



13544





035303

Chemical: Carbamic acid, ?2-???1-(4-chlorophenyl)-

PC Code: 099100
HED File Code 11000 Chemistry Reviews
Memo Date: 11/28/2001
File ID: DPD269668
Accession Number: 412-02-0281

HED Records Reference Center
04/30/2002





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES


OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

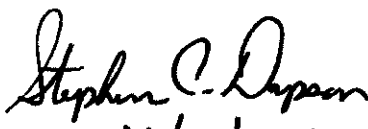
November 28, 2001

MEMORANDUM

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 Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS # 175013-18-0. DP Barcodes: D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, D278429.

MRID #s: 451184-28, 451184-29, 451184-30, 451184-31, 451184-32, 451184-33, 451184-34, 451184-35, 451184-36, 451184-37, 451185-01, 451185-02, 451185-03, 451185-04, 451185-05, 451185-06, 451185-07, 451185-08, 451185-09, 451185-10, 451185-11, 451185-12, 451185-14, 451185-15, 451185-16, 451185-17, 451185-18, 451185-19, 451185-20, 451185-21, 451185-22, 451185-23, 451185-24, 451185-25, 451185-26, 451185-27, 451185-28, 451185-29, 451185-30, 451185-31, 451185-32, 451185-33, 451185-34, 451185-35, 451185-36, 451185-37, 451186-01, 451186-02, 451186-03, 451186-04, 451186-05, 451186-06, 451186-07, 451186-08, 451186-09, 451186-10, 451186-11, 451186-12, 451186-13, 451186-14, 451186-15, 451186-16, 451186-17, 451186-18, 451186-19, 451186-20, 451186-21, 451186-22, 451186-23, 451186-24, 451186-25, 451605-01, 452728-01, 452749-01, 453211-01, 453675-01, 453994-01 (replaced 451184-28 with minor corrections), 454299-01

FROM: Leung Cheng, Chemist 
Registration Action Branch 3
Health Effects Division (7509C)

THROUGH: Stephen Dapson, Branch Senior Scientist 
Registration Action Branch 3
Health Effects Division (7509C)

11/29/2001

TO: Cynthia Giles-Parker/John Bazuin, Team 22

Fungicide Branch
Registration Division (7505C)

Following is the chemistry assessment of a petition from BASF Corp. for the establishment of permanent tolerances for residues of the fungicide, pyraclostrobin [carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy[methyl]phenyl]methoxy-, methyl ester], in/on many 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, tuberous and corm vegetables, and wheat. The review was performed by the Dynamac Corp. under the supervision of RAB3, HED. The data assessment has undergone secondary review within the branch and has been revised to reflect current HED and OPP policy. If any additional input is needed, please advise.

Executive Summary of Residue Chemistry Deficiencies

- Product chemistry (under the purview of the Registration Division).
- Amend Section B and labels.
- Agency validation of enforcement methods.
- Revise Section F.
- Submit final storage stability data for livestock commodities.
- Submit additional crop field trials.
- Submit sample storage intervals for the confined rotational crop study.

cc:RAB3 Reading F, Cheng, Wassell
RD/I:Team:6/21/2001:ChemSAC|PMRA|CDPR:8/2/2001:SDapson:11/6/2001
7509C:RAB3:LCheng:CM#2:RM810A:11/21/2001:3rab/pyraclostrobin

PYRACLOSTROBIN

PP#0F06139: EVALUATION OF RESIDUE CHEMISTRY DATA TO SUPPORT
PERMANENT TOLERANCES FOR USE OF PYRACLOSTROBIN
ON BANANAS (IMPORT), BARLEY, BERRIES, BULB VEGETABLES, CITRUS FRUITS,
CUCURBIT VEGETABLES, DRIED SHELLLED 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,
TUBEROUS AND CORM VEGETABLES, AND WHEAT
(DP BARCODES D269668, D272771, D272789, D274095, D274192, D274471, D274957,
D275843, and D278429)

INTRODUCTION

BASF Corporation has submitted a petition for the establishment of permanent tolerances for residues of the new foliar fungicide pyraclostrobin (BAS 500 F) in conjunction with a request for Section 3 registrations of a 20% water dispersible granular formulation (WDG; EPA File Symbol 7969-RIT) and a 2 lb/gal emulsifiable concentrate formulation (EC; EPA File Symbol 7969-RIA) for use of pyraclostrobin on many food/feed crops.

Pyraclostrobin [carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester] (CAS name) belongs to the strobilurin class of fungicides (β -methoxyacrylate class of compounds). Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface.

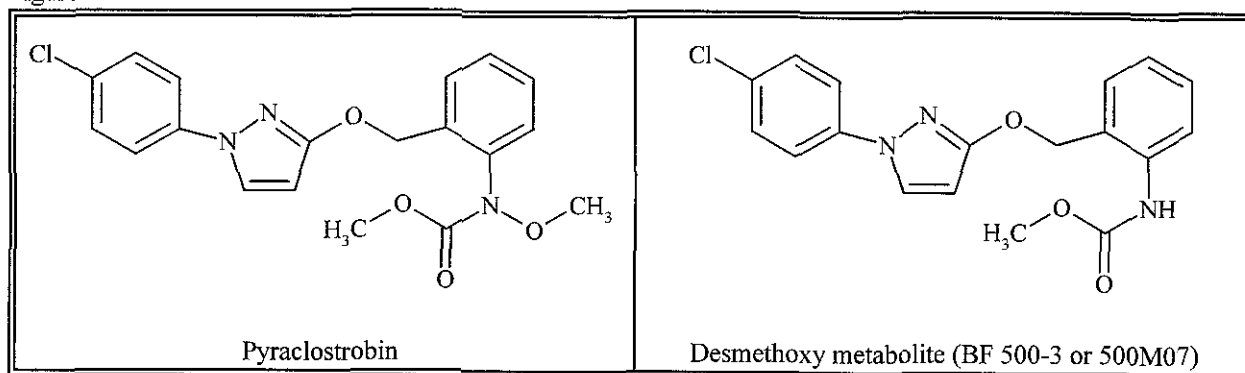
The petitioner is proposing in a revised Section F dated June 12, 2001 the establishment of permanent tolerances for the combined residues of pyraclostrobin methyl-N-[[[1-(4-chlorophenyl)pyrazol-3-yl]oxy]o-tolyl]-N-methoxycarbamate and its desmethoxy metabolite, methyl-N-[[[1-(4-chlorophenyl)pyrazol-3-yl]oxy]o-tolyl] carbamate, expressed as parent compound, in/on the following raw agricultural and processed commodities:

Bananas	0.04 ppm
Barley (grain)	0.4 ppm
Barley (hay)	25 ppm
Barley (straw)	6.0 ppm
Berries (crop group)	1.0 ppm
Bulb vegetables (crop group)	0.7 ppm
Citrus (crop group)	0.7 ppm
Cucurbit vegetables (crop group)	0.5 ppm
Dried shelled pea & bean (except soybean) group (crop subgroup 6-C)	0.5 ppm
Fruiting vegetables (crop group)	1.0 ppm
Grapes	2.0 ppm
Grass (seed screenings)	27.0 ppm
Grass (straw)	14.0 ppm
Grass (forage)	10.0 ppm
Grass (hay)	4.5 ppm
Peanut (nutmeat)	0.05 ppm
Pea hay	26.0 ppm
Pea vines	10.0 ppm
Pistachio	0.5 ppm
Root vegetables (crop subgroup 1-B)	0.4 ppm
Radish (tops)	16.0 ppm
Rye (grain)	0.04 ppm
Rye (straw)	0.5 ppm
Snap bean	0.3 ppm
Stone fruits (crop group)	0.7 ppm
Strawberry	0.4 ppm
Sugar beet (root)	0.2 ppm
Sugar beet (top)	8.0 ppm
Tuberous and corm vegetables (crop subgroup 1-C)	0.04 ppm
Tree nuts (crop group)	0.04 ppm
Almond hulls	1.6 ppm
Wheat (grain)	0.20 ppm
Wheat (hay)	6.0 ppm
Wheat (straw)	8.5 ppm
Wheat (aspirated grain fractions)	2.5 ppm
Orange pulp (dry)	6.3 ppm
Orange oil	4.2 ppm
Tomato paste	2.0 ppm
Raisin	6.0 ppm
Peanut oil	0.1 ppm
Sugar beet pulp (dry)	1.6 ppm
Milk	0.03 ppm

Cattle muscle	0.1 ppm
Cattle liver	0.6 ppm
Cattle kidney	0.1 ppm
Cattle fat	0.1 ppm
Eggs	0.1 ppm
Poultry muscle	0.1 ppm
Poultry liver	0.1 ppm
Poultry fat	0.1 ppm

The structures of pyraclostrobin and its desmethoxy metabolite are depicted in Figure 1 below.

Figure 1.



Associated with this petition are more than 76 volumes of residue chemistry submissions which are evaluated in this document. Supplemental data received by the Agency through June 2001 have been incorporated into the review.

CONCLUSIONS

OPPTS 830 Series GLNs: Product Properties

1. The Registration Division (RD) conducted reviews of the technical grade active ingredient and end-use products Cabrio, Headline and Insignia Fungicide (D269848 & D274191, May 3, May 15, and June 7, 2001, S. Malak). Fulfillment of the product chemistry data requirements is under the purview of the RD.

OPPTS GLN 860.1200: Proposed Uses

- 2a. The proposed use directions are adequate to allow RAB3 to make an assessment of whether residue data reflect the maximum residues likely to occur in food and livestock feeds for all crops for which use of pyraclostrobin is proposed except snap beans and

imported bananas. Additional information is required to delineate the proposed use of pyraclostrobin on snap beans (use rate in lbs ai/A and pre-harvest interval (PHI)) and imported bananas. For bananas, the petitioner should submit a copy of the product label(s), with English translation, for each pyraclostrobin product intended for use on bananas targeted for import to the U.S.

- 2b. A revised Section B must be submitted. The label must be modified to specify that aerial applications to orchard crops be made in a minimum of 10 gal/A. Based on the submitted data for barley and wheat hay, the petitioner must modify the proposed label to add a 14-day PHI for barley and wheat hay. In addition, based on the submitted data for grass forage and hay, a pregrazing and prehayage interval of 27 days must be added to the label for the 2 lb/gal EC formulation. For use on peanut, the EC formulation needs to be revised to include "Do not feed green immature growing plants to livestock or do not harvest for livestock feed."

OPPTS GLN 860.1300: Nature of the Residue in Plants

- 3a. Grape: The submitted grape metabolism is acceptable. Following treatment of established grape vines with six foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.11-0.43 lb ai/A/application (126-480 g ai/ha/application) for a total application rate for each label of ~1.34 lb ai/A (~1500 g ai/ha; ~1.5x the maximum proposed seasonal application rate for grapes), grapes were harvested 40 days after the final application. Total radioactive residues (TRR) in grapes were 0.951 ppm (chlorophenyl label) and 1.56 ppm (tolyl label); TRR in grape leaves were 39-40 ppm.
- 3b. Approximately 93% (chlorophenyl label) and 86% (tolyl label) TRR were characterized/identified in grapes. Pyraclostrobin was the major residue identified at 61.8% TRR (0.588 ppm) in chlorophenyl-label samples and 55.7% TRR (0.860 ppm) in tolyl-label samples. The desmethoxy metabolite BF 500-3 (also referred to as 500M07) accounted for 16.7% TRR (0.159 ppm) and 11.0% TRR (0.170 ppm) in chlorophenyl- and tolyl-label grapes, respectively. The following minor metabolites were also identified at <5% TRR: M54 (also referred to as 500M54, both labels), M55 (chlorophenyl label only), and M56 (both labels).
- 3c. Nonextractable residues comprised 12-16% TRR (0.116-0.245 ppm) following initial extraction. Data indicate that lignin accounted for 4.1-4.6 % TRR and cellulose accounted for 1.8-2.8% TRR from both labels. The petitioner attributed the lignin and cellulose residues to the grape stem that was homogenized with the grape bunches.
- 4a. Potato: The submitted potato metabolism study is acceptable. Following treatment of young potato plants with three or six foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.27 lb-0.36 ai/A/application (300-400 g ai/ha/application), potatoes were harvested 7 days after three

applications (immature; total application rate for each label of 0.8 lb ai/A; ~0.7x) or 7 days after six applications (mature; total application rate for each label of 1.7 lb ai/A; 1.4x the maximum proposed rate for any tuberous and corm crop). In chlorophenyl-label samples, TRR were 19.6 ppm and 0.009 ppm in immature foliage and tubers, respectively, and 69.8 ppm and 0.040 ppm in mature foliage and tubers. In tolyl-label samples, TRR were 9.86 ppm and 0.014 ppm in immature foliage and tubers, respectively, and 47.8 ppm and 0.048 ppm in mature foliage and tubers.

- 4b. Approximately 40-55% TRR and 89-96% TRR were characterized/identified in potato tubers and foliage, respectively from both labels. Pyraclostrobin was the major residue identified in all matrices except tolyl-label tubers. Pyraclostrobin accounted for 21% and 29.4% TRR (0.002 ppm and 0.012 ppm) in immature and mature chlorophenyl-label tubers, but for only 2.5% TRR (<0.001 ppm) in immature tolyl-label tubers; residues were nondetectable in mature tolyl-label tubers. In potato foliage, pyraclostrobin accounted for 56.5% and 55.1% TRR (11.1 and 38.5 ppm) in chlorophenyl-label foliage (mature and immature) and 65.2% and 64.6% TRR (6.43 and 30.9 ppm) in mature and immature tolyl-label foliage. The following metabolites were also detected in chlorophenyl-label tubers (mature and immature, respectively): the desmethoxy metabolite, 500M07 (BF 500-3), at 5.8% and 6.6% TRR; metabolite 500M54 at 6.2% and 2.6% TRR; the glucose conjugate of pyraclostrobin, 500M68, together with the chlorophenyl pyrazolol metabolite, 500M04, at 1.5% and 1.7% TRR; and the cleavage product, 500M79, at 0.4% and 3.3% TRR. These same metabolites were identified in chlorophenyl-label immature and mature foliage. In tolyl-label tubers, the major identified residue was the amino acid L-tryptophan, 500M72, which accounted for 10% TRR (0.001 ppm) and 29.2% TRR (0.014 ppm) in immature and mature tubers, respectively; L-tryptophan was also identified at 2.9% TRR (0.001 ppm) in the nonextractable residues of tolyl-label mature tubers following extraction with ammonia. One additional metabolite, 500M07, was identified at 0.6% TRR in immature tubers. In tolyl-label foliage, metabolite 500M07 was identified at 16.2% TRR (immature) and 21.4% TRR (mature). Metabolites 500M68 and 500M54 were also identified in immature tolyl-label foliage at 0.6% and 1.8% TRR, respectively.
- 5a. Wheat: The submitted wheat metabolism study is acceptable. Following treatment of summer wheat plants with two foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.27 lb ai/A/application (300 g ai/ha/application) for a total application rate of 0.54 lb ai/A (~1.6x), samples of wheat forage were harvested 0 and 31 days following the second application, and samples of mature wheat (straw, grain, and chaff) were harvested 41 days following the second application. In chlorophenyl-label samples TRR were 6.53 ppm in forage, 37.8 ppm in straw, 0.098 ppm in grain, and 24.3 ppm in chaff. In tolyl-label samples, TRR were 6.79 ppm in forage, 40.5 ppm in straw, 0.441 ppm in grain, and 30.6 ppm in chaff.
- 5b. Approximately 85-91% TRR were characterized/identified in wheat forage, straw, and grain from both labels. Pyraclostrobin was the major residue identified in all matrices

except tolyl-label grain. In chlorophenyl-label and tolyl-label forage and straw, pyraclostrobin accounted for at least 53-58% TRR (3.72 and 3.60 ppm in forage, and 21.2 and 23.3 ppm in straw). In grain, pyraclostrobin accounted for 36.1% TRR (0.036 ppm) in the chlorophenyl-label sample, but only 7.8% TRR (0.034 ppm) in tolyl-label grain. The desmethoxy metabolite, 500M07 (BF 500-3), was also a significant component in forage and straw from both labels (at least 12-15% TRR) and in chlorophenyl-label grain (10.5% TRR); it accounted for 3.2% TRR in tolyl-label grain. The major identified component in tolyl-label grain was 500M72 (L-tryptophan), which accounted for 36.8% TRR (0.162 ppm) and the cleavage product 500M24 accounted for 10.4% TRR (0.047 ppm) in tolyl-label grain; these metabolites were not detected in any other wheat matrix. The following additional metabolites were identified in chlorophenyl- and tolyl-label forage and straw at $\leq 4\%$ TRR: 500M68, 500M70, and 500M71 (glucose conjugates), 500M76, 500M54, and 500M34. In addition, metabolite 500M04 was identified in chlorophenyl-label wheat forage and straw at 1.7% and 3.7% TRR. Together the metabolites 500M68, 500M70, and 500M71 accounted for 4.3% TRR in chlorophenyl-label grain.

- 5c. Nonextractable residues in forage, straw, and grain were subjected to extensive procedures to characterize crude cellulose and lignin. In chlorophenyl-label forage and straw, cellulose accounted for 1.8% and 1.0% TRR and lignin accounted for 4.4% and 6.8% TRR in forage and straw. In tolyl-label samples, cellulose accounted for 1.8% and 2.6% TRR in forage and straw, and lignin accounted for 6.8% and 7.9% TRR in forage and straw. In grain, 10.5% and 5.0% TRR were characterized as starch in chlorophenyl- and tolyl-label grain, and 1.7% TRR in tolyl-label grain were characterized as cellulose.
6. The HED Metabolism Assessment Review Committee (MARC) discussed the metabolism of pyraclostrobin in plants on September 20, 2001 and has concluded that, based on the results of three dissimilar crop studies (grape, potato, and wheat), the nature of the residue in plants is understood for pyraclostrobin, and the residues of concern in plant commodities consist of pyraclostrobin and its desmethoxy metabolite for tolerance and risk assessment (D278044, L. Cheng, October 9, 2001).
7. In addition to the above metabolism studies, the petitioner submitted a translocation study with wheat which demonstrated that very little radioactivity translocated from the treated leaves to the untreated plant part.

OPPTS GLN 860.1300: Nature of the Residue in Livestock

- 8a. Ruminants: The submitted goat metabolism study adequately delineates the nature of the residue in ruminants. Following oral administration of [^{14}C]pyraclostrobin, labeled in either the chlorophenyl ring or the tolyl ring, to lactating goats for 5 consecutive days at a feeding level of 12.2 ppm ($\sim 0.34\times$ the maximum theoretical dietary burden, MTDB, for beef cattle and dairy cattle), the TRR were 0.013-0.058 ppm in milk, 0.018 and 0.022

ppm in muscle, 0.082 and 0.094 ppm in fat, 0.054 and 0.085 ppm in kidney, and 0.241 and 0.383 ppm in liver.

- 8b. Following oral administration of [¹⁴C]pyraclostrobin to lactating goats for 5 consecutive days at feeding levels of 70 ppm (tolyl label) or 78 ppm (chlorophenyl label) (~1.9-2.2x the MTDB for beef cattle and dairy cattle), TRR were 0.051-0.247 and 0.283-0.659 ppm in milk, 0.063 and 0.117 ppm in muscle, 0.380 and 0.928 ppm in fat, 0.316 and 0.335 ppm in kidney, and 0.828 and 1.51 ppm in liver. Residue levels were generally comparable for the two labels. Residues in milk plateaued about 36 hours after the first dose (tolyl label).
- 8c. Approximately 79-101% of the TRR were characterized/identified in the milk and tissues from the high-dose group. The parent, pyraclostrobin, was the major residue identified in muscle and fat, at 76.2-88.2% TRR (0.048-0.819 ppm). The parent was also identified in liver (1.4-8.4% TRR, 0.021-0.070 ppm) and in milk and kidney (17.4-23.2% TRR, 0.027-0.074 ppm). However, in milk and kidney, the parent was not resolved from the desmethoxy metabolite, 500M07 (elsewhere referenced as BF 500-3). Metabolite 500M07 was also identified in muscle, fat, and liver, at 1.5-15.4% TRR (0.005-0.082 ppm). Additional major metabolites identified were 500M04 (in chlorophenyl-label milk at 16.3% TRR and in chlorophenyl-label kidney at 4.4% TRR), 500M05 (in chlorophenyl-label milk at 14.1% TRR and in chlorophenyl-label kidney at 13.4% TRR), 500M51 (in tolyl-label kidney at 12.4% TRR), and 500M67 (in kidney at 7.8-13.0% TRR and in milk at 2.1-2.8% TRR). Several additional metabolites were identified in milk, kidney, and liver, each at <6% TRR; see Figure 2 (Attachment II) for the chemical structures of identified metabolites.
- 8d. Nonextractable residues in kidney and liver were further characterized by pronase digestion and acid hydrolysis. Pronase digestion released ~50% TRR in liver and 10-17% TRR in kidney. In general, higher levels of residue were released by refluxing with hydrochloric acid. Acid hydrolysis released ~60% TRR in liver and ~20% TRR in kidney. The bound residues in chlorophenyl-label kidney and liver were converted to chlorophenylpyrazole derivatives with acid hydrolysis.
- 9a. Poultry: The submitted hen metabolism study adequately delineates the nature of the residue in poultry. Following oral administration of [¹⁴C]pyraclostrobin, labeled in either the chlorophenyl ring or the tolyl ring, to laying hens for 7 consecutive days at a feeding level of 12-13 ppm (35-36x the maximum theoretical dietary burden for poultry), the TRR were 0.002-0.037 ppm in eggs, 0.007 and 0.009 ppm in muscle, 0.065 and 0.083 ppm in fat, and 0.317 and 0.474 ppm in liver. Residue levels were comparable for the two labels. Residues in eggs gradually increased during the study and had not reached a plateau at the time of sacrifice.
- 9b. Approximately 55-99% of the TRR were characterized/identified in eggs, fat, and liver; muscle samples were not analyzed because TRR levels were <0.010 ppm. The parent,

pyraclostrobin, was identified in eggs (8.5-8.8% TRR, 0.002-0.003 ppm) and fat (10.2-15.2% TRR, 0.008-0.010 ppm) but was not identified in liver. Metabolite 500M07 (BF 500-3) was a major metabolite identified in eggs (8.3-11.2% TRR, 0.003 ppm) and fat (27.3-38.9% TRR, 0.022-0.025 ppm); it was not identified in liver. The major metabolite identified in liver was 500M32, a glucuronide conjugate, at 10.9-13.1% TRR (0.035-0.062 ppm); this metabolite was not identified in eggs or fat. Several additional metabolites were identified in eggs, fat, and liver, each at <10% TRR; see Figure 2 (Attachment II) for the chemical structures of identified metabolites.

- 9c. In liver, a large portion of the TRR remained bound after initial extractions (43-48% TRR). A significant portion of this radioactivity (15-21% TRR) was released following pronase digestion, indicating that a large portion of the nonextractable residues were protein bound. HPLC analysis of the digestate (chlorophenyl label) indicated the presence of 500M04 and 500M64; however, no quantitative data were provided.
10. The HED MARC discussed the metabolism of pyraclostrobin in livestock on September 20, 2001 and concluded that the residues of concern in livestock commodities consist of pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol for tolerance and risk assessment (D278044, L. Cheng, October 9, 2001).

OPPTS GLN 860.1340: Residue Analytical Method - Plant Commodities

- 11a. The petitioner has proposed two tolerance enforcement methods for the determination of residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3) in/on plant commodities: LC/MS/MS method D9808 (U.S.) or 421/0 (Germany), and HPLC/UV method D9904. The validated method limits of quantitation (LOQs) for pyraclostrobin and BF 500-3 for both the LC/MS/MS or HPLC/UV methods are 0.02 ppm for each analyte in plant matrices. Adequate independent method validation and radiovalidation data have been submitted for both methods. LC/MS/MS method D9808 and HPLC/UV method D9904 have been forwarded to ACB/BEAD for petition method validation (D269850, L. Cheng, November 8, 2000). The petitioner must modify the proposed enforcement methods to include any modifications made by the EPA laboratory during the Agency laboratory validation.
- 11b. Based on the submitted concurrent method validation data, the LC/MS/MS method is adequate for data collection of residues of pyraclostrobin and BF 500-3 in/on almond (nutmeat and hulls); banana; barley (hay, grain, and straw); bean (dry and snap); blueberry (highbush); cabbage (with and without wrapper leaves); dry field pea (hay, vine, and seed); cantaloupe; carrot; cherry (tart); cucumber; grape; grapefruit; grass (forage, hay, straw, and seed screenings); lemon; lentil (seed); onion (dry bulb and green); orange; peach; peanut (hay and nutmeat); pecan (nutmeat); pepper (bell and chili); pistachio; potato; plum; radish (roots and tops); raspberry (red); rye (grain and straw); squash (summer); strawberry; sugar beet (roots and tops); tomato; wheat (forage, hay,

grain, straw, and aspirated grain fractions); and the processed commodities of grapes, oranges, peanuts, plums, sugar beets, tomatoes, and wheat.

