
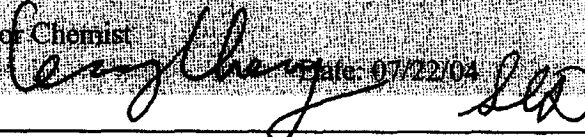


US EPA ARCHIVE DOCUMENT



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 IIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Citrus Fruits Crop Group

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

This DER was originally prepared under contract by Dynamac Corporation (20440 Century Boulevard, Suite 100; Germantown, MD 20874; submitted 02/26/2004). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

45903601 Jordan, J. (2002) Magnitude of BAS 500 02 F and BAS 510 02 F Residues in Citrus: Final Report: Lab Project Number: 2002/5002446:BASF Study Number 64978. Unpublished study prepared by BASF Agro Research. 129 p.

EXECUTIVE SUMMARY:

BASF Corporation has submitted field trial data for residues of pyraclostrobin and its metabolite 500-3 in/on citrus fruits (grapefruit, lemon, and orange). A total of 24 citrus fruit field trials were conducted during the 2001-2002 growing season. Six trials were conducted on grapefruit encompassing Regions 3 (FL; 3 trials), 6 (TX; 1 trial), and 10 (CA, 2 trials); five trials were conducted on lemon encompassing Regions 3 (FL; 1 trial) and 10 (AZ and CA; 4 trials); and thirteen trials were conducted on oranges encompassing Regions 3 (FL; 8 trials), 6 (TX; 1 trial), and 10 (CA; 4 trials).

At each test location, a total of four broadcast foliar applications of the 20% BAS 500 F WG formulation were made to citrus fruit trees (grapefruit, lemon, and orange) at ~0.2 lb ai/A/application (first and second applications) and ~0.25 lb ai/A/application (third and fourth applications) with 7- to 11-day retreatment intervals, for a total seasonal application rate of ~0.9 lb ai/A. Applications were made using ground equipment in either concentrate spray volumes (50-100 GPA) or dilute spray volumes (100-400 GPA) with a spray adjuvant added to



Pyraclostrobin/BAS 500 3/PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86 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 - Citrus Fruits Crop Group

limit of quantitation (LOQ) was 0.02 ppm for each analyte (pyraclostrobin and BF 500-3) in/on all citrus fruit matrices. This method is adequate for data collection based on acceptable concurrent method recovery data.

The maximum storage intervals of crop samples from harvest to analysis were 146 days (4.8 months) for grapefruit whole fruit, 136 days (4.5 months) for lemon whole fruit, 186 days (6.1 months) for orange whole fruit, 160 days (5.3 months) for orange pulp, and 180 days (5.9 months) for orange peel. No storage stability data have been submitted with this petition. 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 citrus fruits for this study (D269668, etc., L. Cheng, 11/2001).

The results from the citrus fruit field trials show that the maximum combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.627 ppm in/on grapefruit, 1.137 ppm in/on lemon, and 1.278 ppm in/on orange harvested 0 days following the last of four applications for a total application rate of 0.88-0.1 lb ai/A. The residue data reflect trials with both concentrate and dilute spray volumes.

Residues in oranges were primarily located in/on the orange peel. The combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.184-3.634 ppm in/on orange peel and <0.04-0.118 ppm in/on orange pulp separated from whole oranges harvested at the 0-day PHI.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/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 D290369.

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.



Pyraclostrobin/BAS 500 F/PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 860.1500/OECD II A 6.3.1, 6.3.2, 6.3.3 and III A 8.3.1, 8.3.2, 8.3.3
 Crop Field Trial - Citrus Fruits Crop Group

Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl <i>N</i> -{2-[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yloxymethyl]phenyl}(<i>N</i> -methoxy)carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use products/EPs	20% water dispersible granular formulation (WG; product name: Cabrio™ EG Fungicide; EPA Reg. No. 7969-187/EPA File Symbol 7969-RIT) and 2 lb/gal emulsifiable concentrate formulation (EC; Headline® Fungicide; EPA Reg. No. 7969-186/EPA File Symbol 7969-RIA)

Pyraclostrobin technical is a white to light beige solid.

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
Vapour 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)



Pyraclostrobin/BAS 500 /PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86 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 - Citrus Fruits Crop Group

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.

