

US EPA ARCHIVE DOCUMENT



Pyraclostrobin/BAS 500 F/PC Code 099100/BASF Corporation  
 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

Primary Evaluator	Manning Xue, Chemist RAB3/HED (7509C)	Date: 07/22/04
Approved by	Leung Cheng, Ph.D. Senior Chemist RAB3/HED (7509C)	Date: 07/22/04

### STUDY REPORTS:

MRID No. 46109102, Chen, H (2002) BAS 516 (BAS 510 F Plus BAS 500 F): Magnitude of the Residue on Celery: IR-4 PR No. 08091, Lab. Identification Number 08091.01-BAR02, Unpublished study prepared by IR-4, 274 pages.

### EXECUTIVE SUMMARY:

IR-4 Project on behalf of the Agricultural Experiment Stations of Texas, Oregon, and California has submitted celery field trial data for pyraclostrobin in/on celery. Twelve trials were conducted in regions: III: FL (2 trial), X: CA (4 trials), XI: OR (1 trials), V: OH (1 trials) and Quebec (equivalent to EPA Region V, 2 trial), and Ontario (equivalent to EPA Region I, 2 trial) during the 2001 growing season. The number and locations of field trials, including the three trials conducted in year 2001 (MRID 46109102), are in accordance with OPPTS Guideline 860.1500. The number and location of the field trials are sufficient to support a tolerance for celery.

At each test location, celery received two sequential foliar applications of BAS 500 02 F at a rate of approximately 0.2 lb ai/A per application in combination with BAS 510 UCF for a total of approximately 0.8 lb ai/A. The retreatment intervals between the sequential applications were 6-9 days. Celery were harvested with preharvest intervals (PHIs) of 0 day, 7(±1) days and 14 (±1) days following the last application.

Samples were analyzed at BASF Agro Research, Research Triangle Park, NC for residues of pyraclostrobin and BF 500-3 in celery using LC/MS/MS BASF Method D9908. The method is adequate for data collection based on acceptable concurrent method recovery data. The limit of quantitation (LOQ) was 0.02 ppm for BAS 500 F and BF 500-3 in celery.

The maximum storage interval of celery samples from harvest to analysis was 9.6 months. No celery storage stability data have been submitted. Available storage stability data indicated 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. The storage stability data can be translated to support the storage intervals for celery samples for this study (D269668, etc., L. Cheng, 11/28/2001).

The combined residues of pyraclostrobin and its metabolite ranged from 1.02 ppm to 10.7 ppm



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with a PHI of 0 day, 0.39 ppm to 6.68 ppm with a PHI of 7 days and <0.02 ppm to 7.88 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on celery at the seasonal application rate of 0.8 lb ai/A.

**STUDY CLARIFICATIONS**

Under the conditions and parameters used in the study, the 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 DP Barcode D298178.

**COMPLIANCE:**

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported.

**A. BACKGROUND INFORMATION**

Pyraclostrobin is a fungicide that is structurally related to the naturally occurring strobilurins, compounds derived from some fungal species. Pyraclostrobin is also in the same chemical class as azoxystrobin (PC 128810), registered for many crops and turf/lawn, and trifloxystrobin (PC 129112) which recently was granted a "reduced risk" status as a fungicide on many crops. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi.

TABLE A.1. Test Compound Nomenclature	
Compound	Chemical Structure
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl N-(2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl)methoxycarbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	17013-18-0
End-use product/EP	BAS 500 02 F and BAS 510 UCF



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Pyraclostrobin technical is a white to light beige solid.

Parameter	Value	Reference <sup>1</sup>
Boiling point/boiling range	N/A	D290351
pH	N/A	D290351
Density	1.285g/cm <sup>3</sup> at 20°C	D290351
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	D290351
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).	D290351
Vapour pressure at 25°C	2.6 x 10 <sup>-10</sup> hPa (at 20°C); 6.4 x 10 <sup>-10</sup> hPa	D290351
Dissociation constant (pK <sub>a</sub> )	Does not dissociate in water. There are no dissociable moieties.	D290351
Octanol/water partition coefficient Log(K <sub>ow</sub> )	n-Octanol/water partition coefficient (K <sub>ow</sub> ) at room temperature (=K <sub>ow</sub> of 3.80, pH 6.2; =log K <sub>ow</sub> 4.18, pH 6.5).	D290351

