



Primary Evaluator

Date: 5/5/2008

Amelia M. Acierto, Chemist
Registration Action Branch 3
Health Effects Division (7509P)

Approved by

Date: 5/8/2008

Stephen Funk, Ph.D., Senior Science Adviser
Immediate Office
Health Effects Division (7509P)

In the absence of signatures, this document is considered to be a draft with deliberative material for internal use only.

This DER was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713; submitted 4/03/08). The DER has been reviewed by the HED and revised to reflect current OPP policies.

STUDY REPORT:

47214701 Duah, F. and Harbin, A. (2007) JAU6476 480 SC– Magnitude of the Residue in/on Peanuts. Project Number: RAJAY035, 0504011, N106806A. Unpublished study prepared by Bayer Crop., Gustafson Seed Technology Center and Battelle. 271 p.

EXECUTIVE SUMMARY:

Bayer CropScience has submitted three side-by-side field trials conducted in 2005 on peanuts grown in Zones 2 and 3, comparing prothioconazole residues in/on peanuts and peanut hay resulting from applications of prothioconazole (4 lb/gal FIC) as either (i) only broadcast foliar applications or (ii) a combination of a seed treatment, an in-furrow application at planting, and broadcast foliar applications. For the foliar only applications, prothioconazole was applied as four broadcast foliar applications at 0.170-0.183 lb ai/A beginning around flowering or pegging, at retreatment intervals (RTIs) of 13-14 days, for a total seasonal rate of 0.69-0.73 lb ai/A. For the combination treatment, prothioconazole was first applied to peanut seed at 10 g ai/100 kg seed, which was equivalent to 0.010-0.012 lb ai/A based on the seeding rate. An in-furrow soil application was then made at planting at 0.172-0.178 lb ai/A, followed 56-64 days later by four broadcast foliar applications at 0.086-0.094 lb ai/A at RTIs of 13-14 days, for a total seasonal rate of 0.543-0.547 lb ai/A. The peanut plants were dug and the hay was cut at either 8 or 14 days after the last foliar application (DAT), and peanut and hay samples were allowed to dry for 3-6 days prior to collecting a single control and duplicate treated samples of each commodity from each test.

Samples were stored frozen for up to ~14 months prior to analysis. The available storage stability data support this storage interval for the prothioconazole-related residues and for



residues of triazolylalanine (TA) and triazolylacetic acid (TAA). However, the data indicate that residues of 1,2,4-triazole are not likely to be stable for this interval in either peanut nutmeats or hay. However, the instability of triazole residues is not considered a major deficiency for this study, because any instability in triazole residues would affect residues from both treatments similarly, and the main purpose of these field trials was to compare residues between the two treatments.

Residues of prothioconazole and its desthio metabolite were determined using an LC/MS/MS method (Bayer Report No. RPA JA/03/01), which was adequately validated in conjunction with the analysis of field trial samples. Residues were extracted for 2 hours at 65°C with a mixture of methanol, 30% hydrogen peroxide, and 5% aqueous sodium bicarbonate, which converts prothioconazole to its sulfonic acid derivative but does not change the desthio metabolite. Residues were then cleaned up using a C₁₈ solid-phase extraction (SPE) cartridge and analyzed by LC-MS/MS, using internal standards. Residues of prothioconazole sulfonic acid and prothioconazole-desthio are reported in parent equivalents and then summed to yield “total prothioconazole derived residues.” For nutmeats, the limits of quantitation (LOQ) and detection (LOD) for each analyte were 0.01 and 0.002 ppm, respectively, for a combined LOQ of 0.02 ppm and a combined LOD of 0.004 ppm. For peanut hay, the LOQ was 0.05 ppm for each analyte, for a combined LOQ of 0.10 ppm, and the LODs were 0.004 ppm for the desthio-metabolite and 0.007 ppm for the sulfonic acid of prothioconazole, for a combined LOD of 0.011 ppm.

