UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

Date: October 27, 2005

Subject: Pyraclostrobin. Reduction of Pre-harvest Interval for Almonds.

DP Barcode:	D314869, D316931	Decision No.:	354038
PC Code:	099100	Chemical Class:	Fungicide
Petition No.:	5F6906	MRID Nos.:	46407701
40 CFR 180.	582		

From: Leung Cheng, Chemist
Registration Action Branch 3
Health Effects Division (7509C)

Through: Stephen Dapson, Branch Senior Scientist
Registration Action Branch 3
Health Effects Division (7509C)

To: John Bazuin/Cynthia Giles-Parker, Team 22
Fungicide Branch
Registration Division (7505C)

Executive Summary

Pyraclostrobin belongs to the strobilurin class of fungicides that inhibit spore germination, mycelial growth, and sporulation of pathogenic fungi on leaf surfaces. Pyraclostrobin is registered to BASF Corporation and is formulated as water-dispersible granules (WDG or WG) and an emulsifiable concentrate (EC) for use on numerous crops as foliar applications using ground or aerial equipment. Two WDG formulations are currently registered for up to four broadcast foliar applications at up to 0.12 lb ai/A/application, at 7- to 14-day re-treatment intervals, for a maximum of 0.48 lb ai/A/season.

Permanent tolerances for pyraclostrobin in plant commodities are listed in 40 CFR §180.582 (a)(1) and expressed in terms of the combined residues of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its

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desmethoxy metabolite (methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl carbamate), BF 500-3, expressed as parent compound. The established tolerances for plant commodities range from 0.02 ppm (wheat grain) to 27 ppm (grass seed screenings), and include a tolerance of 1.6 ppm on almond hulls.

BASF has submitted additional field trials to support a reduction of the pre-harvest interval (PHI) from 5 weeks after petal fall to 25 days for use on almonds, and proposed a revised tolerance of 7.0 ppm in/on almond hulls. The use rate will remain the same: up to 4 applications at 0.12 lb ai/A with a re-treatment interval of 7 to 14 days.

HED has determined that the nature of the residue in plants and livestock is adequately understood. For purposes of both tolerance and risk assessment, the residues of concern in plant commodities consist of pyraclostrobin and metabolite BF 500-3, expressed as parent. The residues of concern in livestock commodities consist of pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol (BF 500-8), expressed as parent.

Adequate residue analytical methods are available for the enforcement of established tolerances. These methods have successfully passed independent laboratory validation and have been forwarded to ACB/BEAD for petition method validations. Residues in the current almond field trials were determined using an adequate LC/MS/MS method (BASF Method Number D9908), which is similar to the enforcement method. The method was adequately validated in conjunction with the field trial analyses and has an LOQ of 0.02 ppm and an LOD of 0.005 ppm for each analyte.

As the proposed increase in the almond hull tolerance will not increase the maximum theoretical dietary burden of livestock to pyraclostrobin, reassessment of tolerances for livestock commodities is not necessary for this petition.

The new almond field trial data from CA are adequate and reflect the revised use pattern for pyraclostrobin (WDG) on almond. The number and geographic distribution of the new field trials are adequate and an appropriate number of samples were collected at the proposed PHI. Samples were analyzed using an adequate method, and the sample storage intervals are supported by the available storage stability data. The results from these trials show that residues of pyraclostrobin and its desmethoxy metabolite were each below the LOQ of 0.02 ppm in/on all treated nutmeat samples (n = 20) harvested 24-26 days after the last of four concentr[illegible]r dilute spray applications of pyraclostrobin totaling 0.48-0.49 lb ai/A/season. Total pyraclostrobin residues were 1.09-[illegible] ppm (concentrate spray) and 1.2-5.75 ppm (dilute spray) in/on 20 treated almond hull sample[illegible] significant differences in the residues were observed in samples taken from trees treated with the concentrate spray as opposed to those treated with the dilute spray.

Adequate confined and limited field rotational crop studies are available. Tolerances for rotated crops are not required and the available data support the current label-specified 14-day plant-back interval for crops not listed on the label.