**B. EXPERIMENTAL DESIGN**

**B.1. Study Site Information**

Trial Identification (City, State/Year)	Soil characteristics				Meteorological data	
	Type	%OM <sup>1</sup>	pH <sup>1</sup>	CEC <sup>1</sup> meq/g	Monthly rainfall average	Mean T (°C)
Gainesville, FL/2001	sand	2.1	5.7	NA <sup>2</sup>	NA	31-33
Gainesville, FL/2001	sand	2.1	5.7	NA		31-33
Holtville, CA/2001	silty clay loam	0.68	7.7	NA		14-37
Visalia, CA/2001	loam	1.24	7.6	NA		22-28
Brooks, OR/2001	silt loam	2.0	5.9	NA		15-31
Celeryville, OH/2001	muck	45.9	5.8	NA		19-28
Salinas, CA/2001	loam	1.8	7.5	NA		13-21
Salinas, CA/2001	loam	1.8	7.5	NA		14-20
Quebec, Canada/2001	muck	NA	NA	NA		25-28
Quebec, Canada/2001	muck	NA	NA	NA		12-26
Ontario, Canada/2001	silty loam	1.21	7.9	NA		11-21
Ontario, Canada/2001	silty loam	2.24	7.3	NA		11-21

<sup>1</sup> These parameters (percent organic matter, pH, and cation exchange capacity) are optional except in cases where



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their value affects the use pattern for the chemical.

<sup>2</sup> Not available.

**TABLE B.1.2. Study Use Pattern.**

Location (City, State/Year)	EP <sup>1</sup>	Application				Tank Mix Adjuvants	
		Method/Timing	Vol, GPA <sup>2</sup>	Rate, (lb a.i./A) )	RTI, <sup>3</sup> days		Total Rate, (lb a.i./A)
Gainesville, FL/2001	BAS 500 02 F	Vegetative	36-37	0.2	7±1	0.8	None
Gainesville, FL/2001	BAS 500 02 F	Vegetative	35-36	0.2	7±1	0.8	None
Holtville, CA/2001	BAS 500 02 F	Very young stalks	40-43	0.2	7±1	0.8	None
Visalia, CA/2001	BAS 500 02 F	Harvestable vegetative plant parts 70% of final size	45-49	0.2	7±1	0.8	None
Brooks, OR/2001	BAS 500 02 F	12-14 stalks per row avg. 1" size	42-43	0.2	7±1	0.8	None
Celeryville, OH/2001	BAS 500 02 F	Vegetative	53-58	0.2	7±1	0.8	None
Salinas, CA/2001	BAS 500 02 F	Vegetative, stalks 2-2.5" in diameter	60-87	0.2	7±1	0.8	None
Salinas, CA/2001	BAS 500 02 F (20% WG)	Foliar/Vegetative, medium sized stalks 2-3" in diameter	35-66	0.2	7±1	0.8	None
Quebec, Canada/2001	BAS 500 02 F (20% WG)	Foliar/Vegetative	48-52	0.2	7±1	0.8	None
Quebec, Canada/2001	BAS 500 02 F (20% WG)	Foliar/Vegetative	47-51	0.2	7±1	0.8	None
Ontario, Canada/2001	BAS 500 02 F (20% WG)	Foliar/Vegetative	37-38	0.2	7±1	0.8	None
Ontario, Canada/2001	BAS 500 02 F (20% WG)	Foliar/Vegetative	37-38	0.2	7±1	0.8	None

<sup>1</sup> EP = End-use Product

<sup>2</sup> Gallons per acre, L/ha

<sup>3</sup> Retreatment Interval

**TABLE B.1.3. Trial Numbers and Geographical Locations**

Growing Region	Celery	
	Submitted	Requested
1A	2	
3	3	2

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5	1	1
5A	2	
10	4	5

## B.2. Sample Handling and Preparation

After harvest, samples were placed in a freezer ( $< -20^{\circ}\text{C}$ ) upon arrival at BASF Agro Research. Celery samples were homogenized with dry ice before analysis.

The maximum storage interval of celery samples from harvest to analysis were 9.6 months. No celery storage stability data have been submitted. Available storage stability data indicated 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. The storage stability data can be translated to support the storage intervals for celery samples for this study (D269668, etc., L. Cheng, 11/28/2001).