For analysis of triazole, TA and TAA residues, samples were analyzed using an LC/MS/MS method (Morse Method Meth-160), which was adequately validated in conjunction with the analysis of field trial samples. Residue were extracted with methanol/water and then separately cleaned up and derivatized for analysis by LC/MS/MS. The validated LOQs were 0.01 ppm for triazole and TAA in nutmeats and hay, and TA in hay, and 0.05 ppm for TA in nutmeats. The data were reported as triazole residues and total conjugated residues (TA + TAA), expressed in TA equivalents.

Total prothioconazole residues were non-detectable (<0.004 ppm) in/on all samples of peanut nutmeats, regardless of the type of treatment (foliar only vs. in-furrow + foliar). For peanut hay, total prothioconazole residues were 0.71-2.58 ppm (average 1.41 ppm) for the combined in-furrow and foliar applications and were 2.33-6.44 ppm (average 4.03 ppm) for the foliar only treatment.

Residues of triazole were <LOQ ppm for all samples of peanut nutmeat and hay, regardless of treatment. The total conjugated triazole residues in/on nutmeats were 0.30-0.92 ppm (average 0.63 ppm) for the combined in-furrow and foliar applications and were 0.40-1.44 ppm (average 0.80 ppm) for the foliar only treatment. The total conjugated triazole residues in/on peanut hay were 0.08-0.16 ppm (average 0.11 ppm) for the combined in-furrow and foliar applications and 0.12-0.20 ppm (average 0.16 ppm) for the foliar only treatment.

The data suggest that use of an in-furrow (or seed treatment) at planting will not result in higher residues in/on peanut nutmeats and hay than from use of only foliar applications.



However, these findings are equivocal as the two treatments had different seasonal application rates. The seasonal use rate for the combined applications was ~0.8x compared to the seasonal rate for the foliar only applications.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Although there are questions about the stability of triazole residues in peanut nutmeats and hay during frozen storage, the peanut field trials are classified as scientifically acceptable for the purposes for which they were intended. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Chemistry Summary Document, DP Number 347039.

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

Prothioconazole is a systemic demethylation inhibitor fungicide which belongs to the triazolinthione class of fungicides (Group 3). In the U.S., a 4 lb/gal FIC formulation of prothioconazole (Proline™ 480 SC; EPA Reg. No. 264-825) is registered to Bayer CorpScience for use on canola, rapeseed, chickpeas, lentils, dried shelled peas and beans (except soybean), peanuts, barley, and wheat. The current use on peanuts allows for up to four broadcast foliar applications at 0.178 lb ai/A/application at a minimum RTI of 14 days, for a total of 0.713 lb ai/A/season. A 14-day preharvest interval is specified, and the use of peanut hay or threshings for livestock feed is prohibited.

Bayer has requested an amendment to the label directions on peanuts to allow for inclusion of either an in-furrow application at planting or a pre-emergence banded application at 0.178 lb ai/A. To support this request, Bayer has submitted side-by-side field trials comparing the use of only foliar applications to a combination of an in-furrow and foliar applications.

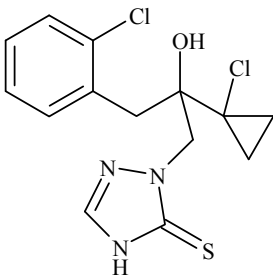
TABLE A.1. Nomenclature of Prothioconazole and its Regulated Metabolite.	
Parent Compound	
Common name	Prothioconazole



TABLE A.1. Nomenclature of Prothioconazole and its Regulated Metabolite.	
Company experimental names	JAU6476
IUPAC name	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione
CAS name	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione
CAS #	178928-70-6
End-use products/EP	Proline™ 480 SC (4 lb/gal FIC; EPA Reg. No. 264-825)
Regulated Metabolite	
Common name	Prothioconazole-desthio
Company Code	JAU6476-desthio
IUPAC name	2-(1-chlorocyclopropyl)-1-(2-chlorophenyl)-3-(1H-1,2,4-triazol-1-yl)propan-2-ol
CAS name	∇-(1-chlorocyclopropyl)-∇-(2-chlorophenyl)methyl-1H-1,2,4-triazole-1-ethanol
CAS #	120983-64-4