OPPTS GLN 860.1340: Residue Analytical Methods - Livestock Commodities

- 12a. The petitioner has proposed two tolerance enforcement methods for ruminant commodities: HPLC/UV method 439/0 and Method 446, consisting of GC/MS method 446/0 and LC/MS/MS method 446/1. The HPLC/UV method determines residues of pyraclostrobin *per se*. Method 446 has a hydrolysis step and determines residues of pyraclostrobin and its metabolites as BF 500-5 and BF 500-8; see Figure 3 (Attachment III) for the chemical structures of these analytes. The validated method LOQs for BF 500-5 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues, and the validated LOQs for BF 500-8 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues. Independent method validation data for the HPLC/UV and LC/MS/MS methods are acceptable. Radiovalidation data submitted for the GC/MS and LC/MS/MS methods are adequate for liver and milk, and marginal for muscle. Method 446 has been forwarded to ACB/BEAD for petition method validation. The petitioner must modify the proposed enforcement method to include any modifications made by the EPA laboratory during the Agency laboratory validation.
- 12b. The petitioner has proposed Method D9902 as an enforcement method for poultry commodities. The method contains a hydrolysis step and determines residues of pyraclostrobin and its metabolites as BF 500-5 and BF 500-9 in poultry commodities; see Figure 3 (Attachment III) for the chemical structures of these analytes. The validated method LOQs for BF 500-5 type residues and for BF 500-9, in parent equivalents, are 0.05 ppm each for eggs and tissues.
- 12c. Independent validation and radiovalidation data were not submitted for Method D9902. These data are not relevant for the current petition since tolerances on poultry and eggs are not needed (see Conclusion 54b). These data may be required in the future when tolerances on poultry and eggs need to be established.
- 12d. The proposed enforcement methods were used for data collection in the ruminant and poultry feeding studies. The concurrent method validation recoveries demonstrate that the methods are adequate for data collection.

OPPTS GLN 860.1360: Multiresidue Method

13. Pyraclostrobin was successfully evaluated through several of the FDA protocols, while recovery of BF 500-3 was unsuccessful in all protocols. Pyraclostrobin was completely recovered through Protocol D (in grape) and E (in grape), and partially recovered through Protocol F (in peanut). Metabolite BF 500-3 had poor peak shape and inadequate sensitivity with Protocol C columns and therefore was not further analyzed under

Protocols D, E, and F. The results of the multiresidue testing for pyraclostrobin will be forwarded to FDA for inclusion in PAM Volume I.

OPPTS GLN 860.1380: Storage Stability Data

- 14a. Plant commodities: The submitted 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. The plant commodities chosen for the storage stability study are representative of all crops: an oilseed (peanut nutmeat), a non-oily grain (wheat grain), a leafy vegetable (sugar beet tops), a root crop (sugar beet roots), a fruit/fruited vegetable (tomatoes), a dry feed (wheat straw), and processed oil (peanut) and juice (grape) commodities.
- 14b. The available storage stability data support the storage intervals (≤ 19 months) of the samples of almond nutmeat and hulls, banana, barley hay, straw, and grain, bean (dry and snap), blueberry, cabbage, cantaloupe, carrot, cherry (sweet and tart), cucumber, grape and grape juice and raisin, grapefruit, grass forage, hay, straw, and seed screenings, lemon, lentils, onion (bulb and green), orange, orange processed commodities, dry pea hay, vine, and seed, peach, peanut hay and nutmeat, peanut processed commodities, pecan, pepper (bell and chili), pistachio, plum and its processed commodity prune, potato, radish roots and tops, raspberry (red), rye grain and straw, squash (summer), strawberry, sugar beet (roots and tops), sugar beet processed commodities, tomato, tomato processed commodities, wheat forage, hay, grain, aspirated grain fractions, and straw, and wheat processed commodities from the submitted field trial, field rotational crop, and processing studies.
- 15a. Livestock commodities: Cow commodity samples from the submitted ruminant feeding studies were stored frozen from collection to analysis for up to 3 months for whole and skim milk, 6.1 months for milk fat, 6.5 months for fat, 5.7 months for liver, 5.4 months for kidney, and 5 months for muscle. The submitted interim storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-10 (the latter representing the type of metabolites hydrolyzable to BF 500-8) are relatively stable under frozen storage conditions in/on fortified samples of cow milk, liver, and muscle for up to 90 days (~ 3 months). The submitted storage stability data are adequate to support the storage conditions and intervals of the whole and skim milk samples from the ruminant feeding study; however, additional storage stability data are required to support the storage conditions and intervals of the milk fat and tissue samples from the ruminant feeding study. When the final report of the ruminant storage stability study becomes available, RAB3 will validate the stability of pyraclostrobin and its metabolites in milk and cow tissues stored under the conditions and intervals of the ruminant feeding study.

- 15b. Hen commodity samples from the submitted poultry feeding study were stored frozen from collection until analysis for up to 5 months for eggs, 4 months for fat, 3 months for liver, and 6 months for muscle. The submitted storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-16 (the latter representing the type of metabolites hydrolyzable to BF 500-9) are relatively stable under frozen storage conditions in/on fortified samples of eggs for up to 7 months. The submitted storage stability data for eggs are adequate to support the storage conditions and intervals of the egg samples from the poultry feeding study. The petitioner has referenced the ruminant storage stability data to support the storage conditions and intervals of the remaining poultry matrices. The storage stability data for ruminant commodities can be translated to poultry commodities.

OPPTS GLN 860.1500: Crop Field Trials

Root Vegetables (Except Sugar Beet) - Crop Subgroup 1-B:

16. Carrot and Radish: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern for pyraclostrobin on carrots and radishes, the representative commodities of the root vegetables (except sugar beet) subgroup. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on carrots and radish roots harvested immediately (0-day PHI) following the last of three foliar applications of the WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.59-0.62 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-<0.26 ppm in/on 12 treated samples of carrots and <0.06-<0.33 ppm in/on 10 treated samples of radish roots; residues of BF 500-3 were below the LOQ in/on all samples.

Tuberous and Corm Vegetable - Crop Subgroup 1-C:

- 17a. Potato: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on potato, the representative commodity of the tuberous and corm vegetables subgroup. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tuberous and corm vegetables (crop subgroup 1-C) tolerance level of 0.04 ppm in/on potatoes harvested 3 days following the last of six foliar applications of the WDG formulation at 0.18-0.22 lb ai/A/application for a total seasonal application rate of 1.24 lb ai/A (~1x the maximum proposed seasonal rate). The combined residues were <0.04 ppm (below the LOQ) in/on all (34) samples of potatoes grown in the U.S., including residue decline samples.
- 17b. In the Canadian trials, the combined residues of pyraclostrobin and BF 500-3 were <0.04 ppm in/on all samples of potatoes harvested 3 days following the last of: (i) four foliar applications of the WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.80-0.82 lb ai/A; (ii) four foliar applications of the EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.80-0.81 lb ai/A; or (iii) four foliar applications of a tank mix of pyraclostrobin (WDG)

at 0.19-0.21 lb ai/A/application plus metiram (WDG) at 1.55-1.66 lb ai/A/application for total seasonal application rates of 0.79-0.81 lb ai/A pyraclostrobin and 6.34-6.50 lb ai/A metiram.

Sugar Beet:

18. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on sugar beet roots. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.2 ppm in/on sugar beet roots harvested 7-8 days following the last of four foliar applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application for a total seasonal application rate of 0.75-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.15 ppm in/on 24 samples of sugar beet roots.

Leaves of Root and Tuber Vegetables

19. Radish tops: The petitioner has submitted adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on radish tops. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 16.0 ppm in/on radish tops harvested immediately (0-day PHI) following the last of three foliar applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.59-0.62 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 7.17-15.8 ppm in/on 10 samples of radish tops.
20. Sugar beet tops: The petitioner has submitted adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on sugar beet tops. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 8.0 ppm in/on sugar beet tops harvested 7-8 days following the last of four foliar applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application for a total seasonal application rate of 0.75-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.42-7.37 ppm in/on 24 samples of sugar beet tops.

Bulb Vegetables:

21. Dry Bulb and Green Onion: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin and its metabolite BF 500-3 on dry bulb onions and green onions, the representative commodities of the bulb vegetable crop group. The combined residues of pyraclostrobin and BF 500-3 in/on dry bulb and green onions harvested seven days following the last of six broadcast foliar applications of the WDG formulation at 0.15-0.16 lb ai/A/application for a total seasonal application rate of 0.90-0.91 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.04-0.15 ppm in/on bulb onions (12 samples) and <0.05-0.65 ppm in/on green onions (6 samples) treated with the WDG formulation. RAB3 recommends that the bulb vegetables (crop group) tolerance be proposed at 0.9 ppm. A revised Section F is required.

Dried Shelled Pea and Bean (Except Soybean) - Subgroup 6C:

- 22a. Pea, drv. seed: The petitioner has not provided adequate residue data for field pea in support of the subgroup crop tolerance. Three field pea trials should be conducted in Region 11 reflecting application of the 2 lb/gal WDG formulation according to the maximum proposed use pattern. Because Canadian trials were conducted in Region/Zone 14 which does not border Region 11, these data cannot be translated to the U.S. registration.
- 22b. The submitted U.S. field pea field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 are <0.04 ppm in/on field pea seed harvested 30 days following the last of two foliar applications of the EC formulation at 0.2 lb ai/A/application for a total seasonal application rate of ~0.4 lb ai/A (~1.5x the maximum proposed seasonal rate). The combined residues were 0.05-0.37 ppm in/on field pea seed grown in Canada treated with the EC formulation at 1.5x the maximum proposed use pattern.
- 22c. Lentil: The petitioner has not provided adequate residue data on lentil seed because the submitted field trials were conducted at twice the proposed maximum application rate. The petitioner should conduct trials at the 1x rate in Region 11 to support the proposed subgroup crop tolerance for dry shelled pea and bean (except soybean).
23. Bean, dry and snap: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on dry bean. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed 0.21 ppm in/on dry bean (20 samples) and snap bean (18 samples) harvested 21 and 7 days, respectively following the last of two foliar applications of the EC formulation at 0.19-0.20 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1.5x the maximum proposed seasonal application rate for dry bean).
24. To establish a tolerance for the dried shelled pea and bean (except soybean) subgroup, the petitioner should conduct the three field pea trials or lentil field trials described above. The submitted residue data support a tolerance of 0.3 ppm for the combined residues of pyraclostrobin and its metabolite BF 500-3 in/on dry bean. A revised Section F deleting the tolerance proposed for this crop subgroup 6C and proposing a tolerance at 0.3 ppm in/on dry bean must be submitted.
25. Pending submission of a proposed label specifying application rates and PHI, the residue data may support the proposed tolerance of 0.3 ppm in/on snap bean (bean, succulent).

Foliage of Legume Vegetables Except Soybeans:

- 26a. The petitioner has not provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on field pea vines and hay because geographic representation of data is inadequate. Three trials of field pea reflecting application of the 2 lb/gal WDG formulation according to the maximum proposed use pattern in Region 11

are required. Because Canadian trials were conducted in Region/Zone 14 which does not border Region 11, these data cannot be translated to the U.S. registration.

- 26b. The submitted U.S. field pea field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 were 4.90-25.2 ppm in/on field pea hay and 0.37-9.50 ppm in/on pea vines harvested 0-2 days following the last of two foliar applications of the EC formulation at 0.2 lb ai/A/application for a total seasonal application rate of 0.4 lb ai/A (~1.5x the maximum proposed seasonal rate). The combined residues were 6.92-21.6 ppm in/on field pea hay and 4.28-7.75 ppm in/on field pea vines grown in Canada treated with the EC formulation at 1.5x the maximum proposed use pattern.
27. For establishment of the subgroup foliage of legume vegetables except soybeans subgroup (7A) tolerance, the petitioner would be required to conduct three field pea trials and three field trials on a cultivar of bean (cowpea is the preferred commodity) reflecting the maximum proposed use pattern for the 2 lb/gal WDG formulation on field pea and a bean.

Fruiting Vegetables (Except Cucurbits):

- 28a. Pepper (Bell and Non-bell) and Tomato: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on peppers (bell and non-bell) and tomatoes, representative commodities of the fruiting vegetables crop group. The results of the pepper and tomato field trials indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 in/on peppers and tomatoes harvested on the day (0-day PHI) of the last of six foliar applications of either the WDG (peppers) or EC (tomatoes) formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.04-<0.30 ppm in/on bell peppers (12 samples), <0.14-0.99 ppm in/on non-bell (chili) peppers (6 samples), and <0.08-<0.25 ppm in/on tomatoes (30 samples). RAB3 recommends that a fruiting vegetables (crop group) tolerance of 1.4 ppm be proposed. A revised Section F is required.
- 28b. In side-by-side tomato field trials conducted to compare the use of the EC and WDG formulations, tomatoes were harvested on the day (0-day PHI) of the last of six foliar applications of either the EC or WDG formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.08-0.20 ppm following applications of the EC formulation and <0.08-<0.15 ppm following applications of the WDG formulation. These data indicate that there were no significant differences in residue levels between tomato samples treated with the EC formulation and the WDG formulation.

Cucurbit Vegetables:

- 29a. Cucumber, Muskmelon (Cantaloupe), and Summer Squash: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on cucumber, muskmelon (cantaloupe), and summer squash, the representative commodities of the cucurbit vegetables crop group. The results of the cucurbit field trials indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed cucurbit vegetables (crop group) tolerance level of 0.5 ppm in/on cantaloupes, cucumbers, and summer squash harvested on the day (0-day PHI) of the last of six foliar applications of the EC formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.08-0.16 ppm in/on cantaloupes (12 samples), <0.04-<0.43 ppm in/on cucumbers (16 samples), and <0.07-<0.22 ppm in/on summer squash (10 samples).
- 29b. In side-by-side cucurbit field trials conducted to compare the use of the EC and WDG formulations, cantaloupes, cucumbers, and summer squash were harvested on the day (0-day PHI) of the last of six foliar applications of either the EC or WDG formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.15-<0.16 ppm in/on cantaloupe, <0.14-<0.15 ppm in/on cucumber, and <0.04-<0.05 ppm in/on summer squash following applications of the EC formulation and <0.08-<0.12 ppm in/on cantaloupe, <0.15-<0.16 ppm in/on cucumber, and <0.04-<0.06 ppm in/on summer squash following applications of the WDG formulation. These data indicate that there were no significant differences in residue levels in/on cucurbit vegetable samples treated with the EC formulation or the WDG formulation.

Citrus Fruits (Citrus Spp., Fortunella Spp.):

- 30a. The available citrus field trial data are adequate to support the proposed crop group tolerance (0.7 ppm) because the three bridging studies (conducted with tomato, cucurbits, and grape) indicate no significant difference in the residue levels between the use of the WDG formulation or the EC formulation. The field trial data reflecting application of the WDG formulation can be extrapolated to project the residue levels for the EC formulation for which use on citrus is proposed.
- 30b. The combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.08-0.28 ppm in/on grapefruit (12 samples), <0.13-0.45 ppm in/on lemons (10 samples), and <0.11-0.61 ppm in/on oranges (26 samples) harvested 13-14 days following the last of four foliar applications of the WDG formulation at ~0.15 lb ai/A/application (first and second applications) and ~0.25 lb ai/A/application (third and fourth applications) for a total seasonal application rate of ~0.8 lb ai/A (~1x the maximum proposed seasonal application rate).
- 30c. In addition, the pulp and peel were analyzed separately in selected samples of grapefruit and oranges. These data indicate that combined residues were <0.04 ppm in/on 6 citrus pulp samples and <0.08-0.54 ppm in/on 6 citrus peel samples.

- 30d. Trials conducted with dilute and concentrate sprays did not indicate that higher residues were likely to result from either type of application. Combined residues for concentrate and dilute spray applications were, respectively, <0.08-<0.24 ppm and <0.09-0.28 ppm in/on grapefruit; <0.13-0.45 ppm and <0.21-0.35 ppm in/on lemons; and <0.11-0.61 ppm and <0.19-0.46 ppm in/on oranges.

Stone Fruits:

- 31a. Cherry (Sweet and Tart), Peach, and Plum: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on cherries (sweet and tart), peaches, and plums, the representative commodities of the stone fruits crop group. The combined residues of pyraclostrobin and its metabolite BF 500-3 in/on cherries (sweet and tart), peaches, and plums harvested immediately (0-day PHI) following the last of five foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.6 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.27-<0.44 ppm in/on sweet cherries (6 samples), 0.45-0.67 ppm in/on tart cherries (6 samples), <0.09-<0.33 ppm in/on peaches (18 samples), and <0.04-<0.21 ppm in/on plums (12 samples). RAB3 recommends that a stone fruits (crop group) tolerance of 0.9 ppm (as opposed to 0.7 ppm) be proposed. A revised Section F is required.
- 31b. Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.27-0.53 ppm and <0.29-0.67 ppm in/on cherries, <0.09-<0.28 ppm and <0.10-<0.33 ppm in/on peaches, and <0.04-<0.21 ppm and <0.04-<0.15 ppm in/on plums treated with concentrate or dilute sprays, respectively.

Berries:

32. Blueberry and Raspberry: The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on blueberries and raspberries, the representative commodities of the berries crop group. The combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.12-0.69 ppm in/on highbush blueberries (12 samples) and <0.46-0.97 ppm in/on red raspberries (6 samples) harvested immediately (0-day PHI) following the last of four foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.72 lb ai/A (~1x the maximum proposed seasonal application rate). RAB3 recommends that the tolerance in berries (crop group) be proposed at 1.3 ppm.

Tree Nuts:

- 33a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on almonds and pecans, the representative commodities of the tree nuts crop group.
- 33b. Almond and Pecan nutmeat: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tree nuts (crop group) tolerance level of 0.04 ppm

in/on almonds (10 samples) harvested 108-148 days and pecans (10 samples) harvested 14 days following the last of four foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.48 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm in/on all samples of almond and pecan nutmeat.

- 33c. Trials conducted with dilute and concentrate sprays did not indicate that higher residues were likely to result from either type of application. Combined residues in/on almond and pecan nutmeat were <0.04 ppm in all samples whether treated with concentrate or dilute sprays.
- 33d. Almond hulls: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed almond hulls tolerance level of 1.6 ppm in/on almond hulls harvested 108-148 days following the last of four foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.48 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm to 0.67 ppm in/on almond hulls sampled at normal harvest. The maximum combined residue (1.59 ppm) was detected in an almond hull sample from the decline study harvested 148 days following the last application.
- 33e. Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.04-0.56 ppm in/on almond hulls treated with concentrate sprays, and <0.04-0.67 ppm in/on almond hulls treated with dilute sprays.

Pistachio:

- 34a. The petitioner has provided adequate data reflecting the maximum proposed use pattern of pyraclostrobin on pistachios. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.5 ppm in/on pistachios harvested 14-15 days following the last of four foliar applications of the WDG formulation at 0.12-0.21 lb ai/A/application for a total seasonal application rate of 0.72-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.48 ppm in/on pistachios (6 samples). RAB3 recommends that the tolerance in pistachio be proposed at 0.7 ppm.
- 34b. Trials conducted with dilute and concentrate sprays did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.04-0.46 ppm in/on pistachios treated with concentrate sprays, and <0.04-0.48 ppm in/on pistachios treated with dilute sprays.

Small Grains:

Barley:

- 35a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on barley.

- 35b. Barley hay: The combined residues of pyraclostrobin and BF 500-3 support the proposed tolerance level of 25.0 ppm in/on barley hay harvested 9-16 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 1.06-25 ppm in/on 24 samples of barley hay grown in the U.S. and 0.80-5.51 ppm in/on 26 samples of barley hay grown in Canada.
- 35c. Barley grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on barley grain harvested 38-70 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.19 ppm in/on 24 samples of barley grain grown in the U.S. and <0.04-0.33 ppm in/on 26 samples of barley grain grown in Canada.
- 35d. Barley straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 6.0 ppm in/on barley straw harvested 38-70 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-3.17 ppm in/on 24 samples of barley straw grown in the U.S. and 0.26-5.55 ppm in/on 26 samples of barley straw grown in Canada.

Rye

- 36a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on rye.
- 36b. Rye grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.04 ppm in/on rye grain harvested 58-66 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.40-0.414 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm in/on 10 samples of rye grain.
- 36c. Rye straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 0.5 ppm in/on rye straw harvested 55-66 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.40-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.13-0.43 ppm in/on 10 samples of rye straw.
- 36d. Rye forage: The petitioner did not provide residue data or propose a tolerance for rye forage because applications are made after the growth stages at which rye is foraged.

Based on the proposed use pattern, the Agency will not require residue data or a tolerance for rye forage.

Wheat:

- 37a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on wheat in the U.S. Adequate field trial data were submitted supporting applications made to wheat at the earlier growth stage (applications made at flag leaf and 50% head emergence) and applications made to wheat at later growth stages with a shorter PHI (applications made at full head emergence and the end of anthesis; expanded use application schedule) for control of Fusarium head blight.
- 37b. Wheat grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.2 ppm in/on wheat grain following earlier and later (expanded use) application schedules to wheat. In the early treatment schedule, wheat grain was harvested 40-57 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following the earlier application schedule were <0.04 ppm in/on 44 samples of wheat grain grown in the U.S. and <0.04-<0.05 ppm in/on 22 samples of wheat grain grown in Canada. In the later application schedule, wheat grain was harvested 24-60 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.39-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following later application schedules were <0.04-0.16 ppm in/on 34 samples of wheat grain grown in the U.S. and <0.04-0.09 ppm in/on 22 samples of wheat grain grown in Canada.
- 37c. Wheat hay: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 6.0 ppm in/on wheat hay following earlier application schedules to wheat. In the early treatment schedule, wheat hay was harvested 12-19 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following early application schedules were 0.21-5.95 ppm in/on 44 samples of wheat hay grown in the U.S. and 0.90-4.3 ppm in/on 22 samples of wheat hay grown in Canada.
- 37d. Wheat straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 8.5 ppm in/on wheat straw following earlier and later (expanded use) application schedules to wheat. In the early treatment schedule, wheat straw was harvested 40-57 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following early application schedules were <0.05-5.7 ppm in/on 44 samples of wheat straw grown in the U.S. and 0.11-2.56 ppm in/on 22 samples of

wheat straw grown in Canada. In the later treatment schedule, wheat straw was harvested 24-60 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.39-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following later application schedules were 0.65-8.23 ppm in/on 34 samples of wheat straw grown in the U.S. and 0.21-6.31 ppm in/on 22 samples of wheat straw grown in Canada.

- 37e. Wheat forage: The petitioner did not provide residue data or propose a tolerance for wheat forage because applications are made after the growth stages at which wheat is foraged. Based on the current proposed use patterns, the Agency will not require residue data or a tolerance for wheat forage.

Small grains - European trials:

- 38a. The submitted European field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.04 ppm to 0.15 ppm in/on barley and wheat grain and 0.66-7.33 ppm in/on barley and wheat straw harvested 33-64 days following treatment according to one of the following application patterns: (i) pyraclostrobin (250 g/L) formulated as an EC formulation and applied to barley and wheat plants as two spray applications at 194-265 g ai/ha/application (0.17-0.24 lb ai/A/application for a total rate of 0.37-0.45 lb ai/A); (ii) pyraclostrobin (133 g/L) and epoxiconazole (50 g/L) formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 211-285 g ai/ha/application (0.19-0.25 lb ai/A/application for a total rate of 0.39-0.46 lb ai/A); or (iii) pyraclostrobin (133 g/L), epoxiconazole (50 g/L), and kresoxim-methyl (67 g/L) formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 231-266 g ai/ha/application (0.21-0.24 lb ai/A/application for a total rate of 0.42-0.45 lb ai/A).
- 38b. Although small grain data from Europe are not required to support the subject petition, the submitted European field trial data are useful in demonstrating that combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed U.S. tolerance levels of 0.2 ppm for wheat grain, 0.4 ppm for barley grain, 6.0 ppm for barley, and 8.5 ppm for wheat straw following treatment according to the use patterns utilized in the studies.

