- 8. PLANT UPTAKE: N/A.
- **9. LEACHING:** Propiconazole and its transformation products were not detected below the 0-15 cm soil depth with the exception of a single detection of CGA-71019 (one of three replicates) in the 30-45 cm soil depth (Tables 14-18, pp. 58-62).
- 10. RUN OFF: Run off was not studied.
- 11. RESIDUE CARRYOVER: The total carryover of residues of propiconazole and its transformation products was 39.6% and 6.7% of the theoretical amount (determined based on a theoretical concentration of 61.0 ppb per application for the 0-15 cm soil depth and four test applications), respectively, at 479 days after the fourth application, the last sampling interval that samples were analyzed (Tables 14-18, pp. 58-62). A DT90 value was not determined for propiconazole.
- **12. SUPPLEMENTARY STUDY RESULTS:** Results from the stability study indicated that propiconazole was stable in soil for the duration of the 12-month storage interval, with recoveries ranging from 77.7% to 110.0%, with no pattern of decline (Table 19, pp. 63-64). However, recoveries of the transformation products CGA-271495, CGA-91305, Hydroxy Isomers and CGA-71019 decreased slightly over time and exhibited questionable stability for the storage interval. Recoveries are reported in the table below.

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Mean recoveries from soil samples.

Storage Interval					Recovery (%)	у (%)				
(montns)	Propiconazole	lazole	CGA-217495	7495	CGA-91305	1305	Hydroxy Isomers	somers	CGA-71019	1019
	Replicates	Mean	Replicates	Mean	Replicates	Mean	Replicates	Mean	Replicates	Mean
0	87.1	9.68	8.86	8.86	97.6	95.1	9.98	90.1	9.06	85.7
	92.1				92.5		93.6		80.8	
—	104.9	0.86	9.66	103.5	102.0	103.6	100.3	101.9	84.8	76.1
	92.1		107.4		105.2		103.4		67.4	
ĸ	78.7	84.6	120.3	122.2	91.9	93.0	103.5	103.6	9.99	0.99
3	90.4		124.0		94.1		103.6		65.3	
9	115.3	110.0	79.2	6.92	68.5	70.9	69.7	70.4	64.6	66.7
	104.6		74.6		73.2		71.1		8.89	
6	72.9	T.T.	47.1	44.8	62.5	67.7	6.89	9.69	43.9	45.4
	82.5		42.4		72.8		70.3		46.9	
12	85.4	88.8	77.1	71.1	83.9	85.4	78.7	79.8	TBA	
	92.1		65.1		86.9		80.8		TBA	

Data were obtained from Table 19, pp. 63-64 and Appendix V, Table 6, p. 230 of the study report. TBA = To be analyzed.

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III. STUDY DEFICIENCIES: No deficiencies were noted.

IV. REVIEWER'S COMMENTS:

- 1. Recoveries of the transformation products CGA-271495, CGA-91305, Hydroxy Isomers, and CGA-71019 from the frozen storage stability study indicated questionable stability for all analytes through the 12-month storage interval (Table 19, pp. 63-64). The reviewer notes that while recoveries generally decreased during the storage interval, recoveries were variable between intervals. The stability of the transformation products in frozen storage should be re-evaluated after data for the subsequent storage intervals are submitted and any trends in the data become more clear.
- 2. The chemical names and molecular weights of the transformation products of propiconazole were not reported. As a result, the reviewer could not convert transformation product concentrations to parent equivalent values to determine the percentage of each transformation product, in terms of percent of the total applied propiconazole.
- 3. Registrant-calculated half-lives for propiconazole using linear regression were 77 days based on 0- to 118-day data and 462 days based on 0- to 479-day data (Figures 8-9, pp. 75-76). The half-life of propiconazole in soil calculated using the two-compartment model, ModelMaker, was 43.8 days (pp. 37-38; Appendix VI, pp. 294-299).
- 4. The study authors stated that the soil method was previously validated and described in a previous study report (Novartis Analytical Method AG-677 titled "Analytical Method for the Determination of Propiconazole (CGA-64250) and its Transformation products CGA-217495, CGA-91305, CGA-118244, CGA-118245, CGA-136735, and CGA-71019 by using High Performance Liquid Chromatography with Mass Spectrometric Detection Including Method Validation Data). The results from the method validation report were not reproduced in the terrestrial field dissipation study report.
- 5. Concurrent recoveries were determined for propiconazole and its transformation products in soil at concentrations of 5.0, 50.0, 250, and 500 ppb (p. 34). Mean recoveries of propiconazole, CGA-217495, CGA-91305, Hydroxy Isomers, and CGA-71019 from soil were 91.6 ± 10.3%, 92.6 ± 12.5%, 96.8 ± 9.5%, 96.9 ± 8.8%, and 87.8 ± 17.6%, respectively (p. 34; Appendix V, Table 4, p. 227).
- 6. No residues of propiconazole or its transformation products were found at or above the LOQ in any of the control samples analyzed (p. 34).
- 7. The study authors stated that an addendum/amendment to this report providing information on the remaining sampling events would be submitted (p. 21).
- 8. A copy of the Tilt® label was provided in Appendix 1 (pp. 104-110) of the study report.



