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 - Celery

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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 1/14/2005). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

46145102 Chen, H. (2003) BAS 516 (BAS 510 F Plus BAS 500 F): Magnitude of the Residue on Celery. Lab Project Number: IR-4 PR No. 08091. Unpublished study prepared by IR-4 Project Center for Minor Crop Pest Management. 274 p. {OPPTS 860.1500}

EXECUTIVE SUMMARY:

Twelve celery fields trials were conducted during 2001, with eight field trials in the US and four in Canada. In each test, boscalid (70% WDG) was applied to celery plants using ground equipment as two directed foliar applications at 0.39-0.42 lb ai/A/application, for a total of 0.78-0.82 lb ai/A/season. Applications were made during the vegetative stage when plants were ~12-24" tall and the retreatment interval (RTI) was 6-8 days. 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 (46109102.der), it is not included in this report. A single control (0 days after treatment (DAT) only) and duplicate treated samples of celery plants were collected from each test at commercial maturity the same day as the last treatment (0-DAT), 6-8 DAT, and 13-15 DAT. Samples were stored frozen from collection to analysis for 3.2-9.6 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 celery is adequate for data collection. For this method, residues are extracted with methanol:water:2 N HCl, concentrated, and cleaned up by solvent partitioning and using a silica gel SPE cartridge, prior to LC/MS/MS analysis. 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 1.8-19.7 ppm in/on 24 celery samples harvested immediately following (0-DAT) the last of two foliar applications. Boscalid residues were 0.3-11.0 ppm in/on 24 celery samples harvested 6-8 DAT and 0.2-9.8 ppm in/on 24 celery samples harvested 13-15 DAT. Average boscalid residues were 8.7 ppm from 0-DAT samples, 3.6 ppm from 7-DAT samples, and 2.3 ppm from 14-DAT samples.

(1)

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the celery 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 celery. 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

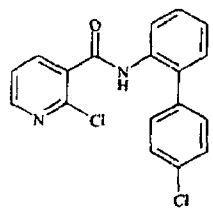
Compound	
Common name	Boscalid
Company experimental names	BAS 510 F
IUPAC name	2-chloro-N-(4'-chlorobiphenyl-2-yl)-nicotinamide
CAS name	3-pyridinecorboxamide,2-chloro-N-(4'-chloro[1,1'-biphenyl]-2-yl
CAS #	188425-85-6
End-use products/EP	70% WDG (Endura™ fungicide; EPA Reg. No. 7969-197)

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TABLE A.2. Physicochemical Properties for Boscalid		
Parameter	Value	Reference
Melting point	143.4-143.6°C (TGAI); 142.8-143.8°C (PAI)	D278385, M. Nelson, 8/15/03
pH (23°C)	5.5 (1% solution)	
Density	1.394g/cm^3 (TGAI); 1.381g/cm^3 (PAI)	
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)
Gainesville, FL, 2001	Sandy	NA = Not Applicable			8.8-9.8	Not reported = NR
Gainesville, FL, 2001	Sandy	NA			8.8-9.8	NR
Holtville, CA, 2001	Silty Clay Loam	NA			NR	NR
Visalia, CA, 2001	Loam	NA			NR	NR
Brooks, OR, 2001	Silt Loam	NA			NR	NR
Celeryville, OH, 2001	Muck	NA			NR	NR
Salinas, CA, 2001	Loam	NA			NR	NR
Salinas, CA, 2001	Loam	NA			NR	NR
Quebec, Canada, 2001	Muck	NA			NR	NR
Quebec, Canada 2001	Muck	NA			dry in July and early August	excess temperature in July and early August[1]
Ontario, Canada, 2001	Silt Loam	NA			NR	early October frost[1]
Ontario, Canada, 2001	Silt Loam	NA			dry in August	early October frost[1]

[1] Detailed meteorological data were not provided.

Weather conditions were reported to be normal, with the following exceptions: (i) conditions were wetter than normal in June and July at the two FL locations; (ii) conditions were drier and warmer than normal at one Quebec location in July and early August, and drier in August at one

Ontario location; and (iii) early October frost was reported from both Ontario locations. 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.

Twelve celery field trials were conducted during 2001, eight in the US and four in Canada. In each test, boscalid (70% WDG) was applied to celery plants using ground equipment as two directed foliar applications (Table B.1.2), with a RTI of 6-8 days. Applications were made during the vegetative stage when plants were ~12-24" tall, at approximately commercial maturity. 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 (46109102.der, M. Xue, 7/22/04).

TABLE B.1.2. Study Use Pattern on Celery.

