



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 - Spinach

Primary Evaluator Douglas A. Dotson, Chemist, RAB2 *D. Dotson* Date: 9/22/2005

Peer Reviewer William Drew, Chemist, RAB2 *W. Drew* Date: 10/7/2005

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Rd., Building 100, Suite B; Durham, NC 27713; submitted 1/14/2005). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

46145101 Chen, H. (2003) BAS 516 (BAS 510 F Plus BAS 500 F): Magnitude of the Residue on Spinach. Lab Project Number: IR-4 PR No. 08090. Unpublished study prepared by IR-4 Project Center for Minor Crop Pest Management. {OPPTS 860.1500}

EXECUTIVE SUMMARY:

In eight spinach field trials conducted during 2001, boscalid (70% WDG) was applied using ground equipment as two directed foliar applications to spinach at commercial maturity, at a retreatment interval (RTI) of 6-8 days. The application rate was 0.39-0.42 lb ai/A/application, for a total of 0.78-0.82 lb ai/A/season. The boscalid was tank mixed with the last two of four foliar applications of the fungicide pyraclostrobin (20% WDG); as the pyraclostrobin data from these tests were previously reviewed (46109101.der), it is not included in this report. A single control (designated 0-DAT (days after treatment)) and duplicate treated samples of spinach leaves were collected from each test at commercial maturity the same day as the last treatment (0-DAT), 6-7 DAT, and 13-15 DAT. Samples were stored frozen from collection to analysis for 3.2-11.3 months, an interval supported by available stability data.

The LC/MS/MS method (BASF Method Number D9908) used to determine residues of boscalid in/on spinach leaves is adequate for data collection. For this method, residues are extracted with methanol:water:2 N HCl, concentrated, cleaned up by solvent partitioning and silica gel SPE, and analyzed by LC/MS/MS. The lowest limit of method validation (LLMV) was 0.05 ppm. Based on recovery data at the LLMV, the LOQ and LOD were calculated to be 0.06 and 0.02 ppm, respectively.

Residues of boscalid were 12.6-41.8 ppm in/on 16 spinach leaf samples harvested immediately following (0-DAT) the last of two foliar applications. Boscalid residues were 4.5-21.3 ppm in/on 16 spinach leaf samples harvested 6-7 DAT and 0.17-17.8 ppm in/on 16 spinach leaf samples harvested 13-15 DAT. Average boscalid residues were 24.9 ppm (HAFT = 39.5 ppm) from 0 DAT samples, 10.4 ppm (HAFT = 21.0 ppm) from 7 DAT samples, and 6.4 ppm (HAFT = 17.1 ppm) from 14 DAT samples.



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STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the spinach field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming 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, animal, and rotational crop commodities, ranging from 0.02 ppm in/on eggs to 35 ppm in/on dried hops. Tolerances have been established for two of the representative commodities of the leafy vegetables crop group: head lettuce at 6.5 ppm and leaf lettuce at 11.0 ppm. The current field trials were submitted by IR-4 to support the use of boscalid on spinach. The proposed use rate cited in the study was for two broadcast foliar applications of boscalid (70% WDG) at 0.4 lb ai/A/application for a total of 0.8 lb ai/A/season, with a RTI of 7 days and a 0-Day PHI. The nomenclature and physicochemical properties of boscalid are presented below in Tables A.1. and A.2.

TABLE A.1. Nomenclature of Boscalid	
Compound	
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)



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TABLE A.2. Physicochemical Properties for Boscalid (BAS 510 F)

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

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 average monthly temperature range (°C)
Freeville, NY, 2001	Silty Clay Loam	NA = Not Applicable			Not reported = NR	NR
Salisbury, MD, 2001	Loamy Sand	NA			NR	NR
Salisbury, MD, 2001	Loamy Sand	NA			NR	NR
Weslaco, TX, 2001	Sandy Loam	NA			NR	NR
Holtville, CA, 2001	Silty Clay Loam	NA			NR	NR
Salinas, CA, 2001	Loam	NA			NR	NR
Fort Collins, CO, 2001	Clay/Clay Loam	NA			NR	NR
Weslaco, TX, 2001	Sandy Clay	NA			NR	NR

¹Detailed meteorological data were not provided.

Weather conditions were reported to be normal; no further details were provided. No unusual conditions that would affect the integrity of the study were reported. Rainfall was supplemented with irrigation as needed.

In eight spinach field trials conducted during 2001, boscalid (70% WDG) was applied to spinach plants using ground equipment as two directed foliar applications (Table B.1.2) at commercial maturity. The applications were made when plants were at the 5-8 leaf stage and the RTI was 6-8



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days. The application rate was 0.39-0.42 lb ai/A/application, for a total of 0.78-0.82 lb ai/A/season.