Trial Identification (City, State; Year)	Soil type	Soil characteristics			Meteorological data	
		%OM	pH	CEC	Overall monthly rainfall range (inches)	Overall temperature range (°C) ¹
Grapefruit field trials						
Oviedo, FL; 2001	and		Not applicable		Not reported	18-28
Loxahatchee, FL; 2001	and		Not applicable		Not reported	22-27
Clermont, FL; 2001-2002	and		Not applicable		Not reported	9-31
Raymondville, TX; 2001-2002	Sandy clay loam		Not applicable		Not reported	9-23
Porterville, CA; 2001	loam		Not applicable		Not reported	11-23
Terra Bella, CA; 2001	clay		Not applicable		Not reported	9-21
Lemon field trials						
Palm City, FL; 2002	and		Not applicable		Not reported	29-33
Porterville, CA; 2002	clay		Not applicable		Not reported	12-17
Porterville, CA; 2002	clay		Not applicable		Not reported	7-17
Waddell, AZ; 2001	Sandy loam		Not applicable		Not reported	9-16
Hyder, AZ; 2001	Sandy loam		Not applicable		Not reported	16-22
Orange field trials						
Oviedo, FL; 2002	and		Not applicable		Not reported	20-25
Oviedo, FL; 2001	and		Not applicable		Not reported	18-28
Oviedo, FL; 2001	and		Not applicable		Not reported	19-28
Loxahatchee, FL; 2001	and		Not applicable		Not reported	26-29
Stuart, FL; 2002	and		Not applicable		Not reported	21-27
Hobe Sound, FL; 2001-2002	and		Not applicable		Not reported	14-24
Winter Garden, FL; 2001-2002	and		Not applicable		Not reported	9-32
Clermont, FL; 2002	and		Not applicable		Not reported	30-35
Raymondville, TX; 2001-2002	Sandy clay loam		Not applicable		Not reported	8-22
Porterville, CA; 2002	Clay		Not applicable		Not reported	8-13
Richgrove, CA; 2002	Sandy loam		Not applicable		Not reported	8-14
Porterville, CA; 2002	Clay		Not applicable		Not reported	11-15
Porterville, CA; 2002	loam		Not applicable		Not reported	12-24

¹ Air temperature was only provided for days of application.

The petitioner did not include any information pertaining to weather conditions over the course of the field trials except to describe the conditions which occurred during application of the test substance. The petitioner did indicate that weather conditions including temperature were normal for the duration of the trials except for below average rainfall in the orange CA sites, lemon AZ sites, and one grapefruit and one orange FL site.



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 IIA 8.3.1, 8.3.2, 8.3.3
 Crop Field Trial - Citrus Fruits Crop Group

TABLE B.1.2. Study Use Pattern.							
Location (City, State; Year)	EP ¹	Method; Timing	Vol. (GPA ²)	Rate (lb ai/A)	RTI ³ (days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
Oviedo, FL; 2001	20% WG	1: Broadcast foliar; starting color break	179.79	0.20	—	0.90	Triangle DW
		2: Broadcast foliar; color developing	179.37	0.20	9		Triangle DW
		3: Broadcast foliar; color developing	180.32	0.25	11		Triangle DW
		4: Broadcast foliar; mature fruit	179.95	0.25	10		Triangle DW
Loxahatchee, FL; 2001	20% WG	1: Broadcast foliar; mature fruit	89.8	0.21	—	0.91	Latron B-1956
		2: Broadcast foliar; mature	87.1	0.20	11		Latron B-1956
		3: Broadcast foliar; mature	87.3	0.25	10		Latron B-1956
		4: Broadcast foliar; mature	90.03	0.25	10		Latron B-1956
Clermont, FL; 2001-2002	20% WG	1: Broadcast foliar; mature	272.43	0.20	—	0.90	Diamond R Spread-R
		2: Broadcast foliar; mature	275.42	0.20	10		Diamond R Spread-R
		3: Broadcast foliar; mature	282.71	0.25	9		Diamond R Spread-R
		4: Broadcast foliar; mature	288.72	0.25	10		Diamond R Spread-R
Raymondville, TX; 2001-2002	20% WG	1: Broadcast foliar; medium-large fruit, 4" diameter	73.88	0.20	—	0.90	R-56
		2: Broadcast foliar; medium-large fruit, 4" diameter	74.13	0.20	10		R-56
		3: Broadcast foliar; medium-large fruit, 4" diameter	74.43	0.25	10		R-56
		4: Broadcast foliar; medium-large fruit, 4" diameter	74.2178	0.25	10		R-56
Porterville, CA; 2001	20% WG	1: Broadcast foliar; fruit sizing	89.58	0.20	—	0.90	Latron B-1956
		2: Broadcast foliar; fruit size 5-6"	89.53	0.20	10		Latron B-1956
		3: Broadcast foliar; fruit sizing, near maturity 5.5-7"	89.23	0.25	10		Latron B-1956
		4: Broadcast foliar; mature, 6-7" fruit	90.75	0.25	10		Latron B-1956
Terra Bella, CA; 2001	20% WG	1: Broadcast foliar; fruit set 5-6"	222.1	0.20	—	0.90	Latron B-1956
		2: Broadcast foliar; fruit set 6-7"	226.03	0.20	10		Latron B-1956
		3: Broadcast foliar; fruit sizing, near maturity 6-7"	227.44	0.25	10		Latron B-1956
		4: Broadcast foliar; mature, 6-7" fruit	224.7	0.25	9		Latron B-1956