## B.3. Analytical Methodology

The method used to analyze the residues of pyraclostrobin (BAS 500 F) and BF 500-3 in celery was the LC/MS/MS BASF Method. Homogenized spinach samples are extracted with methanol:water:2N HCl (70:25:5, v:v:v) and filtered. An aliquot of the extract is removed and cleaned by liquid/liquid partitioning. Residues are further purified on a silica gel Speedisk micro column. Residues are analyzed by LC/MS/MS. For quantitation, the product/daughter ion for the transition  $m/z$  388  $\rightarrow$  194 for pyraclostrobin (BAS 500 F) and  $m/z$  358  $\rightarrow$  164 for BAS 500-3 are measured. The limit of quantitation (LOQ) was 0.02 ppm for BAS 500 F and BF 500-3 in spinach.

Recoveries of pyraclostrobin from celery samples fortified over the concentration range of 0.02 ppm to 20.0 ppm averaged 81% to 90 $\pm$ 4% for BAS 500 F and 78 $\pm$ 12% to 90 $\pm$ 9 for BF 500-3.

## C. RESULTS AND DISCUSSION

The analytical method (LC/MS/MS BASF Method D9908) is adequate as a data collection method. As shown in Table C.1, adequate method validation data for celery have been provided. The limit of quantitation (LOQ) was 0.02 ppm for 500 F and BF 500-3 in celery.

As shown in Table C.2, the available information indicated that celery samples were stored for a maximum of about 9.6 months. As indicated in the previous studies, 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



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25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for celery samples for this study (D269668, etc., L. Cheng, 11/28/2001).

As indicated in Table C.3., twelve trials were conducted in regions: III: FL (2 trial), X: CA (4 trials), XI: OR (1 trials), V: OH (1 trials) and Quebec (equivalent to EPA Region V, 2 trial), and Ontario (equivalent to EPA Region I, 2 trial) during the 2001 growing season(MRID 46109102).

The combined residues of pyraclostrobin and its metabolite ranged from 1.02 ppm to 10.7 ppm with a PHI of 0 day, 0.39 ppm to 6.68 ppm with a PHI of 7 days and <0.02 ppm to 7.88 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on celery at the seasonal application rate of 0.8 lb ai/A.

Matrix	Spike level (mg/kg)	Sample Size (n)	Recoveries (%)		Mean ± std dev		
			BAS 500F	BF 500-3	BAS 500F	BF 500-3	
Celery	0.02	NA	13	NA	65-109	NA	78±12
	1.0	8	8	71-96	68-99	89±8	90±9
	2.0	1	1	88	89	88	89
	10	3	3	80-82	77-84	81	81±4
	20	2	2	87-92	87-91	90±4	89±3

Matrix (RAC)	Storage Temp. (°C)	Actual Storage Duration (months)	Interval of Demonstrated Storage Stability (months)
Analyte: Pyraclostrobin (BAS 500F & BF 500-3)			
Celery	< -20	9.6	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. The storage stability data can be translated to support the storage intervals for celery samples for this study (D269668, etc., L. Cheng, 11/28/2001).

Trial ID (City, State/Year)	Region	Crop Variety	Total Rate, (lb a.i./A)	PHI (days)	Residues (ppm)		
					BAS 500F	BF 500-3	Total
Gainesville, FL/2001	3	Dane bell 1622	0.8	0	5.78, 6.30	0.22, 0.23	6.00, 6.53
				7	4.26, 3.78	0.38, 0.35	4.64, 4.13

