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STUDY REPORTS:

MRID No. 46109101, Chen, H (2002) BAS 516 (BAS 510 F Plus BAS 500 F): Magnitude of the Residue on Spinach: IR-4 PR No. 08090, Lab. Identification Number 08091.01-BAR01, Unpublished study prepared by IR-4, 222 pages.

EXECUTIVE SUMMARY:

IR-4 Project on behalf of the Agricultural Experiment Stations of Texas, Oregon, and California has submitted field trial data for pyraclostrobin in/on spinach. Eight trials were conducted in regions: I: NY (1 trial), II: MD (2 trials), VI: TX (2 trials), X: CA (2 trials), and VIII: CO (1 trial) during the 2001 growing season. The number and locations of field trials, including the three trials conducted in year 2001 (MRID 46109101), are in accordance with OPPTS Guideline 860.1500. The number and location of the field trials are sufficient to support a tolerance for spinach.

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

Samples were analyzed at BASF Agro Research, Research Triangle Park, NC for residues of pyraclostrobin and its metabolites in spinach using LC/MS/MS BASF Method D9908. The method is adequate as a data collection method based on the concurrent method recovery data.

The maximum storage interval of spinach samples from harvest to analysis was 11 months. No spinach storage stability data have been submitted. Available storage stability data indicated that residues of pyraclostrobin (BAS 500 F) 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 spinach samples for this study (D269668, etc., L. Cheng, 11/28/2001) .

Residues of pyraclostrobin and its metabolite ranged from 5.62 ppm to 23.38 ppm with a PHI of

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0 day, 1.18 ppm to 8.99 ppm wi ı a PHI of 7 days and 0.05 ppm to 5.72 ppm with a PHI of 14 days reflecting the use of pyracl strobin with the treatment of BAS 500 02 F on spinach at the seasonal application rate of 0.8 ! ai/A.

STUDY CLARIFICATIONS:

Under the conditions and param ters used in the study, the field trial residue data are classified as scientifically acceptable.

The acceptability of this study f r regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary D cument DP Barcode D298178.

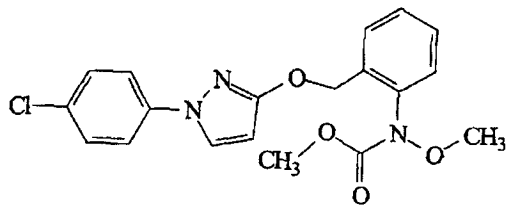
COMPLIANCE:

Signed and dated GLP, Quality ssurance and Data Confidentiality statements were provided. No deviations from regulatory ı quirements were reported.

A. BACKGROUND INF(RMATION

Pyraclostrobin is a fungicide th : is structurally related to the naturally occurring strobilurins, compounds derived from some ungal species. Pyraclostrobin is also in the same chemical class as azoxystrobin (PC 128810), ı gistered for several crops and turf/lawn, and trifloxystrobin (PC 129112) which recently was gr ıted a "reduced risk" status as a fungicide on several crops. The biochemical mode of action of ıese compounds is inhibition of electron transport in pathogenic fungi.

TABLE A.1. Test Compound omenclature

Compound	Ch nical Structure
	
Common name	Py clostrobin
Company experimental name	B/ 500 F
IUPAC name	me ıyl N-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(N-me ıoxy)carbamate
CAS name	me ıyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	17)13-18-0
End-use product/EP	B/ 500 02 F and BAS 510 UCF

Pyraclostrobin technical is a white to light beige solid.

TABLE A.2. Physicochemical Properties

Parameter	Value	Reference[1]
Boiling point/boiling range	N/A	D290351
pH	N/A	D290351
Density	1.285g/cm^3 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^{-10} hPa (at 20°C); 6.4 x 10^{-10} hPa	D290351
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D290351
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).	D290351

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1 Trial Site Conditions

Trial Identification (City, State/Year)	Soil characteristics				Meteorological data	
	Type	%OM[1]	pH[1]	CEC[1] meq/g	Monthly rainfall average	Mean T (°C)
Freeville, NY/2001	silty clay loam	6.26	6.81	NA[2]	NA	23-27
Salisbury, MD/2001	loamy sand	0.8	6.0	NA		16-18
Salisbury, MD/2001	loamy sand	0.8	6.0	NA		16-18
Weslaco, TX/2001	sandy loam	0.5	8.1	NA		15-24
Holtville, CA/2001	silty clay loam	0.68	7.7	NA		16-29
Salinas, CA/2001	loam	NA	7.5	NA		19-25
Fort Collins, CO/2001	clay loam	2.3	7.8	NA		9-18
Weslaco, TX/2001	sandy loam	1.0	8.3	NA		18-26

[1] These parameters (percent organic matter, pH, and cation exchange capacity) are optional except in cases where their value affects the use pattern for the chemical.
[2] Not available.

