

US EPA ARCHIVE DOCUMENT



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This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Suite B, Durham, NC 27713; submitted 6/12/2006). The DER was reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

44548402 Vincent, T. (1998) Propiconazole--Magnitude of the Residues in or on Wheat, Including Processed Fractions, Following an Application of TILT; Lab Project Number: 46-96: ABR-97143: 411124. Unpublished study prepared by Novartis Crop Protection, Inc. 189 p.

EXECUTIVE SUMMARY:

Two wheat field trials were conducted in ID and ND in 1996 to compare residues in/on wheat grain and straw resulting from a late-season application of propiconazole. At each site, propiconazole (3.6 lb/gal EC) was applied to 4 separate plots of wheat as a single broadcast foliar application at booting (Feekes Growth Stage 10) or at heading (Feekes Growth Stage 10.5) at 0.11-0.12 lb ai/A or 0.55-0.62 lb ai/A (1x and 5x rates). All applications were made using ground equipment in volumes of 15-21 gal/A, and did not include any adjuvants. Single control and single or duplicate treated samples of grain and straw were harvested 41 and 63-67 days following the application at booting and 30-31 and 55-57 days following the application at heading. Samples were stored up to 3.4 months prior to analysis, an interval supported by available storage stability data.

Combined residues of propiconazole and its 2,4-dichlorobenzoic acid (DCBA) containing metabolites in/on wheat grain and straw were determined using an adequate GC/ECD method (Method AG-454B). For this method, residues are extracted and converted to 2,4-DCBA by base hydrolysis and oxidization with $KMnO_4$. Residues of DCBA are then partitioned into diethyl ether:hexane, concentrated, methylated, and cleaned-up using an acidic alumina cartridge. Methylated DCBA is determined by GC/ECD using external standards, and residues are expressed in parent equivalents. The validated method limit of quantitation (LOQ) is 0.05 ppm, and the limit of detection (LOD) is 0.02 ppm.

Following a single application at 0.11-0.12 lb ai/A (1x), total propiconazole residues in/on grain averaged 0.03 ppm at 41 and 63-67 days after an application at booting (FGS 10). For the application at heading (FGS 10.5), grain residues averaged 0.06 ppm at ~30 days after treatment (DAT) and declined to 0.03 ppm at 55-57 DAT. For straw, average residues following the application at booting were 1.1 ppm at 41 DAT and 0.56 ppm at 63-67 DAT, and average



residues following the application at heading were 1.6 ppm at ~30 DAT and 0.95 ppm at 55-57 DAT.

Following a single application at 0.55-0.62 lb ai/A (5x) at booting, average residues in/on grain were 0.07 ppm at 41 DAT and 0.03 ppm at 63-67 DAT and average residues in/on straw were 6.1 ppm at 41 DAT and 4.1 ppm at 63-67 DAT. Following the application 5x application at heading, average residues in/on grain were 0.30 ppm at ~30 DAT and 0.18 ppm at 55-57 DAT and average residues in/on straw were 7.8 ppm at ~30 DAT and 5.0 ppm at 55-57 DAT.

The tests conducted at both use rates indicate that propiconazole residues in/on wheat grain and straw are higher following an application at the heading stage then at the booting stage. The tests also indicate that residues in both grain and straw decline at longer post-treatment intervals.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the wheat field trial data are classified as scientifically acceptable for purposes of comparing residues resulting from a late season application to wheat at either booting or heading (FGS 10 or 10.5). The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP Barcode D238458.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. The study author cited minor deviations from GLP compliance, pertaining to the collection of weather data, tank mix storage stability data and maintenance of records. None of these deviations affect the overall acceptability of the study.



A. BACKGROUND INFORMATION

Propiconazole is a triazole-type fungicide that provides broad spectrum disease control through inhibition of sterol biosynthesis in fungi. It is registered to Syngenta Crop Protection for the control of fungal diseases on a variety of crops. Tolerances for propiconazole are currently established for the combined residues of propiconazole and its metabolites determined as 2,4-dichlorobenzoic acid (expressed as parent) in/on a variety of plant and animal commodities, including permanent tolerances of 0.1 and 1.5 ppm on wheat grain and straw [40 CFR §180.434(a)].