Grass (Grown for Seed):

- 39a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on grasses grown for seed.
- 39b. Grass straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 14.0 ppm in/on grass straw harvested 13-15 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were 1.91-13.8 ppm in/on grass straw.

- 39c. Grass seed screenings: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 27.0 ppm in/on grass seed screenings harvested 13-15 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were 1.6-26.6 ppm in/on grass seed screenings.
- 39d. Grass forage: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 10.0 ppm in/on grass forage harvested 27-115 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were <0.04-9.29 ppm in/on grass forage cut when the postharvest regrowth was approximately 2 to 5 inches in height.
- 39e. Grass hay: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 4.5 ppm in/on grass hay harvested 27-115 days and field dried for 2-7 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were <0.04-4.3 ppm in/on grass forage cut when the postharvest regrowth was approximately 2 to 5 inches in height.

Miscellaneous Commodities

Banana:

40. The petitioner has provided adequate residue data reflecting the stated maximum proposed use pattern for pyraclostrobin on imported bananas. The petitioner has indicated that the maximum seasonal rate is 800 g ai/ha; however, specimen labels were not included to confirm the proposed use patterns for pyraclostrobin on imported bananas. A sufficient number of field trials, reflecting the stated maximum proposed use pattern, were conducted in the major banana-growing regions of Central and South America. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance of 0.04 ppm in/on imported bagged or unbagged bananas (whole fruit including peel) harvested immediately (0-day PHI) following the last of eight foliar applications of an EC formulation at 0.08-0.13 lb ai/A/application (90.0-141 g ai/ha) for a total seasonal application rate of 0.66-0.80 lb ai/A (743-902 g ai/ha; ~1x the stated proposed maximum seasonal rate). The combined residues were <0.04 ppm in/on all (24) samples of bagged and unbagged bananas.

Grape:

- 41a. The available grape field trial data are adequate to support the proposed tolerance because the grape bridging study (as well as those conducted with tomato and cucurbits) indicates no significant difference in the residue levels between the use of the WDG formulation or the EC formulation. The field trial data reflecting application of the EC formulation can

be extrapolated to project the residue levels for the WDG formulation for which use on grape is proposed.

- 41b. The petitioner has provided residue data reflecting the maximum proposed use pattern of pyraclostrobin (for the WDG formulation) following application of the 2 lb/gal EC formulation at 1x on grapes. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 2.0 ppm in/on grapes harvested 14 days following the last of six foliar applications of the EC formulation at ~0.15 lb ai/A/application for a total seasonal application rate of ~0.9 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.23-1.92 ppm in/on 50 samples of grapes. Data from trials conducted with dilute and concentrate sprays indicate that higher residues would be unlikely to result from different spray volumes. Combined residues were 0.23-1.66 ppm in/on grapes treated with a concentrate spray and <0.35-1.92 ppm in/on grapes treated with a dilute spray.
- 41c. The petitioner also provided residue data reflecting application of the 20% WDG formulation at 0.6x on grapes. The combined residues did not exceed the proposed grapes tolerance level of 2.0 ppm in/on grapes harvested 14 days following the last of three foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.54 lb ai/A (~0.6x the maximum proposed seasonal application rate). The combined residues were 0.10-1.31 ppm in/on grapes treated with the WDG formulation at 0.6x the maximum proposed seasonal application rate. Combined residues were 0.10-1.31 ppm in/on grapes treated with a concentrate spray and <0.12-1.0 ppm in/on grapes treated with a dilute spray.
- 41d. In side-by-side bridging trials conducted to compare the use of the EC and WDG formulations, grapes were harvested 14-15 days following the last of three foliar applications of either the EC or WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.54 lb ai/A (~0.6x the maximum proposed seasonal application rate). The combined residues were 0.24-1.01 ppm in/on grapes following applications of the EC formulation and 0.32-0.83 ppm in/on grapes following applications of the WDG formulation. These data indicate that there were no significant differences in residue levels between grape samples treated with the EC formulation and the WDG formulation.

Peanut:

- 42a. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on peanuts.
- 42b. Peanut nutmeat: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.05 ppm in/on peanut nutmeat harvested 14-18 days following the last of five foliar applications of the EC formulation at 0.24-0.27 lb ai/A/application for a total seasonal application rate of 1.24-1.28 lb ai/A (~1x the

maximum proposed seasonal application rate). The combined residues were <0.04- <0.045 ppm in/on 24 samples of peanut nutmeat.

- 42c. Peanut hay: The submitted peanut hay field trial data indicate that combined residues of pyraclostrobin and BF 500-3 were 1.45-34.3 ppm in/on peanut hay harvested 14-18 days following the last of five foliar applications of the EC formulation at 0.24-0.27 lb ai/A/application for a total seasonal application rate of 1.24-1.28 lb ai/A (~1x the maximum proposed seasonal application rate). These data are not adequate to support a tolerance for peanut hay because the moisture content was not provided for the peanut hay samples from the 1997 field trials and ranged 22.5-45.2% in peanut hay samples from the 1998 peanut field trials. According to Table 1 of OPPTS 860.1000, peanut hay consists of vines and leaves that have been sun-dried to a moisture content of 10 to 20 percent.
- 42d. A tolerance for peanut hay will not be required if the label for the EC formulation is amended to include the following feeding restriction: "Do not feed green immature growing plants to livestock or do not harvest for livestock feed." Alternatively, additional field trials will be required depicting residues of pyraclostrobin in peanut hay dried to <20% following application of the EC formulation at 1x the maximum proposed use pattern.

Strawberry:

43. The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on strawberries. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on strawberries harvested immediately (0-day PHI) or one day following the last of five foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.9 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.07-<0.39 ppm in/on 16 samples of strawberries.

Residue Decline Studies:

44. The petitioner conducted residue decline studies with carrot; potato; sugar beet (root and tops); onion (dry bulb); peas, dry, seed; bean, dry; bean, snap; lentil seed; dry pea (hay and vine); tomato; cucumber; peach; plum; raspberry; almond (nutmeat and hulls); barley (grain, hay, and straw); wheat (grain, hay, and straw); grape; peanut (nutmeat and hay); and strawberry. These studies indicate that combined residues of pyraclostrobin and BF 500-3 do not increase with increasing posttreatment intervals.

OPPTS GLN 860.1520: Processed Food/Feed

Citrus Fruits:

- 45a. The submitted orange processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in juice processed

from oranges bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate 8.2-9.5x in dried pulp and 5.3-6.8x in oil processed from oranges bearing detectable residues.

- 45b. The highest average field trial (HAFT) residue of citrus treated at 1x the maximum seasonal rate (0.8 lb ai/A/season; 14-day PHI) from the submitted citrus field trial studies was 0.505 ppm pyraclostrobin and 0.075 ppm BF 500-3. Based on the HAFT (0.58 ppm) and an average concentration factor of 8.9x in dried pulp and 6.1x in citrus oil, the maximum expected pyraclostrobin and BF 500-3 residues would be 5.16 ppm in dried pulp and 3.54 ppm in citrus oil. RAB3 recommends that the petitioner propose tolerances of 5.5 ppm for citrus, dry pulp and 4 ppm for citrus, oil. We note that the tolerances will have to be revised to be expressed for citrus commodities instead of orange commodities.

Grapes:

- 46a. The submitted grape processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in juice processed from grapes bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate in raisins at 3.4x.
- 46b. The HAFT residue of grape treated at 1x the maximum seasonal rate (0.9 lb ai/A/season; 14-day PHI) from the submitted field trial studies was 1.71 ppm pyraclostrobin and 0.21 ppm BF 500-3 (1.92 ppm combined residues). Based on the HAFT (1.92 ppm) and a concentration factor of 3.4x in raisin, the maximum expected pyraclostrobin and BF 500-3 residues would be 6.53 ppm in raisin. Data from the processing study indicate that the proposed tolerance of 6.0 ppm for raisin is too low. RAB3 recommends that the petitioner propose a tolerance of 7 ppm for raisin.

Peanut:

- 47a. The submitted peanut processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in peanut meal processed from peanut nutmeat bearing detectable residues of pyraclostrobin. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate in peanut oil at 1.6x and 2.2x (average concentration factor of 1.9x).
- 47b. The HAFT residue of peanut nutmeat treated at 1x the maximum seasonal rate (1.25 lb ai/A/season; 14-day PHI) from the submitted peanut field trial studies was 0.0225 ppm pyraclostrobin and <0.02 ppm BF 500-3 (<0.0425 ppm combined residues). Based on the HAFT (<0.0425 ppm) and an average concentration factor of 1.9x, the maximum expected pyraclostrobin and BF 500-3 residues in peanut oil would be 0.081 ppm. Data from the peanut processing study indicate that the proposed tolerance of 0.1 ppm for peanut oil is appropriate.

Plum:

- 48a. The submitted plum processing data are adequate for the purposes of this petition. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate slightly in prunes at 1.2x and 1.3x.
- 48b. The HAFT residue of plums treated at 1x the maximum seasonal rate (0.6 lb ai/A/season; 0-day PHI) from the submitted plum field trial studies was 0.19 ppm pyraclostrobin and <0.02 ppm BF 500-3 (<0.21 ppm combined residues). Based on the HAFT (0.21 ppm) and an average concentration factor of 1.25x, the maximum expected pyraclostrobin and BF 500-3 residues in prunes would be 0.273 ppm, which is lower than the proposed RAC tolerance of 0.7 ppm for the stone fruits crop group. Therefore, a tolerance for pyraclostrobin residues in prunes is not warranted.

Potato:

49. The submitted potato processing data are adequate for the purposes of this petition. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 are below the LOQ (<0.04 ppm) in/on potato samples following treatment at 5x the maximum proposed rate. Therefore, no potato processing study or tolerances for potato processed commodities are required.

Sugar Beet:

- 50a. The submitted sugar beet processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in molasses and refined sugar processed from sugar beet roots bearing detectable residues of pyraclostrobin. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate in dried pulp at 6.9x and 7.5x (average concentration factor = 7.2x).
- 50b. The HAFT residue of sugar beet roots treated at 1x the maximum seasonal rate (0.8 lb ai/A/season; 7-day PHI) from the submitted sugar beet field trial studies was 0.105 ppm pyraclostrobin and 0.03 ppm BF 500-3 (0.135 ppm combined residues). Based on the HAFT (0.135 ppm) and an average concentration factor of 7.2x, the maximum expected pyraclostrobin and BF 500-3 residues in dried pulp would be 0.972 ppm. Data from the sugar beet processing study indicate that the proposed tolerance of 1.6 ppm for dried sugar beet pulp is too high. RAB3 recommends that the petitioner propose a tolerance of 1 ppm for beet, sugar, dried pulp.

Tomato:

- 51a. The submitted tomato processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in tomato puree processed from whole tomatoes bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrate in tomato paste at 1.5x and 2.6x (average concentration factor = 2.1x).

- 51b. The HAFT residue of tomatoes treated at 1x the maximum seasonal rate (1.2 lb ai/A/season; 0-day PHI) from the submitted tomato field trials was 0.21 ppm pyraclostrobin and <0.025 ppm BF 500-3 (0.235 ppm combined residues). Based on the HAFT (0.235 ppm) and an average concentration factor of 2.1x, the maximum expected pyraclostrobin and BF 500-3 residues in tomato paste would be 0.494 ppm, which is within the proposed RAC tolerance of 1.0 ppm for the fruiting vegetables crop group. A revised Section F deleting the proposed tolerance of 2.0 ppm in/on tomato paste is needed.

Wheat:

- 52a. The submitted wheat processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 is observed in flour, bran, middlings, shorts, and germ processed from wheat grain bearing detectable residues, except in bran from the expanded use application schedule. However, based on the HAFT (0.145 ppm) in wheat grain treated at 1x the maximum proposed seasonal rate (expanded use; 36-day PHI) and a concentration factor of 1.3x, residues in processed wheat bran (0.189 ppm) are not expected to exceed the proposed tolerance for wheat grain (0.2 ppm). Based on the results of the processing studies, tolerances for residues of pyraclostrobin in the processed commodities of wheat are not required.
- 52b. Aspirated grain fractions: The combined residues of pyraclostrobin and its metabolite BF 500-3 do not exceed the proposed tolerance level of 2.5 ppm in/on wheat aspirated grain fractions following application of pyraclostrobin at 1x to wheat according to the earlier and later (expanded use) application schedules. Combined residues of pyraclostrobin and BF 500-3 are <0.067-0.445 ppm and 1.87-2.17 ppm in/on aspirated grain fractions from wheat treated at the earlier and the expanded use application schedules, respectively.
- 52c. The petitioner must submit a revised Section F to change the proposed commodity definition from “Wheat (aspirated grain fractions)” to “Aspirated grain fractions.” The Agency does not set tolerances for the aspirated grain fractions of individual crops.

OPPTS GLN 860.1480: Meat, Milk, Poultry, Eggs

- 53a. Ruminants: The submitted dairy cattle feeding data are adequate for the purpose of establishing tolerances for pyraclostrobin residues of concern in livestock commodities. Dairy cows were orally dosed twice daily for 28 consecutive days with pyraclostrobin at dose levels equivalent to 8.8 ppm, 27.2 ppm (mid dose), and 89.6 ppm (high dose), corresponding to ≈0.25x, ≈0.75x, and 2.5x the maximum theoretical dietary burdens (MTDB) of pyraclostrobin for beef (36.3 ppm) and dairy (35.4 ppm) cattle. The HED MARC discussed the metabolism of pyraclostrobin in livestock on September 20, 2001 and has concluded that the residues of concern in livestock commodities consist of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 (D278044, L. Cheng, October 9, 2001).

- 53b. The maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were <0.02-<0.0235 ppm (mid dose) and <0.02-0.175 ppm (high dose) in whole milk, <0.02 ppm (mid dose) and 0.0393-0.102 ppm (high dose) in skim milk, and <0.02-<0.0561 ppm (mid dose) and 0.131-0.258 ppm (high dose) in milk fat. These data suggest that the proposed tolerance of 0.03 ppm for milk is not adequate. RAB3 recommends that the registrant propose a tolerance of 0.1 ppm in milk.
- 53c. The maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were 0.464-0.607 ppm (mid dose) and 2.06-2.78 ppm (high dose) in liver. These data suggest that the proposed tolerance of 0.6 ppm is not adequate. RAB3 recommends the registrant propose a tolerance of 1.5 ppm in liver.
- 53d. The maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were <0.1 ppm (mid dose) and 0.396 ppm (high dose) in kidney, and <0.1 ppm (mid dose) and <0.1 ppm (high dose) in fat and muscle. These data suggest that the proposed tolerance levels of 0.1 ppm for muscle and fat are adequate. However, the proposed tolerance of 0.1 ppm for kidney is not adequate and not appropriate. RAB3 recommends that the registrant propose a tolerance of 0.2 ppm in meat byproducts (except liver) to cover residues in kidney.
- 53e. The petitioner needs to submit a revised Section F for livestock commodity tolerances. The tolerance expression should be revised to residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-8. In addition, tolerances for ruminant commodities in addition to cattle are required. Tolerances must be proposed for the fat, meat, and meat byproducts of goats, hogs, horses, and sheep; these tolerances should be set at the same levels as those for the cattle commodities.
- 53f. Overall, residues of pyraclostrobin increase in milk and tissues with the increase in the dose level. Residues in whole milk appear to plateau at Day 15 and do not significantly increase with subsequent doses. In tissues, residues were highest in liver. The depletion study (cows sacrificed 2 and 7 days following withdrawal from treatment) demonstrates that residues decline in milk and tissues once exposure is discontinued.
- 54a. Poultry: The submitted poultry feeding data are adequate for the purpose of determining the potential for secondary transfer of pyraclostrobin residues of concern to poultry eggs and tissues. Laying hens were orally dosed once daily for 30 consecutive days with pyraclostrobin at dose levels equivalent to 0.28 ppm, 0.88 ppm, and 3.01 ppm (8.6x the maximum theoretical dietary burden for poultry). The MTDB of pyraclostrobin for poultry is estimated to be 0.35 ppm. At the feeding level of 3.01 ppm, residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 are less than the method LOQ (0.05 ppm) in all egg and tissue samples, except for one egg sample (Day 17) where residues of pyraclostrobin were detected at 0.064 ppm and <0.05 ppm upon re-analysis. Residue analysis of BF 500-8 was not conducted (the metabolism data show all metabolites hydrolyzable to BF 500-8 would be less than 10% TRR), but instead an

isomeric compound (BF 500-9) was measured. Levels of BF 500-9 also were all <0.05 ppm. Samples from the low and mid dose groups, and depletion samples from the high dose group were not analyzed.

- 54b. The poultry metabolism studies were conducted at doses equivalent to 35-36x the MTDB. When extrapolated to the 1x burden, the TRRs in eggs, fat and liver would be at least 3 times below 0.05 ppm, which is the LOQ for BF 500-5 or BF 500-8. In combination with the poultry feeding data, RAB3 concludes that tolerances in poultry and eggs are not needed. A revised Section F in which the proposed tolerances for poultry commodities are deleted needs to be submitted.

OPPTS GLN 860.1850: Confined Accumulation in Rotational Crops

- 55a. Provided the petitioner submit additional information confirming that rotational crop samples were analyzed within the interval represented by the storage stability study, the submitted confined rotational crop study is adequate. In the RACs of radishes, lettuce, and wheat planted 30, 120, and 365 days following soil treatment with [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at total application rates for each label of 0.8 lb ai/A or 1.3 lb ai/A (~0.7x and 1x, respectively, the maximum proposed seasonal rate for annual crops), TRR (expressed as pyraclostrobin equivalents) accumulated at levels >0.01 ppm in samples of radish roots and tops, head lettuce, and wheat forage, straw and grain planted 30 days after treatment (DAT); 120-DAT radish tops, head lettuce, and wheat forage, straw, and grain; and 365-DAT radish roots and tops, head lettuce, and wheat forage straw, and grain.
- 55b. The petitioner successfully characterized/identified ~35-121% TRR in rotational crop commodities. Pyraclostrobin and its metabolite 500M07 (elsewhere named BF 500-3) were identified at 7.5-36.4% TRR (0.0017-0.0176 ppm) in 30-DAT rotational crop commodities except head lettuce and wheat grain, at 0.8-54.1% (0.0006-0.0013 ppm) TRR in 120-DAT wheat forage and straw, and at 1.4-3.3% TRR (0.0004-0.0023 ppm) in 365-DAT wheat forage and straw. Because TRR levels were low, additional extractable residues were characterized as polar, medium polar, or nonpolar fractions; of these fractions, the polar region is the most significant, accounting for up to 36.9% TRR, and the nonpolar region is the least significant. The petitioner also successfully demonstrated incorporation of ¹⁴C-residues into cellulose and lignin in all rotational crop commodities and incorporation into starch in wheat grain.
- 55c. The study indicates that metabolism of pyraclostrobin in rotated crops is similar but more extensive than that in primary crops, with pyraclostrobin undergoing demethoxylation to yield 500M07 (BF 500-3), followed by further degradation to medium polar and polar metabolites, and subsequent conjugation reactions and incorporation into natural products. The HED MARC at the September 20, 2001 meeting concluded that the residues of concern in rotational crops consist of pyraclostrobin and its desmethoxy metabolite (D278044, L. Cheng, October 9, 2001).

OPPTS GLN 860.1900: Field Accumulation in Rotational Crops

- 56a. The limited field rotational crop study is acceptable. Residues of pyraclostrobin and its metabolite BF 500-3 are each less than the method LOQ (<0.02 ppm) in/on rotational crop matrices (radish, roots and tops; cabbage, with and without wrapper leaves; and wheat forage, hay, and grain) planted 14 days following the last of six sequential foliar applications to the primary crop, cucumbers, of the 2 lb/gal EC formulation at 0.19-0.20 lb ai/A/application (~1x the maximum proposed seasonal rate for annual crops). Residues of pyraclostrobin in/on one sample of wheat straw from the CA test site are at the LOQ (0.02 ppm), but residues of pyraclostrobin in/on a replicate sample from the same plot are below the LOQ (0.012 ppm) for an average residue of <0.02 ppm. Residues of metabolite BF 500-3 are nondetectable (<0.02 ppm) in/on all samples of wheat straw.
- 56b. The submitted data indicate that a 14-day plantback interval (PBI) restriction for all crops that are not registered is required.

International Harmonization Issues

- 57. No Codex or Mexican maximum residue limits (MRLs) have been proposed or are established for residues of pyraclostrobin. Canadian MRLs have been proposed on a variety of raw agricultural commodities. An International Residue Limit Status sheet is attached.

RECOMMENDATIONS

RAB3 cannot recommend for the proposed tolerances for residues of pyraclostrobin and its desmethoxy metabolite in/on various plant and livestock commodities, expressed as the parent compound, for reasons given in Conclusions 2 (a,b), 11a, 12a, 15a, 21, 22a, 22c, 24, 25, 26a, 27, 28a, 31a, 32, 34a, 42d, 45b, 46b, 50b, 51b, 52c, 53b, 53c, 53d, 53e, 54b, 55a, and 56b above.

Provided the petitioner submit a revised Section B/label and revised Section F and EPA's method validation is satisfactory (Conclusions 2, 11a, 21, 24, 28a, 31a, 32, 34a, 45b, 46b, 51b, 52c, and 56b above), there will be no residue chemistry data requirements that would preclude the establishment of tolerances for the combined residues of pyraclostrobin and its desmethoxy metabolite, methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenylcarbamate, expressed as the parent compound, in/on the following commodities at the indicated levels:

Almond, hulls	1.6 ppm
Aspirated grain fractions	2.5 ppm
Banana	0.04 ppm
Barley, grain	0.4 ppm

Barley, hay	25 ppm
Barley, straw	6 ppm
Bean, dry	0.3 ppm
Beet, sugar, root	0.2 ppm
Beet, sugar, tops	8 ppm
Beet, sugar, dried pulp	1 ppm
Berry group	1.3 ppm
Citrus, dry pulp	5.5 ppm
Citrus, oil	4 ppm
Fruit, citrus, group	0.7 ppm
Fruit, stone, group	0.9 ppm
Grape	2 ppm
Grape, raisin	7 ppm
Grass, forage	10 ppm
Grass, hay	4.5 ppm
Grass, seed screenings	27 ppm
Grass, straw	14 ppm
Nut, tree, group	0.04 ppm
Peanut, nutmeat	0.05 ppm
Peanut, refined oil	0.1 ppm
Pistachio	0.7 ppm
Radish, tops	16 ppm
Rye, grain	0.04 ppm
Rye, straw	0.5 ppm
Strawberry	0.4 ppm
Vegetable, bulb, group	0.9 ppm
Vegetable, cucurbit, group	0.5 ppm
Vegetable, fruiting, group	1.4 ppm
Vegetable, root, except sugar beet, subgroup	0.4 ppm
Vegetable, tuberous and corm, subgroup	0.04 ppm
Wheat, grain	0.2 ppm
Wheat, hay	6 ppm
Wheat, straw	8.5 ppm

Provided the petitioner submit a revised Section F and EPA's method validation is satisfactory (Conclusions 12a, 53b, 53c, 53d, 53e, and 54b above), and pending review of the final report for the storage stability data in livestock commodities, there will be no residue chemistry data requirements that would preclude the establishment of tolerances for the combined residues of pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as the parent compound, in/on the following commodities at the indicated levels:

Cattle*, fat	0.1 ppm
Cattle*, liver	1.5 ppm

Cattle*, meat	0.1 ppm
Cattle*, meat byproducts, except liver	0.2 ppm
Milk	0.1 ppm

* also to include goats, hogs, horses, and sheep

RAB3 will initiate a human health risk assessment for the supported uses.