5



Pyraclostrobin/BAS 500 /PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86 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 - Citrus Fruits Crop Group

TABLE B.1.2. Study Use Pattern								
Location (City, State; Year)	EP ¹	Method; Timing	Vol. (GPA ²)	Rate (lb ai/A)	RTI ³ (days)	Total Rate (lb ai/A)	Tank Mix Adjuvants	
Lemon Field Trials								
Palm City, FL; 2002	20% WG	1: Broadcas	foliar; fruit	82.5	0.20	--	0.91	Latron B-1956
		2: Broadcas	foliar; fruiting	91.28	0.21	10		Latron B-1956
		3: Broadcas	foliar; fruiting	89.44	0.25	10		Latron B-1956
		4: Broadcas	foliar; mature	90.75	0.25	10		Latron CS-7
Porterville, CA; 2002	20% WG	1: Broadcas	foliar; fruit maturation	226.69	0.20	--	0.90	Latron B-1956
		2: Broadcas	foliar; fruit maturation	241.78	0.20	11		Latron B-1956
		3: Broadcas	foliar; fruit maturation	238.96	0.25	10		Latron B-1956
		4: Broadcas	foliar; mature fruit	234.71	0.25	11		Latron B-1956
Porterville, CA; 2002	20% WG	1: Broadcas	foliar; fruit maturation	77.04	0.20	--	0.90	Latron B-1956
		2: Broadca:	foliar; fruit maturation	76.68	0.20	10		Latron B-1956
		3: Broadca:	foliar; mature fruit	73.96	0.25	10		Latron B-1956
		4: Broadca:	foliar; mature fruit	76.09	0.25	10		Latron B-1956
Waddell, AZ; 2001	20% WG	1: Broadca:	foliar; mature fruit	77.75	0.19	--	0.88	Agri-Dex
		2: Broadca:	foliar; mature fruit	76.82	0.20	10		Agri-Dex
		3: Broadca:	foliar; mature fruit with 70% color	76.7	0.25	11		Agri-Dex COC
		4: Broadca:	foliar; mature fruit with 100% color	76.65	0.25	10		Agri-Dex COC
Hyder, AZ; 2001	20% WG	1: Broadca:	foliar; mature fruit, 30% fruit color	195.6	0.20	--	0.89	Agri-Dex
		2: Broadca:	foliar; mature fruit, 30- 35% color	198.25	0.20	10		Agri-Dex
		3: Broadca:	foliar; mature 80% color	198.25	0.25	11		Agri-Dex COC
		4: Broadca:	foliar; mature fruit, 10% color	197	0.25	10		Agri-Dex COC
Orange Field Trials								
Oviedo, FL; 2002	20% WG	1: Broadca:	foliar; 3-4" diameter fruit	149.82	0.20	--	0.90	Triangle DW
		2: Broadca:	foliar; 3-4" fruit	148.94	0.20	9		Triangle DW
		3: Broadca:	foliar; nearing maturity	150.55	0.25	10		Triangle DW
		4: Broadca:	foliar; mature fruit	150.12	0.25	10		Triangle DW
Oviedo, FL; 2001	20% WG	1: Broadca:	foliar; some color break, nearing maturity	91.47	0.20	--	0.91	Triangle DW
		2: Broadca:	foliar; color developing	89.74	0.20	9		Triangle DW
		3: Broadca:	foliar; color developing	91.32	0.25	11		Triangle DW
		4: Broadca:	foliar; mature fruit	92.99	0.26	10		Triangle DW



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 - Citrus Fruits Crop Group

TABLE B.1.2. Study Use Pattern.