Each field test also included applications of the fungicide pyraclostrobin (BAS 500 F; 20% WDG) as four broadcast foliar applications at ~0.2 lb ai/A for a total of 0.8 lb ai/A/season, at RTIs of ~7 days. The final two pyraclostrobin applications were tank mixed with the two boscalid applications. Residue data for pyraclostrobin and its regulated metabolite were included in the submission; however, these data are not included in this report as the data were previously reviewed (46109101.der, M. Xue, 7/22/04).

TABLE B.1.2. Study Use Pattern on Spinach.

Location (City, State), Year	EP ¹	Method ² ; Timing	Volume (gal/A)	Single Rate (lb ai/A) ³	No. of Appl.	RTI (days)	Total Rate (lb ai/A) ³	Tank Mix Adjuvants
Freeville, NY, 2001	70% WDG	Foliar directed; 5-12 leaf stage	40-42	0.40, 0.42	2	6	0.82	None
Salisbury, MD, 2001	70% WDG	Foliar directed; mature spinach	33	0.40	2	8	0.80	None
Salisbury, MD, 2001	70% WDG	Foliar directed; mature spinach	33-34	0.40, 0.41	2	8	0.81	None
Weslaco, TX, 2001	70% WDG	Foliar directed; 12-16 leaf stage	39	0.39	2	7	0.78	None
Holtville, CA, 2001	70% WDG	Foliar directed; mature spinach	39-41	0.39, 0.40	2	7	0.79	None
Salinas, CA, 2001	70% WDG	Foliar directed; vegetative/mature	62-75	0.40, 0.41	2	7	0.81	None
Fort Collins, CO, 2001	70% WDG	Foliar directed; vegetative stage	40	0.40	2	8	0.80	None
Weslaco, TX, 2001	70% WDG	Foliar directed; vegetative stage	42-44	0.40-0.41	2	7	0.81	None

¹ EP = End-use Product.

² The applications were made using ground equipment.

³ The Endura™ 70% WDG label rate for lettuce is 0.48 lb ai/A/application and 0.96 lb ai/A/season. The target rate for the spinach field trials was 0.40 lb ai/A/application and 0.80 lb ai/A/season.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Region ¹	Spinach		
	Submitted	Requested	
		Canada	US
1	1	NA	1
2	2	NA	2
3	--	NA	--
4	--	NA	--
5	--	NA	--
6	2	NA	2
7	--	NA	--
8	1	NA	--
9	--	NA	1
10	2	NA	2
11	--	NA	--
12	--	NA	--



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TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Region ¹	Spinach		
	Submitted	Requested	
		Canada	US
13	--	NA	--
Total	8	NA	8

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

Spinach was harvested at commercial maturity, the same day as the last application (0-DAT), 6-7 DAT, and 13-15 DAT from all tests. A single control (0 DAT only) and duplicate treated spinach leaf samples (3-5 lbs each) were collected from each test and placed in frozen storage at the test facility within 40 minutes. Samples were stored frozen for 1-44 days, then shipped frozen by ACDS freezer truck, FedEx, or Airborne Express to the analytical laboratory, BASF Agro Research, RTP, NC, and stored frozen (<-10° C) prior to analysis. Samples were stored frozen from collection to analysis for up to 11.3 months.

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.

Residues are extracted with methanol:water:2 N HCl (70:25:5, v/v/v), concentrated, and cleaned up by partitioning into cyclohexane. Residues are then concentrated, cleaned up using a silica gel solid phase extraction cartridge eluted with 4% ethyl acetate in methylene chloride. Residues are analyzed by LC/MS/MS using the positive ionization mode monitoring ion transitions from *m/z* 343 to 307. Quantitation is obtained using an external calibration curve of boscalid. The LLMV for boscalid residues is 0.05 ppm in/on spinach. The LOQ and LOD were determined to be 0.06 ppm and 0.02 ppm, respectively.

In conjunction with the current field trials, control samples of spinach were fortified with boscalid at 0.05, 1.0, and 50 ppm and analyzed concurrently with the field samples.

C. RESULTS AND DISCUSSION

The number and geographic representation of the spinach field trials are adequate. Eight field trials were conducted in Regions 1, 2 (two tests), 6 (two tests), 8, and 10 (two tests).

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The LC/MS/MS method (BASF Method Number D9908) used to determine residues of boscalid in/on spinach leaves is adequate for data collection. Average concurrent recoveries were $84 \pm 10\%$ for boscalid (Table C.1). Apparent residues of boscalid were <LOQ in/on all control samples. Based on the LLMV, the LOQ was estimated to be 0.06 ppm for residues of boscalid in/on spinach; the LOD was estimated to be 0.02 ppm. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for 3.2-11.3 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 spinach field trials.