Pending submission of a proposed label, the residue data may support the proposed tolerance of 0.3 ppm in/on snap bean (bean, succulent).

In the interim, a plantback interval of 14 days is required for crops other than those supported in this petition. Pending submission of the storage intervals for the confined rotational crop samples, the PBI may be revised.

RAB3 cannot recommend in favor for the establishment of a subgroup tolerance on pea and bean, shelled, dried (except soybean), or pea, field, hay and vines until the petitioner submits data relating to crop field trials (Conclusions 24 and 26a).

DETAILED CONSIDERATIONS

OPPTS 830 Series GLNs: Product Properties

The Registration Division (RD) conducted reviews of the technical grade active ingredient and end-use products Cabrio, Headline and Insignia Fungicide (D269848 & 274191, May 3, May 15, and June 7, 2001, S. Malak). Fulfillment of the product chemistry data requirements is under the purview of the RD.

OPPTS GLN 860.1200: Proposed Uses

The petitioner provided specimen labels for two pyraclostrobin formulations, a 20% water dispersible granular (WDG) formulation (Product Name = Cabrio™ EG, formerly named Headline™ WG Fungicide; EPA File Symbol No. 7969-RIT) and a 2 lb/gal emulsifiable concentrate (EC) formulation (Product Name = Headline™ EC, formerly named Attitude™ Fungicide; EPA File Symbol No. 7969-RIA). The 20% WDG formulation is proposed for use on berries, bulb vegetables, cucurbit vegetables, fruiting vegetables, grapes, pistachio, root vegetables, tree nuts, stone fruits, and strawberries. The 2 lb/gal EC formulation is proposed for use on barley, citrus fruits, dried peas and beans, grass grown for seed, peanuts, rye, tuberous and corm vegetables, sugar beets, and wheat. We note that the specimen label for the 2 lb/gal EC label actually states that the active ingredient content is equivalent to 2.09 lb/gal.

For both products, applications may be made using ground, aerial, and chemigation (sprinkler irrigation) equipment. Ground applications should be made using sufficient volumes for

adequate coverage of foliage, bloom, and fruit; and aerial applications must be made in a minimum of 5 gal/A. An additive such as crop oil concentrate or methylated seed oil may be added to the spray volumes to improve coverage. Tank mixing with most recommended fungicides and insecticides is permitted. No rotational crop restrictions are specified.

The specimen labels contain two sets of resistance management options. Resistance management Option A consists of a **general** restriction for all crops: “Do not make more than two (2) applications of [the product] before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application.” Resistance management Option B consists of **crop specific** restrictions. The proposed use patterns for each formulation and the restrictions and limitations for resistance management are presented in Table 1.

Table 1. Pyraclostrobin maximum use patterns

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations *
Almond						
20% WDG	0.12	4	0.48	7-14	Apply no later than 5 weeks after petal fall	Resistance management Option A. Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application." Apply the first application at pink bud and continue up to 5 weeks after petal fall.
Barley						
2 lb/gal EC	0.2	2	0.34	10-14	Apply no later than the end of flowering	Resistance management Option A. Resistance management Option B: "Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." For powdery mildew, net blotch, rust, scald, Septoria, spot blotch and tan spot, application may begin immediately after flag leaf emergence and a second application may be made 10-14 days later. For Fusarium head scab/blight, a single application may be made at 0.15-0.20 lb ai/A during flowering.

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Berries [including blackberry (all varieties), blueberry, currant, elderberry, gooseberry, huckleberry, loganberry, and raspberry (black and red)]						
20% WDG	0.18	4	0.7	7-14	0	Resistance management Option A.
	0.18	2	0.35	7-14	0	Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."
Bulb vegetables [including onions (all varieties), garlic, leek, and shallot], See "Onion"						
Carrot						
20% WDG	0.2	3	0.6	7-14	0	Resistance management Option A.
	0.2	3	0.3	7-14	0	Resistance management Option B: "Do not make more than three applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Citrus fruits [including Calamondin, citrus citron, citrus hybrids (chironja, tangelo, tangor), grapefruit, kumquat, lemon, lime, mandarin (tangerine), orange (sweet and sour), pummelo and satsuma mandarin]						
2 lb/gal EC	0.24	4	0.8	Not specified (NS)	14	Resistance management Option A.
	0.24	3 (fresh) 2 (processing)	0.73 (fresh) 0.49 (processing)	NS	14	Resistance management Option B: (i) "On fresh market citrus, do not make more than three applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season."; (ii) "On citrus for processing, do not make more than two applications per season."; and (iii) "Do not make more than two sequential applications of the 2 lb/gal EC formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action."
Cucurbit vegetables [including Chayote, Chinese waxgourd, citron melon, cucumber, gherkin, edible gourd (hyotan, cucuzza, chinese okra), <i>Momorida</i> spp. (balsam apple, balsam pear, bitter melon, and Chinese cucumber), muskmelon (cantaloupes, casaba, creshaw melon, golden pershaw melon, honeydew melon, honey balls, mango melon, Persian melon, pineapple melon, Santa Claus melon, and snake melon), pumpkin, summer squash (crookneck squash, scallop squash, straightneck squash, vegetable marrow, and zucchini), winter squash (butternut squash, calabaza, hubbard squash, acorn squash, and spaghetti squash), and watermelon]						
20% WDG	0.2	6	1.2	7-14	0	Resistance management Option A.
	0.2	4	0.8	7-14	0	Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than one application of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
<p>Dried shelled pea and bean (except soybean) [including dried cultivars of bean (<i>Lupinus</i> spp., includes grain lupin, sweet lupin, white lupin, and white sweet lupin); (<i>Phaseolus</i> spp., includes field bean, kidney bean, lima bean (dry), navy bean, pinto bean, tepary bean); bean (<i>Vigna</i> spp., includes adzuki bean, blackeyed pea, catjang, cowpea, Crowder pea, moth bean, mung bean, rice bean, southern pea, urd bean); broad bean, chickpea, guar, lablab bean, lentil, pea (<i>Pisum</i> spp.; includes field pea) and pigeon pea], See “Dry pea”</p>						
Dry pea						
2 lb/gal EC	0.13	2	0.26	NS	30	<p>Resistance management Option A. Resistance management Option B: “Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season.”</p> <p>Application may be made at the beginning of flowering or at the onset of disease. A second application may be made if conditions are favorable for disease development or if heavy disease has already set in.</p>
<p>Fruiting vegetables [including eggplant, ground cherry, pepino, pepper (all varieties), tomatillo, and tomato], See “Pepper” and “Tomato”</p>						

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Grape (<i>Vitis vinifera</i> only)						
20% WDG	0.15	6	0.9	10-21	14	Resistance management Option A.
	0.15	4	0.6	10-21	14	Resistance management Option B: "On wine and table grapes, do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop. On grapes for all other uses, do not make more than three applications per season." and "Do not make more than three sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action."
Grass seed						
2 lb/gal EC	0.20	2	0.39	14-21	14	Resistance management Option A. Resistance management Option B: "Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season."
Lentils						
2 lb/gal EC	0.13	2	0.18	7-10	30	Resistance management Option A. Resistance management Option B: "Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Onion						
20% WDG	0.15	6	0.9	14	7	Resistance management Option A.
	0.15	4	0.6	14	7	Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."
Peanut						
2 lb/gal EC	0.24	5	1.22	14-21	14	Resistance management Option A.
	0.24	4	0.98	14-21	14	Resistance management Option B: "Do not make more than four applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." and "Do not make more than three sequential applications of the 2 lb/gal EC formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Pecan						
20% WDG	0.12	4	0.48	7-21 for pecan 7-28 for all other tree nuts except almonds	14 for tree nuts except almonds	Resistance management Option A.
	0.12	3	0.36	7-21 for pecan 7-28 for all other tree nuts except almonds	14 for tree nuts except almonds	Resistance management Option B: "Do not make more than three applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than three sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Pepper						
20% WDG	0.2	6	1.2	5-14	0	Resistance management Option A.
	0.2	5	1.0	5-14	0	Resistance management Option B: (i) "Do not make more than five applications of the 20% WDG formulation or other strobilurin fungicides per crop."; (ii) "For control of late blight, do not make more than one application of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."; and (iii) "For control of diseases other than late blight, do not make more than three sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."
Pistachio						
20% WDG	0.2	4	0.8	7-28	14	Resistance management Option A. Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than three sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Potato						
2 lb/gal EC	0.2	6	1.2	5-14	3	Resistance management Option A. Resistance management Option B: "Do not make more than six applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." and "Do not make more than one application of the 2 lb/gal EC formulation before alternating to a labeled nonstrobilurin fungicide with a different mode of action for at least one application."
Radish						
20% WDG	0.2	3	0.6	7-14	0	Resistance management Option A.
	0.2	3	0.3	7-14	0	Resistance management Option B: "Do not make more than three applications of the 20% WDG formulation or other strobilurin fungicides per season." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."
Root vegetables [including carrot, radish, garden beet, edible burdock, celeriac, chervil (turnip-rooted), chicory, ginseng, horseradish, parsley (turnip-rooted), parsnip, oriental radish, rutabaga, black salsify, Spanish salsify, skirret, and turnip], see "Carrot" and "Radish"						

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Rye						
2 lb/gal EC	0.2	2	0.34	10-14	Apply no later than the end of flowering	Resistance management Option A. Resistance management Option B: "Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." For powdery mildew, net blotch, rust, scald, Septoria, spot blotch and tan spot, application may begin immediately after flag leaf emergence and a second application may be made 10-14 days later. For Fusarium head scab/blight, a single application may be made at 0.15-0.20 lb ai/A during flowering.
Stone fruits [including apricot, cherry (sweet and tart), nectarine, peach, plum (all varieties), plumcot, and prune]						
20% WDG	0.12	5	0.59	7-14	0	Resistance management Option A.
	0.12	4	0.48	7-14	0	Resistance management Option B: "Do not make more than four applications of the 20% WDG formulation or other strobilurin fungicides per crop." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Strawberry						
20% WDG	0.18	5	0.88	7-14	0	Resistance management Option A. Resistance management Option B: "Do not make more than five applications of the 20% WDG formulation or other strobilurin fungicides per season." and "Do not make more than two sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least two applications."
Sugar beet						
2 lb/gal EC	0.2	4	0.78	14	7	Resistance management Option A. Resistance management Option B: "Do not make more than four applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." and "Do not make more than one application of the 2 lb/gal EC formulation before alternating to a labeled nonstrobilurin fungicide with a different mode of action for at least one application."

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Tomato						
20% WDG	0.2	6	1.2	5-14	0	Resistance management Option A.
	0.2	5	1.0	5-14	0	Resistance management Option B: (i) "Do not make more than five applications of the 20% WDG formulation or other strobilurin fungicides per crop."; (ii) "For control of late blight, do not make more than one application of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."; and (iii) "For control of diseases other than late blight, do not make more than three sequential applications of the 20% WDG formulation before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."
Tree nuts [(excluding almond) beech nut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert, hickory nut, macadamia nut, pecan, and walnut (black and English)], See "pecan"						
Tuberous and corm vegetables [including arracacha, arrowroot, Chinese artichoke, Jerusalem artichoke, edible canna, cassava (bitter and sweet), chayote (root), chufa, dasheen, ginger, leren, potato, sweet potato, tanier, turmeric, yam bean, and true yam], see "Potato"						

Table 1 (continued).

Formulation	Rate (lb ai/A)	Number of Apps/Season	Maximum Rate/Season (lb ai/A)	Retreatment Interval (days)	PHI (days)	Use Directions and Limitations ^a
Wheat						
2 lb/gal EC	0.2	2	0.34	10-14	Apply no later than the end of flowering	Resistance management Option A. Resistance management Option B: "Do not make more than two applications of the 2 lb/gal EC formulation or other strobilurin fungicides per season." For powdery mildew, net blotch, rust, scald, Septoria, spot blotch and tan spot, application may begin immediately after flag leaf emergence and a second application may be made 10-14 days later. For Fusarium head scab/blight, a single application may be made at 0.15-0.20 lb ai/A during flowering.

^a Resistance management, Option A is specified for all crops: "Do not make more than two sequential applications of [the product] before alternating to a labeled non-strobilurin fungicide with a different mode of action for at least one application."

Comments: The proposed use directions are adequate to allow RAB3 to make an assessment of whether residue data reflect the maximum residues likely to occur in food and livestock feeds for all crops for which use of pyraclostrobin is proposed except snap beans and imported bananas. Additional information is required to delineate the proposed use of pyraclostrobin on snap beans and imported bananas. The petitioner should submit a copy of the product label(s), with English translation, for each pyraclostrobin product intended for use on bananas targeted for import to the U.S.

Because no data reflecting aerial applications to orchard crops were submitted, the label must be modified to specify that aerial applications to orchard crops be made in a minimum of 10 gal/A.

Based on the submitted data for barley and wheat hay, the petitioner must modify the proposed label to add a 14-day PHI for barley and wheat hay.

In addition, based on the submitted data for grass forage and hay, a pregrazing and prehayage interval of 27 days must be added to the label for the 2 lb/gal EC formulation.

OPPTS GLN 860.1300: Nature of the Residue in Plants

The test substances for the plant metabolism studies were uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin (specific activity 4.34 MBq/mg (260,400 dpm/ μ g); radiochemical purity >99%) and [tolyl-¹⁴C]pyraclostrobin (specific activity 4.5 MBq/mg (270,000 dpm/ μ g); radiochemical purity >99%). The petitioner noted in the potato metabolism study that both radiolabeled test substances contained the desmethoxy metabolite 500M07 (or BF 500-3) as an impurity (at 5%). The presence of this impurity was not expected to influence the study results.

For all plant metabolism studies, the in-life and analytical phases of the study were conducted by BASF (BASF Agricultural Center, Limburgerhoff, Germany)

Grape

BASF submitted a grape metabolism study (citation listed below) in support of the current petition.

45118430 Hamm, R.T. (1998) Metabolism of BAS-500 F in Grapes. Laboratory Project Identification No. 35507, 1998/10988. Unpublished study submitted by BASF Corporation. 91 p.

The radioactive test substances, [chlorophenyl-¹⁴C]pyraclostrobin and [tolyl-¹⁴C]pyraclostrobin, were combined with EC formulation blank and diluted to volume with water. The formulated test substances (final specific activity unspecified) were each applied by hand sprayer to four established grape vines (~5 years old) as six foliar applications, with 16- to 19-day retreatment intervals, at 0.11-0.43 lb ai/A/application (126-480 g ai/ha/application). The total application

rate for each label was ~1.34 lb ai/A (~1500 g ai/ha; ~1.5x the maximum proposed seasonal application rate for grapes). The first application was made at growth stage 53-55 (inflorescences visible to fully developed), and the last application was made at growth stage 81 (beginning of ripening). The petitioner did not mention establishment of experimental controls for the study.

Samples of grapes and leaves were harvested 40 days after the final application (proposed PHI for grapes is 14 days), and were stored at ≤ -18 C prior to and throughout the analytical phase of the study.

Total radioactive residues (TRR)

Homogenized samples of grapes and leaves were subjected to combustion/LSC (liquid scintillation counting) for TRR determinations within 79 days of sampling. Because of the high water content of the samples, the TRR in all samples were calculated by summing the radioactivity in plant sample extracts and non-extractable fractions. The reported LOQ for LSC determinations was 0.001 ppm. The TRR (expressed as parent equivalents) are presented in Table 2. The petitioner noted that the relatively low levels of radioactivity in grapes might be attributed to their having been protected from spray residues by the leaf canopy.

Table 2. TRR in grapes and grape leaves harvested following six foliar applications of [14 C]pyraclostrobin at 1.3 lb ai/A (~1.5x).

Matrix	TRR, ppm [14 C]pyraclostrobin equivalents	
	Chlorophenyl Label	Tolyl Label
Grapes	0.951	1.559
Leaves	40.029	39.244

Extraction of residues

Samples of homogenized grapes and grape leaves were subjected to extraction procedures for residue characterization and identification. During the fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for radioactivity by LSC or combustion/LSC. The general extraction procedures are summarized below. Quantitative results were not reported for the extraction of grape leaves, which were intended for use in characterizing residues in grapes.

Homogenized samples of grapes and leaves from both labels were extracted with methanol (3x) and centrifuged. The supernatants were filtered, combined, and subsamples were reserved for HPLC and LC/MS analysis. Following concentration to remove methanol, subsamples of the extracts were subjected to partitioning with cyclohexane (3x). The resulting organic phases were subjected to peak fractionation and clean-up using preparative HPLC, and were reserved for

LC/MS analysis. The aqueous phases were partitioned with ethyl acetate (3x). For grape leaves, the resulting aqueous and organic phases were subjected to further peak fractionation and clean-up. The organic and aqueous phases for grapes and leaves were reserved for HPLC and LC/MS analysis.

Nonextractable residues of grapes were extracted with water (chlorophenyl label) or ammonium hydroxide (tolyl label; details unspecified). The resulting aqueous phases were not further analyzed. Remaining nonextractable residues were subjected to base hydrolysis (10% NaOH for 3 hours at reflux).

The distribution of ¹⁴C-activity in the extracts of grapes are presented in Tables 3a (chlorophenyl label) and 3b (tolyl label).

Characterization/identification of residues

The methanol extracts of grapes and leaves were analyzed by HPLC for isolation and identification of metabolites. Purified metabolites were identified by ion-spray LC/MS and/or LC/MS/MS. HPLC was conducted using a Spherisorb ODS II or Inertsil phenyl column and gradient mobile phases of water:formic acid (1000:5, v:v) and acetonitrile (ACN):formic acid (1000:5, v:v). The detector for nonradiolabeled standards was not identified (probably UV, see discussions under potato and wheat studies). Metabolites were identified by cochromatography with radiolabeled reference standards for pyraclostrobin and BF 500-3 (elsewhere named 500M07), and with the following metabolites isolated from grape leaf extracts by MS: M54 (elsewhere named 500M54), M55, and M56. Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

Minor metabolites M54 (the tolylmethoxy derivative of BF 500-3), M55 (the scillabiose or glucosidorhamnose conjugate of the Cl-phenyl pyrazol moiety), and M56 (the OH-pyrazolglycoside of M54) were isolated from the methanol extract of grape leaves and identified by LC/MS and LC/MS/MS. These metabolites were determined in grapes by HPLC cochromatography of the methanol extracts and cyclohexane and ethyl acetate phases with the metabolites isolated from grape leaves. The petitioner stated that further characterization of minor metabolites detected in the methanol extract (unknown peaks P1, P2, and P5) was not possible due to low radioactivity concentrations.

The petitioner stated that partitioning with cyclohexane and ethyl acetate was conducted to aid in characterization of pyraclostrobin metabolites as organosoluble or aqueous-soluble compounds. Quantitative results for HPLC analysis of the organic phases following partitioning were not reported; however, the petitioner stated that components in the organic and aqueous phases following partitioning were minor metabolites present at <0.05 ppm. Chromatograms provided for the tolyl label indicate that M54 was identified in the cyclohexane phase, and M56 was identified in the ethyl acetate phase by cochromatography.

The nonextractable residues were treated with water or ammonia and then subjected to 10% NaOH at reflux. The supernatant following NaOH reflux was adjusted to pH 1 with concentrated HCl, resulting in precipitation of "raw lignin", which accounted for 4.1% TRR (0.039 ppm) in the chlorophenyl-label grapes, and 4.6% TRR (0.071 ppm) in the tolyl-label grapes. The petitioner postulated that radioactivity remaining in the supernatants following precipitation was comprised of low molecular weight lignins. The nonextractable residue remaining following NaOH reflux was characterized as "raw cellulose". The petitioner noted that the lignin and cellulose residues probably resulted from grape stems homogenized with grape bunches since grapes themselves are comprised of primarily water (80%) and sugar (15%), with only 2% fiber composition.

A summary of the characterized and identified ¹⁴C-residues in chlorophenyl- and tolyl-label grapes is presented in Table 4.

Table 3a. Distribution and characterization of radioactive residues in/on grapes harvested 40 days following six applications of [chlorophenyl-¹⁴C]pyraclostrobin at 1.34 lb ai/A (~1.5x).

Fraction	% TRR	ppm	Characterization/Identification ^a
Grapes (TRR = 0.951 ppm)			
Methanol	87.8	0.835	<u>HPLC analysis resolved:</u> Pyraclostrobin 61.79% TRR 0.588 ppm BF 500-3 16.68% TRR 0.159 ppm M54 1.55% TRR 0.015 ppm M55 4.01% TRR 0.038 ppm M56 1.69%TRR 0.016 ppm Unknown P1 2.09% TRR 0.020 ppm Partitioned with cyclohexane.
Cyclohexane	69.7	0.663	Results of HPLC analysis were not provided.
Aqueous	N/R ^b	N/R	Partitioned with ethyl acetate
Ethyl acetate	8.1	0.077	Results of HPLC analysis were not provided.
Aqueous	7.8	0.075	N/A ^c .
Nonextractable	12.2	0.116	Extracted with water
Aqueous	0.6	0.006	N/A.
Nonextractable	N/R	N/R	Subjected to hydrolysis with 10% sodium hydroxide at reflux.
Base hydrolysate	N/R	N/R	Adjusted to pH 1 with concentrated HCl.
Precipitate	4.1	0.039	Characterized as "raw lignin".
Supernatant	2.8	0.027	N/A.
Nonextractable	1.8	0.017	Characterized as "raw cellulose".

^a Metabolites BF 500-3 and M54 are named 500M07 and 500M54, respectively, in the potato, wheat, and livestock metabolism studies.

^b N/R = Not reported.

^c N/A = Not analyzed.

Table 3b. Distribution and characterization of radioactive residues in/on grapes harvested 40 days following six applications of [tolyl-¹⁴C]pyraclostrobin at 1.34 lb ai/A (~1.5x).

Fraction	% TRR	ppm	Characterization/Identification ^a
Grapes (TRR = 1.559 ppm)			
Methanol	84.3	1.314	<u>HPLC analysis resolved:</u> Pyraclostrobin 55.71% TRR 0.860 ppm BF 500-3 11.02% TRR 0.170 ppm M54 2.90% TRR 0.045 ppm M56 3.11% TRR 0.048 ppm Unknown P1 4.66% TRR 0.072 ppm Unknown P2 3.21% TRR 0.050 ppm Unknown P5 2.18% TRR 0.034 ppm Partitioned with cyclohexane.
Cyclohexane	65.5	1.011	HPLC analysis resolved M54; quantitative results were not provided.
Aqueous	N/R ^b	N/R	Partitioned with ethyl acetate.
Ethyl acetate	7.7	0.119	HPLC analysis resolved M56; quantitative results were not provided.
Aqueous	6.2	0.096	HPLC analysis resolved several minor metabolites which were not further characterized.
Nonextractable	15.7	0.245	Extracted with NH ₄ OH.
Aqueous	1.5	0.023	N/A ^c .
Nonextractable	16.7	0.261	Subjected to hydrolysis with 10% sodium hydroxide at reflux.
Base hydrolysate	N/R	N/R	Adjusted to pH 1 with concentrated HCl.
Precipitate	4.6	0.071	Characterized as "raw lignin".
Supernatant	7.1	0.111	N/A.
Nonextractable	2.8	0.044	Characterized as "raw cellulose".

^a Metabolites BF 500-3 and M54 are named 500M07 and 500M54, respectively, in the potato, wheat, and livestock metabolism studies.

^b N/R = Not reported.

^c N/A = Not analyzed.

Table 4. Identification/characterization of radioactive residues in/on grapes harvested 40 days following six applications of [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 1.34 lb ai/A (~1.5x).