Regulatory Recommendations and Residue Chemistry Deficiencies

There are no residue chemistry data deficiencies that will preclude the establishment/amendment of the tolerance for residues of pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester) and its desmethoxy metabolite (methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl carbamate), expressed as parent compound, in/on the following raw agricultural commodity:

Almond, hulls . . . . . 7.0 ppm

Furthermore, the reduction of the pre-harvest interval on almonds does not lead to an increase in residues in almond nutmeat. Hence, the current tolerance of 0.04 ppm in nut, tree, group is adequate to cover the amended use.

Background

Pyraclostrobin is a foliar fungicide that is structurally related to the naturally occurring strobilurins. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi. Pyraclostrobin is currently registered for use on a number of crops, including almond. Permanent tolerances have been established [40 CFR §180.582(a)(1)] for residues of pyraclostrobin in/on a number of plant commodities, including residues in/on almond hulls at 1.6 ppm.

The nomenclature and physicochemical properties of pyraclostrobin are presented below in Tables 1 and 2.

Table 1. Nomenclature of Pyraclostrobin.

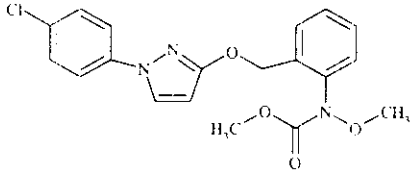
Compound	
Common name	Pyraclostrobin
Company experimental names	BAS 500 F
IUPAC name	Methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate
CAS name	Methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use products/EPs	20% WDG (Cabrio® Fungicide; EPA Reg. No. 7969-187) 12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199; also contains 25.2% boscalid)

Table 2. Physicochemical Properties for Pyraclostrobin (BAS 500 F).

Parameter	Value	Reference[1]
Melting point	63.7-65.2 °C	D269848 & D274191
Density	1.285g/cm^3 at 20°C	D269848 & D274191

Table 2. Physicochemical Properties for Pyraclostrobin (BAS 500 F).

Parameter	Value	Reference[1]
Water solubility (20°C)	2.41 mg/L in deionized water at 20°C 1.9 mg/L in buffer system pH 7 at 20°C 2.3 mg/L in buffer system pH 4 at 20°C 1.9 mg/L in buffer system pH 9 at 20°C	D269848 & D274191
Solvent solubility (mg/L at 20°C)	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (>110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L); DMF (>62 mg/L).	D269848 & D274191
Vapor pressure at 25°C	2.6×10^{-10} hPa (at 20°C); 6.4×10^{-10} hPa	D269848 & D274191
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D269848 & D274191
Octanol/water partition coefficient Log(K_{OW})	n-Octanol/water partition coefficient (K_{ow}) at room temperature (=K_{ow} of 3.80, pH 6.2; =log K_{ow} 4.18, pH 6.5).	D269848 & D274191

[1] Product Chemistry data were reviewed by the Registration Division (D269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak)

860.1200 Directions for Use

Cabrio® is a WDG formulation which contains 20% of pyraclostrobin by weight. A summary of the proposed use is presented in the following table.

Table 3. Summary of Proposed Uses of Pyraclostrobin.

Trade Name	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Almond					
Cabrio®	9.5 oz per acre (0.12)	4	38 oz per acre (0.48)	25	Apply in sufficient water to ensure thorough coverage of foliage, blooms, and fruit. For aerial application, use no less than 10 gallons of spray solution per acre. Applications to begin at pink bud and continue on a 7- to14-day interval up to 25 days before harvest. Almond hulls may be fed to livestock.

Conclusions. The proposed use directions for the Cabrio formulation are adequate to allow RAB3 an assessment of whether the submitted residue data reflect the maximum residues likely to occur in/on almond nutmeat and hulls.

860.1500 Crop Field Trials

46407701.der.wpd (almond)

Five trials were conducted on almonds during the 2003 growing season in NAFTA Growing Region 10 (California). At each test location four broadcast applications of pyraclostrobin (20% WG) were made as a tank mix with boscalid (70% WG) to almonds. Applications were made at 0.12 lb ai/A/application, with a 6- to 8-day re-treatment interval. The total application rates were 0.48-0.49 lb ai/A. The applications were made to side-by-side plots at each site using either concentrate (56-100 gal/A) or dilute (140-210 gal/A) spray volumes. An adjuvant was added to the spray mixture for all applications. Mature almond RAC samples were harvested at 24-26 days after the last application. The number and locations of field trials conducted in year 2003 (MRID 46407701) are in accordance with OPPTS Guideline 860.1500.