Location (City, State; Year)	EP ¹	Method; Timing	Vol. (GPA ²)	Rate (lb ai/A)	RTI ³ (days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
Oviedo, FL; 2001	20% WG	1: Broadcast foliar; 2-3" diameter - starting color break	150.08	0.20	--	0.90	Triangle DW
		2: Broadcast foliar; color developing	149.21	0.20	9		Triangle DW
		3: Broadcast foliar; color developing	151.44	0.25	11		Triangle DW
		4: Broadcast foliar; mature fruit	150.2	0.25	10		Triangle DW
Loxahatchee, FL; 2001	20% WG	1: Broadcast foliar; mature fruit	88.9	0.20	--	0.90	Latron B-1956
		2: Broadcast foliar; mature	86.9	0.20	11		Latron B-1956
		3: Broadcast foliar; mature	88.1	0.25	10		Latron B-1956
		4: Broadcast foliar; mature	90.03	0.25	10		Latron B-1956
Stuart, FL; 2002	20% WG	1: Broadcast foliar; mature fruit	165.57	0.20	--	0.90	Latron B-1956
		2: Broadcast foliar; mature fruit	163.43	0.20	11		Latron B-1956
		3: Broadcast foliar; mature fruit	161.9	0.25	10		Latron B-1956
		4: Broadcast foliar; mature fruit	163.43	0.25	10		Latron B-1956
Hobe Sound, FL; 2001-2002	20% WG	1: Broadcast foliar; full size maturing	88.43	0.20	--	0.90	None
		2: Broadcast foliar; mature	87.94	0.20	11		Latron B-1956
		3: Broadcast foliar; mature	86.4	0.25	10		Latron B-1956
		4: Broadcast foliar; mature	87.4	0.25	10		Latron B-1956
Winter Garden, FL; 2001-2002	20% WG	1: Broadcast foliar; mature	198.79	0.20	--	0.90	Diamond R Spread-R
		2: Broadcast foliar; mature	198.74	0.20	10		Diamond R Spread-R
		3: Broadcast foliar; mature	203.65	0.25	9		Diamond R Spread-R
		4: Broadcast foliar; mature	207.55	0.25	10		Diamond R Spread-R
Clermont, FL; 2002	20% WG	1: Broadcast foliar; mature crop	75.29	0.20	--	0.90	Diamond R Spread-R
		2: Broadcast foliar; mature	74.45	0.20	9		Diamond R Spread-R
		3: Broadcast foliar; mature	74.08	0.25	11		Diamond R Spread-R
		4: Broadcast foliar; mature	74.81	0.25	10		Diamond R Spread-R

7



Pyraclostrobin/BAS 5007/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 - Citrus Fruits Crop Group

TABLE B.1.2. Study Use Pattern

Location (City, State; Year)	EP ¹	Application Method; Timing	Vol. (GPA ²)	Rate (lb ai/A)	RTI ³ (days)	Total Rate (lb ai/A)	Tank Mix Adjuvants
Raymondville, TX; 2001-2002	20% WG	1: Broadcast foliar; medium-large fruit, 3-3.5" diameter	250.4	0.20	--	0.91	R-56
		2: Broadcast foliar; medium-large fruit, 3-3.5" diameter	251.68	0.20	10		R-56
		3: Broadcast foliar; medium-large fruit, 3-3.5" diameter	253.36	0.25	10		R-56
		4: Broadcast foliar; medium-large fruit, 3-3.5" diameter	253.95	0.25	10		R-56
Porterville, CA; 2002	20% WG	1: Broadcast foliar; mature fruit	351.25	0.20	--	0.90	Latron B-1956
		2: Broadcast foliar; mature fruit	355.55	0.20	10		Latron B-1956
		3: Broadcast foliar; mature fruit	361.94	0.25	10		Latron B-1956
		4: Broadcast foliar; mature fruit	352.38	0.25	10		Latron B-1956
Richgrove, CA; 2002	20% WG	1: Broadcast foliar; mature fruit	77.47	0.20	--	0.90	Latron B-1956
		2: Broadcast foliar; mature fruit	81.3	0.20	10		Latron B-1956
		3: Broadcast foliar; mature fruit	77.22	0.25	10		Latron B-1956
		4: Broadcast foliar; mature fruit	78.38	0.25	11		Latron B-1956
Porterville, CA; 2002	20% WG	1: Broadcast foliar; mature fruit	348.64	0.20	--	0.90	Latron B-1956
		2: Broadcast foliar; mature fruit	350.73	0.20	7		Latron B-1956
		3: Broadcast foliar; mature fruit	350.65	0.25	10		Latron B-1956
		4: Broadcast foliar; mature fruit	345.7	0.25	10		Latron B-1956
Porterville, CA; 2002	20% WG	1: Broadcast foliar; mature fruit	78.22	0.20	--	0.89	Latron B-1956
		2: Broadcast foliar; mature fruit	78.4	0.20	10		Latron B-1956
		3: Broadcast foliar; mature fruit	77.13	0.25	10		Latron B-1956
		4: Broadcast foliar; mature fruit	76.65	0.25	11		Latron B-1956