Metabolite/Fraction	Grapes (chlorophenyl label) TRR = 0.951 ppm		Grapes (tolyl label) TRR = 1.559 ppm	
	% TRR	ppm	% TRR	ppm
Identified ^a				
Pyraclostrobin	61.79	0.588	55.71	0.860
BF 500-3 (500M07)	16.68	0.159	11.02	0.170
M54 (500M54)	1.55	0.015	2.90	0.045
M55	4.01	0.038	--	--
M56	1.69	0.016	3.11	0.048
Total Identified	85.72	0.816	72.74	1.123
Characterized				
Lignin	4.1	0.039	4.6	0.071
Aqueous	0.6	0.006	1.5	0.023
Acidified supernatant	2.8	0.027	7.1	0.111
Cellulose	1.8	0.017	2.8	0.044
Total Characterized/Identified	95.02	0.905	88.74	1.372

^a Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

Storage stability

Grape samples were stored at ≤-18 C prior to and throughout the analytical phase of the study. Initial HPLC analyses were conducted 37 (chlorophenyl label) and 86 (tolyl label) days after sampling, and subsequent/second HPLC analyses were conducted 188 days (chlorophenyl label) and 97 days (tolyl label) after the initial analyses. Residue characterization was completed ~11 months following initial analysis. The petitioner compared the initial and second HPLC analyses and found little change in residue profiles for periods of 3 months (tolyl label) and 6 months (chlorophenyl label) under frozen conditions. While these periods do not cover the time between sampling and residue characterization, stability data from the wheat metabolism study (forage and straw: 20 months) and the grape juice storage stability study (18 months) support the stability of pyraclostrobin and its desmethoxy metabolite for the duration of residue identification. RAB3 concludes that no additional storage stability data are required.

Proposed metabolic pathway

Based on the results of the grape metabolism study, the petitioner proposed that pyraclostrobin is metabolized in grapes at two sites of the molecule and with cleavage of the chlorophenyl-pyrazol moiety from the tolyl moiety. Desmethoxylation in the tolyl moiety side chain produces BF 500-3 (500M07) and methoxylation of the aromatic ring produces M54 (500M54).

Hydroxylation of M54 in the chlorophenyl pyrazol moiety, followed by glucosidation results in formation of M56, and cleavage of the moiety from the tolyl moiety results in formation of M55.

Study summary

Following treatment of established grape vines with six foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.11-0.43 lb ai/A/application (126-480 g ai/ha/application) for a total application rate for each label of ~1.34 lb ai/A (~1500 g ai/ha; ~1.5x the maximum proposed seasonal application rate for grapes), grapes were harvested 40 days after the final application. Total radioactive residues (TRR) in grapes were 0.951 ppm (chlorophenyl label) and 1.559 ppm (tolyl label); TRR in grape leaves were 39-40 ppm.

Approximately 95% (chlorophenyl label) and 89% (tolyl label) TRR were characterized/identified in grapes. Pyraclostrobin was the major residue identified at 61.79% TRR (0.588 ppm) in chlorophenyl-label samples and 55.71% TRR (0.860 ppm) in tolyl-label samples. The desmethoxy-metabolite BF 500-3 (also referred to as 500M07) accounted for 16.68% TRR (0.159 ppm) and 11.02% TRR (0.170 ppm) in chlorophenyl- and tolyl-label grapes, respectively. The following minor metabolites were also identified at <5% TRR: M54 (also referred to as 500M54, both labels), M55 (chlorophenyl label only), and M56 (both labels).

Nonextractable residues comprised 12-16% TRR (0.116-0.245 ppm) following initial extraction. Data indicate that lignin accounted for 4.1-4.6 % TRR and cellulose accounted for 1.8-2.8% TRR from both labels. The petitioner attributed the lignin and cellulose residues to grape stem that was homogenized with the grape bunches.

The submitted grape metabolism study is acceptable.

Potato

BASF submitted a potato metabolism study (citation listed below) in support of the current petition. We note that extraction efficiency data included in the subject MRID are presented in the Residue Analytical Method section under Radiovalidation.

45118431 Bross, M. and Mackenroth, C. (1999) The Metabolism of ¹⁴C-BAS 500 F in Potato. Laboratory Project Identification No. 35751; 1999/11419. Unpublished study submitted by BASF Corporation. 175 p.

The radioactive test substances, [chlorophenyl-¹⁴C]pyraclostrobin and [tolyl-¹⁴C]pyraclostrobin, were combined with EC formulation blank and diluted to volume with water. The formulated test substances (final specific activity unspecified) were each applied by hand sprayer to young potato plants in pots as six foliar applications, with 6- to 10-day retreatment intervals, at 0.27 lb ai/A/application (300 g ai/ha/application), except for the fourth application, which was made at

0.36 lb ai/A (400 g ai/ha). Each test substance was applied to 12 pots containing one potato plant each; plants were at BBCH 31 (main stem elongation) at the first application. The total application rate for each label was 0.8 lb ai/A (~0.7x the maximum proposed rate for any root crop) after 3 applications and 1.7 lb ai/A (1900 g ai/ha, 1.4x the maximum proposed rate) after 6 applications. The petitioner did not mention establishment of experimental controls for the study.

Samples of potato foliage, tubers, and roots were collected 7 days after the third application (at growth stage 70; immature) and 7 days after the sixth treatment (at growth stage 85-89; mature), and were stored at ≤ -18 C prior to and throughout the analytical phase of the study. We note that the proposed PHI is 3 days for potatoes.

Total radioactive residues (TRR)

Samples of frozen potato foliage, tubers, and roots were homogenized by sample homogenizers or mills and subjected to combustion/LSC for TRR determinations. The reported LOD for LSC determinations was 0.0003 ppm. Because the results of replicate combustion analyses varied considerably, apparently due to the inhomogeneity of samples, the petitioner also determined TRR by summing extractable and nonextractable residues following initial methanol extraction. The TRR in/on potato matrices are presented in Table 5. Summed TRR values were used for calculation of percent TRR for the remainder of the study.

Table 5. Total radioactive residues (TRR) in potatoes following three or six foliar applications of [¹⁴C]pyraclostrobin.

Matrix	TRR, ppm [¹⁴ C]pyraclostrobin equivalents			
	Chlorophenyl Label		Tolyl Label	
	Combustion/LSC	Summed ^a	Combustion/LSC	Summed ^a
Immature - sampled after 3 applications (0.8 lb ai/A; ~0.7x)				
Foliage	24.047	19.636	12.686	9.860
Tubers	0.010	0.009	0.014	0.014
Roots	0.450	NA ^b	0.208	NA
Mature - sampled after 6 applications (1.7 lb ai/A; ~1.4x)				
Foliage	68.671	69.846	58.293	47.785
Tubers	0.039	0.040	0.049	0.048
Roots	0.986	NA	0.678	NA

^a Summed = Sum of extractable and nonextractable radioactivity.

^b Not analyzed.

The petitioner stated that the TRR determination for potato roots was conducted for purposes of determining any translocation pattern in potatoes. No further extraction or analysis was conducted on potato roots.

Extraction and hydrolysis of residues

Samples of homogenized immature and mature potato foliage and tubers from each label were subjected to extraction procedures for residue characterization and identification. After each extraction step, samples were centrifuged. The resulting supernatants were filtered and analyzed by LSC, then combined prior to the next extraction step. The petitioner indicated that beakers and flasks were cooled with methanol/dry ice or water/ice mixtures during extraction to reduce degradation during extraction. During the fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for radioactivity by LSC or combustion/LSC. The general extraction procedures are summarized below.

Homogenized samples of potato foliage and tubers were extracted with methanol (3x), and the resulting extracts were combined and reduced by evaporation. The dried residue was resuspended in water:methanol (70:10, v:v) and centrifuged. The resulting supernatant was reserved for HPLC analysis, and the pellet was dissolved in methanol and/or water and reserved for HPLC analysis. Following evaporation to remove methanol, subsamples of selected combined methanol extracts were also subjected to sequential partitioning with iso-hexane (3x), DCM (3x), and ethyl acetate (3x). Respective organic and aqueous phases were combined and reserved for HPLC analysis.

Nonextractable residues generated from methanol extraction of a second subsample of tolyl-label mature tubers (summed TRR = 0.50 ppm) were subjected to extraction with ammonia (concentration unspecified) to release bound residues. The resulting ammonia extract was reserved for HPLC analysis.

The distribution of ¹⁴C-activity in the extracts of potatoes is presented in Tables 6a (chlorophenyl label) and 6b (tolyl label).

Characterization/identification of residues

Methanol extracts and the organic and aqueous phases of potato foliage and tubers were analyzed by reversed-phase HPLC. HPLC was conducted using an Inertsil phenyl or Spherisorb ODS-2 column with gradient mobile phases of water:formic acid (1000:5, v:v) and ACN:formic acid (1000:5, v:v). An HPLC system using a Hypersil Green ENV column with gradient mobile phase of water:ACN:formic acid (900:100:1, v:v:v) and water:ACN:formic acid (100:900:1, v:v:v) was used for confirmation of parent and 500M07 (BF 500-3) quantitations. All systems were equipped with UV (230 nm) and radioactivity detectors and fraction collectors. Metabolites were identified by retention time comparisons with the following reference standards or metabolites isolated from foliage: pyraclostrobin, BF 500-3 (also referred to as 500M07), BF 500-5 (also referred to as 500M04), methyl-N-[[[1-(4-chlorophenyl)-pyrazol-3-yl]oxy]-o-tolyl]-

N-hydroxy carbamate, N-(2-[[1-(4-chlorophenyl)-pyrazol-3-yl]oxy]-o-tolyl)-hydroxyl-amine, 1-(4-chlorophenyl)-2-methyl-1,2-dihydro-pyrazol-3-one, 1-(4-chlorophenyl)-3-(2-nitrobenzyloxy)-1H-pyrazole, and ¹⁴C-L-tryptophan (500M72). In HPLC analyses of chlorophenyl-label samples, metabolites 500M68 and 500M04 shared a common peak. Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

The methanol extract, DCM, and EA phases of chlorophenyl-label mature foliage were used for the isolation of metabolites for identification by LC/MS. Metabolites were fractionated by preparative HPLC on an Inertsil phenyl column. Following isolation, relevant fractions were subjected to ion-spray LC/MS analysis. Metabolites 500M68, 500M04, and 500M54 were identified in the DCM phase by LC/MS, and pyraclostrobin, 500M07, and 500M79 were identified in the ethyl acetate phase. The petitioner stated that HPLC quantitation (using the ENV column) confirmed that 500M07 was formed by metabolism of pyraclostrobin in potatoes, and was not present merely as an impurity of the radiolabeled test substances. Metabolite 500M72 (L-tryptophan) was identified by retention time comparison and MS analysis in the wheat metabolism study (see below), and identification in potato tubers was confirmed by HPLC retention time comparison with the isolated metabolite. The petitioner attributed the reduced extractability of tolyl-label tuber residues to the presence of L-tryptophan, which is not readily extractable by methanol.

Following partitioning with organic solvents, it was observed that most of the metabolites in foliage were detected in the organic phases. For tubers, the majority of radioactivity from chlorophenyl-label samples partitioned into the organic phases, and the majority of radioactivity from tolyl-label samples partitioned into the aqueous phases. This pattern was again attributed to the presence of tryptophan, which is water soluble, in tolyl-label tubers.

The petitioner made only one attempt to characterize bound residues in potato tubers. L-Tryptophan was identified by HPLC analysis of the ammonia extract of tolyl-label mature tubers; however, even after ammonia extraction, a significant portion of the nonextractable residues remained unextractable (38.5% TRR, 0.019 ppm).

A summary of the characterized and identified ¹⁴C-residues in potato foliage and tubers is presented in Tables 7a (chlorophenyl label) and 7b (tolyl label).

Table 6a. Distribution and characterization of radioactive residues in/on potato foliage and tubers following three (totaling 0.8 lb ai/A; ~0.7x) or six (totaling 1.7 lb ai/A; ~1.4x) applications of [chlorophenyl-¹⁴C]pyraclostrobin.

Fraction	% TRR	ppm	Characterization/Identification
Immature potato foliage (sampled after 3 applications; TRR = 19.636 ppm)			
Methanol	94.4	18.531	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 56.5% TRR 11.098 ppm 500M07 (BF 500-3) 16.1% TRR 3.157 ppm 500M68, 500M04 2.9% TRR 0.570 ppm 500M54 1.38% TRR 0.271 ppm 500M79 0.37% TRR 0.072 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 16.7% TRR (3.282 ppm).</p> <p>Sequentially partitioned with hexane, DCM, and ethyl acetate.</p>
Hexane	76.8	15.075	Not further analyzed (N/A).
DCM	7.8	1.528	N/A.
Ethyl acetate	2.5	0.499	N/A.
Aqueous	0.7	0.143	N/A.
Nonextractable	5.6	1.105	N/A.
Immature potato tubers (sampled after 3 applications; TRR = 0.009 ppm)			
Methanol	38.0	0.004	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 20.1% TRR 0.002 ppm 500M07 (BF 500-3) 5.4% TRR 0.001 ppm 500M68, 500M04 1.2% TRR <0.001 ppm 500M54 4.3% TRR <0.001 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 7.1% TRR (0.001 ppm).</p>
Pellet	11.7	0.001	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 0.9% TRR <0.001 ppm 500M07 (BF 500-3) 0.4% TRR <0.001 ppm 500M68, 500M04 0.3% TRR <0.001 ppm 500M54 2.0% TRR <0.001 ppm 500M79 0.4% TRR <0.001 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 7.8% TRR (0.001 ppm).</p>
Nonextractable	51.3	0.005	N/A.

Table 6a (chlorophenyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
Mature potato foliage (sampled after 6 applications; TRR = 69.846 ppm)			
Methanol	80.7	56.352	<p><u>HPLC analysis resolved:</u></p> <p>Pyraclostrobin 50.9% TRR 35.564 ppm</p> <p>500M07 (BF 500-3) 19.0% TRR 13.299 ppm</p> <p>500M68, 500M04 4.1% TRR 2.874 ppm</p> <p>500M54 2.46% TRR 1.719 ppm</p> <p>500M79 trace trace</p> <p>Peak (Rt = 48 min.) 4.1% TRR 2.896 ppm</p> <p>Sequentially partitioned with hexane, DCM, and ethyl acetate.</p>
Hexane	75.4	52.630	N/A.
DCM	6.2	4.304	N/A.
Ethyl acetate	1.4	0.970	N/A.
Aqueous	1.4	0.969	N/A.
Pellet 1 (dissolved in methanol)	8.1	5.662	<p><u>HPLC analysis resolved:</u></p> <p>Pyraclostrobin 4.2% TRR 2.952 ppm</p> <p>500M07 (BF 500-3) 1.7% TRR 1.203 ppm</p> <p>500M68, 500M04 0.3% TRR 0.194 ppm</p> <p>500M54 0.09% TRR 0.063 ppm</p> <p>500M79 0.10% TRR 0.072 ppm</p> <p>Peak (Rt = 48 min.) 0.4% TRR 0.246 ppm</p> <p>Plus minor HPLC peaks, each <1% TRR, accounting for 1.3% TRR (0.931 ppm).</p>
Pellet 2 (dissolved in water)	0.5	0.377	N/A.
Nonextractable	9.2	6.433	N/A.
Mature potato tubers (sampled after 6 applications; TRR = 0.040 ppm)			
Methanol	52.2	0.021	<p><u>HPLC analysis resolved:</u></p> <p>Pyraclostrobin 29.4% TRR 0.012 ppm</p> <p>500M07 (BF 500-3) 6.6% TRR 0.003 ppm</p> <p>500M68, 500M04 1.7% TRR 0.001 ppm</p> <p>500M54 2.6% TRR 0.001 ppm</p> <p>500M79 3.3% TRR 0.001 ppm</p> <p>Plus one minor HPLC peak accounting for 8.5% TRR (0.003 ppm).</p> <p>Sequentially partitioned with hexane, DCM, and ethyl acetate.</p>
Hexane	33.7	0.014	HPLC analysis resolved pyraclostrobin and 500M07; quantitative results were not provided.

Table 6a (chlorophenyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
DCM	4.5	0.002	HPLC analysis resolved pyraclostrobin, 500M07, 500M68, 500M54, and 500M01; quantitative results were not provided.
Ethyl acetate	2.7	0.001	HPLC analysis resolved several minor peaks.
Aqueous	9.6	0.004	HPLC analysis resolved several minor peaks.
Pellet	2.7	0.001	N/A.
Nonextractable	38.9	0.016	N/A.

Table 6b. Distribution and characterization of radioactive residues in/on potato foliage and tubers following three (totaling 0.8 lb ai/A; ~0.7x) or six (totaling 1.7 lb ai/A; ~1.4x) applications of [tolyl-¹⁴C]pyraclostrobin.

Fraction	% TRR	ppm	Characterization/Identification
Immature potato foliage (sampled after 3 applications; TRR =9.860 ppm)			
Methanol	94.7	9.337	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 65.2% TRR 6.427 ppm 500M07 (BF 500-3) 16.2% TRR 1.600 ppm 500M68 0.6% TRR 0.058 ppm 500M54 1.8% TRR 0.177 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 12.3% TRR (1.212 ppm).</p> <p>Sequentially partitioned with hexane, DCM, and ethyl acetate.</p>
Hexane	77.0	7.595	HPLC analysis resolved pyraclostrobin and 500M07 as a single peak; quantitative results were not provided.
DCM	8.7	0.858	HPLC analysis resolved numerous minor peaks.
Ethyl acetate	1.7	0.166	HPLC analysis resolved numerous minor peaks.
Aqueous	2.4	0.232	HPLC analysis resolved numerous minor peaks.
Nonextractable	5.3	0.523	Not further analyzed (N/A).
Immature potato tubers (sampled after 3 applications; TRR = 0.014 ppm)			
Methanol	30.0	0.004	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 2.5% TRR <0.001 ppm 500M07 (BF 500-3) 0.6% TRR <0.001 ppm 500M72 (tryptophan) 10.0% TRR 0.001 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 16.9% TRR (0.002 ppm).</p>
Pellet	9.7	0.001	N/A.
Nonextractable	61.0	0.009	N/A.
Mature potato foliage (sampled after 6 applications; TRR = 47.785 ppm)			
Methanol	90.8	43.370	<p><u>HPLC analysis resolved:</u> Pyraclostrobin 64.6% TRR 30.888 ppm 500M07 (BF 500-3) 21.4% TRR 10.231 ppm Plus one minor HPLC peak accounting for 4.7% TRR (2.251 ppm).</p> <p>Sequentially partitioned with hexane, DCM, and ethyl acetate.</p>
Hexane	77.9	37.201	N/A.
DCM	11.6	5.542	N/A.
Ethyl acetate	2.3	1.104	N/A.
Aqueous	1.7	0.835	N/A.

Table 6b (toyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
Pellet	0.2	0.091	N/A.
Nonextractable	5.4	2.588	N/A.
Mature potato tubers - Subsample 1 (sampled after 6 applications; TRR = 0.048 ppm)			
Methanol	41.6	0.020	<u>HPLC analysis resolved:</u> 500M72 (tryptophan) 26.1% TRR 0.013 ppm Plus minor HPLC peaks accounting for 15.5% TRR (0.007 ppm).
Pellet	5.6	0.003	<u>HPLC analysis resolved:</u> 500M72 (tryptophan) 3.1% TRR 0.002 ppm Plus minor HPLC peaks accounting for 2.5% TRR (0.001 ppm).
Nonextractable	51.8	0.025	
Mature potato tubers - Subsample 2 (sampled after 6 applications; TRR = 0.050 ppm)			
Methanol (extract 1 of 3)	18.5	0.009	Sequentially partitioned with hexane, DCM, and ethyl acetate.
Hexane	4.5	0.002	HPLC analysis resolved pyraclostrobin and 500M07; quantitative results were not provided.
DCM	1.7	0.001	HPLC analysis resolved numerous minor peaks.
Ethyl acetate	1.5	0.001	HPLC analysis resolved numerous minor peaks.
Aqueous	10.5	0.005	HPLC analysis resolved 500M72; quantitative results were not provided.
Pellet	20.9	0.010	Sequentially partitioned with hexane, DCM, and ethyl acetate.
Hexane	0.5	0.002	N/A.
DCM	0.3	<0.001	N/A.
Ethyl acetate	0.4	<0.001	N/A.
Aqueous	18.4	0.009	N/A.
Nonextractable	52.3	0.026	Extracted with ammonia.
Ammonia	23.4	0.012	<u>HPLC analysis resolved:</u> 500M72 (tryptophan) 2.9% TRR 0.001 ppm Plus minor HPLC peaks, each <5% TRR, accounting for 20.5% TRR (0.011 ppm).
Nonextractable	38.5	0.019	N/A.

Table 7a. Identification/characterization of radioactive residues in immature and mature potato foliage and tubers collected following three (immature; totaling 0.8 lb ai/A; ~0.7x) or six (mature; totaling 1.7 lb ai/A; ~1.4x) applications of [chlorophenyl-¹⁴C]pyraclostrobin.

Fraction	Immature potato foliage (TRR = 19.636 ppm)		Immature potato tubers (TRR = 0.009 ppm)		Mature potato foliage (TRR = 69.846 ppm)		Mature potato tubers (TRR = 0.040 ppm)	
	% TRR	ppm	% TRR	ppm	% TRR	ppm	% TRR	ppm
Identified ^a								
Pyraclostrobin	56.5	11.098	21.0	0.002	55.1	38.515	29.4	0.012
500M07(BF 500-3)	16.1	3.157	5.8	0.001	20.8	14.502	6.6	0.003
500M68, 500M04	2.9	0.570	1.5	<0.001	4.4	3.068	1.7	0.001
500M54	1.38	0.271	6.2	0.001	2.6	1.782	2.6	0.001
500M79	0.37	0.072	0.4	<0.001	0.1	0.072	3.3	0.001
Total Identified	77.25	15.168	34.9	<0.006	83.0	57.939	43.6	0.018
Characterized								
Unidentified peak	--	--	--	--	4.5	3.143	8.5	0.003
Unidentified minor peaks (<5% TRR)	16.7	3.282	14.8	0.001	1.3	0.931	--	--
Methanol pellet	--	--	--	--	0.5	0.377	2.7	0.001
Total Characterized/Identified	93.95	18.45	49.7	<0.007	89.3	62.390	54.8	0.022
Nonextractable	5.6	1.105	51.3	0.005	9.2	6.433	38.9	0.016

^a Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

Table 7b. Identification/characterization of radioactive residues in immature and mature potato foliage and tubers collected following three (immature; totaling 0.8 lb ai/A; ~0.7x) or six (mature; totaling 1.7 lb ai/A; ~1.4x) applications of [tolyl-¹⁴C]pyraclostrobin.

Fraction	Immature potato foliage (TRR = 9.860 ppm)		Immature potato tubers (TRR = 0.014 ppm)		Mature potato foliage (TRR = 47.785 ppm)		Mature potato tubers (TRR = 0.048 ppm)	
	% TRR	ppm	% TRR	ppm	% TRR	ppm	% TRR	ppm
Identified ^a								
Pyraclostrobin	65.2	6.427	2.5	<0.001	64.6	30.888	--	--
500M07 (BF 500-3)	16.2	1.600	0.6	<0.001	21.4	10.231	--	--
500M68	0.6	0.058	--	--	--	--	--	--
500M54	1.8	0.177	--	--	--	--	--	--
500M72 (tryptophan)	--	--	10.0	0.001	--	--	29.2	0.014
Total Identified	83.8	8.262	13.1	<0.003	86.0	41.119	29.2	0.014
Characterized								
Unidentified peak	--	--	--	--	4.7	2.251	--	--
Unidentified peaks (<5% TRR)	12.3	1.212	16.9	0.002	--	--	18.0	0.009
Methanol pellet	--	--	9.7	0.001	0.2	0.091	--	--
Total Characterized/Identified	96.1	9.474	39.7	<0.006	90.9	43.461	47.2	0.023
Nonextractable ^b	5.3	0.523	61.0	0.009	5.4	2.588	51.8 ^b	0.025 ^b

^a Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

^b Extraction of a separate subsample of nonextractable residues (52.3% TRR, 0.026 ppm) with ammonia resulted in identification of 500M72 (2.9% TRR, 0.001 ppm), with 20.5% TRR (0.011 ppm) characterized as minor peaks; see Table 6b for details.

Storage stability

Potato foliage and tuber samples were stored at ≤ -18 C prior to and throughout the analytical phase of the study. Analytical work-up for residue characterization/identification was completed within two years of sampling.