The residues of pyraclostrobin on almond RAC samples (nutmeat and hulls) were quantitated using a validated LC/MS/MS method, BASF Analytical Method D9908. Acceptable concurrent method validation data for almond commodities were obtained. The validated limit of quantitation (LOQ) was 0.02 ppm each for residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3; BAS 500-3) in/on almond nutmeat and hulls, with a limit of detection (LOD) estimated at 0.005 ppm.

The field residue samples were stored frozen (<-10°C) a maximum of 5 months from harvest to analysis. The available storage stability data indicate that residues of pyraclostrobin and its desmethoxy metabolite are stable in/on a variety of frozen plant matrices for 19 months.

TABLE 4. Summary of Residue Data for Almonds from Crop Field Trials using a 20% WDG Formulation of Pyraclostrobin at a Total Rate of 0.48-0.49 lb ai/A.

Commodity	PHI (days)	Compound	Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median (STMdR[2])	Mean (STMR[2])	Std. Dev.
Nutmeat (Conc.)	24-26	BAS 500	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		BAS 500-3	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		Combined	10	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Nutmeat (Dilute)	24-26	BAS 500	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		BAS 500-3	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		Combined	10	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Nutmeat (Overall)	24-26	Total	20	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Hulls (Conc.)	24-26	BAS 500	10	1.05	3.42	3.1	1.18	1.59	0.85
		BAS 500-3	10	0.06	0.30	0.14	0.12	0.14	0.09
		Combined	10	1.09	3.72	3.4	1.37	1.73	0.93
Hulls (Dilute)	24-26	BAS 500	10	1.07	5.30	4.79	1.61	2.38	1.50
		BAS 500-3	10	0.11	0.45	0.40	0.17	0.22	0.12
		Combined	10	1.20	5.75	5.19	1.91	2.60	1.60
Hulls (Overall)	24-26	Total	20	1.09	5.75	5.19	1.42	2.16	1.34

[1] HAFT = Highest Average Field Trial.
[2] STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.

The results from these trials show that residues of pyraclostrobin and its desmethoxy metabolite were each below the LOQ of 0.02 ppm in/on all treated nutmeat samples (n = 20) harvested 24-26 days after the last of four concentrate or dilute spray applications of pyraclostrobin totaling 0.48-0.49 lb ai/A/season. Total pyraclostrobin residues were 1.09-3.72 ppm (concentrate spray) and 1.2-5.75 ppm (dilute spray) in/on 20 treated almond hulls samples. No significant differences in the residues were observed in samples taken from trees treated with the concentrate spray as opposed to those treated with the dilute spray (Table 4).

Conclusions. The submitted field trial data for almond are adequate to support the amended tolerance of 7.0 ppm in/on almond hulls, and are also adequate to support the retention of the established tolerance at 0.04 ppm in/on nut, tree, group.

860.1550 Proposed Tolerances

Tolerances for plant commodities are listed in 40 CFR §180.582 (a)(1) and expressed in terms of the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent compound. The established tolerances for plant commodities range from 0.02 ppm (wheat grain) to 27 ppm (grass seed screenings), and include a tolerance of 1.6 ppm in/on almond hulls.

In the current petition, BASF is requesting an increase in the existing permanent tolerance on almond hulls from 1.6 ppm to 7.0 ppm.

In the current three CA field trials, the maximum combined residues of pyraclostrobin and metabolite BF 500-3 in/on almond hulls were 5.75 ppm (dilute spray) and 3.72 ppm (concentrate spray). Following the *2005 Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the residue data for almond hulls support a tolerance of 7.0 ppm. Therefore, the Agency recommends increasing the current permanent tolerance for almond hulls from 1.6 ppm to 7.0 ppm (Table 5).

Table 5. Tolerance Summary for Pyraclostrobin.

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments (*Correct commodity definition*)
Almond, hulls	7.0	7.0	The available residue data are adequate.

No Canadian or Mexican maximum residue limits (MRLs) are established for residues of pyraclostrobin in/on almond hulls (see attached International Residue Limit Status sheet). There is a Codex MRL established at 2 ppm for almond hulls (step 8/CXL). The US tolerance level and residue definition both differ from Codex.