Location (City, State), Year	EP [1]	Method [2]; Timing [3]	Volume (gal/A)	Single Rate (lb ai/A) [4]	No. of Appl.	RTI (days)	Total Rate (lb ai/A) [4]	Tank Mix Adjuvants
Gainesville, FL, 2001	70% WDG	Foliar directed; vegetative	36	0.41	2	8	0.82	None
Gainesville, FL, 2001	70% WDG	Foliar directed; vegetative	35, 36	0.40, 0.41	2	8	0.81	None
Holtville, CA, 2001	70% WDG	Foliar directed; vegetative	41, 43	0.40, 0.41	2	7	0.81	None
Visalia, CA, 2001	70% WDG	Foliar directed; vegetative	49	0.41	2	7	0.82	None
Brooks, OR, 2001	70% WDG	Foliar directed; vegetative	42, 43	0.40, 0.41	2	8	0.81	None
Celeryville, OH, 2001	70% WDG	Foliar directed; vegetative	53, 54	0.39, 0.40	2	8	0.79	None
Salinas, CA, 2001	70% WDG	Foliar directed; vegetative	63, 87	0.41, 0.42	2	6	0.83	None
Salinas, CA, 2001	70% WDG	Foliar directed; vegetative	63, 66	0.41, 0.42	2	7	0.83	None
Napierville, Quebec, Canada, 2001	70% WDG	Foliar directed; vegetative	48, 52	0.38, 0.40	2	7	0.78	None
Napierville, Quebec, Canada, 2001	70% WDG	Foliar directed; vegetative	50, 51	0.39, 0.40	2	7	0.79	None
Ontario, Canada, 2001	70% WDG	Foliar directed; vegetative	37	0.40	2	6	0.80	None
Ontario, Canada, 2001	70% WDG	Foliar directed; vegetative	37, 38	0.40, 0.41	2	6	0.81	None

[1] EP = End-use Product.
[2] The applications were made using ground equipment.
[3] Applications were made when plants were approximately at commercial maturity.
[4] The target rate for the celery field trials was 0.40 lb ai/A/application and 0.80 lb ai/A/season.

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TABLE B.1.3. Trial Numbers and Geographical Locations.

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

[1] Regions 14-21 and 1A, and 7A were not included as the proposed use is for the US only.
[2] Although the proposed use is for the US, additional tests were conducted in Regions 5A (Ontario) and 5B (Quebec).
NA = not applicable.

B.2. Sample Handling and Preparation

Celery plants were harvested at commercial maturity, the same day as the last application (0-DAT), 6-8 DAT, and 13-15 DAT from all tests. A single control (0 DAT only) and duplicate treated celery samples (12 whole plants each) were collected from each test and placed in frozen storage at the test facility within 7 hours. Samples were stored frozen for 0-132 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 9.6 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 partitioned into cyclohexane. Residues were then concentrated and 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 with boscalid. The LLMV for boscalid residues is 0.05 ppm in/on celery. Using the recovery data from the lowest fortification level, a LOD of 0.02 ppm and a LOQ of 0.06 ppm were calculated based on a method described in Roy-Keith Smith's Handbook of Environmental Analysis, 4th Ed.

In conjugation with the current field trials, control samples of celery were fortified with boscalid at 0.05-20 ppm and analyzed concurrently with the field samples.

C. RESULTS AND DISCUSSION

The number and geographic representation of the celery field trials are adequate. Eight field trials were conducted in the U.S. in Regions 3 (two tests), 5 (one test), 10 (four tests), and 12 (one test). Four field trials were also conducted in Canada in Regions 5A (2 tests) and 5B (2 tests).

The LC/MS/MS method (BASF Method Number D9908) used to determine residues of boscalid in/on celery is adequate for data collection. Average concurrent recoveries were 73% with a standard deviation of 12% for boscalid (Table C.1). Apparent residues of boscalid were <LOQ in/on all control samples. Based on the LLMV, the LOQ and LOD were calculated to be 0.06 and 0.02 ppm, respectively. Adequate sample calculations and chromatograms were provided.

Samples were stored frozen from collection to analysis for 3.2-9.6 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 celery field trials.