To support the storage intervals of the study, the petitioner extracted and analyzed samples of immature tolyl-label foliage and mature chlorophenyl-label tubers at the beginning (~2.4 months for foliage and 1.6 months for tuber) and at the end (3 years for foliage and 2.6 years for tubers) of the analytical phase. Extraction procedures varied from initial storage stability analyses to final analyses. For tolyl-label immature foliage, the initial storage stability sample was extracted with methanol (3x) followed by water (2x) to yield a methanol extract (76.5% TRR), a methanol pellet (9.2% TRR), and an aqueous extract (1.1% TRR); both the methanol extract and the pellet were subjected to HPLC analysis. At the end of the study the tolyl-label foliage sample was extracted with methanol only (3x) to yield a methanol extract (90.0% TRR). For the chlorophenyl-label tuber, the beginning storage stability sample was extracted with methanol (3x) and water (2x); the resulting methanol extracts were combined and centrifuged to yield a methanol extract and three pellets. The first two pellets were dissolved in methanol and combined with the methanol extract. Following centrifugation, the supernatant (25.4% TRR) and resulting pellet (dissolved in methanol; 29.5% TRR) were subjected to HPLC analysis. The chlorophenyl-label tuber sample at the end of the study was extracted with methanol:water, and the resulting methanol:water extract (68.8% TRR) was subjected to HPLC analysis. The results of HPLC analysis of storage stability samples are presented in Table 8.

Table 8. Results of HPLC analysis of storage stability samples of immature tolyl-label foliage and mature chlorophenyl-label tuber.

Fraction	Initial analysis		Final analysis	
	% TRR	ppm	% TRR	ppm
Tolyl-label immature foliage	TRR = 10.271 ppm		TRR = 9.963 ppm	
Pyraclostrobin, 500M07	69.4	7.125	87.8	8.749
Unidentified peaks	16.3	1.678	2.2	0.219
Chlorophenyl-label mature tuber	TRR = 0.036 ppm		TRR = 0.035 ppm	
Pyraclostrobin, 500M07	45.1	0.016	32.8	0.011
500M68, 500M04	1.5	0.001	n.d.	n.d.
500M54	2.8	0.001	10.7	0.004
Unidentified peaks	5.5	0.002	25.3	0.009

The petitioner attributed differences in the levels of identified metabolites and characterized residues in foliage samples to differences in integration parameters and in total amounts injected

into the HPLC system. For tubers, differences in the metabolite profile were attributed to the different extraction solvents. Based on the frozen storage stability conducted on sugar beet root (18 months for pyraclostrobin and its desmethoxy metabolite), RAB3 concludes that the metabolites remained stable during frozen storage over the course of the study. The petitioner is advised for future storage stability determinations to standardize as many aspects of the extraction and analysis procedures as possible to eliminate the influence of such factors on the analytical results.

Metabolic pathway

Based on the results of the potato metabolism study, the petitioner proposed that pyraclostrobin is metabolized in potatoes by three key transformation steps. As was observed in the grape metabolism study, desmethoxylation in the side chain of the tolyl moiety produces 500M07 (BF 500-3), which in turn may undergo methoxylation of the aromatic ring to produce 500M54. Hydroxylation followed by glucosylation led to formation of 500M68. Also, as observed in grapes, ether cleavage between the chlorophenylpyrazole and the tolyl moieties was observed leading to formation of the chlorophenylpyrazolol metabolite, 500M04, which was subsequently glucosylated to 500M79. One difference in the pathway observed following cleavage in the molecule in potatoes versus grapes was the production of the amino acid tryptophan (500M72) from an anthranilic acid intermediate (500M24) via the shikimate pathway. The petitioner stated that L-tryptophan accumulated in potato tubers as the free amino acid and as a component of the storage protein.

Study summary

Following treatment of young potato plants with three or six foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.27 lb-0.36 ai/A/application (300-400 g ai/ha/application), potatoes were harvested 7 days after three applications (immature; total application rate for each label of 0.8 lb ai/A; ~0.7x) or 7 days after six applications (mature; total application rate for each label of 1.7 lb ai/A; 1.4x the maximum proposed rate for any tuberous and corm crop). In chlorophenyl-label samples, TRR were 19.636 ppm and 0.009 ppm in immature foliage and tubers, respectively, and 69.846 ppm and 0.040 ppm in mature foliage and tubers. In tolyl-label samples, TRR were 9.860 ppm and 0.014 ppm in immature foliage and tubers, respectively, and 47.785 ppm and 0.048 ppm in mature foliage and tubers.

Approximately 40-55% TRR and 89-96% TRR were characterized/identified in potato tubers and foliage, respectively from both labels. Pyraclostrobin was the major residue identified in all matrices except tolyl-label tubers. Pyraclostrobin accounted for 21.0% and 29.4% TRR (0.002 ppm and 0.012 ppm) in immature and mature chlorophenyl-label tubers, but for only 2.5% TRR (<0.001 ppm) in immature tolyl-label tubers; residues were nondetectable in mature tolyl-label tubers. In potato foliage, pyraclostrobin accounted for 56.5% and 55.1% TRR (11.098 and 38.515 ppm) in chlorophenyl-label foliage (mature and immature) and 65.2% and 64.6% TRR (6.427 and 30.888 ppm) in mature and immature tolyl-label foliage. The following metabolites

were also detected in chlorophenyl-label tubers (mature and immature, respectively): the desmethoxy metabolite, 500M07 (BF 500-3), at 5.8% and 6.6% TRR; metabolite 500M54 at 6.2% and 2.6% TRR; the glucose conjugate of pyraclostrobin, 500M68, together with the chlorophenyl pyrazolol metabolite, 500M04, at 1.5% and 1.7% TRR; and the cleavage product, 500M79, at 0.4% and 3.3% TRR. These same metabolites were identified in chlorophenyl-label immature and mature foliage. In tolyl-label tubers, the major identified residue was the amino acid L-tryptophan, 500M72, which accounted for 10.0% TRR (0.001 ppm) and 29.2% TRR (0.014 ppm) in immature and mature tubers, respectively; L-tryptophan was also identified at 2.9% TRR (0.001 ppm) in the nonextractable residues of tolyl-label mature tubers following extraction with ammonia. One additional metabolite, 500M07, was identified at 0.6% TRR in immature tubers. In tolyl-label foliage, metabolite 500M07 was identified at 16.2% TRR (immature) and 21.4% TRR (mature). Metabolites 500M68 and 500M54 were also identified in immature tolyl-label foliage at 0.6% and 1.8% TRR, respectively.

The submitted potato metabolism study is acceptable.

Wheat

BASF submitted a wheat metabolism study (citation listed below) in support of the current petition.

45118428 Reinhard, K. (1999) Metabolism of ¹⁴C-BAS-500 F in Wheat. Laboratory Project Identification No. 1999/11137. Unpublished study submitted by BASF Corporation. 216 p.

The radioactive test substances, [chlorophenyl-¹⁴C]pyraclostrobin and [tolyl-¹⁴C]pyraclostrobin, were combined with EC formulation blank and diluted to volume with water. The formulated test substances (final specific activity unspecified) were each applied by hand sprayer to summer wheat plants in pots as two foliar applications, with 24- to 25-day retreatment intervals, at 0.27 lb ai/A/application (300 g ai/ha/application) for a total application rate for each label of 0.54 lb ai/A (600 g ai/ha; ~1.6x the maximum proposed application rate for the cereal grain crops wheat, rye, and barley). Each test substance was applied to 60 pots containing one wheat plant each; plants had been transplanted to the pots from an outdoor test site and were maintained in the greenhouse for the duration of the study. Applications were made at growth stages BBCH 32 and BBCH 61. The petitioner did not mention establishment of experimental controls for the study.

Wheat samples were collected 0, 31, and 41 days following the second application. Wheat forage was collected at the 0- and 31-day sampling intervals; mature wheat plants (BBCH 89) were collected 41 days after treatment (DAT) and were separated into straw, grain, and chaff. Samples were stored at ≤-18 C prior to and throughout the analytical phase of the study.

Total radioactive residues (TRR)

Samples of 31-DAT forage and mature straw, grain, and chaff were homogenized and subjected to combustion/LSC for TRR determinations. The reported LODs for LSC determinations were 0.0007-0.0008 ppm for forage and grain, and 0.0016-0.0017 ppm for straw. Because the results of replicate combustion analyses varied, possibly due to the inhomogeneity of samples or water content, the petitioner also determined TRR by summing extractable and nonextractable residues following initial methanol and water extractions. The TRR in/on wheat matrices are presented in Table 9. Summed TRR values were used for calculation of percent TRR for the remainder of the study.

Table 9. Total radioactive residues (TRR) in wheat following two foliar applications of [¹⁴C]pyraclostrobin at 0.54 lb ai/A (~1.6x).

Matrix	DAT ^a	TRR, ppm [¹⁴ C]pyraclostrobin equivalents			
		Chlorophenyl Label		Tolyl Label	
		Combustion/LSC	Summed ^b	Combustion/LSC	Summed ^b
Forage	31	7.424	6.527 (5.738)	8.393	6.793 (6.221)
Straw	41	50.511	37.768 (47.018)	47.539	40.461 (44.482)
Grain	41	0.078	0.098 (0.082)	0.447	0.441
Chaff	41	26.297	24.251	34.456	30.617

^a DAT = Days after treatment.

^b Summed = Sum of extractable and nonextractable radioactivity. Where two values are presented, initial values are for samples used in characterization/ identification of extractable residues (Sample 1), and values in parentheses are for samples used in characterization/ identification of nonextractable residues (Sample 2).

Extraction and hydrolysis of residues

Samples of wheat matrices were subjected to extraction procedures for residue characterization and identification. To prepare them for extraction procedures, samples were homogenized in the presence of dry ice (forage), chopped, frozen in liquid nitrogen and crushed (straw and chaff), or homogenized in an analytical mill (grain). During the fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for radioactivity by LSC or combustion/LSC. The general extraction procedures are summarized below.

Samples of forage, straw, grain, and chaff were extracted with methanol (3x) followed by water (3x), and centrifuged. The resulting like supernatants were combined and reserved for HPLC analysis. Following evaporation to remove methanol, a subsample of the combined methanol extract was subjected to sequential partitioning with cyclohexane (3x) and ethyl acetate (3x). The respective organic and aqueous phases were combined and reserved for HPLC analysis. The nonextractable residues following methanol and water extractions were subjected to extraction

with 0.5% aqueous ammonia at 40 C for 1.5 hours. The ammonia extract was reserved for HPLC analysis. Samples from this work-up are referred to hereafter as Sample 1 for each matrix.

For characterization of nonextractable residues, separate samples of forage, straw, and grain (referred to hereafter as Sample 2 for each matrix) were subjected to the extraction procedures described above, except that the methanol extracts of straw were partitioned with ethyl acetate only, and the methanol extracts of chlorophenyl-label grain and tolyl-label forage were not subjected to any partitioning. The resulting ammonia extracts were reserved for HPLC analysis, and the nonextractable residues following ammonia extraction were reserved for further procedures to characterize cellulose and lignin. In general, Sample 2 work-up was conducted within 7-9 months of Sample 1 work-up for forage and straw, and within 14-19 months for grain.

The distribution of ^{14}C -activity in the extracts of wheat matrices is presented in Tables 10a (chlorophenyl label) and 10b (tolyl label). We note that the flow chart depicting extraction procedures for chlorophenyl-label chaff was omitted from the MRID; however, because chaff is not identified as a significant RAC in Table 1 (OPPTS 860.1000), no action is required by the petitioner.

Characterization/identification of residues

Methanol, water, and ammonia extracts, as well as the organic and aqueous phases following partitioning of wheat forage, straw, and grain were analyzed by reversed-phase HPLC. For the extracts, HPLC was conducted using an Inertsil phenyl column or an ODS II column (confirmatory analysis for methanol extracts) with gradient mobile phases of water:formic acid (1000:5, v:v) and ACN:formic acid (1000:5, v:v). Another HPLC system using a Hypersil Green ENV column with gradient mobile phases of water:ACN:formic acid (90:10:0.1, v:v:v) and water:ACN:formic acid (10:90:0.1, v:v:v) was used to separate the parent and 500M07 metabolite. Organic and aqueous phases were also analyzed using an Inertsil phenyl column and mobile phases of water:formic acid and ACN:formic acid. All systems were equipped with UV (230 nm) and radioactivity detectors and fraction collectors. Metabolites were identified by retention time comparisons with the following radiolabeled reference standards: pyraclostrobin, tryptophan, and 500M24 (isolated and identified from the rat metabolism study). In HPLC analyses of chlorophenyl-label samples, metabolites later identified as 500M68 and 500M04 (see below) eluted at similar retention times.

The following fractions resulting from the Sample 2 extraction procedures were used for the isolation of metabolites for identification and qualitative confirmation by LC/MS/MS: the cyclohexane phase of chlorophenyl-label forage, the ethyl acetate phases of chlorophenyl- and tolyl-label straw, and the water extract and the aqueous phase following ethyl acetate partitioning of tolyl-label grain. To isolate extractable, organosoluble radioactivity from natural products, the fractions were subjected to various purification procedures including extraction and partitioning steps, silica gel column cleanup, gel permeation chromatography, acetylation with acetic anhydride, and/or methylation with diazomethane. The purified extracts were then subjected to preparative HPLC (on an Inertsil-phenyl or Shandon Hypercarb column), and the fractions

containing significant radioactivity were analyzed by HPLC, ion-spray LC/MS/MS, and/or GC/MS analysis.

The following metabolites were identified by LC/MS and/or LC/MS/MS in wheat forage and straw: pyraclostrobin; 500M07 (BF 500-3); 500M54; the glucosides 500M68, 500M70, and 500M71; 500M76; 500M04; and 500M34. The petitioner noted that, for a number of metabolites which were identified by LC/MS/MS from a single chromatographic peak, it was impossible to quantify individual compounds. Therefore, for certain metabolites, calculated values were reported as follows: Metabolite 500M76 was quantitated in Sample 2 chlorophenyl-label straw by HPLC (Shandon Hypercarb column); the % TRR value determined was subsequently applied to Sample 1 chlorophenyl-label and tolyl-label straw based on the assumption that, because of its structure, the relative amounts of 500M76 would be similar for the two labels. For the glucosides 500M68, -M70, and -M71, which shared peak 15 in HPLC analysis with 500M76, the petitioner calculated the glucoside summed % TRR by subtracting the % TRR of 500M76 in tolyl-labeled straw from the total peak value for peak 15. The calculated value for the glucosides was then transferred directly to chlorophenyl-label straw. For metabolite 500M04, which due to its structure would be detected only in chlorophenyl-label samples, the petitioner calculated the difference between the amount of 500M76 plus the summed glucosides and the total radioactivity in peak 15. Analogous calculations were applied to quantitation of these metabolites in forage.

Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

In wheat grain, the parent and 500M07 (BF 500-3) were confirmed by comparison with forage and straw chromatograms and metabolites 500M72 (tryptophan) and 500M24 were identified by LC/MS and LC/MS/MS in tolyl-label grain. Metabolite 500M24 in grain was confirmed by methylation with diazomethane and HPLC and GC/MS analysis. A peak (4.3% TRR, 0.004 ppm) in chlorophenyl-label grain was considered most likely 500M04, because it did not appear in the tolyl-label grain; however, insufficient material was available to further characterize/identify the peak.

The petitioner utilized three separate procedures to characterize radioactivity associated with lignin and cellulose in the bound residues of Sample 2 wheat forage and straw. To isolate lignin and cellulose, the petitioner subjected the nonextractable residues following ammonia extraction to hydrolysis with 10% NaOH at reflux for 3 hours. Following filtration, the filter cake was washed with 10% NaOH at 80 C followed by water at 25 C. Lignin was precipitated by adjusting the filtrate and individual wash solutions to pH 1 with concentrated HCl. The petitioner characterized the remaining filter cake as cellulose. To characterize cellulose and hemicelluloses, the nonextractable residues following ammonia extraction were subjected to enzyme hydrolysis with a mixture of cellulase and Macerozyme, a mixture of cellulase, hemicellulase, and pectinase (in sodium acetate buffer, pH 4.7, at 37 C for 20 hours). To characterize lignin, the nonextractable residues following ammonia extraction were subjected to hydrolysis with 66% sulfuric acid for 48 hours with gentle shaking. The mixture was then

diluted with water and filtered. The filter cake was washed and subjected to hydrolysis with 0.5% HCl at reflux for 8 hours. Following filtration, the remaining filter cake was characterized as lignin. Cellulose was also characterized in straw by the treatment of nonextractable residues with Schweizer's reagent (saturated solution of $\text{Cu}(\text{OH})_2$ in 25% ammonia) at room temperature for 16 hours. Following centrifugation, the supernatant was adjusted to pH 5 with concentrated HCl to precipitate cellulose.

For characterization of nonextractable residues in grain, the nonextractable residues following ammonia extraction were extracted with DMSO:water (9:1, v:v; 2x) at room temperature overnight. Following centrifugation, the DMSO:water extracts were combined with ethanol to precipitate starch. For tolyl-label grain, the nonextractable residues remaining following DMSO:water extraction were heated in water at reflux for 3 hours and centrifuged. The resulting supernatant was checked for starch with I_2/KI solution, and the nonextractable residues were subjected to hydrolysis with 10% NaOH at reflux for 3 hours.

The ammonia extract of tolyl-label grain was also subjected to further procedures to precipitate grain protein. The extract was adjusted to pH 4.2 with phosphoric acid, and the resulting precipitate was subjected to digestion with protease in 0.2 M TRIS-HCl buffer, pH 7.2, overnight at 37 C. Following centrifugation, the resulting supernatant was subjected to HPLC analysis using an ODS II column and a gradient mobile phase of phosphate buffer, pH 5.4:methanol (20:80 and 80:20, v:v).

A summary of the characterized and identified ^{14}C -residues in wheat forage, grain, and straw is presented in Tables 11a (chlorophenyl label) and 11b (tolyl label).

Table 10a. Distribution and characterization of radioactive residues in wheat forage, straw, and grain following two foliar applications of [chlorophenyl-¹⁴C]pyraclostrobin at 0.54 lb ai/A (~1.6x).

Fraction	% TRR	ppm	Characterization/Identification
Wheat forage (Sample 1: TRR = 6.527 ppm)			
Methanol	80.9	5.282	HPLC analysis resolved: Pyraclostrobin 57.0% TRR 3.724 ppm 500M07 (BF 500-3) 12.0% TRR 0.782 ppm 500M68, -70, and -71 2.5% TRR 0.163 ppm 500M54 2.1% TRR 0.136 ppm 500M04 1.7% TRR 0.111 ppm 500M76 0.8% TRR 0.052 ppm Unknown P9 3.6% TRR 0.233 ppm Unknown P13 1.2% TRR 0.078 ppm Sequentially partitioned with cyclohexane and ethyl acetate.
Cyclohexane	57.5	3.753	HPLC chromatograms indicated that the majority of metabolites partitioned into organic phases.
Ethyl acetate	11.4	0.742	
Aqueous	12.0	0.781	
Water	4.2	0.274	HPLC analysis resolved pyraclostrobin, 500M07, 500M34, and unknowns P9 and P13; quantitative results were not provided.
Nonextractable	14.9	0.970	Extracted with ammonia.
Ammonia	5.9	0.383	HPLC - see Sample 2 for resolved metabolites.
Nonextractable	6.5	0.420	N/A.
Wheat forage (Sample 2: TRR = 5.738 ppm)			
Methanol	80.2	4.6	Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	76.5	4.385	Worked up (partitioned with ACN:isohexane and preparative HPLC) for LC/MS/MS.
Ethyl acetate	17.7	1.013	N/A.
Aqueous	4.9	0.279	N/A.
Water	4.4	0.253	N/A.
Nonextractable	15.4	0.885	Extracted with ammonia.
Ammonia	3.0	0.173	HPLC analysis resolved pyraclostrobin, 500M07, 500M04, 500M68, 500M70, 500M71, 500M76, and 500M34; quantitative results were not provided.
Nonextractable (SS1)	12.4	0.712	Refluxed with NaOH.
NaOH	12.5	0.717	Adjusted to pH 1 with concentrated HCl.
HCl	5.3	0.306	N/A.

Table 10a (chlorophenyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification																					
Precipitate	5.0	0.289	Characterized as lignin.																					
Nonextractable	0.7	0.039	Characterized as cellulose.																					
Nonextractable (SS2)	12.4	0.712	Subjected to enzyme hydrolysis.																					
Hydrolysate	2.9	0.168	Characterized as cellulose.																					
Nonextractable	10.5	0.601	N/A.																					
Nonextractable (SS3)	12.4	0.712	Hydrolyzed with sulfuric acid.																					
Hydrolysate	8.7	0.497	N/A.																					
Nonextractable	3.8	0.221	Characterized as lignin.																					
Wheat straw (Sample 1: TRR = 37.768 ppm)																								
Methanol	74.6	28.191	<p><u>HPLC analysis resolved:</u></p> <table> <tr> <td>Pyraclostrobin</td> <td>56.0% TRR</td> <td>21.155 ppm</td> </tr> <tr> <td>500M07 (BF 500-3)</td> <td>12.9% TRR</td> <td>4.885 ppm</td> </tr> <tr> <td>500M68, -70, and -71</td> <td>1.9% TRR</td> <td>0.718 ppm</td> </tr> <tr> <td>500M54</td> <td>1.2% TRR</td> <td>0.462 ppm</td> </tr> <tr> <td>500M04</td> <td>1.1% TRR</td> <td>0.415 ppm</td> </tr> <tr> <td>500M76</td> <td>0.6% TRR</td> <td>0.227 ppm</td> </tr> <tr> <td>Unknown P9</td> <td>0.9% TRR</td> <td>0.335 ppm</td> </tr> </table> <p>Sequentially partitioned with cyclohexane and ethyl acetate.</p>	Pyraclostrobin	56.0% TRR	21.155 ppm	500M07 (BF 500-3)	12.9% TRR	4.885 ppm	500M68, -70, and -71	1.9% TRR	0.718 ppm	500M54	1.2% TRR	0.462 ppm	500M04	1.1% TRR	0.415 ppm	500M76	0.6% TRR	0.227 ppm	Unknown P9	0.9% TRR	0.335 ppm
Pyraclostrobin	56.0% TRR	21.155 ppm																						
500M07 (BF 500-3)	12.9% TRR	4.885 ppm																						
500M68, -70, and -71	1.9% TRR	0.718 ppm																						
500M54	1.2% TRR	0.462 ppm																						
500M04	1.1% TRR	0.415 ppm																						
500M76	0.6% TRR	0.227 ppm																						
Unknown P9	0.9% TRR	0.335 ppm																						
Cyclohexane	69.4	26.209	HPLC chromatograms indicated that the majority of metabolites partitioned into organic phases.																					
Ethyl acetate	8.0	3.005																						
Aqueous	2.4	0.918																						
Water	9.9	3.755	<p><u>HPLC analysis resolved:</u></p> <table> <tr> <td>Pyraclostrobin/500M07</td> <td>2.4% TRR</td> <td>0.895 ppm</td> </tr> <tr> <td>500M68, -70, and -71</td> <td>2.1% TRR</td> <td>0.793 ppm</td> </tr> <tr> <td>500M04</td> <td>2.6% TRR</td> <td>0.982 ppm</td> </tr> <tr> <td>500M76</td> <td>0.9% TRR</td> <td>0.340 ppm</td> </tr> <tr> <td>500M34</td> <td>1.3% TRR</td> <td>0.491 ppm</td> </tr> <tr> <td>Unknown P2</td> <td>0.3% TRR</td> <td>0.112 ppm</td> </tr> </table>	Pyraclostrobin/500M07	2.4% TRR	0.895 ppm	500M68, -70, and -71	2.1% TRR	0.793 ppm	500M04	2.6% TRR	0.982 ppm	500M76	0.9% TRR	0.340 ppm	500M34	1.3% TRR	0.491 ppm	Unknown P2	0.3% TRR	0.112 ppm			
Pyraclostrobin/500M07	2.4% TRR	0.895 ppm																						
500M68, -70, and -71	2.1% TRR	0.793 ppm																						
500M04	2.6% TRR	0.982 ppm																						
500M76	0.9% TRR	0.340 ppm																						
500M34	1.3% TRR	0.491 ppm																						
Unknown P2	0.3% TRR	0.112 ppm																						
Nonextractable	15.4	5.822	Extracted with ammonia.																					
Ammonia	4.2	1.585	HPLC - see Sample 2 for resolved metabolites.																					
Nonextractable	10.2	3.870	N/A.																					
Wheat straw (Sample 2: TRR = 47.018 ppm)																								
Methanol	73.2	34.425	Partitioned with ethyl acetate.																					
Ethyl acetate	68.8	32.373	Worked up (silica gel chromatography and preparative HPLC) for LC/MS and LC/MS/MS.																					