¹ EP = End-use Product
² GPA = Gallons per acre
³ RTI = Retreatment Interval

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Region	Grapefruit		Lemon				Orange			
	Submitted	Canada	Requested		Submitted	Requested				
			Canada	US ¹		Submitted	Canada	US ¹		
3	3		3		1		1	8		8
6	1		1					1		1
10	2		2		4		4	4		3

¹ As required under OPPTS 860.1500, Tables 2 and 5 for grapefruit, lemon, and orange as the representative crops of the Citrus Fruits crop group.

8



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 - Citrus Fruits Crop Group

B.2. Sample Handling and Preparation

A single untreated and duplicate treated samples of grapefruit, lemon, and orange whole fruit were harvested on the day (0-day PHI) of the last application. Specific harvesting procedures were not described. Samples were bagged and stored frozen (temperature not specified) on the day of harvest. Samples of citrus fruits were shipped frozen within 4-35 days of harvest to BASF Agro Research (Research Triangle Park, NC) for analysis. At BASF, a portion of the orange whole fruit sample from each trial site was separated by hand into peel and pulp samples.

B.3. Analytical Methodology

Samples of whole citrus fruits (grapefruit, lemon, and orange), and orange pulp and peel were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using LC/MS/MS, BASF Method Number D9908. A brief description of the method was included in the submission. BASF Method Number D9908 is similar to the proposed enforcement method (LC/MS/MS BASF Method Number D9808) submitted in conjunction with a previous pyraclostrobin petition (PP#0F06139; DP Barcodes D269668, etc., L. Cheng, 11/28/01). Method D9908 used an alternate extraction option: citrus fruit commodities were extracted with methanol:water:2 N HCl (7:2.5:0.5; v:v:v) instead of methanol:water (7:3; v:v). Residues are analyzed by LC/MS/MS. For quantitation, the product/daughter ion for the transition m/z 388 → 194 for pyraclostrobin (BAS 500 F) and m/z 358 → 164 for BAS 500-3 are measured. The method limit of quantitation (LOQ) was 0.02 ppm for each analyte (pyraclostrobin and BF 500-3) in/on all citrus fruit matrices. The limit of detection (LOD), defined as the lowest standard level injected with an analysis set, was 0.1 ng/mL for each analyte.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.2. The maximum storage intervals of crop samples from harvest to analysis were 146 days (4.8 months) for grapefruit whole fruit, 136 days (4.5 months) for lemon whole fruit, 186 days (6.1 months) for orange whole fruit, 160 days (5.3 months) for orange pulp, and 180 days (5.9 months) for orange peel. No 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 citrus fruits for this study (D269668, etc., L. Cheng, 11/28/2001).

Concurrent method recovery data are presented in Table C.1. Samples of whole citrus fruits (grapefruit, lemon, and orange), and orange pulp and peel were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using LC/MS/MS, BASF Method Number D9908. The method LOQ was 0.02 ppm for each analyte. This method is adequate for data collection based on acceptable concurrent method recovery data. Apparent residues of pyraclostrobin and



Pyraclostrobin/BAS 500 3/PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86 .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 - Citrus Fruits Crop Group

its metabolite BF 500-3 were each below the method LOQ (<0.02 ppm) in/on all untreated samples of grapefruit, lemon, orange, orange peel, and orange pulp.

Residue data from the citrus field trials are reported in Table C.3. A summary of residue data for whole citrus fruit (grapefruit, lemon, and orange), and orange peel and pulp following treatment with the 20% WG formulation is presented in Table C.4. The combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.074-0.627 ppm in/on grapefruit, 0.403-1.137 ppm in/on lemon, and 0.168-1.78 ppm in/on orange whole fruits harvested 0 days following the last of four applications for a total application rate of 0.88-0.91 lb ai/A. Residues in oranges were primarily located in/on the orange peel. The combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.18-3.634 ppm in/on orange peel and <0.04-0.118 ppm in/on orange pulp separated from whole oranges harvested at the 0-day PHI. The residue data reflect trials with both concentrate and diluted spray volumes.