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- 9. The reviewer notes that an additional field dissipation study was conducted on separate bare ground and turf plots in California (MRID 45528701).
- 10. No quantifiable residues (at or above the LOQ) of CGA-64250 was found in the 6-12 or 12-18 inch soil soil layers through 479 DALA.

No quantifiable residues (at or above the LOQ) of CGA-217495 was found in the 6-12 or 12-18 inch soil soil layers through 479 DALA.

No quantifiable residues (at or above the LOQ) of CGA-91035 was found in the 6-12 or 12-18 inch soil soil layers through 479 DALA.

No quantifiable residues (at or above the LOQ) of Hydroxy Isomerers was found in the 0-6, 6-12 or 12-18 inch soil soil layers through 479 DALA.

No quantifiable residues (at or above the LOQ) of CGA-71019 were found in the 6-12 or 12-18 inch soil soil layers through 479 DALA with the exception of one replicate at 180 DALA (6-12 inch) which had 5.4 ppb.

V. REFERENCES:

- U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 164-1, Terrestrial Field Dissipation Studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.
- 2. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010.
- 3. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.



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Data Requirement: PMRA DATA CODE:

EPA DP Barcode: NA OECD Data Point:

EPA Guideline: Non-guideline

Test material: Propiconazole

End Use Product name: Tilt 3.6 EC

Concentration of a.i.: 42.2%

Formulation type: Emulsifiable concentrate

Active ingredient

Common name: Chemical name

Propiconazole.

IUPAC:

cis-trans-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-

1*H*-1,2,4-triazole.

CAS name:

1-[[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1*H*-1,2,4-

triazole.

CAS No:

60207-90-1.

Synonyms:

CGA-64250.

SMILES string:

Clc1cc(ccc1C1(Cn2cncn2)OC(CO1)CCC)Cl.

Primary Reviewer: Dan Hunt

Signature:

Dynamac Corporation

Date:

QC Reviewer: Joan Gaidos

Dynamac Corporation

Signature:

Date:

Secondary Reviewer: James Lin

EPA

Signature:

Company Code:

Active Code:

Use Site Category:

EPA PC Code: 122101

CITATION: Jacobson, B., N.J. Snyder and P.J. Manuli. 1999. Foliar washoff and field runoff monitoring of Tilt® fungicide applied to celery in California. Unpublished study performed by Waterborne Environmental, Inc., Leesburg, VA, Plant Sciences, Inc., Watsonville, CA, and Novartis Crop Protection, Inc., Greensboro, NC; sponsored and submitted by Novartis Crop Protection, Inc., Greensboro, NC. Novartis No.: 116-97. WEI Study No.: 242.29. Study initiation October 30, 1997, and completion March 3, 1999 (p. 7). Final report issued March 3, 1999.



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Administrative Conclusions: This study was not submitted to fulfill EPA Subdivision N Guideline requirements. The foliar washoff study on celery may provide useful information when assessing the celery use of propiconazole. The runoff study proved that propiconazole can contaminate receiving water bodies when rainfall occurred after the chemical applications.