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Location	Replicates	Genotype	PHI	14	7	0	14
Gainesville, FL/2001	3	June bell 1622	0.8	14	2.24, 1.94	0.29, 0.29	2.53, 2.23
				0	5.50, 7.38	0.12, 0.13	5.62, 7.51
				7	1.81, 1.94	0.19, 0.25	2.00, 2.19
				14	1.88, 1.43	0.23, 0.21	2.11, 1.64
Holtville, CA/2001	10	Conquistador	0.8	0	8.24, 9.44	0.30, 0.35	8.54, 9.79
				7	6.36, 6.38	0.31, 0.30	6.67, 6.68
				14	7.42, 6.70	0.46, 0.42	7.88, 7.12
				0	4.10, 3.79	0.23, 0.19	4.33, 3.98
Visalia, CA/2001	10	Conquistador	0.8	7	2.14, 2.10	0.22, 0.22	2.36, 2.32
				14	1.35, 1.55	0.19, 0.23	1.54, 1.78
				0	2.38, 3.07	0.07, 0.08	2.45, 3.15
				7	2.10, 2.15	0.09, 0.10	2.19, 2.25
Brooks, OR/2001	12	Picador	0.8	14	1.25, 1.55	0.07, 0.07	1.32, 1.62
				0	3.65, 3.54	0.10, 0.08	3.75, 3.62
				8	0.95, 0.90	0.09, 0.10	1.04, 1.00
				14	0.45, 0.61	0.06, 0.07	0.51, 0.68
Celeryville, OH/2001	5	Ventura	0.8	0	1.63, 1.49	0.05, 0.04	1.68, 1.53
				7	0.81, 0.66	0.04, 0.04	0.85, 0.70
				14	0.52, 0.49	0.04, 0.03	0.56, 0.52
				0	0.98, 1.16	0.04, 0.04	1.02, 1.20
Salinas, CA/2001	10	Conquistador	0.8	6	0.69, 0.53	0.04, 0.04	0.73, 0.57
				13	0.37, 0.48	0.03, 0.03	0.40, 0.51
				0	1.29, 1.14	<0.02, <0.02	1.29, 1.14
				8	0.56, 0.39	<0.02, <0.02	0.56, 0.39
Salinas, CA/2001	10	Conquistador	0.8	15	0.20, 0.34	<0.02, <0.02	0.20, 0.34
				0	3.10, 3.30	0.06, 0.07	3.16, 3.37
				7	0.61, 1.1	0.06, 0.06	0.67, 1.16
				14	0.40, 0.18	0.02, <0.02	0.42, 0.20
Quebec, Canada/2001	5	Calmario	0.8	0	10.4, 10.6	0.10, 0.10	10.5, 10.7
				7	3.49, 2.58	0.08, 0.07	3.57, 2.65
				14	1.82, 2.38	0.06, 0.07	1.88, 2.45
				0	9.7, 9.6	0.12, 0.12	9.82, 9.72
Quebec, Canada/2001	5	Calmario	0.8	7	3.93, 3.27	0.12, 0.10	4.05, 3.37
				14	2.16, 2.33	0.09, 0.09	2.25, 2.42
				0	10.4, 10.6	0.10, 0.10	10.5, 10.7
				7	3.49, 2.58	0.08, 0.07	3.57, 2.65
Ontario, Canada/2001	1	Florida 683	0.8	14	1.82, 2.38	0.06, 0.07	1.88, 2.45
				0	9.7, 9.6	0.12, 0.12	9.82, 9.72
				7	3.93, 3.27	0.12, 0.10	4.05, 3.37
				14	2.16, 2.33	0.09, 0.09	2.25, 2.42
Ontario, Canada/2001	1	Florida 683	0.8	0	9.7, 9.6	0.12, 0.12	9.82, 9.72
				7	3.93, 3.27	0.12, 0.10	4.05, 3.37
				14	2.16, 2.33	0.09, 0.09	2.25, 2.42
				0	9.7, 9.6	0.12, 0.12	9.82, 9.72

**TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyraclostrobin.**

Commodity	Total Applic. Rate, (lb a.i./A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAPT*	Median (STMdR <sup>2</sup> )	Mean (STMR <sup>3</sup> )	Std. Dev.

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Analyte: Pyraclostrobin (BAS 500F) & its metabolite (BF 500-3)									
Celery	0.8	0	24	1.02	10.7	10.06	3.87	5.02	3.34
	0.8	6-8	24	0.39	6.68	6.68	2.19	2.36	1.83
	0.8	13-15	24	<0.02	7.88	7.5	1.58	1.79	1.94

<sup>1</sup> HAFT = Highest Average Field Trial.

<sup>2</sup> STMdR = Supervised Trial Median Residue.

<sup>3</sup> STMR = Supervised Trial Mean Residue.

#### D. CONCLUSION

The combined residues of pyraclostrobin and its metabolite ranged from 1.02 ppm to 10.7 ppm with a PHI of 0 day, 0.39 ppm to 6.68 ppm with a PHI of 7 days and <0.02 ppm to 7.88 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on celery at the seasonal application rate of 0.8 lb ai/A.

#### E. REFERENCES

DP Barcodes: D269668, D27271, 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, Tuberos and Corn 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 & Bazuin

Dated: 11/28/01

MRIDs: 45118428-45118437, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 5429901

#### F. DOCUMENT TRACKING

RDI: ChemTeam:06/29/04:L. Cheng:07/22/04

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