A total of 24 citrus fruit field trials were conducted during the 2001-2002 growing season. Six trials were conducted on grapefruit encompassing Regions 3 (FL; 3 trials), 6 (TX; 1 trial), and 10 (CA, 2 trials); five trials were conducted on lemon encompassing Regions 3 (FL; 1 trial) and 10 (AZ and CA; 4 trials); and thirteen trials were conducted on oranges encompassing Regions 3 (FL; 8 trials), 6 (TX; 1 trial), and 10 (CA; 4 trials). The number and locations of field trials are in accordance with OPPTS Guideline 860.1500.

TABLE C.1. Summary of Current Recoveries of Pyraclostrobin and its Metabolite BF 500-3 from Citrus Fruit Commodities.		Concentration (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev
Pyraclostrobin					
Grapefruit	0.2	2	2	73, 73	79 ± 7
			2	85, 85	
Lemon	0.2	2	3	76, 94, 94	89 ± 8
			1	89	
			1	94	
Orange	0.2	2	4	73, 79, 84, 91	91 ± 14
			3	92, 105, 113	
Orange pulp	0.2	2	3	78, 82, 83	85 ± 9
			1	87	
			2	80, 102	
Orange peel	0.2	2	3	65, 78, 148 ¹	91 ± 20
			3	82, 97, 122	
			1	102	
BF 500-3					
Grapefruit	0.2	2	2	64, 68	76 ± 12
			2	86, 86	
Lemon	0.2	2	3	84, 94, 121	94 ± 16



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 - Citrus Fruits Crop Group

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin and its Metabolite BF 500-3 from Citrus Fruit Commodities.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev
	1	1	85	
	2	1	86	
Orange	0.02	4	66, 71, 90, 118	89 ± 18
	2	3	85, 89, 102	
Orange pulp	0.02	3	69, 75, 77	79 ± 8
	2	1	80	
	10	2	77, 95	
Orange peel	0.02	3	64, 69, 91	85 ± 18
	2	3	74, 99, 113	
	5	1	86	

¹ This fortification recovery of pyraclostrobin is above the acceptable level. Due to residue levels in the samples run with the sets being significantly greater than the LOQ the set was passed based on the acceptability of the high fortification. These recoveries are not used for the statistical calculations but are reported.

TABLE C.2. Summary of Storage Conditions.

Matrix (RAC or Extract)	Storage Temp. (°C)	Actual Storage Duration ¹	Interval of Demonstrated Storage Stability ²
Grapefruit, whole fruit	<-10	84-146 days (2.8-4.8 months)	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.
Lemon, whole fruit	<-10	14-136 days (0.5-4.5 months)	
Orange, whole fruit	<-10	31-186 days (1.0-6.1 months)	
Orange, pulp	<-10	30-160 days (1.0-5.3 months)	
Orange, peel	<-10	32-180 days (1.1-5.9 months)	

¹ All citrus fruit samples were analyzed within 0-3 days of extraction.

² Refer to storage stability data reviewed in conjunction with a previous pyraclostrobin petition (PP#0F06139; DP Barcode D269668, etc., L. Cheng, 11/28/01).

TABLE C.3. Residue Data from Citrus Fruit Field Trials with Pyraclostrobin.

Trial ID (City, State, Year)	Region	Crop; Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Total
Grapefruit field trials								
Oviedo, FL; 2001	3	Grapefruit; Flame	whole fruit	0.90	0	0.228, 0.25	<0.02, <0.02	<0.248, <0.27
Loxahatchee, FL; 2001	3	Grapefruit; White Marsh	whole fruit	0.91	0	0.58, 0.591	0.038, 0.036	0.618, 0.627
Clermont, FL; 2001-2002	3	Grapefruit; Flame	whole fruit	0.90	0	0.054, 0.066	<0.02, <0.02	<0.074, <0.086
Raymondville, TX; 2001-2002	6	Grapefruit; Rio Red	whole fruit	0.90	0	0.0667, 0.081	<0.02, <0.02	<0.0867, <0.101
Porterville, CA; 2001	10	Grapefruit; Mello Gold	whole fruit	0.90	0	0.1, 0.115	<0.02, <0.02	<0.12, <0.135

11



Pyraclostrobin/BAS 500 F/PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86.1500/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 - Citrus Fruits Crop Group