TABLE A.2. Physicochemical Properties of Prothioconazole Technical Grade Test Compound.		
Parameter	Value	Reference (MRID)
Melting point	139.1 to 144.5 EC	46246003
pH	5.8 (1% solution)	46246002
Density	1.36 g/mL at 20 EC	46246003
Water solubility (mg/L at 20 EC)	pH 4 5 pH 8 300 pH 9 2000	46246001, 46246003
Solvent solubility (g/L at 20 EC)	Acetone >250 Acetonitrile 69 Dichloromethane 88 Dimethylsulfoxide 126 Ethyl acetate >250 n-Heptane <0.1 1-Octanol 58 Polyethylene glycol >250 2-Propanol 87 Xylene 8	46246001
Vapor pressure (at 20 or 25 EC)	<<4 x 10 ⁻⁷ Pa (calculated from determinations at 70 EC)	46246001, 46246003
Dissociation constant, pK _a	6.9 (calculated from K _{OW})	46246001, 46246003
Octanol/water partition coefficient (at 20 EC) [Log K _{ow}]	unbuffered water 4.05 pH 4 4.16 pH 7 3.82 pH 9 2.00	46246001
UV/visible absorption	Peak maxima at 257 nm	46246003



B. EXPERIMENTAL DESIGN

Three side-by-side field trials were conducted in Zones 2 and 3 during 2005 comparing the use of prothioconazole (4 lb/gal FIC) on peanuts as either (i) only broadcast foliar applications with or (ii) a combination of a seed treatment, an in-furrow application at planting, and broadcast foliar applications (Table B.1.2). For the treatment using only foliar applications, prothioconazole was applied as four broadcast foliar applications at 0.170-0.183 lb ai/A/application beginning around flowering or pegging, at RTIs of 13-14 days, for a total of 0.691-0.726 lb ai/A. For the combination treatment, prothioconazole was first applied to peanut seed at 10 g ai/100 kg of seed, which was equivalent to 0.010-0.012 lb ai/A based on the seeding rate. An in-furrow soil application was then made at planting at 0.172-0.178 lb ai/A, followed 56-64 days later by four broadcast foliar applications at 0.086-0.094 lb ai/A and RTIs of 13-14 days. The total seasonal rate for the combined applications was 0.543-0.547 lb ai/A.

The seed treatment was made using an aqueous dilution of the 4 lb/gal FIC formulation and a Hege 22 Seed Treater. All the field applications were made with ground equipment using 5-10 gal/A for the in-furrow application and 12-18 gal/A for the foliar applications. None of the applications included the use of an adjuvant.

B.1. Study Site Information

Trial Identification (City, State, Year)	Soil characteristics			
	Type	%OM	pH	CEC
Seven Springs, NC 2005	Sandy Loam	0.9	5.8	25.1
Tifton, GA 2005	Sandy Loam	0.95	5.9	3.9
Molino FL 2005	Sandy Loam	2.2	6.3	7.7

The peanuts were grown and maintained at each test site using typical agricultural practices for the respective geographical regions (Table B.1.1). Detailed temperature and precipitation data were reported for all sites, and fell within historical averages for the regions. Detailed information was also provided on maintenance chemicals and other pesticides used at each site.

Location (City, State), Year	Application Information ¹							
	End-use Product	Trt#	Method ² ; Timing	Volume (gal/A)	Single Rates (lb ai/A)	No. of App.	RTI ³ (days)	Total Rate (lb ai/A)



TABLE B.1.2. Study Use Pattern on Peanuts.