EXECUTIVE SUMMARY:

Propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4triazole), the active ingredient in Tilt® (containing 42.2% propiconazole), was broadcast four times (6- to 8-day intervals) at a target application rate of 0.124 lb a.i./A/application to a plot of clay loam soil planted with celery in California to determine foliar washoff and field runoff. The type of application and crop was considered to offer one of the worst-case scenarios for field runoff; the application rate represents 110% of the maximum use rate for Tilt® on celery, which represents the highest use rate for Tilt® for any crop. The slope in the test area was estimated to be approximately 2%. Diversion walls were constructed alongside the treated plot to direct overland flow to a single collection point on the east-end of the plot where a flume was installed with a ISCO 6700 autosampler and flow meter configured to collect water samples at the flume. The first test application was made on November 12, 1997 when the celery was at the 12-14 leaves/plant stage and at a height of 12 inches. Mean recoveries of propiconazole from application monitors placed in the treated plot prior to each application indicated that the target application rate was achieved for each of the four applications. Soil (0- to 3-inch depth) and foliage samples were collected from the treated plot prior to the first application, immediately after each of the four test applications, after the initial rainfall event following the first two applications, and at 6 days and 15 days after the last application. Runoff samples were collected at intervals adequate to characterize the rising and recession limbs of each runoff event.

There were a total of 16 runoff events during the 8-week study period, of which 15 followed rainfall events. Total rainfall during the study period was 227% of the normal 6.12 inches of rainfall for the study period. Rainfall of at least 0.27 inches occurred within 24 hours following each of the first three applications, and 2.25 inches of irrigation were applied approximately 24 hours after the last application to force runoff.

Foliage. Propiconazole residues on celery foliage decreased significantly following precipitation/irrigation events following each application, indicating that washoff was occurring. The mean concentration of propiconazole in the celery foliage was 0.492 μ g/cm² following the first application and decreased to 0.037 μ g/cm² after the first runoff event, was 0.171 μ g/cm² following the second application and decreased to 0.057 μ g/cm² following the first runoff event following the second application, and was 0.386 μ g/cm² following the fourth runoff event and decreased to 0.136 μ g/cm² following the forced runoff event following the fourth application.



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The mean percent propiconazole extracted and potentially available for runoff ranged from 63 to 87% following each of the four applications and ranged from 20 to 27% following each runoff event.

Runoff. A total of 2.666 g of propiconazole, representing 5.8% of the total applied propiconazole (based on four applications) was lost from the treated plot during the study period in runoff. The highest concentrations in runoff occurred in the first runoff event following each application, with the highest concentrations generally occurring during the ascending limb or around the peak of the runoff event. The first runoff event following each of the four applications accounted for 72% of the total propiconazole lost in runoff. Subsequent rainfall events produced less runoff of propiconazole because residues had already moved into the soil and were not available to runoff.

Propiconazole was detected in runoff samples collected from the first runoff event following the first application at a concentration of 44-62 ppb, representing a total mass loss of 0.068 g of propiconazole. Following the second application, propiconazole was detected in runoff samples collected from the first runoff event following that application at a concentration of 83-136 ppb, representing a total mass loss of 0.193 g of propiconazole. Propiconazole was detected in runoff samples collected from the first runoff event following the third application at a concentration of 26-110 ppb, representing a total mass loss of 0.703 g of propiconazole. Following the forced runoff event within 24 hours of the fourth application, propiconazole was detected in runoff samples at a concentration of 37-200 ppb, representing a total mass loss of 0.964 g of propiconazole. The forced runoff event was the most intense of all the runoff events, with over 2 inches of irrigation occurring in under two hours. Subsequent rainfall events following the last application produced decreasing propiconazole concentrations in runoff samples, 28-42 ppb following the second runoff event, 13-26 ppb following the third event, 8.9-12 ppb following the fourth event, 7.4-12 ppb following the fifth event and 2.6-5.4 ppb following the seventh event.

Soil. The concentration of propiconazole in the 0- to 3-inch soil depth under the celery canopy ranged from 0.05 to 0.11 ppm following the first three applications, was 0.16 ppm following the fourth application, was 0.18 ppm at 6 days and was 0.14 ppm at 15 days posttreatment of the fourth application. In contrast, propiconazole residues in soil collected from between the crop rows was more variable. The concentration of propiconazole in the 0- to 3-inch soil depth between rows was 0.01 ppm following the first application and increased to 0.15 ppm after the first runoff event, was 0.19 ppm following the second application and increased to 0.37 ppm following the first runoff event following the second application, and ranged from 0.49-0.53 ppm following the fourth runoff event and at 6 and 14 days posttreatment.