References

DP Barcode: D278044
Subject: PP# 0F06139. Pyraclostrobin. Outcome of the HED Metabolism Assessment Review Committee (MARC) Meeting Held on September 20, 2001.
From: L. Cheng
To: Y. Donovan
Dated: 10/9/01
MRIDs: None

DP Barcodes: D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, and D278429
Subject: PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS #175013-18-0.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

DP Barcode: D269850
Subject: PP# 0F06139. Pyraclostrobin (BAS 500F) in or on Various Crops. Request for Tolerance Method Validation (TMV) Trial.
From: L. Cheng
To: F. D. Griffith, Jr.
Dated: 11/8/00
MRIDs: 45118505, 45118504, 45118509, 45118510, 45118501, 45118503, 45118507, 45118514

RD/I:NDodd:WWassell:9/22/2005:SDapson://2005

Attachments:
DER for MRID 46407701

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name:	Common Name:		Date:
Methyl [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl] methoxycarbamate	pyraclostrobin (BAS 500 F); PC Code 099100	☐ Proposed tolerance X Reevaluated tolerance ☐ Other	

Codex Status (Maximum Residue Limits)	U. S. Tolerances
☐ No Codex proposal step 6 or above ☐ No Codex proposal step 6 or above for the crops requested	Petition Number: 5F6906 DP Barcode: D314869 Other Identifier:
Residue definition (step 8/CXL): pyraclostrobin (fat soluble)	Reviewer/Branch: Leung Cheng/RAB3
	Residue definition:Pyraclostrobin and its desmethoxy metabolite methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl carbamate, expressed as parent compound

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
almond hulls	2	almond, hulls	7.0

Limits for Canada	Limits for Mexico
X No Limits ☐ No Limits for the crops requested	X No Limits ☐ No Limits for the crops requested
	Residue definition: N/A

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)

Notes/Special Instructions:
S.Funk, 09/06/2005.

Rev. 1998

Residue values (parent plus desmethoxy metabolite) in/on almond hulls: MRID 46407701

1.09

1.17

1.17

1.18

1.2

1.22

1.27

1.33

1.37

1.37

1.46

1.81

1.92

2.01

3.08

3.17

3.35

3.72

4.63

5.75

Primary Evaluator	Leung Cheng, Chemist RAB3/HED	Date: 10/27/2005
Approved by	Stephen Dapson, BSS RAB3/HED	Date: 10/27/2005

In the absence of signatures, this document is considered to be a draft with deliberative material for internal use only.

STUDY REPORT:

46407701 The Magnitude of BAS 500 F and BAS 510 F Residues in Almonds with a 25 Day PHI. BASF Study Number 146467. Unpublished study prepared by BASF Corporation, 6-15-2004, 105 p.

EXECUTIVE SUMMARY:

Field trial data have been generated for pyraclostrobin on almonds. Five trials were conducted on almonds during the 2003 growing season in NAFTA Growing Region 10 (California). At each test location four broadcast applications of boscalid (70% WG) and pyraclostrobin (20% WG) were made as a tank mix to almonds; this DER addresses the pyraclostrobin residues only. Applications were made at 0.12 lb ai/A/application, with a 6- to 8-day retreatment interval. The total application rates were 0.48-0.49 lb ai/A. The applications were made to side-by-side plots at each site using either concentrate (56-100 gal/A) or dilute (140-210 gal/A) spray volumes. An adjuvant was added to the spray mixture for all applications. Mature almond RAC samples were harvested at 24-26 days after the last application.

The residues of pyraclostrobin on almond RAC samples (nutmeat and hulls) were quantitated using a validated LC/MS/MS method, BASF Analytical Method D9908. Acceptable concurrent method validation data for almond commodities were obtained. The validated limit of quantitation (LOQ) was 0.02 ppm each for residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3 or BAS 500-3) in/on almond nutmeat and hulls, with a limit of detection (LOD) estimated at 0.005 ppm.

The field residue samples were stored frozen (<-10°C) a maximum of 5 months from harvest to analysis. The available storage stability data indicate that residues of pyraclostrobin and its desmethoxy metabolite are stable in/on a variety of frozen plant matrices for at least 19 months.