Location (City, State), Year	Application Information ¹							
	End-use Product	Trt#	Method ² ; Timing	Volume (gal/A)	Single Rates (lb ai/A)	No. of App.	RTI ³ (days)	Total Rate (lb ai/A)
Seven Springs, NC 2005	4 lb/gal FIC	Trt# 1	Seed treatment	NA	0.011	1	NA	0.543
			In-furrow soil application at planting	10	0.177	1	NA	
			Broadcast foliar applications from pegging to 70% crop maturity (BBCH 66-87)	13-15	0.087-0.091	4	67; 13	
		Trt# 2	Broadcast foliar applications from pegging to 70% crop maturity (BBCH 66-87)	14-15	0.179-0.183	4	13	0.726
Tifton, GA 2005	4 lb/gal FIC	Trt# 1	Seed treatment	NA	0.012	1	NA	0.547
			In-furrow soil application at planting	5.3	0.178	1	NA	
			Broadcast foliar applications from beginning of flowering to maturity (BBCH 61-89)	17-18	0.089	4	56; 14	
		Trt# 2	Broadcast foliar applications from beginning of flowering to maturity (BBCH 61-89)	17-18	0.178-0.179	4	14	0.714
Molino FL 2005	4 lb/gal FIC	Trt# 1	Seed treatment	NA	0.010	1	NA	0.546
			In-furrow soil application at planting	5.2	0.172	1	NA	
			Broadcast foliar applications from pegging to crop maturity (BBCH 66-89)	13-16	0.086-0.094	4	64; 13-14	
		Trt# 2	Broadcast foliar applications from pegging to crop maturity (BBCH 66-89)	12-16	0.170-0.176	4	13-14	0.691

¹ None of the field applications included the use of any adjuvants.

² Seed treatments were made using a Hege 11 Seed Treater, and all field applications were made using ground equipment.

³ The RTI between the in-furrow application and the first foliar application was 56-67 days, and the RTI for all foliar applications was 13-14 days.



TABLE B.1.3. Trial Numbers and Geographical Locations.

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

¹ Regions 14-21 and 1A, 5A, 5B, and 7A were not included as the use on peanuts is in the U.S. only.

² A specific number of side-by-side tests were not required.

NA = not applicable

B.2. Sample Handling and Preparation

Single control and duplicate treated samples of peanuts (≥ 1 kg/sample) and peanut hay (≥ 500 g/sample) were harvested at commercial maturity (BBCH 89). The plants were dug and the hay was cut at either 8 (1 test) or 14 (2 tests) days after treatment (DAT). As per standard commercial practices, the peanuts and hay were allowed to dry in the field or under shelter until attaining commercial dryness (3-6 days), after which composite samples were placed in labeled cloth bags and placed in frozen storage ($< -15^{\circ}\text{C}$) for 138-141 days until shipment via freezer truck to Bayer Research Park (BRP), Stilwell, KS, where the samples were stored at $\leq -15^{\circ}\text{C}$. All samples were later shipped via freezer truck to Battelle Agri-Food, Columbus, OH. At Battelle, the frozen peanuts were shelled and the nutmeat and hay samples were ground with dry ice and stored at $\leq -20^{\circ}\text{C}$ until analysis for residues of prothioconazole and its metabolite prothioconazole-desthio. Frozen subsamples of homogenized nutmeats and hay were also shipped back to BRP, and then shipped to Pyxant Labs, Colorado Springs, CO, for analysis of triazole-related residues. Samples were stored at $\leq -20^{\circ}\text{C}$ at Pyxant Labs until analysis.

B.3. Analytical Methodology

Samples of peanut nutmeat and hay were analyzed for residues of prothioconazole and its desthio metabolite using an LC/MS/MS method (Bayer Report No. RPA JA/03/01), which is the current tolerance enforcement method for plant commodities. The method was slightly modified to use a different solvent for preparation of the fortification solutions and to use slightly different m/z values for the quantitation.



For this method, residues are extracted with a mixture of methanol, 30% hydrogen peroxide, and 5% aqueous sodium bicarbonate at 65°C for 2 hours. This oxidative extraction procedure converts prothioconazole to its sulfonic acid derivative, while the desthio metabolite remains unchanged. The cooled extract is spiked with isotopically labeled internal standards, cleaned up by C₁₈ solid-phase extraction (SPE), and diluted with 1% acetic acid for analysis by LC-MS/MS, using internal standards. The results for prothioconazole sulfonic acid and prothioconazole desthio are reported in prothioconazole equivalents and then totaled to yield “total prothioconazole derived residues.” For nutmeats, the LOQ and LOD for each analyte were 0.01 and 0.002 ppm, respectively, and the LOQ and LOD for combined residues in nutmeats were 0.02 and 0.004 ppm. For peanut hay, the LOQ was 0.05 ppm for each analyte, for a combined LOQ of 0.10 ppm, and the LODs were 0.004 ppm for the desthio-metabolite and 0.007 ppm for the sulfonic acid of prothioconazole, for a combined LOD of 0.011 ppm.