TABLE C.1 Summary of Concurrent Recoveries of Boscalid from Spinach using LC/MS/MS Method D9908.

Analyte	Spinach Matrix	Spiking Level (mg/kg)	Sample size	Recoveries (%)	Mean Recovery \pm SD
Boscalid (BAS 510 F)	Leaves	0.05	8	68-105 (1) ¹	84 \pm 10
		1.0	2	85, 97	
		50.0	6	75-89	

¹ The number of recoveries outside the 70-120% range is in parentheses.

TABLE C.2 Summary of Freezer Storage Conditions

Spinach Matrix	Storage Temp. (°C)	Actual Storage Duration (months) ¹	Limit of Demonstrated Storage Stability (months) ²
Leaves	< -10	3.2-11.3	12

¹ Extracts were stored frozen for 0-1 days prior to analysis.

² 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).

Residues of boscalid were 12.6-41.8 ppm in/on 16 spinach leaf samples harvested immediately following (0-DAT) the last of two foliar applications of the 70% WDG totaling 0.78-0.82 lb/A/season (Table C.3). Boscalid residues were 4.5-21.3 ppm in/on 16 spinach leaf samples harvested 6-7 DAT and 0.17-17.8 ppm in/on 16 spinach leaf samples harvested 13-15 DAT. Average boscalid residues were 24.9 ppm (HAFT = 39.5 ppm) from 0 DAT samples, 10.4 ppm (HAFT = 21.0 ppm) from 7 DAT samples, and 6.4 ppm (HAFT = 17.1 ppm) from 14 DAT samples (Table C.4).

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. In addition, the application volume has minimal or no impact on residue levels.



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TABLE C.3 Residue Data from Spinach Field Trials with 70% WDG Formulation of Boscalid.

Trial ID (City, State, Year)	EPA Region	Spinach Variety	Matrix	Total Rate (lb ai/A)	PHI (days) ¹	Boscalid Residues (ppm)
Freeville, NY, 2001	1	Olympia	Leaves	0.82	0	25.9, 27.5
					6	4.54, 4.95
					14	0.18, 0.17
Salisbury, MD, 2001	2	Vienna	Leaves	0.80	0	22.8, 21.9
					7	17.6, 21.3
					14	16.4, 17.8
Salisbury, MD, 2001	2	Vancouver	Leaves	0.81	0	28.7, 28.2
					7	20.9, 21.0
					14	14.7, 14.5
Weslaco, TX, 2001	6	Olympia	Leaves	0.78	0	41.6, 34.0
					7	9.12, 9.34
					15	4.21, 3.75
Holtville, CA, 2001	10	Bolero	Leaves	0.79	0	13.0, 12.6
					7	10.2, 8.90
					14	5.12, 5.68
Salinas, CA, 2001	10	El Palmar	Leaves	0.81	0	14.3, 16.3
					6	7.66, 5.40
					13	3.68, 3.08
Fort Collins, CO, 2001	8	Unipack 151	Leaves	0.80	0	17.9, 14.7
					7	4.91, 4.49
					14	1.05, 2.20
Weslaco, TX, 2001	6	Fall Green	Leaves	0.81	0	37.2, 41.8
					6	9.10, 6.65
					13	4.76, 4.53

The current PHI for lettuce is 14 days; the proposed PHI for spinach is 0 days.

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

Commodity	Total Rate (lb a.i./A)	PHI (days) ¹	Boscalid Residue Levels (ppm)						
			n	Min.	Max.	HAFT ²	Median (STMdR ³)	Mean (STMR ³)	Std. Dev.
Spinach Leaves	0.78-0.82	0	16	12.6	41.8	39.5	24.4	24.9	9.9
		6-7	16	4.49	21.3	21.0	9.0	10.4	6.2
		13-15	16	0.17	17.8	17.1	4.37	6.36	5.93

The current PHI for lettuce is 14 days; the proposed PHI for spinach is 0 days.

² HAFT = Highest Average Field Trial.

³ STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.

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D. CONCLUSION

The spinach field trial data are adequate and reflect the use of up to two foliar directed applications of boscalid (70% WDG) at 0.4 lb ai/A/application, for a total of ~0.80 lb ai/A/season. The data would support a 0-day, 7-day, or 14-day PHI. Maximum boscalid residues were 41.8 ppm from 0-day PHI samples, 21.3 ppm from 7-day PHI samples, and 17.8 ppm from 14-day PHI samples.

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: 1F6313
DP Barcode: D316092
PC Code: 128008

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