The results from these trials show that residues of pyraclostrobin and its desmethoxy metabolite were each below the LOQ of 0.02 ppm in/on all treated nutmeat samples (n = 20) harvested 24-26 days after the last of four concentrate or dilute spray applications of pyraclostrobin totaling 0.48-0.49 lb ai/A/season. Total pyraclostrobin residues were 1.09-3.72 ppm (concentrate spray) and 1.2-5.75 ppm (dilute spray) in/on 20 treated almond hulls samples. No significant differences in the residues were observed in samples taken from trees treated with the concentrate spray as opposed to those treated with the dilute spray.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the almond field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the associated U.S. EPA Residue Chemistry Summary Document D314869.

COMPLIANCE:

Signed and dated GLP, quality assurance, and data confidentiality statements were provided. No deviations from regulatory requirements were noted that would impact the study results or their interpretation.

A. BACKGROUND INFORMATION

Pyraclostrobin is a foliar fungicide that is structurally related to the naturally occurring strobilurins. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi. Pyraclostrobin is currently registered for use on a number of crops, including almond. The current field trials were submitted by BASF to support the reduction of the pre-harvest interval (PHI) of almond to 25 days.. Both the Pristine and Cabrio labels currently specify that pyraclostrobin is to be applied no later than 5 weeks after petal fall. The use rate will remain the same: up to 4 applications at 0.12 lb ai/A with a re-treatment interval of 7 to 14 days.

The nomenclature and physicochemical properties of pyraclostrobin are presented below in Tables A.1. and A.2.

Table A.1. Pyraclostrobin Nomenclature.

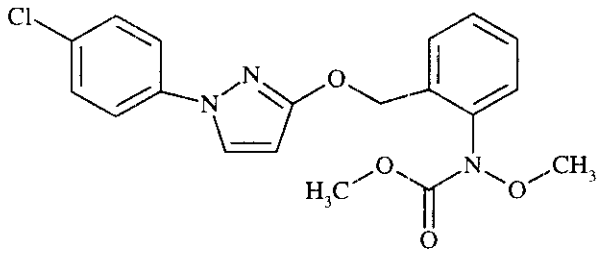
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	Methyl *N*-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate
CAS name	Methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use products/EPs	20%WDG (Cabrio® EG Fungicide; EPA Reg. No. 7969-187) and 12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199; also contains 25.2% boscalid)

TABLE A.2. Physicochemical Properties.

Parameter	Value	Reference[1]
Melting point	63.7-65.2 °C	D269848 & D274191
Density	1.285g/cm^3 at 20°C	D269848 & D274191
Water solubility (20°C)	2.41 mg/L in deionized water at 20°C 1.9 mg/L in buffer system pH 7 at 20°C 2.3 mg/L in buffer system pH 4 at 20°C 1.9 mg/L in buffer system pH 9 at 20°C	D269848 & D274191
Solvent solubility (mg/L at 20°C)	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (≥110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L); DMF (≥62 mg/L).	D269848 & D274191
Vapor pressure at 25°C	2.6 x 10^{-10} hPa (at 20°C); 6.4 x 10^{-10} hPa	D269848 & D274191
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D269848 & D274191
Octanol/water partition coefficient Log(K_{OW})	n-Octanol/water partition coefficient (K_{ow}) at room temperature (=K_{ow} of 3.80, pH 6.2; =log K_{ow} 4.18, pH 6.5).	D269848 & D274191

[1] Product Chemistry data were reviewed by the Registration Division (D269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1 Trial Site Conditions.

Trial Identification (City, State, Year)	Soil characteristics				Meteorological data[1]	
	Type	%OM	pH	CEC	Overall total monthly rainfall range (inches)	Overall monthly temperature range (°C)
Terra Bella, CA/2003 RCN 2003131	Nord, fine sandy loam	ND = No Data Collected			0.0 - 0.01	12-33
Wasco, CA /2003 RCN 2003132	Panche Clay Loam	ND			0.00 - 0.00	17-34
Madera, CA /2003 RCN 2003133	Hanford Fine Sandy Loam	ND			0.00 - 0.03	13-37
Glenn, CA /2003 RCN 2003134	Loam	ND			0.00 - 0.8	14-34
Hughson, CA /2003 RCN 2003135	Loam	ND			0.00 - 0.04	17-37

[1] Detailed meteorological data were not provided.