For analysis of triazole, TA and TAA residues, samples were analyzed using an LC/MS/MS method (Morse Method Meth-160; MRID 46492901), which was also used in the analysis of peanut samples from earlier field trials (DP# D303508, S. Funk, 8/21/2006). For this method, homogenized samples of peanut nutmeats and hay were extracted with methanol/water (80/20), and isotopically labeled internal standards were added for each analyte. Aliquots were then taken for the separate analysis of triazole, TA and TAA. For triazole, an aliquot was mixed with dansyl chloride to form the dansyl derivative of triazole, which was partitioned into ethyl acetate and then redissolved in acetonitrile (ACN)/water for LC/MS/MS analysis. For TA, an aliquot was cleaned up using a Certify II SPE cartridge, derivatized to the butyl ester using butanolic HCl, and then further derivatized using heptafluorobutyric anhydride (HFBA). The mixture was then redissolved in ACN/water for LC/MS/MS analysis. For determination of TAA, the aliquot was cleaned up by C₁₈ SPE, derivatized to the butyl ester using butanolic HCl, and then redissolved in ACN/water for LC/MS/MS analysis. Residue levels were quantified using reference standards of dansyl-1,2,4-triazole, triazolylalanine butyl ester HFBA, and triazolylacetic acid butyl ester. The method was modified to use different calibration standards and gradient for HPLC. The validated LOQs were 0.01 ppm for triazole and TAA in nutmeats and hay, and TA in hay, and 0.05 ppm for TA in nutmeats. LODs were also calculated for each analyte in each matrix; however, due to the presence of endogenous triazole-related residues in controls, the calculated LOD were higher than the validated LOQs. Therefore, only the LOQs were used. The data were reported as triazole residues and total conjugated residues (TA + TAA), expressed in TA equivalents.

The above LC/MS/MS methods were validated in conjunction with the analysis of the field trial samples using control samples of nutmeat and hay fortified separately with prothioconazole and prothioconazole-desthio at 0.01-0.20 ppm, and triazole, TA, and TAA at 0.01-7.4 ppm.



C. RESULTS AND DISCUSSION

The number and geographic representation of the peanut field trials are adequate as a side-by-side comparison between the two application method (foliar application only vs. combined seed treatment, in-furrow, and foliar applications).

The LC/MS/MS methods used to determine prothioconazole derived residues and residues of triazole, TA and TAA in/on peanut nutmeat and hay were adequately validated in conjunction with the analysis of field trial samples. For the prothioconazole derived residues, the average concurrent recoveries (\pm S.D.) for prothioconazole were $84 \pm 20\%$ for nutmeats and $84 \pm 9\%$ for hay. For the triazole-related residues, average concurrent recoveries were 90-109% from nutmeats with standard deviations of 6-10%, and 81-91% from hay with standard deviations of 6-12%. The validated LOQ for prothioconazole and desthio-prothioconazole were each 0.01 ppm in nutmeats and 0.05 ppm in hay, for combined LOQs of 0.02 and 0.10 ppm in nutmeats and hay, respectively. For the triazole-related residues, the validated LOQs were 0.01 ppm for each compound in hay and for triazole and TAA in nutmeats, and 0.05 ppm for TA in nutmeats. Apparent residues in/on control samples of nutmeats and hay were $<$ LOQ for the prothioconazole-related residues and for triazole. However, combined residues of TA and TAA were \geq LOQ in control samples, although the levels of control residues were well below the residues in treated samples (Table C.3.2). Adequate sample calculations and example chromatograms were provided for both methods, and the fortification levels used for the concurrent recoveries bracketed the measured residue levels.