Table 10a (chlorophenyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification		
Aqueous	1.3	0.614	N/A.		
Water	8.8	4.144	N/A.		
Nonextractable	18.0	8.449	Extracted with ammonia.		
Ammonia	3.4	1.582	HPLC analysis resolved 500M04, 500M68, 500M70, 500M71, and 500M76; quantitative results were not provided.		
Nonextractable (SS1)	14.6	6.867	Refluxed with NaOH.		
NaOH	13.1	6.138	Adjusted to pH 1 with concentrated HCl.		
HCl	6.7	3.137	N/A.		
Precipitate	4.6	2.172	Characterized as lignin.		
Nonextractable	0.6	0.300	Characterized as cellulose.		
Nonextractable (SS2)	14.6	6.867	Subjected to enzyme hydrolysis.		
Hydrolysate	1.6	0.766	Characterized as cellulose.		
Nonextractable	11.6	5.453	N/A.		
Nonextractable (SS3)	14.6	6.867	Extracted with Schweizer's reagent; supernatant adjusted to pH 5 with concentrated HCl; precipitate dissolved in ammonia.		
Hydrolysate	2.3	1.100	N/A.		
Precipitate	0.8	0.360	Characterized as cellulose.		
Nonextractable	4.6	2.165	N/A.		
Nonextractable (SS4)	14.6	6.867	Hydrolyzed with sulfuric acid.		
Hydrolysate	5.3	2.477	N/A.		
Nonextractable	8.9	4.183	Characterized as lignin.		
Wheat grain (Sample 1: TRR = 0.098 ppm)					
Methanol	55.8	0.055	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin	36.1% TRR	0.036 ppm
			500M07 (BF 500-3)	10.5% TRR	0.010 ppm
			500M68, -70, -71, and 500M04 and 500M76	4.3% TRR	0.004 ppm
			Unknown P2	2.4% TRR	0.002 ppm
			Unknown P9	2.6% TRR	0.003 ppm
			Sequentially partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	43.9	0.043	N/A.		
Ethyl acetate	10.8	0.011	N/A.		

Table 10a (*chlorophenyl label, continued*).

Fraction	% TRR	ppm	Characterization/Identification
Aqueous	6.7	0.007	N/A.
Water	15.2	0.015	HPLC analysis resolved more than 10 minor peaks.
Nonextractable	29.0	0.028	Extracted with ammonia.
Ammonia	14.2	0.014	N/A.
Nonextractable	20.7	0.020	N/A.
Wheat grain (Sample 2: TRR = 0.082 ppm)			
Methanol	54.0	0.044	N/A.
Water	12.4	0.010	N/A.
Nonextractable	33.7	0.027	Extracted with ammonia.
Ammonia	11.3	0.009	N/A.
Nonextractable (SS1)	22.4	0.018	Extracted with DMSO:water.
DMSO:water	N/R	N/R	Extracted with ethanol.
Ethanol	5.2	0.004	N/A.
Precipitate	10.5	0.009	Characterized as starch.
Nonextractable	9.9	0.008	N/A.

Table 10b. Distribution and characterization of radioactive residues in wheat forage, straw, grain, and chaff following two foliar applications of [tolyl-¹⁴C]pyraclostrobin at 0.54 lb ai/A (~1.6x).

Fraction	% TRR	ppm	Characterization/Identification																														
Wheat forage (Sample 1: TRR = 6.793 ppm)																																	
Methanol	80.0	5.436	<p><u>HPLC analysis resolved:</u></p> <table border="0"> <tr> <td>Pyraclostrobin</td> <td>52.9% TRR</td> <td>3.598 ppm</td> </tr> <tr> <td>500M07 (BF 500-3)</td> <td>13.1% TRR</td> <td>0.892 ppm</td> </tr> <tr> <td>500M68, -70, and -71</td> <td>2.5% TRR</td> <td>0.170 ppm</td> </tr> <tr> <td>500M76</td> <td>0.8% TRR</td> <td>0.054 ppm</td> </tr> <tr> <td>500M54</td> <td>3.8% TRR</td> <td>0.260 ppm</td> </tr> <tr> <td>500M34</td> <td>1.2% TRR</td> <td>0.083 ppm</td> </tr> <tr> <td>Unknown P5</td> <td>1.8% TRR</td> <td>0.120 ppm</td> </tr> <tr> <td>Unknown P6</td> <td>1.8% TRR</td> <td>0.125 ppm</td> </tr> <tr> <td>Unknown P9</td> <td>1.2% TRR</td> <td>0.081 ppm</td> </tr> <tr> <td>Unknown P13</td> <td>0.8% TRR</td> <td>0.053 ppm</td> </tr> </table> <p>Sequentially partitioned with cyclohexane and ethyl acetate.</p>	Pyraclostrobin	52.9% TRR	3.598 ppm	500M07 (BF 500-3)	13.1% TRR	0.892 ppm	500M68, -70, and -71	2.5% TRR	0.170 ppm	500M76	0.8% TRR	0.054 ppm	500M54	3.8% TRR	0.260 ppm	500M34	1.2% TRR	0.083 ppm	Unknown P5	1.8% TRR	0.120 ppm	Unknown P6	1.8% TRR	0.125 ppm	Unknown P9	1.2% TRR	0.081 ppm	Unknown P13	0.8% TRR	0.053 ppm
Pyraclostrobin	52.9% TRR	3.598 ppm																															
500M07 (BF 500-3)	13.1% TRR	0.892 ppm																															
500M68, -70, and -71	2.5% TRR	0.170 ppm																															
500M76	0.8% TRR	0.054 ppm																															
500M54	3.8% TRR	0.260 ppm																															
500M34	1.2% TRR	0.083 ppm																															
Unknown P5	1.8% TRR	0.120 ppm																															
Unknown P6	1.8% TRR	0.125 ppm																															
Unknown P9	1.2% TRR	0.081 ppm																															
Unknown P13	0.8% TRR	0.053 ppm																															
Cyclohexane	60.9	4.134	HPLC chromatograms indicated that the majority of metabolites partitioned into organic phases.																														
Ethyl acetate	9.2	0.624																															
Aqueous	8.0	0.545																															
Water	4.1	0.281	HPLC analysis resolved pyraclostrobin, 500M07, 500M34, and unknowns P9 and P13; quantitative results were not provided.																														
Nonextractable	15.8	1.076	Extracted with ammonia.																														
Ammonia	5.6	0.382	HPLC - see Sample 2 for resolved metabolites.																														
Nonextractable	6.1	0.414	N/A.																														
Wheat forage (Sample 2: TRR = 6.221 ppm)																																	
Methanol	76.9	4.786	N/A.																														
Water	5.2	0.324	N/A.																														
Nonextractable	17.9	1.111	Extracted with ammonia.																														
Ammonia	2.6	0.159	HPLC analysis resolved pyraclostrobin, 500M07, 500M68, 500M70, 500M71, and 500M76; quantitative results were not provided.																														
Nonextractable (SS1)	15.3	0.952	Refluxed with NaOH.																														
NaOH	14.3	0.890	Adjusted to pH 1 with concentrated HCl.																														
HCl	6.0	0.373	N/A.																														
Precipitate	5.1	0.317	Characterized as lignin.																														
Nonextractable	1.1	0.068	Characterized as cellulose.																														

Table 10b (toyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable (SS2)	15.3	0.952	Subjected to enzyme hydrolysis.
Hydrolysate	2.4	0.148	Characterized as cellulose.
Nonextractable	12.1	0.753	N/A.
Nonextractable (SS3)	15.3	0.952	Hydrolyzed with sulfuric acid.
Hydrolysate	7.0	0.440	N/A.
Nonextractable	8.5	0.528	Characterized as lignin.
Wheat straw (Sample 1: TRR = 40.461 ppm)			
Methanol	78.5	31.777	HPLC analysis resolved:
			Pyraclostrobin 57.5% TRR 23.295 ppm
			500M07 (BF 500-3) 15.2% TRR 6.159 ppm
			500M68, -70, and -71 1.9% TRR 0.769 ppm
			500M76 0.6% TRR 0.243 ppm
			500M54 1.4% TRR 0.553 ppm
			Unknown P9 0.7% TRR 0.289 ppm
			Unknown P13 1.2% TRR 0.467 ppm
			Sequentially partitioned with cyclohexane and ethyl acetate.
Cyclohexane	71.7	29.018	HPLC chromatograms indicated that the majority of metabolites partitioned into organic phases.
Ethyl acetate	7.4	2.993	
Aqueous	3.2	1.303	
Water	7.2	2.915	HPLC analysis resolved:
			Pyraclostrobin/500M07 1.6% TRR 0.642 ppm
			500M68, -70, and -71 2.1% TRR 0.850 ppm
			500M76 0.9% TRR 0.364 ppm
			500M54 0.2% TRR 0.064 ppm
			500M34 0.7% TRR 0.289 ppm
			Unknown P2 0.2% TRR 0.099 ppm
Plus 8 additional unknowns, accounting for 1.5% TRR (0.612 ppm).			
Nonextractable	14.3	5.769	Extracted with ammonia.
Ammonia	3.2	1.272	HPLC - see Sample 2 for resolved metabolites.
Nonextractable	9.3	3.742	N/A.
Wheat straw (Sample 2: TRR = 44.482 ppm)			
Methanol	70.8	31.497	Partitioned with ethyl acetate.
Ethyl acetate	66.8	29.710	Worked up (silica gel chromatography and preparative HPLC) for LC/MS/MS.
Aqueous	2.2	0.958	N/A.

Table 10b (tolyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
Water	9.5	4.208	N/A.
Nonextractable	19.7	8.777	Extracted with ammonia.
Ammonia	2.8	1.261	HPLC analysis resolved 500M68, 500M70, 500M71, and 500M76; quantitative results were not provided.
Nonextractable (SS1)	16.9	7.516	Refluxed with NaOH.
NaOH	13.6	6.029	Adjusted to pH 1 with concentrated HCl.
HCl	5.4	2.372	N/A.
Precipitate	5.7	2.546	Characterized as lignin.
Nonextractable	1.5	0.663	Characterized as cellulose.
Nonextractable (SS2)	16.9	7.516	Subjected to enzyme hydrolysis.
Hydrolysate	2.4	1.086	Characterized as cellulose.
Nonextractable	12.6	5.586	N/A.
Nonextractable (SS3)	16.9	7.516	Extracted with Schweizer's reagent; supernatant adjusted to pH 5 with concentrated HCl; precipitate dissolved in ammonia.
Hydrolysate	3.1	1.359	N/A.
Precipitate	4.1	1.818	Characterized as cellulose.
Nonextractable	5.9	2.608	N/A.
Nonextractable (SS4)	16.9	7.516	Hydrolyzed with sulfuric acid.
Hydrolysate	6.7	2.990	N/A.
Nonextractable	10.0	4.460	Characterized as lignin.
Wheat grain (TRR = 0.441 ppm)			
Methanol	25.6	0.113	<u>HPLC analysis resolved:</u> Pyraclostrobin 7.8% TRR 0.034 ppm 500M07 (BF 500-3) 3.2% TRR 0.014 ppm 500M72 (tryptophan) 11.0% TRR 0.048 ppm 500M24 2.7% TRR 0.012 ppm Unknown P13 0.9% TRR 0.004 ppm Sequentially partitioned with cyclohexane and ethyl acetate.
Cyclohexane	10.6	0.047	HPLC chromatograms indicated that the majority of metabolites partitioned into organic phases; however, peaks corresponding to 500M72 and 500M24 also appeared in the aqueous phase.
Ethyl acetate	3.9	0.017	
Aqueous	10.3	0.045	

Table 10b (tolyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification		
Water	25.6	0.113	HPLC analysis resolved:		
			Pyraclostrobin/500M07	0.5% TRR	0.002 ppm
			500M72 (tryptophan)	12.0% TRR	0.053 ppm
			500M24	4.0% TRR	0.018 ppm
			Unknown P2	0.3% TRR	0.001 ppm
			Unknown P3	0.7% TRR	0.003 ppm
			Unknown P6	4.0% TRR	0.018 ppm
			Unknown P7	4.0% TRR	0.018 ppm
Unknown P13	0.2% TRR	0.001 ppm			
Nonextractable	48.8	0.216	Extracted with ammonia.		
Ammonia	25.5	0.113	HPLC analysis resolved:		
			500M72 (tryptophan)	3.1% TRR	0.014 ppm
			500M24	3.7% TRR	0.017 ppm
			Unknown P2	1.1% TRR	0.005 ppm
			Unknown P3	2.0% TRR	0.009 ppm
			Unknown P6	3.3% TRR	0.015 ppm
			Unknown P7	2.4% TRR	0.010 ppm
			Unknown P8	6.9% TRR	0.031 ppm
Unknown P13	3.0% TRR	0.013 ppm			
			Extracted with phosphoric acid.		
Phosphoric acid	20.2	0.089	N/A.		
Precipitate	N/R	N/R	Subjected to enzyme hydrolysis with protease.		
Protease	10.7	0.047	HPLC analysis resolved: 500M72 (tryptophan) 10.7% TRR 0.047 ppm Characterized as cleaved protein.		
Pellet	0.9	0.004	N/A.		
Nonextractable	22.1	0.098	Extracted with DMSO:water		
DMSO:water	N/R	N/R	Extracted with ethanol.		
Ethanol	2.7	0.012	N/A.		
Precipitate	5.0	0.022	Characterized as starch.		
Nonextractable	14.9	0.065	Refluxed with water.		
Water	3.4	0.015	Subjected to I ₂ /KI test for residual starch. Results were negative.		
Nonextractable	N/R	N/R	Hydrolyzed with NaOH.		
Hydrolysate	9.8	0.043	N/A.		
Nonextractable	1.7	0.007	Characterized as crude cellulose.		

Table 10b (tolyl label, continued).

Fraction	% TRR	ppm	Characterization/Identification
Wheat chaff (TRR = 30.617 ppm)			
Methanol	59.4	18.183	HPLC analysis revealed a profile similar to that for straw; a peak corresponding to pyraclostrobin (probably containing 500M07) was the only significant component. Sequentially partitioned with cyclohexane and ethyl acetate.
Cyclohexane	49.7	15.217	N/A.
Ethyl acetate	7.2	2.207	N/A.
Aqueous	5.3	1.630	N/A.
Water	11.9	3.639	N/A.
Nonextractable	28.7	8.795	Extracted with ammonia.
Ammonia	6.2	1.888	N/A.
Nonextractable	21.4	6.555	N/A.

Table 11a. Identification/characterization of radioactive residues in wheat forage, straw, and grain following two foliar applications of [chlorophenyl-¹⁴C]pyraclostrobin at 0.54 lb ai/A (~1.6x).

Fraction	Wheat forage (TRR = 6.527 ppm)		Wheat straw (TRR = 37.768 ppm)		Wheat grain (TRR = 0.098 ppm)	
	% TRR	ppm	% TRR	ppm	% TRR	ppm
Identified ^a						
Pyraclostrobin	57.0	3.724	56.0	21.155	36.1	0.036
500M07 (BF 500-3)	12.0	0.782	12.9	4.885	10.5	0.010
Pyraclostrobin + 500M07	--	--	2.4	0.895	--	--
500M68, -70, and -71	2.5	0.163	4.0	1.511	4.3	0.004
500M04	1.7	0.111	3.7	1.397		
500M76	0.8	0.052	1.5	0.567		
500M54	2.1	0.136	1.2	0.462	--	--
500M34	--	--	1.3	0.491	--	--
Total Identified	76.1	4.968	83.0	31.363	50.9	0.050
Characterized						
Unknown P2	--	--	0.3	0.112	2.4	0.002
Unknown P9	3.6	0.233	0.9	0.335	2.6	0.003
Unknown P13	1.2	0.078	--	--	--	--
Water extract ^b	4.2	0.274	--	--	15.2	0.015
Ammonia extract ^c	5.9	0.383	4.2	1.585	14.2	0.014
Total Characterized/Identified	91.0	5.936	88.4	33.395	85.3	0.084
Nonextractable ^d	6.5	0.420	10.2	3.870	20.7	0.020

^a Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

^b HPLC analysis of water extract resolved pyraclostrobin, 500M07, 500M34, and unknowns P9 and P13 in forage, and >10 minor peaks in grain.

^c HPLC analysis of Sample 2 ammonia extracts for forage (3.0% TRR, 0.173 ppm) resolved pyraclostrobin, 500M07, 500M04, 500M68, 500M70, 500M71, 500M76 and 500M34, and for straw (3.4% TRR, 1.582 ppm) resolved 500M04, 500M68, 500M70, 500M71, and 500M76; quantitative results were not reported.

^d Radioactivity in nonextractable residues of Sample 2 forage (12.4% TRR, 0.712 ppm) and straw (14.6% TRR, 6.867 ppm) was characterized as crude cellulose (1.8% TRR, 0.103 ppm in forage and 1.0% TRR, 0.470 ppm in straw) and crude lignin (4.4% TRR, 0.252 ppm in forage and 6.8% TRR, 3.197 ppm in straw); % TRR values represent the mean of two or more characterization methods for each component. Radioactivity in Sample 2 grain (22.4% TRR, 0.018 ppm) was characterized as starch (10.5% TRR, 0.009 ppm).

Table 11b. Identification/characterization of radioactive residues in wheat forage, straw, and grain following two foliar applications of [tolyl-¹⁴C]pyraclostrobin at 0.54 lb ai/A (~1.6x).

Fraction	Wheat forage (TRR = 6.793 ppm)		Wheat straw (TRR = 40.461 ppm)		Wheat grain (TRR = 0.441 ppm)	
	% TRR	ppm	% TRR	ppm	% TRR	ppm
Identified ^a						
Pyraclostrobin	52.9	3.598	57.5	23.295	7.8	0.034
500M07 (BF 500-3)	13.1	0.892	15.2	6.159	3.2	0.014
Pyraclostrobin + 500M07	--	--	1.6	0.642	0.5	0.002
500M72 (tryptophan)	--	--	--	--	36.8	0.162
500M68, -70, -71	2.5	0.170	4.0	1.619	--	--
500M76	0.8	0.054	1.5	0.607	--	--
500M54	3.8	0.260	1.6	0.617	--	--
500M34	1.2	0.083	0.7	0.289	--	--
500M24	--	--	--	--	10.4	0.047
Total Identified	74.3	5.057	82.1	33.228	58.7	0.259
Characterized						
Unknown P2	--	--	0.2	0.099	1.4	0.006
Unknown P3					0.9	0.012
Unknown P5	1.8	0.120	--	--	--	--
Unknown P6	1.8	0.125	--	--	7.3	0.033
Unknown P7					6.4	0.028
Unknown P8					6.9	0.031
Unknown P9	1.2	0.081	0.7	0.289	--	--
Unknown P13	0.8	0.053	1.2	0.467	4.1	0.018
Water extract ^b	4.1	0.281	1.5	0.612	--	--
Ammonia extract ^c	5.6	0.382	3.2	1.272	--	--
Total Characterized/Identified	89.6	6.099	88.9	35.967	85.7	0.387
Nonextractable ^d	6.1	0.414	9.3	3.742	22.1	0.098

^a Chemical structures of identified metabolites are presented in Figure 2, Attachment II.

^b HPLC analysis of water extract resolved pyraclostrobin, 500M07, 500M34, and unknowns P9 and P13 in forage; and 8 additional minor unknowns in straw.

^c HPLC analysis of Sample 2 ammonia extracts for forage (2.6% TRR, 0.159 ppm) resolved pyraclostrobin, 500M07, 500M68, 500M70, 500M71, and 500M76, and for straw (2.8% TRR, 1.261 ppm) resolved 500M68, 500M70, 500M71, and 500M76; quantitative results were not reported. HPLC analysis of the ammonia extract for grain was conducted on Sample 1; thus, results are included with identified fractions from methanol and water.

^d Radioactivity in nonextractable residues of Sample 2 forage (15.3% TRR, 0.952 ppm) and straw (16.9% TRR, 7.516 ppm) was characterized as crude cellulose (1.8% TRR, 0.112 ppm in forage and 2.6% TRR, 1.157 ppm in straw) and crude lignin (6.8% TRR, 0.423 ppm in forage and 7.9% TRR, 3.514 ppm in straw); % TRR values represent the mean of two or more characterization methods for each component. Radioactivity in grain (22.1%

TRR, 0.098 ppm) was characterized as starch (5.0% TRR, 0.022 ppm) and crude cellulose (1.7% TRR, 0.007 ppm).

Storage stability

Wheat samples were stored at ≤ -18 C prior to and throughout the analytical phase of the study. Analytical work-up for residue quantitation and characterization/identification was completed within 11 months of sampling for forage and straw. For grain, although residue characterization/identification analysis continued for 18-22 months after sampling, quantitation of metabolites for chlorophenyl-label grain was completed within 1 month of sample collection, and quantitation for tolyl-label grain was completed using extracts generated 7 months after sample collection.

To support the storage intervals for forage and straw, the petitioner compared HPLC results for methanol extracts of forage (both labels) and chlorophenyl-label straw analyzed at the beginning of the study (<1 month after sampling) and following storage at ~ -18 C for 20-21 months. Based on the results of HPLC analysis, the metabolite profiles did not change significantly over the course of the study in the methanol extracts of chlorophenyl- and tolyl-label forage or in chlorophenyl-label straw.

Quantitation of metabolites in tolyl-label grain was performed with extracts from the third work-up of the sample, which was conducted 7 months after the start of the study. This work-up was essentially the same as the first work-up, which was conducted less than 1 month after sample collection. To support the storage intervals for grain, the petitioner compared the distribution of radioactivity in the methanol and water extracts, nonextractable residues, and the cyclohexane, ethyl acetate, and aqueous phases between the first and third work-ups as well as the results of HPLC analysis of the cyclohexane, ethyl acetate, and aqueous phases. The distribution of residues and metabolite profiles were essentially unchanged between the two work-ups, except that there was a noticeable increase in the peak representing pyraclostrobin and 500M07 (BF 500-3) in the ethyl acetate phase from the third work-up. No additional storage stability data are required to support the wheat metabolism study.

Metabolic pathway

Based on the results of the wheat metabolism study, the petitioner proposed that pyraclostrobin is metabolized in wheat by three key transformation steps. As was observed in the grape and potato metabolism studies, desmethoxylation in the side chain of the tolyl moiety produces 500M07 (BF 500-3). This in turn may undergo methoxylation of the aromatic ring to produce 500M54 or hydroxylation to produce 500M34. The glucoside metabolites 500M68, 500M70, and 500M71 are formed by conjugation of pyraclostrobin, 500M07, and 500M34, respectively. Also, as observed in potatoes and grapes, cleavage between the chlorophenyl and the tolyl moieties led to formation of the chlorophenylpyrazolol metabolite, 500M04 or its tolyl

counterpart 500M24 (tolyl-label grain only). The cleavage process was more significant in grain than in forage or straw. As was observed in the potato metabolism study, the amino acid L-tryptophan (500M72) was formed from 500M24, an anthranilic acid intermediate, via the shikimate pathway. The petitioner stated that L-tryptophan accumulated in wheat grain as the free amino acid and as a component of the storage protein. The petitioner proposed that metabolite 500M76, a structural isomer of pyraclostrobin which was not identified in grapes or potatoes, was formed by intramolecular arrangement under the influence of light; this was corroborated by the photolysis study in which 500M76 was a main product.

Study summary

Following treatment of summer wheat plants with two foliar applications of uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at 0.27 lb ai/A/application (300 g ai/ha/application) for a total application rate of 0.54 lb ai/A (~1.6x), samples of wheat forage were harvested 0 and 31 days following the second application, and samples of mature wheat (straw, grain, and chaff) were harvested 41 days following the second application. In chlorophenyl-label samples TRR were 6.527 ppm in forage, 37.768 ppm in straw, 0.098 ppm in grain, and 24.251 ppm in chaff. In tolyl-label samples, TRR were 6.793 ppm in forage, 40.461 ppm in straw, 0.441 ppm in grain, and 30.617 ppm in chaff.