TABLE B.1.2. Study Use Pattern.

Location (City, State/Year)	EP [1]	Application					Tank Mix Adjuvants
		Method/Timing	Vol, GPA[2]	Rate, (lb a.i./A)	RTI, [3] days	Total Rate, (lb a.i./A)	
Freeville, NY/2001	BAS 500 02 F (20% WG)	oliar/2-4" leaf	40-42	0.2	7±1	0.8	None
Salisbury, MD/2001	BAS 500 02 F (20% WG)	oliar/3" leaf	33	0.2	7±1	0.8	None
Salisbury, MD/2001	BAS 500 02 F (20% WG)	oliar/3" leaf	33	0.2	7±1	0.8	None
Weslaco, TX/2001	BAS 500 02 F (20% WG)	oliar/6-8" true eaf	39	0.2	7±1	0.8	None
Holtville, CA/2001	BAS 500 02 F (20% WG)	oliar/Vegetative	39-42	0.2	7±1	0.8	None
Salinas, CA/2001	BAS 500 02 F (20% WG)	oliar/5-7" true eaf	60-75	0.2	7±1	0.8	None
Fort Collins, CO/2001	BAS 500 02 F (20% WG)	oliar/Vegetative	40	0.2	7±1	0.8	None
Weslaco, TX/2001	BAS 500 02 F (20% WG)	oliar/Vegetative	42-44	0.2	7±1	0.8	None

[1] EP = End-use Product
[2] Gallons per acre, L/ha
[3] Retreatment Interval

TABLE B.1.3. Trial Numbers and Geographical Locations

Growing Region	Spinach	
	Submitted	Requested
1	1	1
2	2	2
6	2	2
8	1	
9		1
10	2	2
Total		

B.2. Sample Handling and Preparation

After harvest, samples were p iced in a freezer (< -20°C) upon arrival at BASF Agro Research. Spinach samples were homog nized with dry ice before analysis.

The maximum storage interva of spinach samples from harvest to analysis was 11 months. No

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spinach 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 interval for spinach 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 spinach was the LC/MS/MS BASF Method D9908. 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 →194 for pyraclostrobin (BAS 500 F) and *m/z* 358 →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.

Recovery values of pyraclostrobin from samples of spinach fortified over the concentration range of 0.02 ppm to 50.0 ppm averaged 86 ± 6% to 92±10% for BAS 500 F and 79±7% to 89±2% 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 spinachs have been provided. The limit of quantitation (LOQ) was 0.02 ppm for 500 F and BF 500-3 in spinach.

As shown in Table C.2, the available information indicate that spinach samples were stored for a maximum of about 11 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 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 spinach samples for this study (D269668, etc., L. Cheng, 11/28/2001).

As indicated in Table C.3., eight trials were conducted in regions: I: NY (1 trial), II: MD (2 trials), VI: TX (2 trials), X: CA (2 trials), and VIII: CO (1 trial) during the 2001 growing season. The number and locations of field trials, including the three trials conducted in year 2001 (MRID 46109101).

The combined residues of pyraclostrobin and its metabolite ranged from 5.62 ppm to 23.38 ppm with a PHI of 0 day, 1.18 ppm to 8.99 ppm with a PHI of 7 days and 0.05 ppm to 5.72 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on spinach at the seasonal application rate of 0.8 lb ai/A.

TABLE C.1. Summary of Concu ent Recoveries of Pyraclostrobin (BAS 500F) & its metabolite (B! 500-3) from Spinach.

Matrix	Spike level (mg/kg)	Sample size (r		Recoveries (%)		Mean ± std dev	
		BAS 500F	BF 500-3	BAS 500F	BF 500-3	BAS 500F	BF 500-3
Spinach	0.02	8	8	80-106	65-86	92±10	79±7
	1.0	2	2	81, 90	80-97	86±6	89±12
	50	6	6	83-91	87-92	87±3	89±2

TABLE C.2. Summary of Stor ge Conditions

Matrix (RAC)	Storage Temp. (°C)	Actual Storage Duration (months)	Interval of Demonstrated Storage Stability (months)
Analyte: Pyraclostrobin (BAS 500F) & s metabolite (BF 500-3)			
Spinach	< -20	11	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 spinach samples for this study (D269668, etc., L. Cheng, 11/28/2001).