TABLE C.3. Residue Data from			Citrus Fruit Field Trials with Pyraclostrobin.					
Trial ID (City, State; Year)	Region	Crop; Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Total
Terra Bella, CA; 2001	10	Grapefruit; Oroblanco	whole fruit	0.90	0	0.0702, 0.1	<0.02, <0.02	<0.0902, <0.12
Lemon field trials								
Palm City, FL; 2002	3	Lemon; Bearss	whole fruit	0.91	0	0.547, 0.568	<0.02, <0.02	<0.567, <0.588
Porterville, CA; 2002	10	Lemon; Prior	whole fruit	0.90	0	0.383, 0.654	<0.02, <0.02	<0.403, <0.674
Porterville, CA; 2002	10	Lemon; Lisbon	whole fruit	0.90	0	0.691, 1.11	0.022, 0.027	0.713, 1.137
Waddell, AZ; 2001	10	Lemon; Lisbon	whole fruit	0.88	0	0.496, 0.574	<0.02, <0.02	<0.516, <0.594
Hyder, AZ; 2001	10	Lemon; Limonaire	whole fruit	0.89	0	0.686, 0.803	0.03402, 0.029	0.720, 0.832
Orange field trials								
Oviedo, FL; 2002	3	Orange; Valencia	whole fruit	0.90	0	0.405, 0.534	0.032, 0.033	0.437, 0.567
			peel	0.90	0	2.52 ¹ , 3.36 ¹	0.180 ¹ , 0.186 ¹	2.700, 3.546
			pulp	0.90	0	0.065, 0.074	<0.02, <0.02	<0.085, <0.094
Oviedo, FL; 2001	3	Orange; Navel	whole fruit	0.91	0	0.148, 0.237	<0.02, <0.02	<0.168, <0.257
			peel	0.91	0	0.164, 0.505	<0.02, <0.02	<0.184, <0.525
			pulp	0.91	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Oviedo, FL; 2001	3	Orange; Hamlin	whole fruit	0.90	0	0.609, 0.616	0.034, 0.038	0.643, 0.654
			peel	0.90	0	1.79, 2.27	0.025, 0.030	1.815, 2.30
			pulp	0.90	0	0.021, 0.025	<0.02, <0.02	<0.041, <0.045
Loxahatchee, FL; 2001	3	Orange; Hamlin	whole fruit	0.90	0	1.060, 1.205	0.062, 0.073	1.122, 1.278
			peel	0.90	0	3.43, 3.6	0.095, 0.034	3.525, 3.634
			pulp	0.90	0	0.048, 0.098	<0.02, <0.02	<0.068, <0.118
Stuart, FL; 2002	3	Orange; Valencia, Swingle	whole fruit	0.90	0	0.411, 0.436	0.028, 0.034	0.439, 0.470
			peel	0.90	0	1.63, 2.15	0.120, 0.168	1.75, 2.318
			pulp	0.90	0	0.020, 0.026	<0.02, <0.02	<0.04, <0.046
Hobe Sound, FL; 2001-2002	3	Orange; Pineapple	whole fruit	0.90	0	0.631, 0.945	0.026, 0.038	0.657, 0.983
			peel	0.90	0	1.53, 1.83	<0.02, 0.027	<1.55, 1.857
			pulp	0.90	0	0.046, 0.052	<0.02, <0.02	<0.066, <0.072
Winter Garden, FL; 2001-2002	3	Orange; Hamlin	whole fruit	0.90	0	0.333, 0.356 ¹	<0.02, <0.02 ¹	<0.353, <0.376
			peel	0.90	0	0.641, 0.793	0.028, 0.027	0.669, 0.820
			pulp	0.90	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Clermont, FL; 2002	3	Orange; Valencia	whole fruit	0.90	0	0.159 ¹ , 0.392 ¹	<0.02 ¹ , 0.043 ¹	<0.179, 0.435
			peel	0.90	0	0.595, 0.954	0.032, 0.081	0.627, 1.035
			pulp	0.90	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

12



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 - Citrus Fruits Crop Group

TABLE C.3. Residue Data from Citrus Fruit Field Trials with Pyraclostrobin.