Weather conditions were reported to be normal. The actual temperature recordings were within average historical values for the residue study period. The actual rainfall average was within the historical rainfall average. No unusual conditions that would affect the integrity of the study were reported. Rainfall was supplemented with irrigation as needed.

Two treated and one untreated control plot were established at each test site. Four broadcast foliar applications of a tank mix containing pyraclostrobin (20% WG) were made to the treated plots at 0.12 lb ai/A, for a total application rate of 0.48-0.49 lb ai/A. The retreatment intervals between applications were 6-8 days. The applications were made using ground equipment in either a concentrate spray volume (56-100 gallons of water per acre) or dilute spray volume (140-210 gallons of water per acre). Applications included a non-silicone based surfactant (rate not specified) in the spray mixture as spray additive.

TABLE B.1.2. Study Use Pattern on Almonds.

Location (City, State), Year	EP	Method; Timing	Volume (gal/A)	Single Rate (lb ai/A)	No. of Appl.	RTI (days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
Terra Bella, CA, 2003	20% WG	Broadcast foliar (airblast, ground) Appl. 1. Pre hull split Appl. 2. ~10% hull split Appl. 3. ~40% hull split Appl. 4. 60% hull split	Conc: 61-63	0.12	4	6-8	0.48	Non-silicone based adjuvant (LI-700)
			Dilute: 140-146	0.12	4	6-8	0.48	Non-silicone based adjuvant (LI-700)
Wasco, CA, 2003	20% WG	Broadcast foliar (airblast, ground) Appl. 1. Pre hull split Appl. 2. ~10% hull split Appl. 3. ~40% hull split Appl. 4. 60% hull split	Conc: 67-100	0.12	4	6-8	0.48	Non-silicone based adjuvant (LI-700)
			Dilute: 148-178	0.12	4	6-8	0.48	Non-silicone based adjuvant (LI-700)
Madera, CA, 2003	20% WG	Broadcast foliar (airblast, ground) Appl. 1. Fruit ~ 80% of final size Appl. 2. Fruit ~ 80% of final size Appl. 3. Fruit ~ 90% of final size Appl. 4. Fruit ~ 90% of final size	Conc: 72-76	0.12	4	7	0.49	Non-silicone based adjuvant
			Dilute: 201-202	0.12	4	7	0.48	Non-silicone based adjuvant
Glenn, CA, 2003	20% WG	Broadcast foliar (airblast, ground) Appl. 1. 46 days before normal harvest Appl. 2. 39 days before normal harvest Appl. 3. 32 days before normal harvest Appl. 4. 46 days before normal harvest	Conc: 56-59	0.12	4	7	0.48	Non-silicone based adjuvant
			Dilute: 197-201	0.12	4	7	0.48	Non-silicone based adjuvant
Hughson, CA, 2003	20% WG	Broadcast foliar (airblast, ground) Appl. 1. Fruit ~ 90% of final size Appl. 2. Fruit ~ 90% of final size Appl. 3. Fruit ~ 90% of final size Appl. 4. Fruit ~ 90% of final size	Conc: 78-81	0.12	4	6-7	0.48	Non-silicone based adjuvant (Penetrator Plus)
			Dilute: 209-210	0.12	4	6-7	0.48	Non-silicone based adjuvant (Penetrator Plus)

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Region [1]	Almond		
	Submitted	Requested	
		Canada	US
1	--	NA	--
2	--	NA	--
3	--	NA	--
4	--	NA	--
5	--	NA	--
6	--	NA	--
7	--	NA	--
8	--	NA	--
9	--	NA	--
10	5	NA	5
11	--	NA	--
12	--	NA	--
13	--	NA	--
Total	5	NA	5

[1] Regions 14-21 and 1A, 5A, 5B, and 7A were not included as the proposed use is for the US only.
NA = not applicable.

B.2. Sample Handling and Preparation

Almond RAC samples were collected 24-26 days after the last application. One sample was collected from the untreated plot at each site and two independent samples were collected from each treated plot at each site. Each RAC sample was commercially acceptable and consisted of at least 2.2 pounds each of nutmeat and hulls from a minimum of four trees.