Following collection, samples were stored frozen for up to 414 days (13.6 months) prior to analysis of prothioconazole residues and for up to 439 days (14.4 months) prior to analysis of triazole residues (Table C.2). Storage stability data are available indicating that prothioconazole-derived residues are stable at ≤ -15 °C for approximately 36 months in wheat forage, wheat hay, wheat grain, and canola seed (DP# 303508, S. Funk, 8/21/06). Data are also available indicating that conjugate triazole residues (TA and TAA) are relatively stable in frozen canola seed and wheat forage and straw for up to 24 months. However, the data also indicate that triazole is not stable in frozen canola seeds and declines by $\sim 24\%$ per year in frozen wheat forage.

As the main purpose of these field trials was to compare residues resulting from the two use patterns, the instability in triazole residues would have the same impact on residues from both treatment types. Therefore, the instability of triazole in peanut nutmeat and hay is not considered to be a substantial deficiency for this study.



TABLE C.1. Summary of Concurrent Method Recoveries of Prothioconazole-related Residues and Triazole-related Residues from Peanut Matrices.					
Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean Recovery \bar{x} SD
Peanut nutmeat	Prothioconazole (JAU6476)	0.01	3	60, 58, 71	63 \pm 7
		0.05	2	95, 98	97
		0.20	2	102, 104	103
		0.01-0.20	7	58-104	84 \pm 20
	Desthio- Prothioconazole	0.01	1	88	NA
	Triazole	0.01	4	108, 101, 83, 78	93 \pm 14
		0.05	2	87, 89	88
		0.20	2	88, 87	88
		0.01-0.20	8	78-108	90 \pm 10
	Triazolylalanine (TA)	0.05	4	116, 106, 113, 98	108 \pm 8
		0.25	2	109, 112	111
		1.0	2	114, 107	111
		2.0	1	103	NA
		0.05-2.0	9	98-116	109 \pm 6
	Triazolylacetic acid (TAA)	0.01	4	88, 88, 88, 95	90 \pm 4
		0.05	2	93, 113	103
0.20		2	106, 101	104	
0.01-0.20		8	88-113	96 \pm 9	
Peanut hay	Prothioconazole (JAU6476)	0.05	4	85, 79, 89, 100	88 \pm 9
		0.25	2	90, 87	89
		0.98	2	85, 88	87
		7.4	3	73, 72, 73	73 \pm 1
		0.05-7.4	11	72-100	84 \pm 9
	Desthio- Prothioconazole	0.05	2	98, 98	98
	Triazole	0.01	3	78, 74, 109	87 \pm 19
		0.05	2	89, 83	86
		0.20	2	91, 80	86
		0.01-0.20	7	74-109	86 \pm 12
	Triazolylalanine (TA)	0.01	3	71, 82, 74	76 \pm 6
		0.05	2	88, 85	87
		0.20	2	81, 84	83
		0.01-0.20	7	71-88	81 \pm 6
	Triazolylacetic Acid (TAA)	0.01	3	83, 94, 94	90 \pm 6
		0.05	2	99, 86	93
0.20		2	93, 86	90	
0.01-0.20		7	83-99	91 \pm 6	

Standard deviations are only reported for spiking levels with ≥ 3 values.



Analytes	Storage Temp. (°C)	Actual Storage Duration ¹ (days)	Limit of Demonstrated Storage Stability (months) ²
Prothioconazole	≤-15	414	36 ²
Desthio-prothioconazole			
Triazole	≤-15	431-439	737-742 ³
TA			
TAA			

¹ Sample extracts were analyzed within 9 days of extraction.
² Data are available indicating that combined prothioconazole residues are stable in frozen canola seed and wheat hay for up to 36 months (DP# 303508, S. Funk, 8/21/06).
³ Data are available from an on-going storage stability study indicating that TA and TAA are relatively stable in frozen canola seeds and wheat forage and straw for up to 24 months; however, residues of triazole were not stable in canola seeds and declined by ~24% per year in wheat forage (DP#s 331663,335154 &340239, S. Funk, 1/31/08).

Total prothioconazole-related residues were non-detectable (<0.004 ppm) in/on all samples of peanut nutmeats, regardless of the type of treatment (foliar only vs. in-furrow + foliar). For peanut hay, total prothioconazole residues were 0.71-2.58 ppm and averaged 1.41 ppm for the combined in-furrow and foliar applications and were 2.33-6.44 ppm and averaged 4.03 ppm for the foliar only treatment (Tables C.3.1 and C.4).