Syngenta has submitted a petition (PP#2F6371) proposing tolerances and the use of propiconazole on a variety of cereal grains, including wheat. The current submission includes residue data from two wheat field trials comparing residues in/on grain and straw resulting from a late season application of propiconazole (EC) at either booting or heading. Propiconazole was applied at 1x and 5x rates to also generate grain samples for processing studies (44548402.der2, under review).

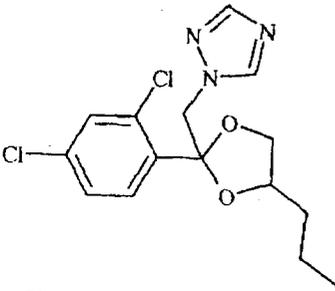
TABLE A.1. Nomenclature of Propiconazole	
Compound	
Common name	Propiconazole
Company experimental names	CGA-64250
IUPAC name	1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole
CAS name	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole
CAS #	60207-90-1
End-use products/EPs	3.6 lb/gal EC (Tilt 3.6E Fungicide, EPA Reg. No. 100-617)



TABLE A.2. Physicochemical Properties of Technical Grade Propiconazole.

Parameter	Value	Reference
Boiling point	120°C at 1.9 Pa, >250°C at 101.325 kPa	MRID No. 43698701
pH	4.9 at 25°C (1% aqueous dispersion)	MRID No. 43698701
Density	1.289 g/cm ³ at 20°C	MRID No. 43698701
Water solubility	0.10 g/L at 20°C	MRID No. 41720301
Solvent solubility (temperature not specified)	Completely miscible in ethanol, acetone, toluene and n-octanol. hexane = 47 g/L	MRID No. 42030201
Vapor pressure	4.2 x 10 ⁻⁷ mm Hg at 25°C	MRID No. 41720301
Dissociation constant (pK _a)	1.09	MRID No. 43698701
Octanol/water partition coefficient Log(K _{ow})	3.72 at pH 6.6 and 25°C	MRID No. 43698701
UV/visible absorption spectrum (λ _{max} , nm)	Not available	MRID No. 40583703

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Wheat was grown and maintained at each test site using typical agricultural practices for the two regions (Table B.1.1). Monthly rainfall and irrigation data were provided for each site, along with temperature data. No usual weather conditions were noted that would have an adverse effect on the field trial data. Information was provided on soil characteristics at each site, along with the maintenance chemicals and other pesticides used.

A total of four treated plots were established at each test site (Table B.1.2). At both sites, propiconazole (3.6 lb/gal EC) was applied to wheat as a single broadcast foliar application at either booting (FGS 10) or heading (FGS 10.5) at target rates of 0.11 lb ai/A (1x) and 0.55 lb ai/A (5x).

TABLE B.1.1. Trial Site Conditions.

Trial Identification (County, State; Year)	Soil characteristics ¹			
	Type	%OM	pH	CEC ² (meq/g)
Latah, ID 1996	Silt Loam	4.4	5.8	17.10
Foster, ND 1996	Loam	4.3	7.5	15.88

¹ These parameters are optional except in cases where their value affects the use pattern for the chemical.

² Cation exchange capacity.



TABLE B.1.2. Study Use Pattern on Wheat.

Location (County, State: Year) Trial ID	End-use Product	Application Information ¹				
		Method; Timing	Volume (GPA)	Rate (lb ai/A)	RTI (days)	Total Rate (lb ai/A)
Latah, ID 1996 0W-FR-672-96	3.6 lb/gal EC	Single broadcast foliar application at Feekes Growth Stage 10 (boot stage)	21	0.12	NA	0.12
			21	0.62	NA	0.62
		Single broadcast foliar application at Feekes Growth Stage 10.5 (heading)	21	0.12	NA	0.12
			21	0.62	NA	0.62
Foster, ND 1996 MW-FR-515-96	3.6 lb/gal EC	Single broadcast foliar application at Feekes Growth Stage 10 (boot stage)	15	0.11	NA	0.11
			15	0.55	NA	0.55
		Single broadcast foliar application at Feekes Growth Stage 10.5 (heading)	15	0.11	NA	0.11
			15	0.55	NA	0.55