Trial ID (City, State; Year)	Region	Crop; Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)		
						Pyraclostrobin	BF 500-3	Total
Raymondville, TX; 2001-2002	6	Orange; Everhard Navel	whole fruit	0.91	0	0.199, 0.275	<0.02, <0.02	<0.219, <0.295
			peel	0.91	0	0.672, 0.717 ¹	0.023, <0.02 ¹	0.695, <0.737
			pulp	0.91	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Porterville, CA; 2002	10	Orange; Navel	whole fruit	0.90	0	0.217, 0.287	<0.02, <0.02	<0.237, <0.307
			peel	0.90	0	0.547, 0.721	<0.02, <0.02	<0.567, <0.741
			pulp	0.90	0	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Richgrove, CA; 2002	10	Orange; Navel	whole fruit	0.90	0	0.216, 0.249 ¹	<0.02, <0.02 ¹	<0.236, <0.269
			peel	0.90	0	0.54, 0.666	0.026, 0.030	0.566, 0.696
			pulp	0.90	0	<0.02, 0.030	<0.02, <0.02	<0.04, <0.05
Porterville, CA; 2002	10	Orange; Navel	whole fruit	0.90	0	0.268, 0.287	<0.02, <0.02	<0.288, <0.307
			peel	0.90	0	0.775, 0.994	<0.02, <0.02	<0.795, <1.014
			pulp	0.90	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Porterville, CA; 2002	10	Orange; Cutter	whole fruit	0.89	0	0.156, 0.188	<0.02, <0.02	<0.176, <0.208
			peel	0.89	0	0.275 ¹ , 0.908 ¹	<0.02 ¹ , 0.029 ¹	<0.295, 0.937
			pulp	0.89	0	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

¹ Duplicate or triplicate analyses of a single sample; the maximum residue is reported.

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

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Analyte	Residue Levels (ppm)						
				n	Min.	Max.	HAFT ¹	Median (STMdR ²)	Mean (STMR ³)	Std. Dev.
Grapefruit, whole fruit	0.90-0.91	0	pyraclostrobin	12	0.054	0.591	0.586	0.10	0.19	0.194
			BF 500-3	12	<0.02	0.038	0.037	0.02	0.02	0.007
			Total	12	0.074	0.627	0.623	0.12	0.21	0.201
Lemon, whole fruit	0.88-0.91	0	pyraclostrobin	10	0.383	1.110	0.901	0.61	0.65	0.199
			BF 500-3	10	<0.02	0.034	0.032	0.02	0.02	0.005
			Total	10	0.403	1.137	0.925	0.63	0.67	0.202
Orange, whole fruit	0.89-0.91	0	pyraclostrobin	26	0.148	1.205	1.133	0.310	0.416	0.282
			BF 500-3	26	<0.02	0.073	0.068	0.02	0.029	0.014
			Total	26	0.168	1.278	1.200	0.330	0.445	0.294
Orange, peel	0.89-0.91	0	pyraclostrobin	26	0.164	3.600	3.515	0.851	1.330	1.006
			BF 500-3	26	<0.02	0.186	0.183	0.027	0.051	0.053
			Total	26	0.184	3.634	3.580	0.879	1.380	1.040
Orange, pulp	0.89-0.91	0	pyraclostrobin	26	<0.02	0.098	0.073	0.020	0.031	0.021
			BF 500-3	26	<0.02	<0.02	<0.02	<0.02	<0.02	0.0
			Total	26	<0.04	0.118	0.093	<0.04	0.051	0.021

¹ HAFT = Highest Average Field Trial.

² STMdR = Supervised Trial Median Residue.

13



Pyraclostrobin/BAS 500 /PC Code 099100/BASF Corporation
 DACO 7.4.1/OPPTS 86.1500/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 - Citrus Fruits Crop Group

³ STMR = Supervised Trial Mean Residue

D. CONCLUSION

The combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.074-0.627 ppm in/on grapefruit, 0.403-1.137 ppm in/on lemon, and 0.168-1.278 ppm in/on orange whole fruits harvested 0 days following the last of four applications for a total application rate of 0.88-0.91 lb ai/A with 7- to 11-day retreatment intervals. Residues in oranges were primarily located in/on the orange peel. The combined residues of pyraclostrobin and its metabolite BF 500-3 were 0.184-3.634 ppm in/on orange peel and <0.04-0.118 ppm in/on orange pulp separated from whole oranges harvested at the 1-day PHI. The residue data reflect trials with both concentrate and dilute spray volumes.

E. REFERENCES

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 Peas & 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: 45118428-45118437, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI:ChemTeam:06/29/04:L.Cheng: 07/22/04
 Petition Number(s): PP#2F06139
 DP Barcode(s): D290342, D290343, and D290369
 PC Code: 099100

Template Version September 2003

14