Residues of triazole were <0.01 ppm for all samples of peanut nutmeat and hay, regardless of treatment (Table C.3.2). The total conjugated triazole residues in/on nutmeats were 0.30-0.92 ppm and averaged 0.63 ppm for the combined in-furrow and foliar applications and were 0.40-1.44 ppm and averaged 0.80 ppm for the foliar only treatment. The total conjugated triazole residues in/on peanut hay were 0.08-0.16 ppm for the combined in-furrow and foliar applications and 0.12-0.20 ppm for the foliar only treatment.

Although both the prothioconazole and triazole residue data indicate that higher residues are likely to result from the use of only the foliar applications vs. the in-furrow plus foliar applications, the total seasonal use rate was not equivalent for the two use patterns (i.e., total rate = 0.71 lb/A vs. 0.54 lb/A). A more appropriate comparison would have utilized an in-furrow application at 0.178 lb ai/A followed by three foliar applications, each at 0.178 lb ai/A, for a total seasonal rate of 0.71 lb ai/A.

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.



TABLE C.3.1. Prothioconazole Residue Data from Peanut Field Trials with Prothioconazole (4 lb/gal FIC).

Trial ID (City, State, Year)	EPA Region	Variety	Application types	Total Rate (lb ai/A)	Commodity	PHI (days)	Residues (ppm) ²	
							Total Prothioconazole-Derived	
Seven Springs, NC 2005	2	NC11	seed trt + in-furrow + broadcast foliar	0.543	Nutmeat	14	ND	ND
					Hay		0.71	0.75
			broadcast foliar	0.726	Nutmeat	14	ND	ND
					Hay		2.33	2.40
Tifton, GA 2005	2	C99R	seed trt + in-furrow + broadcast foliar	0.547	Nutmeat	8	ND	ND
					Hay		1.12	1.12
			broadcast foliar	0.714	Nutmeat	8	ND	ND
					Hay		3.40	3.86
Molino FL 2005	3	Georgia Greens	seed trt + in-furrow + broadcast foliar	0.546	Nutmeat	14	ND	ND
					Hay		2.58	2.19
			broadcast foliar	0.691	Nutmeat	14	ND	ND
					Hay		6.44	5.73

The total prothioconazole-derived residues included residues of prothioconazole, determined as its sulfonic acid, and prothioconazole-desthio. The LOQ and LOD for the combined residues were respectively 0.02 and 0.004 ppm in nutmeats, and 0.10 and 0.011 ppm in hay.

TABLE C.3.2. Triazole Residue Data from Peanut Field Trials with Prothioconazole (4 lb/gal FIC).

Trial ID (City, State, Year)	EPA Region	Variety	Application types	Total Rate (lb ai/A)	Commodity	PHI (days)	Residues (ppm) ¹			
							Triazole		Total Triazole Conjugates ²	
Seven Springs, NC 2005	2	NC11	seed trt + in-furrow + broadcast foliar	0.543	Nutmeat	14	<0.01	<0.01	0.82	0.92
					Hay		<0.01	0.08		
			broadcast foliar	0.726	Nutmeat	14	<0.01	<0.01	1.44	1.23
					Hay		<0.01	0.16		
			control	NA	Nutmeat	14	<0.01	<0.01	0.404	0.033
					Hay		<0.01	0.033		
Tifton, GA 2005	2	C99R	seed trt + in-furrow + broadcast foliar	0.547	Nutmeat	8	<0.01	<0.01	0.69	0.68
					Hay		<0.01	0.16		
			broadcast foliar	0.714	Nutmeat	8	<0.01	<0.01	0.60	0.70
					Hay		<0.01	0.20		
			control	NA	Nutmeat	8	<0.01	<0.01	0.178	0.036
					Hay		<0.01	0.036		
Molino FL 2005	3	Georgia Greens	seed trt + in-furrow + broadcast foliar	0.546	Nutmeat	14	<0.01	<0.01	0.36	0.30
					Hay		<0.01	0.09		
			broadcast foliar	0.691	Nutmeat	14	<0.01	<0.01	0.40	0.41
					Hay		<0.01	0.12		
			control	NA	Nutmeat	14	<0.01	<0.01	0.05	0.01
					Hay		<0.01	0.01		

¹ The validated LOQs are 0.01 ppm for triazole and TAA in each matrix and TA in hay, and 0.05 ppm for TA in nutmeats.