All applications were made using ground equipment, and no adjuvants were included in the spray mix.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones ¹	Wheat	
	Submitted	Requested
		Canada
1	---	---
2	---	---
3	---	1
4	---	---
5	1	1
6	---	5
7	---	1
8	---	5
9	---	6
10	---	---
11	1	---
12	---	1
Total	2	20

¹Regions 13-21 and 1A, 5A, 5B, and 7A were not included as the use is for only in the U.S.
 NA = Not applicable



B.2. Sample Handling and Preparation

Single control samples and either single (5x rate) or duplicate (1x rate) treated samples of wheat grain and straw (weights unspecified) were collected from each test at two intervals. Following the application at booting (FGS 10), samples were collected at 41 DAT and 63-67 DAT. Following the application at heading (FGS 10.5), samples were collected at 30-31 DAT and 55-57 DAT. Grain and straw samples were frozen shortly after harvest and shipped by on dry ice by overnight courier to Novartis Crop Protection (Greensboro, NC), where samples were prepared (homogenized) and stored at -20°C. Samples were later shipped frozen to the analytical laboratory, ABC Laboratories (Columbia, MO), where samples were stored at -20°C until analysis.

B.3. Analytical Methodology

Samples were analyzed for residues of propiconazole and its DCBA-containing metabolites using a GC/ECD method (Method AG-454B), which is an updated version of the current tolerance enforcement method for propiconazole residues in plant commodities. The method converts all residues to 2,4-DCBA through base hydrolysis and oxidation, and residues are then determined as methylated 2,4-DCBA and expressed in parent equivalents.

For this method, propiconazole residues are extracted by refluxing for 1 hour in NH_4OH /methanol (20:80, v/v), and filtered. Residues are concentrated and oxidized to DCBA by refluxing with KMnO_4 in 1N NaOH for 75 minutes. After reflux, the extract is diluted with water, the KMnO_4 is deactivated by the addition of sodium meta-bisulfite, and the extract is acidified by the addition of 6N HCl. Residues of DCBA are partitioned into diethyl ether:hexane (10:90, v/v), evaporated to dryness, and methylated using diazomethane. Residues are then cleaned-up using an acidic alumina Sep-Pak eluted with diethyl ether:hexane (10:90, v/v), and analyzed by GC/ECD using external standards. The validated method LOQ is 0.05 ppm, and the LOD is 0.02 ppm.

Summary tables of the residue data were corrected by the registrant for procedural recoveries of <100%; however, spreadsheets including the uncorrected residue values were available in the raw data and were used by the reviewer to report residue values.

In conjunction with the analysis of field trial samples, the above method was validated using control samples fortified with propiconazole at 0.05-10.0 ppm for straw and at 0.05-20 ppm for grain.

C. RESULTS AND DISCUSSION

In two wheat field trials conducted in ID and ND in 1996, propiconazole (3.6 lb/gal) was applied to 4 separate plots of wheat as a single broadcast foliar application at booting (FGS 10) or heading (FGS 10.5) at 0.11-0.12 lb ai/A or 0.55-0.62 lb ai/A (1x and 5x rates). All applications



were made use ground equipment in volumes of 15-21 gal/A, and did not include the use of any adjuvants. Single control and single or duplicate treated samples of grain and straw were harvested at 41 and 63-67 DAT following the application at booting and at 30-31 and 55-57 DAT following the application at heading.

The GC/ECD method (Method AG-454B) used to determine propiconazole residues in/on grain and straw was adequately validated in conjunction with the analysis of field trial samples. The recovery of propiconazole averaged $85 \pm 15\%$ from grain and $80 \pm 9\%$ from straw (Table C.1). Apparent residues of propiconazole were <LOQ on all control samples of grain and straw. The validated method LOQ for propiconazole is 0.05 ppm, and the LOD is 0.02 ppm. Adequate sample calculations and example chromatograms were provided. Although the study author reported residue values corrected for concurrent recoveries of <100%, uncorrected residues values are used and reported in this review.