Samples were stored frozen at the field sites within 5 hours of harvest, and were shipped within 5-33 days of harvest, via ACDS freezer truck, to the analytical laboratory, BASF Agro Research in Research Triangle Park, NC. The samples were received frozen from the field and were stored in a freezer (<-10°C) prior to homogenization and analysis. The almond RAC samples were homogenized with dry ice to a consistency appropriate for analysis. Samples were stored frozen in plastic bags until the time of analysis.

B.3. Analytical Methodology

Residues of pyraclostrobin were determined using an LC/MS/MS method (BASF Method Number D9908). Method D9908 was validated in conjunction with a previous pyraclostrobin petition (D281042, L. Cheng, 7/26/04) and deemed acceptable for data collection. A brief description of the method follows.

Samples of almond hulls and nutmeat are extracted with methanol:water:2 N HCl (70:25:5, v/v/v) using a Polytron homogenizer. The extract was centrifuged, and an aliquot of the supernatant was removed and cleaned up by liquid/liquid partitioning using cyclohexane. An aliquot of the cyclohexane phase was taken, evaporated to dryness, and re-dissolved in 80:20 methanol:buffer solution (99.9% of 4 mM ammonium formate in water and 0.1% formic acid) for analysis by LC/MS/MS. The method uses external standards. The performance of the detection instrument was evaluated during each analytical set. The correlation coefficients of the calibration curves were >0.99. Residues of BF 500-3 were expressed in parent equivalents.

The LOQ and LOD for each pyraclostrobin and its desmethoxy metabolite were 0.02 and 0.005 ppm, respectively, in/on both almond nutmeat and hulls.

C. RESULTS AND DISCUSSION

The number and geographic representation of the almond field trials are adequate. Five field trials were conducted in Region 5 (California).

The LC/MS/MS method (BASF Method Number D9908) used to determine residues of pyraclostrobin in/on almond nutmeat and hulls is adequate for data collection. Acceptable concurrent method validation data for almond commodities were obtained. Concurrent recoveries ranged from 88 to 97%. Apparent residues of pyraclostrobin were below the LOQ in/on all almond hulls and nutmeat control samples (n=5 each). No interferences were noted in control samples. Recoveries were not corrected, as apparent residues were non-detectable in the associated controls. The concurrent recoveries are presented in Table C.1. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for a maximum of 5 months (Table C.2). Storage stability data are available on representative plant commodities indicating that pyraclostrobin and its desmethoxy metabolite are stable in frozen storage for at least 19 months (D281042, L. Cheng, 7/26/04). These data support the current almond field trials.

TABLE C.1 Summary of Concurrent Recoveries of Pyraclostrobin and BF 500-3 from Almond using LC/MS/MS Method D9908.

Analyte	Almond Matrix	Spiking Level (mg/kg)	Sample size	Recoveries (%)	Mean Recovery ± SD
Pyraclostrobin	Nutmeat	0.02	1	124	
		0.8	1	86	
	Hulls	0.02	2	83, 84	84±0.71
		0.8	1	79	
		15	1	90	
BF 500-3	Nutmeat	0.02	1	91	
		0.8	1	70	
	Hulls	0.02	2	75, 82	79±4.9
		0.8	1	84	
		15	1	79	

TABLE C.2 Summary of Freezer Storage Conditions.

Matrix	Storage Temp. (°C)	Actual Storage Duration (months)	Limit of Demonstrated Storage Stability [1]
Almond Nutmeat	< -10	3 - 5	The available storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months.
Almond Hulls		3 - 5	

[1] Refer to storage stability data reviewed in conjunction with a previous pyraclostrobin petition (PP#0F6139; D269668, etc, L. Cheng, 11/28/01).

TABLE C.3.a. Residue Data from Almond Field Trials Performed with Concentrate Spray.

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	BAS 500 F (ppm)	BAS 500-3 (ppm)	Total (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Nutmeat	0.48	24	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003133 Madera, CA/2003	10	Butte	Nutmeat	0.49	26	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003135 Hughson, CA/2003	10	Carmel	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

TABLE C.3.b. Residue Data from Almond Field Trials Performed with Dilute Spray.