² Total triazole conjugates are the sum of TA and TAA, reported in TA equivalents.



TABLE C.4. Summary of Side-by-side Trial Field Residue Data for Prothioconazole (FIC).¹

Matrix	Appl. Types	Total Rate (lb ai/A)	PHI (days)	Residues (ppm)						
				n	Min.	Max.	HAFT ²	Median (STMdR)	Mean (STMR)	Std. Dev.
Total Prothioconazole-Derived Residues³										
Nutmeat	seed trt + in-furrow + broadcast foliar	0.54-0.55	8-14	6	<0.02	<0.02	<0.02	0.02	0.02	0.00
Hay				6	0.71	2.58	2.39	1.12	1.41	0.78
Nutmeat	broadcast foliar	0.69-0.73	8-14	6	<0.02	<0.02	<0.02	0.02	0.02	0.00
Hay				6	2.33	6.44	6.09	3.63	4.03	1.71
Total Triazole Conjugated Residues⁴										
Nutmeat	seed trt + in-furrow + broadcast foliar	0.54-0.55	8-14	6	0.30	0.92	0.87	0.69	0.63	0.25
Hay				3	0.08	0.16	0.16	0.09	0.11	0.04
Nutmeat	broadcast foliar	0.69-0.73	8-14	6	0.40	1.44	1.34	0.65	0.80	0.44
Hay				3	0.12	0.20	0.20	0.16	0.16	0.04

¹ Triazole residues were not included in the summary table as they were <LOQ in/on all nutmeat and hay samples.

² HAFT = highest average field trial residues.

³ The total prothioconazole-derived residues included residues of prothioconazole, determined as its sulfonic acid, and prothioconazole-desthio. The LOQ for the combined residues is 0.02 ppm in nutmeats and 0.10 ppm in hay.

⁴ Total triazole conjugates are the sum of TA and TAA, reported in TA equivalents. The validated LOQs are 0.01 ppm for TA triazole and TAA in each matrix and TA in hay, and 0.05 ppm for TAA in nutmeats.

D. CONCLUSION

Prothioconazole-related residues and residues of TA and TAA in/on peanut nutmeats and hay following four foliar application totaling ~0.71 lb ai/A were greater or equal to the same residues in/on nutmeat and hay following a combination of a seed treatment, in-furrow, and foliar applications at rates totaling ~0.55 lb ai/A. A more appropriate comparison should have utilized the same total application rate of 0.71 lb ai/A for both the foliar application only and the combination treatment of in-furrow application and foliar applications. However, the peanut field trial data are adequate for purposes of comparing the two use patterns at the rates applied.

E. REFERENCES

DP Numbers: D303508 and D314517

Subject: Prothioconazole. Petition for Establishment of Tolerances for Use on Barley, Oilseed (Except Sunflower and Safflower) Crop Group, Dried Shelled Pea and Bean (Except Soybean) Crop Subgroup, Peanut, Rice, and Wheat. Summary of Analytical Chemistry and Residue Data. PP#4F6830

From: S. Funk

To: L. Coppolino

Date: 8/21/2006

MRID(s): 46246139, 46246141-46246150, 46246201-46246211, 46246213-46246227, 46477701-46477704



DP Numbers: D331663, 335154 & 340239

Subject: Prothioconazole. Petition for Establishment of Tolerances for Use on Sugar Beet (PP#6F7134) and Soybean (PP#6F7073). Summary of Analytical Chemistry and Residue Data.

From: S. Funk

To: B. O'Keefe

Date: 1/31/2008

MRID(s): 46841001, 46841002, 46974608, 46974609 and 47107801.

F. DOCUMENT TRACKING

RDI: A. M. Acierito (05/08/08); S. Funk (5/08/08).

Petition Number: NA

DP Barcode: 347039

PC Code: 113961