

US EPA ARCHIVE DOCUMENT



Boscalid/7969-197/PC Code 128008/BASF Corporation/7969
DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Almond

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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 Unpublished study prepared by BASF Corporation, 6-15-2004, 105 p. {OPPTS 860.1500}

EXECUTIVE SUMMARY:

Field trial data have been generated for boscalid 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% water dispersible granule (WDG)) and pyraclostrobin were made as a tank mix to almonds. As the results of the pyraclostrobin study are not germane to this action, this DER addresses the boscalid residues only. Applications were made at 0.22-0.24 lb ai/A/application, with a 6- to 8-day retreatment interval. The total application rates were 0.92-0.93 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 (DALA).

The residues of boscalid 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 0.05 ppm for residues of boscalid in/on almond nutmeat and hulls. The LOD was 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 boscalid are stable in/on a variety of frozen plant matrices for at least 18 months.

The results from these trials show that residues of boscalid were below the LOQ of 0.05 ppm in/on all treated nutmeat samples (n = 20) harvested 24-26 days after the last of four concentrated or dilute spray applications of boscalid totaling 0.92-0.93 lb ai/A/season. Boscalid residues were 1.8-11.3 ppm (concentrated spray) and 3.1-13.4 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 concentrated spray as opposed to those treated with the dilute spray.



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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 (D322235).

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

Boscalid is an anilide fungicide that inhibits mitochondrial respiration, thereby inhibiting spore germination, germ tube elongation, mycelial growth, and sporulation of pathogenic fungi on the leaf surface. Permanent tolerances have been established in 40 CFR §180.589 for residues of boscalid in/on numerous plant commodities, ranging from 0.05 ppm in/on peanuts and tuberous and corm vegetables (subgroup 1C) to 35 ppm in/on dried hop cones. Separate tolerances have also been established for indirect or inadvertent residues of boscalid in rotational crops, ranging from 0.05 ppm in several commodities to 8.0 ppm in grass forage, fodder, and hay (group 17). Tolerances for the combined residues of boscalid and its glucuronic acid conjugate are also established on animal commodities, ranging from 0.02 ppm in eggs to 0.35 ppm in meat byproducts of cattle, goats, horses, and sheep. The current field trials were submitted by BASF to support the reduction of the almond PHI to 25 days. Both the Pristine and Endura labels currently specify that boscalid is to be applied no later than 5 weeks after petal fall. The use rate will remain the same: up to 4 applications at 0.23 lb ai/A with a re-treatment interval of 7 to 14 days.

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

TABLE A.1. Nomenclature of Boscalid	
Compound	



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Common name	Boscalid
Company experimental names	BAS 510 F
IUPAC name	2-chloro-N-(4'-chlorobiphenyl-2-yl)-nicotinamide
CAS name	3-pyridinecarboxamide,2-chloro-N-(4'-chloro[1,1'-biphenyl]-2-yl
CAS #	188425-85-6
End-use products/EP	70% WDG (Endura™ fungicide; EPA Reg. No. 7969-197)

Parameter	Value	Reference
Melting point	143.4-143.6°C (TGAI)	D278385, M. Nelson, 8/15/03
pH (23°C)	5.5 (1% solution)	
Density	1.394g/cm ³ (TGAI)	
Water solubility (20°C)	4.64 mg/L (PAI)	
Solvent solubility (g/100 mL at 20°C)	PAI: 16-20 in acetone; 4-5 in acetonitrile; 4-5 in methanol; 6.7-8 in ethylacetate; 20-25 in dichloromethane; 2-2.5 in toluene; <1 in 1-octanol	
Vapour pressure at 20°C	7 x 10 ⁻⁹ hPa (PAI)	
Dissociation constant (pK _a)	Does not dissociate in water.	
Octanol/water partition coefficient at 21°C Log(K _{ow})	2.96 (PAI)	
UV/visible absorption spectrum	Not available	

TGAI: technical grade active ingredient
 PAI: pure active ingredient

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

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.



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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 boscalid (70% WDG) were made to the treated plots at 0.22-0.24 lb ai/A, for a total application rate of 0.92-0.93 lb ai/A. The retreatment intervals between applications were 6-8 days. The applications were made using ground equipment in either a concentrated 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	70% WDG	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	0.23	4	6-8	0.92	Non-silicone based adjuvant (LI-700)
			Dilute: 140-146	0.23	4	6-8	0.92	Non-silicone based adjuvant (LI-700)
Wasco, CA, 2003	70% WDG	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	0.23	4	6-8	0.92	Non-silicone based adjuvant (LI-700)
			Dilute: 148-178	0.23	4	6-8	0.92	Non-silicone based adjuvant (LI-700)
Madera, CA, 2003	70% WDG	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	0.23-0.24	4	7	0.93	Non-silicone based adjuvant
			Dilute: 201-202	0.23	4	7	0.92	Non-silicone based adjuvant
Glenn, CA, 2003	70% WDG	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	0.23	4	7	0.92	Non-silicone based adjuvant
			Dilute: 197-201	0.23	4	7	0.92	Non-silicone based adjuvant
Hughson, CA, 2003	70% WDG	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	0.22-0.23	4	6-7	0.92	Non-silicone based adjuvant (Penetrator Plus)
			Dilute: 209-210	0.23	4	6-7	0.93	Non-silicone based adjuvant (Penetrator Plus)



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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 boscalid were determined using an LC/MS/MS method (BASF Method Number D9908). Method D9908 was validated in conjunction with a previous boscalid petition (DP Barcode D278385, M. Nelson, 8/15/03) and deemed acceptable for data collection. A brief description of the method follows.