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METHODOLOGY:

The foliar washoff and field runoff monitoring of propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1*H*-1,2,4-triazole), the active ingredient in Tilt 3.6 EC (containing 42.2% propiconazole), was studied following four applications (6- to 8-day intervals) of Tilt® at 0.124 lb a.i./A/application to a plot of clay loam soil (0-36 inch depth) planted with celery in California (pp. 22-23). The application rate represents 110% of the maximum use rate for Tilt® on celery, which represents the highest use rate for Tilt® for any crop. The study was conducted for 53 days.

The test site was located approximately four miles south of Watsonville in Santa Cruz County, and is representative of a geographic and climatic region for celery production in California (pp. 22 and 24; Figure 2, p. 68). The slope in the test area was estimated to be approximately 2% and the depth to the water table was >10 feet. The soil at the test site was classified as an Elder sandy loam according to the Santa Cruz County Soil Conservation Service Soil Survey; however, the soil was characterized as clay loam from 0 to 36 inches and 42-48 inches (Table 1, p. 46). The soil organic matter content was 3.4-3.5% in the upper 12 inches and pH ranged from 6.3-6.4 from 0 to 48 inches. The study authors stated that the site represents conditions where runoff potential is high relative to celery growing areas in California. An agricultural chemical plot history indicated that Lannate 90S, Rally 40W, Dibrom 8E, Lorsban 4E, Asana XL, Benlate, Roundup, Goal, Benlate 50W and RH-7988 had been applied to the treated plot within the last three years (Table 2, p. 47). The treated plot measured 67 x 134 ft and was divided into seven sampling areas (designated A-G in Figure 4, p. 70), each containing eight subplots (pp. 24-25; Figure 3, p. 69). A cropped control plot measuring 30 x 35 ft and divided into ten subplots for sampling was located 320 feet from the treated plot.

The treated plot was disked and chisel plowed, and beds were lifted and shaped (40-inch centers), roto-tilled and compacted with a ring-roller in July, 1997 (p. 25). Celery plants were transplanted into the plot on August 28, 1997, approximately ten weeks prior to the first test application.

Diversion walls (plywood boards of ½ inch nominal thickness) were constructed alongside the treated plot to direct overland flow to a single collection point on the east-end of the plot (pp. 24-25; Figures 3-4, pp. 69-70). The diversion walls on the north-end and south-end of the plot were buried approximately six inches with six inches exposed above the ground, and the diversion wall on the east-end of the plot was covered with plastic and buried approximately 12-18 inches with 12-14 inches exposed above the ground. Diversion wall panels were secured to wooden posts at 8-ft intervals and the joints between panels were caulked. The west-end of the plot was bordered by a trench; dimensions were not reported. A fiberglass 0.75 ft H-flume was installed at the runoff collection point on the east-end of the test plot for runoff flow measurement and

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sampling (p. 25; Figure 4, p. 70). The flume was installed with a ISCO 6700 autosampler and flow meter configured to collect water samples at the flume using a flow-activated autosampler.

Rainfall and daily air and soil temperatures were recorded on-site and daily pan evaporation data were recorded approximately 3 miles south of the study site (p. 26). In addition, soil moisture was monitored using tensiometers placed at a depth of 6-inches and 12-inches. Historical meteorological data were obtained from the NOAA weather station located 5 miles southeast of the study site in Watsonville. Precipitation was not supplemented with irrigation during the study period with the exception of 2.0 inches of water applied within 24 hours of the last application to force runoff (p. 36).

The first test application was made on November 12, 1997 when the celery was at the 12-14 leaves/plant stage and at a height of 12 inches (p. 27; Table 5, p. 51). Subsequent applications were made at 6- to 8-day intervals (November 18 and 25, 1997 and December 3, 1997). Environmental conditions at the time of each test application were reported in Table 5 (p. 51). Applications were made using a tractor-mounted sprayer equipped with eight TeeJet 8005VK nozzles spaced 20 inches apart and at a height of 18 inches (p. 26).

The application rate was verified for each test application using ten Whatman No. 3 filter papers (15 cm diameter) that were placed in petri dish tops and placed on top of the celery canopy prior to each test application (application monitors were distributed randomly; p. 28). All plate tops were collected, sealed and placed in freezers at the field facility until shipment to the analytical laboratory. The filter papers were extracted by shaking with acetone for 30 minutes and the extracts were analyzed by gas chromatography (GC) with a nitrogen-phosphorous detector (N/P; p. 35; Appendix VIII, p. 194).