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	BAS 500 F (ppm)	BAS 500-3 (ppm)	Total (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Nutmeat	0.48	24	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003133 Madera, CA/2003	10	Butte	Nutmeat	0.48	26	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
RCN 2003135 Hughson, CA/2003	10	Carmel	Nutmeat	0.48	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

TABLE C.3.c. Residue Data from Almond Field Trials Performed with Concentrate Spray.

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	BAS 500 F (ppm)	BAS 500-3 (ppm)	Total (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Hulls	0.48	25	3.42 2.78	0.30 0.30	3.72 3.08
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Hulls	0.48	24	1.86 1.26	0.06 0.07	1.92 1.33
RCN 2003133 Madera, CA/2003	10	Butte	Hulls	0.49	26	1.01 1.09	0.08 0.09	1.09 1.17
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Hulls	0.48	25	1.05 1.13	0.12 0.09	1.17 1.22
RCN 2003135 Hughson, CA/2003	10	Carmel	Hulls	0.48	25	1.22 1.06	0.15 0.12	1.37 1.18

TABLE C.3.d. Residue Data from Almond Field Trials Performed with Dilute Spray.

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	BAS 500 F (ppm)	BAS 500-3 (ppm)	Total (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Hulls	0.48	25	4.28,5.30 [2.46,4.35]*	0.35,0.45 [0.27,0.40]	4.63,5.75 [2.73,4.75]
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Hulls	0.48	24	3.18 3.06	0.17 0.11	3.35 3.17
RCN 2003133 Madera, CA/2003	10	Butte	Hulls	0.48	26	1.51 1.70	0.29 0.31	1.81 2.01
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Hulls	0.48	25	1.30 1.15	0.15 0.12	1.46 1.27
RCN 2003135 Hughson, CA/2003	10	Carmel	Hulls	0.48	25	1.20 1.07	0.17 0.12	1.37 1.20

* The results of a re-extraction and re-analysis of the same field samples are shown in brackets.

TABLE C.4. Summary of Residue Data for Almonds from Crop Field Trials using a 20% WDG Formulation of Pyraclostrobin at a Total Rate of 0.48-0.49 lb ai/A.

Commodity	PHI (days)	Compound	Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median (STMdR[2])	Mean (STMR[2])	Std. Dev.
Nutmeat (Conc.)	24-26	BAS 500	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		BAS 500-3	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		Combined	10	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Nutmeat (Dilute)	24-26	BAS 500	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		BAS 500-3	10	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
		Combined	10	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Nutmeat (Overall)	24-26	Total	20	<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Hulls (Conc.)	24-26	BAS 500	10	1.05	3.42	3.1	1.18	1.59	0.85
		BAS 500-3	10	0.06	0.30	0.14	0.12	0.14	0.09
		Combined	10	1.09	3.72	3.4	1.37	1.73	0.93
Hulls (Dilute)	24-26	BAS 500	10	1.07	5.30	4.79	1.61	2.38	1.50
		BAS 500-3	10	0.11	0.45	0.40	0.17	0.22	0.12
		Combined	10	1.20	5.75	5.19	1.91	2.60	1.60
Hulls (Overall)	24-26	Total	20	1.09	5.75	5.19	1.42	2.16	1.34

[1] HAFT = Highest Average Field Trial.
[2] STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.

D. CONCLUSION

The almond field trial data are adequate and reflect the use of four applications of pyraclostrobin (WDG) at 0.12 lb ai/A/application for a total of 0.48-0.49 lb ai/A/season and PHIs of 24-26 days. Maximum combined residues of pyraclostrobin and its desmethoxy metabolite were below the

LOQ of 0.04 ppm in almond nutmeat treated with either the concentrate spray or the dilute spray. In almond hulls, on the other hand, residues ranged up to 5.75 ppm in trees treated with the dilute spray and 3.72 ppm in trees treated with the concentrate spray.

E. REFERENCES

BAS 500 F (Common Name: Pyraclostrobin), New Fungicide Active Ingredient. PP#0F06139. Residue Chemistry Summary Document, D269668, L. Cheng, 11/28/2001.
PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774. Residue Chemistry Summary Document, D281042, L. Cheng, 7/26/2004.

F. DOCUMENT TRACKING

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