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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.

The method limit of detection (LOD) was 0.005 ppm and the validated limit of quantitation (LOQ) was 0.05 ppm for residues of boscalid in/on almond nutmeat and hulls. The method LOQ and LOD for boscalid residues in/on almond nutmeat and hulls were 0.02 and 0.005 ppm, respectively.

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 boscalid 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 boscalid 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 boscalid is stable in frozen storage for at least 12 months (D278385, M. Nelson, 8/15/03). These data will support the current almond field trials.

Analyte	Almond Matrix	Spiking Level (mg/kg)	Sample size	Recoveries (%)	Mean Recovery ± SD
Boscalid	Nutmeat	0.05	1	106	97
		2.0	1	88	
	Hulls	0.05	2	97, 78	89±8
		2.0	1	88	
		15.0	1	93	



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Matrix	Storage Temp. (°C)	Actual Storage Duration (months)	Limit of Demonstrated Storage Stability (months) ¹
Almond Nutmeat	< 0 < -10	3 - 5	12
Almond Hulls		3 - 5	

¹ Storage stability data are available indicating that boscalid is stable in frozen plant commodities for at least 12 months (D278385, M. Nelson, 8/15/03).

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Nutmeat	0.92	25	<0.05, <0.05
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Nutmeat	0.92	24	<0.05, <0.05
RCN 2003133 Madera, CA/2003	10	Butte	Nutmeat	0.93	26	<0.05, <0.05
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Nutmeat	0.92	25	<0.05, <0.05
RCN 2003135 Hughson, CA/2003	10	Carmel	Nutmeat	0.92	25	<0.05, <0.05

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Nutmeat	0.92	25	<0.05, <0.05
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Nutmeat	0.92	24	<0.05, <0.05
RCN 2003133 Madera, CA/2003	10	Butte	Nutmeat	0.92	26	<0.05, <0.05
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Nutmeat	0.92	25	<0.05, <0.05
RCN 2003135 Hughson, CA/2003	10	Carmel	Nutmeat	0.93	25	<0.05, <0.05



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

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Hulls	0.92	25	11.20, 11.30
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Hulls	0.92	24	4.06, 2.84
RCN 2003133 Madera, CA/2003	10	Butte	Hulls	0.93	26	1.80, 2.61
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Hulls	0.92	25	2.75, 2.52
RCN 2003135 Hughson, CA/2003	10	Carmel	Hulls	0.92	25	3.41, 3.18

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

Trial ID (City, State, Year)	EPA Region	Almond Variety	Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
RCN 2003131 Terra Bella, CA/2003	10	Monterey	Hulls	0.92	25	10.40, 13.40; (7.84, 12.70) ¹
RCN 2003132 Wasco, CA/2003	10	Non-Pareil	Hulls	0.92	24	7.14, 6.42
RCN 2003133 Madera, CA/2003	10	Butte	Hulls	0.92	26	4.92, 5.90
RCN 2003134 Glenn, CA/2003	10	Non-Pareil	Hulls	0.92	25	3.72, 3.11
RCN 2003135 Hughson, CA/2003	10	Carmel	Hulls	0.93	25	4.49, 3.33

¹ Re-analysis of same sample

TABLE C.4. Summary of Residue Data for Almonds from Crop Field Trials using a 70% WDG Formulation of Boscalid.

Commodity	Total Rate (lb a.i./A)	PHI (days)	Boscalid Residue Levels (ppm)						
			n	Min.	Max.	HAFT ¹	Median (STMdR ²)	Mean (STMR ²)	Std. Dev.
Nutmeat (Conc.)	0.92-0.93	24-26	10	<0.05	<0.05	<0.05	<0.05	<0.05	0
Nutmeat (Dilute)	0.92-0.93	24-26	10	<0.05	<0.05	<0.05	<0.05	<0.05	0
Nutmeat (Overall)	0.92-0.93	24-26	20	<0.05	<0.05	<0.05	<0.05	<0.05	0
Hulls (Conc.)	0.92-0.93	24-26	10	1.8	11.3	11.3	3.0	4.6	3.6
Hulls (Dilute)	0.92-0.93	24-26	10	3.1	13.4	11.1	5.4	6.1	3.1
Hulls (Overall)	0.92-0.93	24-26	20	1.8	13.4	11.3	3.9	5.3	3.3

¹ HAFT = Highest Average Field Trial.

² STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.



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D. CONCLUSION

The almond field trial data are adequate and reflect the use of four applications of boscalid (70% WDG) at 0.22-0.24 lb ai/A/application, for a total of 0.92-0.93 lb ai/A/season. The data would support a 24-26 day PHI. Maximum boscalid residues were below the LOQ of 0.05 ppm in almond nutmeat treated with either the concentrated spray or the dilute spray. In almond hulls, on the other hand, residues ranged up to 13.4 ppm in trees treated with the dilute spray and 11.3 ppm in trees treated with the concentrated spray.

E. REFERENCES

PP#0F06313. BAS 510 F (Common Name: Boscalid), New Fungicide Active Ingredient.
Residue Chemistry Summary Document, D278385, M. Nelson, 8/15/03

F. DOCUMENT TRACKING

Petition Number: 4F6875
DP Barcodes: D311246, D311271
PC Code: 128008