Soil and foliage samples were collected from the treated plot prior to the first application, immediately after each of the four test applications, after the initial rainfall event following the first two applications, and at 6 and 15 days after the last application (pp. 28-29). Runoff samples were collected by the autosampler at intervals adequate to characterize the rising and recession limbs of each of the 16 runoff events (pp. 29 and 31-32).

Three soil samples (3 inch diameter) and three foliage samples (100-cm²) were collected from each of four randomly selected subplots in the treated plot at each sampling interval (p. 30). In each subplot, two soil cores were collected from the top of the beds, under the crop canopy, and one core was collected from the bottom of the trough between beds; cores were collected to a depth of 3 inches. Cores were not collected from troughs that were driven on during the applications. Cores were composited into three samples per sampling event by combining one core from each of the four subplots. Foliage samples were collected using a 1.25-cm² leaf sampler by collecting 20 leaf discs from each of the four assigned subplots.

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The 6700 autosampler was programmed to collect runoff samples if the water level exceeded 0.015 feet (p. 31). Samples were collected at intervals adequate to characterize the rising and recession limbs of each runoff event. Three different sampling schemes were used to collect samples. For runoff events 1-9, the first six samples were taken on a 2 cubic foot accumulated flow interval and the remainder of the samples were taken on a 25 cubic foot accumulated flow interval; for the forced runoff event 10, the first six samples were taken on a 5 cubic foot accumulated flow interval and the remainder of the samples were taken on a 75 cubic foot accumulated flow interval; and for the runoff events 11-16, the first six samples were taken on a 5 cubic foot accumulated flow interval and the remainder of the samples were taken on a 50 cubic foot accumulated flow interval and the remainder of the samples were taken on a 50 cubic foot accumulated flow interval (p. 32). Runoff samples were composited according to the schedule reported in Appendix VIII (pp. 225-229). The flow meter provided a continuous record of the water level in the H-flume for runoff flow rate and volume calculations.

Soil samples were reflux extracted for one hour in 90% methanol/water, filtered and an aliquot was partitioned with hexane (Appendix VIII, p. 195). The hexane was evaporated and the sample volume was adjusted with 30% acetonitrile/water and analyzed by HPLC (Zorbax SB-C18 LC MS column, 2.1 x 50 mm, 5 μ) with mass spectrophotometric (MS) detection (Appendix VIII, p. 291). The HPLC mobile phase was A: 4.9% methanol:95% water:0.1% formic acid, B: 99.9% methanol:0.1 formic acid, A:B: 50:50 to 5:95, v:v. The LOQ was 0.01 ppm (p. 35). Soil samples were analyzed following up to a maximum of 160 days of storage (Appendix VIII, pp. 222-223).

Foliage samples were extracted by shaking for 30 minute with acetone and an aliquot was evaporated to dryness (Appendix VIII, p. 195). The extracts were reconstituted in mobile phase and analyzed by LC/MS as previously described for the soil samples (Appendix VIII, p. 309). The LOQ was 0.05 ppm (p. 35).

Runoff water samples were acidified, loaded onto a Varian ENV SPE column and propiconazole was eluted with acetonitrile (Appendix VIII, pp. 194-195). The eluate was concentrated by rotary evaporation, reconstituted in 30% acetonitrile:water and analyzed by LC/MS as previously described for the soil and foliage samples except that the mobile phase gradient was A:B: 40:60 to 10:90, v:v (Appendix VIII, p. 254). The LOQ was 0.10 ppb (p. 35). Water samples were generally analyzed within 168 days of storage (Appendix VIII, pp. 223-224).

Field spikes (transit stability samples) were prepared for propiconazole by fortifying triplicate 0-to 3-inch depth control soil samples at 0.20 ppm and duplicate 100 mL well water samples at 50 ppb (pp. 32-33). The field spikes were placed into frozen storage at the field facility until sent to the analytical laboratory. The soil samples were extracted 41 days after fortification and the water samples were extracted 35 days after fortification. Individual recoveries of propiconazole from soil ranged from 100-105% and duplicate recoveries from water were both 106%; recoveries were not corrected for procedural recoveries (Appendix VIII, p. 218).