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

Analyte	Celery Matrix	Spiking Level (mg/kg)	Sample size	Recoveries (%)	Mean Recovery ± SD
Boscalid	Stems and leaves	0.05	13	41-99 (5)[1]	73 ± 12
		1.0	8	62-93 (1)[1]	
		2.0	1	88	
		10	3	70-85	
		20	2	72, 76	

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

TABLE C.2 Summary of Freezer Storage Conditions			
Celery Matrix	Storage Temp. (°C)	Actual Storage Duration (months) [1]	Limit of Demonstrated Storage Stability (months) [2]
Leaves	< -10	3.2-9.6	12

[1] Extracts were stored frozen for 0-3 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 1.8-19.7 ppm in/on 24 celery samples harvested immediately following (0-DAT) the last of two foliar applications of the 70% WDG totaling 0.78-0.83 lb/A/season (Table C.3). Boscalid residues were 0.3-11.0 ppm in/on 24 celery samples harvested 6-8 DAT and 0.2-9.8 ppm in/on 24 celery samples harvested 13-15 DAT. Average boscalid residues were 8.7 ppm from 0-DAT samples, 3.6 ppm from 7-DAT samples, and 2.3 ppm (HAFT = 9.3 ppm) from 14 DAT samples (Table C.4). In all field trials except one (i.e., the one performed in Holtwell, CA) residues decreased with an increase in PHI.

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.

TABLE C.3. Residue Data from Celery Field Trials with a 70% WDG Formulation of Boscalid.						
Trial ID (City, State, Year)	EPA Region	Celery Variety	Celery Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
Gainesville, FL, 2001	3	June Bell 1622	Stems and Leaves	0.82	0	12.5, 13.4
					7	11.0, 8.6
					14	3.3, 2.7
Gainesville, FL, 2001	3	June Bell 1622	Stems and Leaves	0.81	0	15.6, 18.3
					7	4.4, 4.5
					14	3.1, 3.1
Holtville, CA, 2001	10	Conquistador	Stems and Leaves	0.81	0	9.7, 9.7
					7	8.3, 7.6
					14	9.8, 8.8
Visalia, CA, 2001	10	Conquistador	Stems and Leaves	0.82	0	8.3, 7.6
					7	5.5, 5.0
					14	4.3, 5.0
Brooks, OR, 2001	12	Picador	Stems and Leaves	0.81	0	4.4, 5.6
					7	3.3, 3.7
					14	*0.88, 2.6* (1.7)[2], *2.5, 2.3* (2.4)[2]
Celeryville, OH, 2001	5	Ventura	Stems and Leaves	0.79	0	8.6, 8.1
					8	3.8, 4.0
					14	0.72, 0.78

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

Trial ID (City, State, Year)	EPA Region	Celery Variety	Celery Matrix	Total Rate (lb ai/A)	PHI (days)	Boscalid Residues (ppm)
Salinas, CA, 2001	10	Conquistador	Stems and Leaves	0.83	0	2.7, 2.6
					7	0.88, 0.70
					14	0.40, 0.33
Salinas, CA, 2001	10	Conquistador	Stems and Leaves	0.83	0	1.9, 1.8
					6	0.79, 0.73
					13	0.35, 0.47
Quebec, Canada, 2001	5B	Calmario	Stems and Leaves	0.78	0	2.0, 2.0
					8	0.39, 0.32
					15	0.16, 0.23
Quebec, Canada, 2001	5B	Calmario	Stems and Leaves	0.79	0	6.5, 6.7
					7	1.0, *1.9, 1.9* (1.9)[2]
					14	*0.66, 0.77, 0.61* (0.68)[2], *0.34, 0.34, 0.12* (0.27)[2]
Ontario, Canada, 2001	5A	Florida 683	Stems and Leaves	0.80	0	19.7, 18.4
					7	3.5, 2.3
					14	1.3, 1.4
Ontario, Canada, 2001	5A	Florida 683	Stems and Leaves	0.81	0	12.6, 10.7
					7	2.7, 2.5
					14	1.5, 1.2

[1] The current PHI for lettuce is 14 days; the proposed PHI for celery is 0 days.
[2] Values in *italics* represent multiple analyses of the sample; the average (in parentheses) was used is subsequent calculations.

TABLE C.4. Summary of Residue Data for Celery 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.
Celery	0.78-0.83	0	24	1.8	19.7	19.1	8.2	8.7	5.5
		6-8	24	0.3	11.0	9.8	3.4	3.6	2.9
		13-15	24	0.2	9.8	9.3	1.4	2.3	2.6

[1] The current PHI for lettuce is 14 days; the proposed PHI for celery is 0 days.
[2] HAFT = Highest Average Field Trial.
[3] STMdR = Supervised Trial Median Residue; STMR = Supervised Trial Mean Residue.

D. CONCLUSION

The celery field trial data are adequate and reflect the use of up to two foliar directed applications of a 70% WDG formulation of boscalid totaling ~0.8 lb ai/A/season. The data would support a PHI of 0 days, 7 days, or 14 days. Maximum boscalid residues were 19.7 ppm from 0-day PHI samples, 11.0 ppm from 7-day PHI samples, and 9.8 ppm from 14-day PHI samples.

E. REFERENCES

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

F. DOCUMENT TRACKING

Petition Number: 1F6313
DP Barcode: D316092
PC Code: 128008

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