Grain and straw samples were stored frozen for up to 3.7 months prior to extraction for analysis (Table C.2). Adequate storage stability data are available indicating that the residues of propiconazole and its metabolites are stable at -20°C for up to 39 months in grass forage, straw and seed (DP Barcode D279300, Y. Donovan, 8/18/05). As these matrices are similar to wheat grain and straw, these data will support the storage intervals and conditions for the wheat field trials.

Following a single application at booting at the 1x rate, total residues in/on grain were <0.05 ppm at both sampling intervals, and residues in/on straw were 0.95-1.3 ppm at 41 DAT and 0.31-0.91 ppm at 63-67 DAT (Table C.3). Following an application at heading at the 1x rate, total residues in/on grain were <0.05-0.10 ppm at ~30 DAT and decreased to <0.05 ppm by 55-57 DAT, and residues in/on straw were 1.2-2.2 ppm at ~30 DAT and decreased to 0.75-1.2 ppm by 55-57 DAT. For the 1x applications, average residues in/on grain were 0.03 ppm at 41-67 days after the application at booting and 0.03-0.06 ppm at 30-57 days after the application at heading (Table C.4). Average residues in/on straw following the application at booting were 1.1 ppm at 41 DAT and 0.56 ppm at 63-67 DAT, and average residues in/on straw following the application at heading were 1.6 ppm at 30-31 DAT and 0.95 ppm at 55-57 DAT.

Although residues in/on grain and straw following the 5x application were higher than from the 1x rate, the same trends were observed with regards to residues levels resulting from booting vs. heading applications and for residues at longer post-treatment intervals. Following the application at booting, average residues in/on grain were 0.07 ppm at 41 DAT and 0.03 ppm at 63-67 DAT and average residues in/on straw were 6.1 ppm at 41 DAT and 4.1 ppm at 63-67 DAT. Following the application at heading, average residues in/on grain were 0.30 ppm at ~30 DAT and 0.18 ppm at 55-57 DAT and average residues in/on straw were 7.8 ppm at ~30 DAT and 5.0 ppm at 55-57 DAT.

Common cultural practices were used to maintain plants, and the weather conditions and the maintenance chemicals and fertilizer used in the study did not have a notable impact on the residue data



TABLE C.1. Summary of Concurrent Recoveries of Propiconazole from Wheat Straw and Grain.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean \pm std dev (%)
Grain	0.05	5	101, 75, 73, 61, 77	85 \pm 15
	0.10	4	72, 107, 79, 88	
	0.50	2	105, 95	
	20.0	1	86	
Straw	0.05	1	83	80 \pm 9
	0.10	5	82, 85, 74, 68, 66	
	0.50	1	93	
	10.0	1	85	

TABLE C.2. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration ¹ (months)	Interval of Demonstrated Storage Stability (months) ²
Grain and straw	-20	1.2-3.4	39

¹ From harvest to extraction for analysis. Samples were analyzed within 1-10 days of extraction.
² DP Barcode D279300, Y. Donovan, 8/18/05.

TABLE C.3. Residue Data on Wheat Grain and Straw following a Late Season Applications of Propiconazole (EC) at Booting or Heading.

Trial ID (County, State: Year)	Zone	Wheat Variety	Application Timing	Total Rate (lb ai/A) ¹	PHI (days)	Commodity	Total Propiconazole Residues (ppm) ²
Latah, ID 1996 0W-FR-672-96	11	Walkanz	Feekes Growth stage 10 (booting)	0.12	41	Grain	ND, ND
						Straw	1.3, 0.95
					67	Grain	ND, ND
						Straw	0.91, 0.70
				0.62	41	Grain	0.08
						Straw	7.3
			Feekes Growth Stage 10.5 (heading)	0.12	31	Grain	(0.05, 0.04) ³
						Straw	1.2, 1.4
					57	Grain	(0.04, 0.04)
						Straw	1.2, 0.98
				0.62	31	Grain	0.18
						Straw	6.6
					57	Grain	0.30
						Straw	6.5



TABLE C.3. Residue Data on Wheat Grain and Straw following a Late Season Applications of Propiconazole (EC) at Booting or Heading.