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To determine the frozen storage stability of propiconazole in soil and water samples, soil samples were fortified at 0.20 ppm and water samples were fortified at 50 ppb and stored frozen for up to 180 days (p. 34). Duplicate fortified samples were analyzed at each sampling interval. Recoveries indicated that propiconazole was stable in soil and water for the duration of the 6-month storage interval (Appendix VIII, pp. 215-217). Individual recoveries of propiconazole from soil ranged from 95-110% for all sampling intervals and individual recoveries from water ranged from 74-104%, with no pattern of degradation during storage. Recoveries were not corrected for procedural recoveries.

RESULTS:

Propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) was broadcast four times (6- to 8-day intervals) at a target application rate of 0.124 lb a.i./A/application to a plot of clay loam soil planted with celery in California. The type of application and crop was considered to offer one of the worst-case scenarios for field runoff. The slope in the test area was estimated to be approximately 2%. Diversion walls were constructed alongside the treated plot to direct overland flow to a single collection point on the east-end of the plot where a flume was installed with a ISCO 6700 autosampler and flow meter configured to collect water samples at the flume. The first test application was made on November 12, 1997 when the celery was at the 12-14 leaves/plant stage and at a height of 12 inches. Mean recoveries of propiconazole from application monitors placed in the treated plot prior to each application were 111%, 95%, 95% and 100% of the expected amount for each of the four applications, respectively (p. 38; Table 10, p. 58). Soil and foliage samples were collected from the treated plot prior to the first application, immediately after each of the four test applications, after the initial rainfall or irrigation event following the first two applications, and at 6 days and 15 days after the last application. Runoff samples were collected at intervals adequate to characterize the rising and recession limbs of each runoff event.

Cumulative precipitation plus irrigation during the 8-week study period was 13.89 inches or 189% of the target moisture requirement (120% of the 30-year historical average precipitation or 150% of a celery crop requirement, whichever was greater) for the same time period (7.35 inches; p. 36; Table 3, p. 49). Rainfall of at least 0.27 inches occurred within 24 hours following each of the first three applications, and 2.25 inches of irrigation were applied approximately 24 hours after the last application to force runoff (Table 6, p. 52). Soil moisture data were presented in Table 8 (pp. 55-56) and indicated that soil moisture was high through the 12-inch depth for the study duration (p. 37).



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Foliage. Propiconazole residues on celery foliage decreased significantly following precipitation/irrigation events following each application. The mean concentration of propiconazole in the celery foliage was $0.492~\mu g/cm^2$ following the first application and decreased to $0.037~\mu g/cm^2$ after the first runoff event, was $0.171~\mu g/cm^2$ following the second application and decreased to $0.057~\mu g/cm^2$ following the first runoff event following the second application, and was $0.386~\mu g/cm^2$ following the fourth runoff event and decreased to $0.136~\mu g/cm^2$ following the forced runoff event following the fourth application (Table 13, pp. 62-63; Figure 7, p. 73). The mean percent propiconazole extracted and potentially available for runoff ranged from 63 to 87% following each of the four applications and ranged from 20 to 27% following each runoff event, indicating that washoff was occurring. Propiconazole residues in foliage and the percent extracted are reported in the table below for each sampling interval. All foliage concentrations were reported on a wet-weight basis and were corrected for procedural recoveries (pp. 40-41).

Sampling Event	Days Posttreatment of the Last Application	Total µg/cm	Percent Extracted
Application 1	0	0.492	87
Initial Runoff Event	2	0.037	27
Application 2	0	0.171	63
Initial Runoff Event	2	0.057	20
Application 3	0	0.425	73
Application 4	0	0.386	68
Forced Runoff Event	6	0.136	21
Last Sampling Interval	15	0.179	22

Data obtained from Table 13, pp. 62-63 in the study report.



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Runoff. A total of 2.666 g of propiconazole, representing 5.8% of the total applied propiconazole (based on four applications) was lost from the treated plot during the study period in runoff (p. 41). The highest concentrations in runoff occurred in the first runoff event following each application, with the highest concentrations generally occurring during the ascending limb or around the peak of the runoff event. The first runoff event following each of the four applications accounted for 72% of the total propiconazole lost in runoff.

Following the <u>first application</u>, propiconazole was detected in runoff samples collected from the first runoff event (R01; resulting from 0.43 inches of rainfall; Table 6, p. 52) at a concentration of 44-62 ppb, representing a total mass loss of 0.068 g of propiconazole (Table 14, p. 64). A larger rainfall event, 1.27 inches, occurring 3-4 days after the first application produced a larger net loss of propiconazole, 0.099 g, than the first runoff event, but the concentration of propiconazole in the samples ranged from 9.1-14 ppb.