TABLE C.3a. Residue Data fr n Spinach Field Trials with Pryraclostrobin residues Treated with BAS 500 02 F at 1x th Proposed Use rate.

Trial ID (City, State/Year)	Region	Crop Variety	Total Rate, (lb a.i./A)	PHI (days)	Residues (ppm)		
					BAS 500F	BF 500-3	Total
Freeville, NY/2001	1	(ympia	0.8	0	10.4, 11.0	0.11, 0.11	10.51, 11.11
				6	1.14, 1.15	0.04, 0.04	1.18, 1.19

				14	0.04, 0.03	<0.02, <0.02	0.06, 0.05
Salisbury, MD/2001	2	Vienna	0.8	0	11.3, 9.95	0.23, 0.22	11.53, 10.17
				7	7.1, 8.7	0.25, 0.29	7.35, 8.99
				14	5.5, 4.8	0.22, 0.20	5.72, 5.00
Salisbury, MD/2001	2	Vancouver	0.8	0	14.8, 12.8	0.31, 0.30	15.11, 13.1
				7	7.05, 7.2	0.27, 0.27	7.32, 7.47
				14	4.65, 4.3	0.21, 0.22	4.86, 4.52
Weslaco, TX/2001	6	Olympia	0.8	0	17.4, 14.5	0.25, 0.19	17.65, 14.69
				7	3.52, 3.80	0.15, 0.16	3.67, 3.6
				14	1.08, 0.94	0.06, 0.06	1.14, 1.00
Holtville, CA/2001	10	Bolero	0.8	0	7.05, 7.20	0.19, 0.20	7.24, 7.40
				7	5.05, 4.4	0.21, 0.19	5.26, 4.59
				14	2.97, 3.20	0.14, 0.15	3.11, 3.35
Salinas, CA/2001	10	EL Palmer	0.8	0	6.46, 6.36	0.11, 0.11	6.57, 6.47
				7	2.70, 1.99	0.09, 0.05	2.79, 2.04
				14	1.29, 0.91	0.04, 0.02	1.33, 0.93
Fort Collins, CO/2001	8	Unipack 151	0.8	0	7.5, 5.5	0.15, 0.12	7.65, 5.62
				7	0.90, 1.03	0.06, 0.07	0.96, 1.10
				14	0.22, 0.34	<0.02, 0.02	0.24, 0.36
Weslaco, TX/2001	6	Fall Green	0.8	0	19.7, 22.8	0.47, 0.58	20.17, 23.38
				7	3.39, 2.85	0.18, 0.13	3.57, 2.98
				14	1.26, 1.30	0.06, 0.06	1.32, 1.36

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.	HAFT*	Median (STMdR[2])	Mean (STMR[3])	Std. Dev.
Analyte: Pyroclostrobin (BAS 500F) & its metabolite (BF 500-3)									
Spinach	0.8	0	16	5.62	23.38	21.78	10.81	11.77	5.62
	0.8	6-7	16	1.18	8.99	8.17	3.59	4.00	2.6
	0.8	14	16	0.05	5.72	5.36	1.33	2.15	1.96

* HAFT = Highest Average Field Trial.

[2] STMdR = Supervised Trial Median Residue.
[3] STMR = Supervised Trial Mean Residue.

D. CONCLUSION

The combined residues of pyraclostrobin and its metabolite ranged from 5.62 ppm to 23.38 ppm with a PHI of 0 day, 1.18 ppm to 8.99 ppm with a PHI of 7 days and 0.05 ppm to 5.72 ppm with

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a PHI of 14 days reflecting the u e of pyraclostrobin with the treatment of BAS 500 02 F on spinach at the seasonal applicati n rate of 0.8 lb ai/A.

E. REFERENCES

DP Barcodes: D269668, D272' 71, D272789, D274095, D274192, D274471, D274957, D275843, and D 78429
Subject: PP#0F06139. P Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pe & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachi Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawben , Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review f Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969 UA. CAS #175013-18-0.
From: L. Cheng
To: C. Giles-Parker/ Bazuin
Dated: 11/28/01
MRIDs: 45118428-4511 4-37, 45118501-45118512, 45118514-45118537, 45118601-4511 525, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 4 5429901

F. DOCUMENT TRACI ING

RDI: ChemTeam:06/29/04:L.C eng:07/22/04
Petition Number:3E6774
DP Barcodes: D298178
PC Code:099100

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