Trial ID (County, State, Year)	Zone	Wheat Variety	Application Timing	Total Rate (lb ai/A) ¹	PHI (days)	Commodity	Total Propiconazole Residues (ppm) ²
Foster, ND 1996 MW-FR-515-96	5	Sharp	Feekes growth stage 10 (booting)	0.11	41	Grain	ND, ND
						Straw	1.1, 0.97
					63	Grain	ND, ND
					Straw	0.33, 0.31	
				0.55	41	Grain	0.06
						Straw	4.8
			63		Grain	(0.03)	
				Straw	1.4		
			Feekes growth Stage 10.5 (heading)	0.11	30	Grain	0.10, 0.09
						Straw	1.6, 2.2
					55	Grain	ND, ND
					Straw	0.75, 0.85	
0.55	30	Grain		0.42			
		Straw		9.0			
	55	Grain	0.06				
	Straw	3.5					

¹ The application rates were reported to be at 1x and 5x the proposed use rate for wheat.
² Total propiconazole residues were determined as DCBA and expressed in parent equivalents. Reported values were obtained from the raw data and are not corrected procedural recoveries. The LOQ for propiconazole residues is 0.05 ppm in/on roots and tops, and the LOD is 0.02 ppm.
³ Values in parentheses are residues reported below the LOQ, but \geq LOD.
 ND = Not detected. $<$ 0.02 ppm.

TABLE C.4. Summary of Residue Data from Wheat Field Trials with Propiconazole (EC) Comparing Late Season Applications.

Commodity	Application Timing	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm) ¹						
				n	Min.	Max.	HAFT ²	Median (STMdR) ³	Mean (STMR) ³	Std. Dev.
Grain	Feekes GS 10 (booting)	0.11-0.12	41	4	<0.05	<0.05	<0.05	0.03	0.03	0.00
			63-67	4	<0.05	<0.05	<0.05	0.03	0.03	0.00
			0.55-0.62	41	2	0.06	0.08	0.08	0.07	0.07
			63-67	2	<0.05	<0.05	<0.05	0.03	0.03	0.00
	Feekes GS 10.5 (heading)	0.11-0.12	30-31	4	<0.05	0.10	0.10	0.06	0.06	0.04
			55-57	4	<0.05	<0.05	<0.05	0.03	0.03	0.00
		0.55-0.62	30-31	2	0.18	0.42	0.42	0.30	0.30	0.17
		55-57	2	0.06	0.30	0.30	0.18	0.18	0.17	
Straw	Feekes GS 10 (booting)	0.11-0.12	41	4	0.95	1.3	1.1	1.04	1.1	0.16
			63-67	4	0.31	0.91	0.81	0.52	0.56	0.29
			0.55-0.62	41	2	4.8	7.3	7.3	6.1	6.1
			63-67	2	1.4	6.8	6.8	4.1	4.1	3.8
	Feekes GS 10.5 (heading)	0.11-0.12	30-31	4	1.2	2.2	1.9	1.5	1.6	0.43
			55-57	4	0.75	1.2	1.1	0.92	0.95	0.19
		0.55-0.62	30-31	2	6.6	9.0	9.0	7.8	7.8	1.7
		55-57	2	3.5	6.5	6.5	5.0	5.0	2.1	

¹ The LOQ is 0.05 ppm. Residue data are not corrected for procedural recoveries. For calculation of the median, mean and standard deviation, 1/2 LOQ (0.025 ppm) was used for grain samples with residues <LOQ.
² HAFT = Highest Average Field Trial.
³ STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.



D. CONCLUSION

The two wheat field trials are adequate for the purposes for which they were intended. The tests conducted at both the 1x and 5x rates indicate that propiconazole residues in/on grain and straw are higher following an application at the heading stage than at the booting stage, and that residues in both grain and straw decline at longer post-treatment intervals.

E. REFERENCES

DP Barcode: D279300
Subject: Propiconazole (122101): Reregistration Eligibility Decision (RED) Document;
Residue Chemistry Considerations.
From: Y. Donovan
To: S. Lewis/J. Guerry
Dated: 8/18/05
MRID: None

F. DOCUMENT TRACKING

Yan Donovan, RRB4/HED
Petition Number(s): 2F6371
DP Barcode(s): D238458
PC Code: 122101

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