Following the <u>second application</u>, propiconazole was detected in runoff samples collected from the first runoff event (R03; resulting from 0.56 inches of rainfall; Table 6, p. 52) at a concentration of 83-136 ppb, representing a total mass loss of 0.193 g of propiconazole (Table 14, p. 64). There were no rainfall events after R03 and prior to the third application which resulted in a significant net loss of propiconazole.

Following the third application, propiconazole was detected in runoff samples collected from the first runoff event (R06; resulting from approximately 2.3 inches of rainfall over a two-day period; Table 6, p. 52) at a concentration of 26-110 ppb, representing a total mass loss of 0.703 g of propiconazole (Table 14, p. 64). The second largest net loss of propiconazole occurred following runoff event R08, corresponding to a 0.8-inch rainfall event, and resulted in a net loss of 0.073 g of propiconazole (the concentration of the samples ranged from 8.3-12 ppb).

Following the <u>fourth application</u>, propiconazole was detected in runoff samples collected from the first runoff event (R10; a forced runoff event resulting from 2.25 inches of irrigation; Table 6, p. 52) at a concentration of 37-200 ppb, representing a total mass loss of 0.964 g of propiconazole (Table 14, p. 64). The forced runoff event was the most intense of all the runoff events, with over 2 inches of irrigation occurring in under two hours. Subsequent rainfall events produced decreasing propiconazole concentrations in runoff samples. For example, the second runoff event, occurring just 1-2 days after the last application from a 0.72 inch rainfall event, resulted in sample concentrations ranging from 28-42 ppb and a net loss of 0.237 g of propiconazole (Table 14, p. 65). In comparison, the last runoff event of the study, occurring 32 days after the last application from a 0.88 inch rainfall event, resulted in sample concentrations ranging from 2.6-5.4 ppb and a net loss of 0.039 g of propiconazole. Propiconazole residues in composited runoff samples are reported in the table below. Propiconazole concentrations in runoff water were corrected for procedural recoveries (p. 41).



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Runoff event	Date	Days after previous application (App #)	Concentration range of samples (ppb)		
11	11/14/97	2 (1)	44 - 62	48.5	0.068
2	11/15/97 11/16/97	3-4 (1)	9.1 - 14	292.6	0.099
3 ¹	11/18/97 11/19/97	0-1 (2)	83 - 136	72.6	0.193
4	11/23/97	5 (2)	28 - 41	6	0.006
5	11/25/97	0 (3)	31	8.3	0.007
6 ¹	11/25/97 11/26/97	0-1 (3)	26 - 110	729.2	0.703
7	11/26/97 11/27/97	1-2 (3)	17 - 19	51.3	0.025
8	11/29/97 11/30/97	4-5 (3)	8.3 - 12	28.19	0.073
9	12/03/97	0 (4)	26	10.2	0.008
10¹	12/04/97	1 (4)	37 - 200	787.8	0.964
11	12/04/97 12/05/97	1-2 (4)	28 - 48	269.1	0.237
12	12/06/97 12/07/97	3-4 (4)	13 - 26	356.4	0.146
13	12/07/97 12/08/97	4-5 (4)	8.9 - 12 63.9		0.017
14	12/14/97	11 (4)	7.4 - 12	451.9	0.079
15	01/02/97	30 (4)	6	12.7	0.002
16	01/04/97	32 (4)	2.6-5.4	296.8	0.039

Data obtained from Table 14, pp. 64-65 in the study report. The represented volume (in cubic feet) and the total mass of samples were summed by the reviewer for each runoff event based on discrete runoff samples collected during each runoff event.

¹ First runoff event following the previous application.

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Soil. The concentration of propiconazole in the 0- to 3-inch soil depth under the celery canopy ranged from 0.05 to 0.11 ppm following the first three applications, was 0.16 ppm following the fourth application, was 0.18 ppm at 6 days and was 0.14 ppm at 15 days posttreatment of the fourth application, the last sampling interval (Table 12, p. 61; Figure 6, p. 72). In contrast, propiconazole residues in soil collected from between the crop rows was more variable. The concentration of propiconazole in the 0- to 3-inch soil depth between rows was 0.01 ppm following the first application and increased to 0.15 ppm after the first runoff event, was 0.19 ppm following the second application and increased to 0.37 ppm following the first runoff event following the second application, and ranged from 0.49-0.53 ppm following the fourth runoff event and at 6 and 14 days posttreatment. Propiconazole residues under the crop canopy, between crop rows and the total average are reported in the table below for each sampling interval. All soil concentrations were corrected for procedural recoveries (pp. 39-40).

Sampling Event	Days Posttreatment of the Last Application	Propiconazole residue (ppm)					
		U	nder Crop Ca	nopy	Between rows	Total Average	
		Repl	icates	Average			
Application 1	0	0.06	0.03	0.05	0.01	0.03	
Initial Runoff Event	2	0.05	0.07	0.06	0.15	0.09	
Application 2	0	0.11	0.11	0.11	0.19	0.14	
Initial Runoff Event	2	0.1	0.1	0.1	0.37	0.19	
Application 3	0	0.12	0.02	0.07	0.15	0.1	
Application 4	0	0.12	0.19	0.16	0.53	0.28	
Forced Runoff Event	6	0.16	0.2	0.18	0.52	0.29	
Last Sampling Interval	15	0.13	0.14	0.14	0.49	0.25	

Data obtained from Table 12, p. 61 in the study report.

REVIEWER'S COMMENTS:

1. The reviewer notes that the purpose of the study was to determine the off-site movement of propiconazole through foliar washoff and surface water runoff and that no attempt was made to quantify other dissipation routes of propiconazole under field conditions.

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- 2. The study authors noted that the study was conducted while California was being affected by the 1997 El Nino and that the treated plot received 227% of the normal 6.12 inches of rainfall for the study period (p. 16).
- 3. The study authors stated that the test substance application was timed to coincide with typical fungicide applications for control of early blight (*Cercospora*) and late blight (*Septoria*) in celery in the region (p. 22).
- 4. The study authors stated that the water method was previously validated and described in a previous study report (Novartis Analytical Method AG-677 titled "Analytical Method for the Determination of Propiconazole (CGA-64250) and its Degradates CGA-217495, CGA-91305, CGA-118244, CGA-118245, CGA-136735, and CGA-71019 in Soil and Water by High Performance Liquid Chromatography with Mass Spectrometric Detection Including Method Validation Data). The results from the method validation report were not reproduced in this study report.
- 5. The soil analytical method was validated at concentrations of 0.01, 0.05 and 0.10 ppm using 0- to 3-inch depth control soil from the test site (p. 36). Individual recoveries ranged from 91-103% for the 0.01 ppm fortification, 94-100% for the 0.05 ppm fortification and 93-98% for the 0.10 ppm fortification (Appendix VIII, p. 213). The mean recovery was $97 \pm 4.0\%$.
- 6. Concurrent recoveries were determined for propiconazole in soil (at 0.01, 0.10, 0.20 and 0.50 ppm), foliage (at 0.05, 0.10, 1.0 and 5.0 ppm) and water (at 0.10, 0.5, 1.0 and 10.0 ppm; p. 39; Appendix VIII, pp. 209-211). Mean recoveries of propiconazole were 98 \pm 6.48% from soil, $102 \pm 7.89\%$ from foliage and $87 \pm 8.8\%$ from water.
- 7. Estimated percent celery foliage coverages in the treated plot were $46 \pm 8\%$ at the time of the first application, $53 \pm 9\%$ at the time of the second application, $58 \pm 9\%$ at the time of the third application and $62 \pm 6\%$ at the time of the fourth application (p. 38; Table 11, pp. 59-60).
- 8. In addition to the application verification procedure, a set of six 10-mL spray solution samples were collected from the spray tank at each application (three samples were collected prior to and three samples were collected following each test application) to verify the concentration of propiconazole in the spray solution (p. 28). Spray solution samples were analyzed by gas chromatography equipped with a nitrogen/phosphorous detector (p. 34). The mean concentrations of propiconazole in the tank mix samples represented 94%, 106%, 95% and 98% of the theoretical concentration for each of the four applications, respectively (Table 9, p. 57).



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- A copy of the Tilt® label was provided in Appendix VII (pp. 155-162) of the study report. 9.
- This experiment was conducted in compliance with USEPA FIFRA GLP Standards, with 10. the exceptions noted on page 9 of the study report.
- Form the modeling application viewpoint, the best use of results of this foliar washoff 11. study is to calculate the percent washoff of propiconazole per centimeter (cm) of rainfall amount, if it can be done.