Approximately 85-91% TRR were characterized/identified in wheat forage, straw, and grain from both labels. Pyraclostrobin was the major residue identified in all matrices except tolyl-label grain. In chlorophenyl-label and tolyl-label forage and straw, pyraclostrobin accounted for at least 53-58% TRR (3.724 and 3.598 ppm in forage, and 21.155 and 23.295 ppm in straw). In grain, pyraclostrobin accounted for 36.1% TRR (0.036 ppm) in the chlorophenyl-label sample, but only 7.8% TRR (0.034 ppm) in tolyl-label grain. The desmethoxy metabolite, 500M07 (BF 500-3), was also a significant component in forage and straw from both labels (at least 12-15% TRR) and in chlorophenyl-label grain (10.5% TRR); it accounted for 3.2% TRR in tolyl-label grain. The major identified component in tolyl-label grain was 500M72 (tryptophan), which accounted for 36.8% TRR (0.162 ppm) and the cleavage product 500M24 accounted for 10.4% TRR (0.047 ppm) in tolyl-label grain; these metabolites were not detected in any other wheat matrix. The following additional metabolites were identified in chlorophenyl- and tolyl-label forage and straw at ≤4% TRR: 500M68, 500M70, and 500M71 (glucose conjugates), 500M76, 500M54, and 500M34. In addition, metabolite 500M04 was identified in chlorophenyl-label wheat forage and straw at 1.7% and 3.7% TRR. Together the metabolites 500M68, 500M70, and 500M71 accounted for 4.3% TRR in chlorophenyl-label grain.

Nonextractable residues in forage, straw, and grain were subjected to extensive procedures to characterize crude cellulose and lignin. In chlorophenyl-label forage and straw, cellulose accounted for 1.8% and 1.0% TRR and lignin accounted for 4.4% and 6.8% TRR in forage and straw. In tolyl-label samples, cellulose accounted for 1.8% and 2.6% TRR in forage and straw, and lignin accounted for 6.8% and 7.9% TRR in forage and straw. In grain, 10.5% and 5.0%

TRR were characterized as starch in chlorophenyl- and tolyl-label grain, and 1.7% TRR in tolyl-label grain were characterized as cellulose.

The submitted wheat metabolism study is acceptable.

Translocation study

BASF submitted a study (citation listed below) depicting translocation of [¹⁴C]pyraclostrobin in wheat. The study was conducted by BASF (BASF Agricultural Center, Limburgerhof, Germany).

45118429 Hoffmann, M. (1998) Translocation Study with BAS 500 F and Wheat. Supplementary Study. Study code: 45503, Document No. 1998/11205. Unpublished study submitted by BASF Corporation. 28 p.

Uniformly ring-labeled [tolyl- ¹⁴C]pyraclostrobin (specific 4.55 MBq/mg, radiochemical purity >99%) formulated as an EC was applied by hand sprayer to spring wheat plants grown in pots as two foliar applications at 0.22 lb ai/A/application (250 g ai/ha/application); two separate formulated test substances (made with different formulation blanks) were used for each application. The first application was made to wheat plants at growth stage BBCH 32/33 (second leaf completely developed; flag leaf still incompletely rolled up in sheaf of second leaf). The second application was made to wheat plants at growth stage BBCH 43/47 (ear formed but contained within closed sheath of flag leaf). Wheat plants were harvested 11 and 15 days after the first and second applications, respectively.

To investigate the translocation behavior of pyraclostrobin in wheat, the petitioner subjected selected entire plants to autoradiography. In addition, the following individual plant parts were analyzed by combustion/LSC: from the first application, the flag leaf (untreated) and the second and third leaves (directly treated); and from the second application the wheat ear (untreated) and the first and second leaves (directly treated).

Autoradiograms corroborated the absence of translocation. The results of LSC analysis are presented in Table 12, and confirm that very little radioactivity translocated from the treated leaves to the untreated plant parts.

Table 12. Radioactivity detected in wheat plant parts following treatment with [tolyl- ¹⁴C]pyraclostrobin.

Matrix	[¹⁴ C]Pyraclostrobin equivalents, µg	% of Total radioactivity
Following one application		
Third Leaf	6.145, 2.833	52.77, 45.61
Second Leaf	5.456, 3.322	46.86, 53.48
Flag Leaf (untreated)	0.043, 0.057	0.37, 0.92
Total	11.644, 6.212	
Following two applications		
Second leaf	2.18, 2.902	20.62, 22.12
First leaf	8.246, 9.704	78.01, 73.97
Wheat ear (untreated)	0.144, 0.189	1.36, 1.44
Total	10.57, 12.795	

OPPTS GLN 860.1300: Nature of the Residue in Livestock

Ruminants

BASF has submitted a study (citations listed below) pertaining to the metabolism of [¹⁴C]pyraclostrobin in lactating goats. The in-life portion of the study was performed at BASF Aktiengesellschaft, Department of Toxicology, Ludwigshafen, Germany, and the analytical phase was conducted at BASF Agricultural Center, Limburgerhof, Germany.

45118432 Bross, M.; Tilting, N. (2000) Investigation of the Metabolism of ¹⁴C-BAS 500 F in the Goat. Laboratory Project Identification No. 35634; 2000/100004. Unpublished study submitted by BASF Corporation. 216 p.

45118433 Leibold, E.; Hoffmann, H.; and Hildebrand, B. (1998) ¹⁴C 500 F - Absorption, Distribution and Excretion After Repeated Oral Administration in Lactating Goats. Laboratory Project Identification No. 02B0363/966010; 1998/10636. Unpublished study submitted by BASF Corporation. 63 p.

The study was conducted using pyraclostrobin labeled in either the chlorophenyl ring or the tolyl ring. In addition, a low dose (nominally 12 ppm) and a high dose (nominally 50 ppm) were used for each label. For the low dose studies, the test substances were [chlorophenyl-U-¹⁴C]pyraclostrobin [specific activity 4.34 Mbq/mg (260,400 dpm/μg), radiochemical purity 80%] and [tolyl-U-¹⁴C]pyraclostrobin [specific activity 4.5 Mbq/mg (270,000 dpm/μg), radiochemical purity 80%]. The petitioner stated that the low dose test substances decomposed radiolytically (to 80% radiochemical purity; this was not observed until after dosing), and that approximately 15% of the radioactivity, after decomposition consisted of the N-desmethoxy derivative of pyraclostrobin. Because the petitioner conducted full characterization/identification determinations with the samples from the high dose goats as well as the low dose goats, the relatively low radiochemical purity of the test substance for the low dosing level will not be considered to have a negative impact on the study as a whole.

For the high dose studies, the test substances were [chlorophenyl-U-¹⁴C]pyraclostrobin [specific activity 4.14 Mbq/mg (248,400 dpm/μg), radiochemical purity >98%] and [tolyl-U-¹⁴C]pyraclostrobin [specific activity 4.46 Mbq/mg (267,600 dpm/μg), radiochemical purity >98%]. The test substances were isotopically diluted with non-labeled pyraclostrobin to final specific activities of 52,620 dpm/μg and 166,842 dpm/μg for the low and high dose studies, respectively, with the chlorophenyl label, and 55,380 dpm/μg and 146,622 dpm/μg for the low and high dose studies, respectively, with the tolyl label. For each label, two goats received five daily doses of the test substance at 12.2 ppm (low dose) in the feed and one goat received five daily doses at 78 (chlorophenyl label) or 70 (tolyl label) ppm (high dose); dosing was conducted via capsules for the low dose or by gavage for the high dose. The low dose was ~0.34x the maximum theoretical dietary burden to beef cattle (MTDB; 36.3 ppm) and to dairy cattle (MTDB

35.4 ppm). The high dose was ~1.9-2.2x the MTDB for beef cattle and dairy cattle; see “Meat, Milk, Poultry, Eggs” for calculation of dietary burden.

During the study, the goats were fed a commercial pelleted feed *ad libitum* and apples and hay once per day; water was provided *ad libitum*. The petitioner provided sufficient descriptions of preparation of dose capsules and animal husbandry practices, as well as data concerning daily feed intake, body weights, and milk production.

Milk was collected twice daily, in the morning prior to dosing and in the afternoon. The animals were sacrificed 23 hours after the last dose, and samples of liver, kidney, muscle (back and leg), and fat (kidney and intraperitoneal) were collected. Samples were stored frozen at -18 C prior to transport to the analytical laboratory, where samples were stored frozen prior to analysis.

Total radioactive residues (TRR)

Total radioactive residues (TRR) in milk samples were determined by LSC directly. Fat samples were solubilized (using tissue solubilizer at 50 C overnight) and liver, kidney, and muscle samples were combusted prior to LSC determination. The TRR in milk and tissues are presented in Table 13. The LODs for the radioassay were 0.0002 ppm for milk and kidney, 0.0018 ppm for liver, 0.0022 ppm for muscle, and 0.0029 ppm for fat.

Although the petitioner determined the TRR in individual samples of tissues from each of the goats in the low dose studies, pooled samples of these tissues were prepared and the pooled samples were used for all further analyses. Therefore, the TRR for the pooled samples are presented in Table 13. The petitioner prepared pooled milk samples for characterization and identification purposes; the TRR in these pooled samples are also presented in Table 13. For the low dose study, milk samples from 36-120 hours were pooled. For the high dose study, milk samples from all sampling intervals were pooled for the chlorophenyl label, and milk samples from 36-96 hours were pooled for the tolyl label.

Table 13. Total radioactive residues in milk and tissues from goats dosed for 5 days with [¹⁴C]pyraclostrobin at 12.2 ppm (low dose) and 78 ppm (chlorophenyl label) or 70 ppm (tolyl label; high dose).

Matrix	TRR, ppm [¹⁴ C]pyraclostrobin equivalents			
	Chlorophenyl label		Tolyl label	
	Low dose	High dose	Low dose	High dose
Milk				
12 hours	0.040, 0.039	0.402	0.053, 0.014	0.069
24 hours	0.016, 0.027	0.300	0.015, 0.013	0.078
36 hours	0.043, 0.058	0.470	0.026, 0.026	0.247
48 hours	0.028, 0.030	0.311	0.016, 0.015	0.160
60 hours	0.051, 0.043	0.581	0.052, 0.035	0.148
72 hours	0.030, 0.028	0.195	0.014, 0.022	0.086
84 hours	0.040, 0.058	0.659	0.048, 0.034	0.100
96 hours	0.057, 0.028	0.283	0.015, 0.020	0.051
108 hours	0.027, 0.056	0.593	0.048, 0.039	0.083
120 hours	0.038, 0.028	0.130	0.015, 0.023	0.056
Pooled sample used for characterization	0.038	0.382	0.026	0.127
Muscle	0.018 ^a	0.117	0.022 ^a	0.063
Fat	0.094 ^a	0.928	0.082 ^a	0.380
Liver	0.241 ^a	1.505	0.383 ^a	0.828
Kidney	0.054 ^a	0.335	0.085 ^a	0.316

^a TRR value for pooled samples from two goats.

Samples of urine, feces, and cage washings were collected and analyzed for TRR. These data indicate that a large portion of the radioactivity, 61-75%, was excreted: ~39-64% was eliminated in the feces, ~9-23% was eliminated in the urine, and an additional 0.3-1.4% was found in the cage washings. TRR in milk and tissues accounted for 0.1-0.5% and 0.2-0.6%, respectively, of the administered radioactivity. Overall, TRR levels in the milk and tissue samples were similar for the two labels, although levels were generally lower in goats dosed with the tolyl label than with the chlorophenyl label. TRR in milk plateaued at 36-60 hours.

Extraction and characterization of ¹⁴C-residues

Samples of milk, fat, liver, kidney, and muscle were subjected to extraction and hydrolysis procedures for residue characterization and identification. The petitioner provided adequate descriptions of the fractionation procedures for each matrix. During the extraction and fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for

radioactivity by LSC or combustion/LSC. The general extraction and fractionation procedures are summarized below.

Milk samples were extracted with hexane and ACN, and centrifuged. The aqueous phase was evaporated to dryness and dissolved in ACN. The hexane phase was combined with the nonextractable residues and extracted with ACN. The ACN extracts were combined, evaporated to dryness and dissolved in methanol for HPLC analysis.

Fat samples were extracted with hexane and ACN (2-3x), and the hexane extract was partitioned with ACN. The ACN extracts were combined and reserved for HPLC analysis.

Muscle samples were extracted with methanol (3x), and the extracts were isolated by centrifugation. The methanol extracts were combined and concentrated for HPLC analysis. For samples from the low dose goats, a precipitate formed when the methanol extract was concentrated. This precipitate was isolated and extracted with water. For the tolyl-label low-dose sample, the methanol extract was evaporated to dryness and partitioned between hexane and ACN.

Kidney and liver samples were sequentially extracted with methanol (3x) and water. The methanol extracts of the low dose samples were each concentrated (which resulted in the formation of a precipitate), then combined, evaporated to dryness, and partitioned between hexane and ACN. The methanol extracts of the high dose samples were combined without concentration and partitioned between hexane and ACN. The ACN phases were reserved for HPLC analysis.

For the high-dose kidney samples from both labels, the extraction procedures were repeated with three subsamples. With the second subsample, the methanol extract was subjected to acid hydrolysis (extract evaporated to dryness and dissolved in HCl, heated at reflux for 2 h) and the hydrolysate was partitioned with ethyl acetate (EtOAc). The nonextractable residues of the second subsample were also separately subjected to acid hydrolysis (as described above) and pronase digestion (TRIS buffer, pH 7.0, overnight at 39 C); in both cases the hydrolysate was partitioned with EtOAc. The remaining aqueous phase, after partitioning of the pronase digestate with EtOAc, was subjected to acid hydrolysis as described above. The ethyl acetate phases following acid hydrolysis were reserved for HPLC analysis.

For the third subsample of kidney, the methanol extract was mixed with water, the mixture was concentrated to remove methanol, and the resulting aqueous phase was sequentially extracted with hexane, dichloromethane (DCM), DCM with formic acid (ratio not specified), and EtOAc. The nonextractable residues of the third subsample were subjected to pronase digestion as described above. The digestate was then acidified and applied to a C18 column which was washed with water and eluted with methanol and methanol:formic acid (24:1, v:v).

As with kidney, extraction procedures with the high-dose liver samples were repeated using two subsamples. With the first subsample, the nonextractable residues remaining after methanol and water extraction were separately subjected to acid hydrolysis and pronase digestion as described above for kidney; the hydrolysates were each partitioned with EtOAc. With the second subsample, the methanol extract was mixed with water, concentrated to remove the methanol, and sequentially extracted as described above for kidney (third subsample).

The distribution of ¹⁴C-activity in the extracts and hydrolysates of milk and tissues is presented in Tables 14a (chlorophenyl label) and 14b (tolyl label).

Characterization and identification of residues

Milk and tissue extracts were analyzed by HPLC using a Hypersil or ODS column and a gradient mobile phase of water, ACN, and formic acid. Radioactivity was detected and quantified using a radioactivity monitor. Metabolites were identified by comparison of HPLC retention times with metabolites that were purified and identified in urine and feces. The petitioner stated that some metabolites were identified in kidney and liver by co-chromatography with metabolites isolated from excreta; however, the petitioner did not specify which metabolites were identified in this manner. ¹⁴C-Residue fractions in urine from both labels were isolated by solid phase extraction (SPE) using C18 column chromatography and were further purified by HPLC. Residues in feces were extracted with methanol, applied to a silica gel column, and eluted with hexane:acetone (9:1 and 8:2, v:v) and acetone. Radioactive fractions were further purified by C18 SPE, and individual metabolites were isolated by HPLC. Isolated urinary and fecal metabolites were analyzed by MS and NMR for structural elucidation. In urine, the isolated metabolites were polar and primarily consisted of molecular fragments formed following ring cleavage. Metabolites 500M04, 500M05, and 500M85 were identified from the chlorophenyl label and 500M51 and 500M39 were identified in tolyl-label samples. Residue components identified in chlorophenyl-label feces included 500M84 (OH-500M64: OH ortho to the pyrazole ring), 500M64, 500M66, 500M45, 500M08, 500M67, and 500M04. Pyraclostrobin and the desmethoxy metabolite 500M07 (elsewhere referenced as BF 500-3) were also isolated from feces.

For one of the HPLC systems used for analysis, pyraclostrobin could not be resolved from its desmethoxy metabolite 500M07; therefore, reported residues are listed as the sum of the two components for certain extracts.

The petitioner subjected the organic extract of milk (chlorophenyl label, high dose) and the methanol extract of kidney (chlorophenyl label, high dose) to acid hydrolysis as described previously. HPLC analysis of the hydrolysate demonstrated that all of the metabolites were converted to the chlorophenyl pyrazole derivatives, 500M04 and 500M85. The petitioner also subjected a liver subsample (intact sample, chlorophenyl label, high dose) to acid hydrolysis. HPLC analysis of the hydrolysate also indicated conversion of the majority of the radioactivity to chlorophenyl pyrazole derivatives.

A summary of the characterized and identified ^{14}C -residues in matrices from high-dose goats is presented in Tables 15a (chlorophenyl label) and 15b (tolyl label).

Table 14a. Distribution of total radioactive residues in milk and tissues from lactating goats orally dosed with [chlorophenyl-U-¹⁴C]pyraclostrobin at a feeding level of 12.2 ppm (low dose) or 78 ppm (high dose) in the diet.

Fraction ^a	% TRR	ppm	Characterization/Identification
Milk, Low Dose (TRR = 0.038 ppm)			
ACN	90.1	0.034	HPLC analysis resolved: Pyraclostrobin + 500M07 31.6% TRR 0.012 ppm 500M05 31.1% TRR 0.012 ppm Plus an additional 5 unknowns totaling 27.4% TRR (0.010 ppm), each ≤14.3 % TRR (≤0.005 ppm).
Hexane	4.7	0.002	Not further analyzed (N/A).
Nonextractable	5.8	0.002	N/A.
Milk, High Dose (TRR = 0.382 ppm)			
Organic extract	95.0	0.363	HPLC analysis resolved: Pyraclostrobin + 500M07 17.4% TRR 0.067 ppm 500M04 16.3% TRR 0.062 ppm 500M05 14.1% TRR 0.054 ppm 500M08 1.0% TRR 0.004 ppm 500M45 1.6% TRR 0.006 ppm 500M64 2.6% TRR 0.010 ppm 500M66 1.5% TRR 0.006 ppm 500M67 2.1% TRR 0.008 ppm 500M85 5.5% TRR 0.021 ppm Plus an additional 11 unknowns totaling 32.9% TRR (0.126 ppm), each ≤12.7% TRR (≤0.049 ppm).
Hexane	0.9	0.003	N/A.
Nonextractable	4.4	0.017	N/A.
Muscle, Low Dose (TRR = 0.018 ppm)			
Methanol	88.1	0.016	Partitioned with ACN and hexane.
Hexane	12.1	0.002	N/A.
ACN	72.1	0.013	HPLC analysis resolved: Pyraclostrobin 57.9% TRR 0.010 ppm 500M07 14.2% TRR 0.003 ppm
Methanol precipitate	4.4	0.001	N/A.
Water	4.9	0.001	N/A.
Nonextractable	7.2	0.001	N/A.
Muscle, High Dose (TRR = 0.117 ppm)			
Methanol	84.3	0.099	HPLC analysis resolved: Pyraclostrobin 76.2% TRR 0.089 ppm 500M07 8.1% TRR 0.010 ppm
Nonextractable	11.1	0.013	N/A.
Fat, Low Dose (TRR = 0.094 ppm)			

Table 14a (chlorophenyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
ACN	95.1	0.089	<u>HPLC analysis resolved:</u> Pyraclostrobin 73.4% TRR 0.069 ppm 500M07 21.7% TRR 0.020 ppm
Hexane	5.7	0.006	N/A.
Nonextractable	8.2	0.008	N/A.
Fat, High Dose (TRR = 0.928 ppm)			
ACN	97.0	0.901	<u>HPLC analysis resolved:</u> Pyraclostrobin 88.2% TRR 0.819 ppm 500M07 8.8% TRR 0.082 ppm
Hexane	1.5	0.014	N/A.
Nonextractable	1.3	0.012	N/A.
Liver, Low Dose (TRR = 0.241 ppm)			
Methanol extract 1	26.2	0.063	Combined with other methanol extracts.
Methanol precipitate 1	2.7	0.007	N/A.
Methanol extract 2	5.6	0.013	Combined with other methanol extracts.
Methanol precipitate 2	0.6	0.002	N/A.
Methanol extract 3	1.8	0.004	Combined with other methanol extracts.
Methanol precipitate 3	0.2	<0.001	N/A.
Combined methanol	33.6	0.081	Partitioned with hexane and ACN.
Hexane	10.1	0.024	N/A.
ACN	21.8	0.053	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 3.1% TRR 0.008 ppm Plus an additional 17 unknowns totaling 18.7% TRR (0.045 ppm), each ≤3.1% TRR (≤0.008 ppm).
Water	1.4	0.003	N/A.
Nonextractable	67.5	0.163	N/A.
Liver, High Dose (TRR = 1.505 ppm)			
Methanol	26.0	0.391	Partitioned with hexane and ACN.
Hexane	6.0	0.091	N/A.

Table 14a (chlorophenyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification			
ACN	15.7	0.237	<u>HPLC analysis resolved:</u> Pyraclostrobin 1.4% TRR 0.021 ppm 500M04 0.9% TRR 0.013 ppm 500M05 0.1% TRR 0.002 ppm 500M07 1.5% TRR 0.022 ppm 500M08 0.3% TRR 0.004 ppm 500M39 1.0% TRR 0.015 ppm 500M45 0.2% TRR 0.003 ppm 500M66 1.3% TRR 0.020 ppm 500M67 4.6% TRR 0.069 ppm 500M85 1.6% TRR 0.025 ppm Plus an additional 10 unknowns totaling 2.8% TRR (0.043 ppm), each $\leq 0.6\%$ TRR (≤ 0.009 ppm).			
			Water	1.7	0.025	N/A.
			Nonextractable	Not reported (N/R)	N/R	Split into two subsamples. SS1 subjected to pronase digestion. SS2 subjected to acid (HCl) hydrolysis.
			SS1: pronase digestate	33.5	0.504	HPLC analysis resolved 13 unknowns, each $\leq 5.9\%$ TRR (≤ 0.089 ppm). Partitioned with EtOAc.
			SS1: EtOAc	1.7	0.025	N/A.
			SS1: Aqueous	29.9	0.450	N/A.
			SS1: Solids	N/R	N/R	N/A.
			SS2: Acid hydrolysate	60.8	0.915	Partitioned with EtOAc.
			SS2: EtOAc	43.1	0.648	<u>HPLC analysis resolved:</u> 500M04 26.5% TRR 0.398 ppm 500M85 13.9% TRR 0.208 ppm Plus an additional 2 unknowns totaling 2.8% TRR (0.042 ppm), each $\leq 1.9\%$ TRR (≤ 0.029 ppm).
						SS2: Aqueous
			SS2: Solids	N/R	N/R	N/A.
Liver, High Dose (TRR = 1.505 ppm) - 2nd extraction						
Methanol	28.9	0.434	Water added and mixture concentrated to remove methanol. Aqueous phase sequentially partitioned with hexane, DCM, DCM with formic acid, and EtOAc.			
Hexane	6.5	0.097	N/A.			
DCM	3.6	0.054	N/A.			
Acidic DCM	10.5	0.158	N/A.			
EtOAc	0.8	0.012	N/A.			
Aqueous	2.0	0.031	N/A.			
Water	3.4	0.051	N/A.			

Table 14a (chlorophenyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
Nonextractable	66.3	0.997	Subjected to pronase digestion.
Digestate	42.5	0.640	Applied to C18 column which was washed with water and eluted with methanol and methanol with formic acid.
Filtrate	0.4	0.006	N/A.
Water wash	0.3	0.005	N/A.
Methanol	27.7	0.417	<u>HPLC analysis resolved:</u> 500M04 6.9% TRR 0.104 ppm Plus an additional 16 unknowns totaling 20.8% TRR (0.313 ppm), each ≤8.7% TRR (≤0.131 ppm).
Acidic methanol	7.9	0.119	N/A.
Solids	17.0	0.255	N/A.
Kidney, Low Dose (TRR = 0.054 ppm)			
Methanol extract 1	68.4	0.037	Combined with other methanol extracts.
Methanol precipitate 1	0.4	<0.001	N/A.
Methanol extract 2	10.2	0.005	Combined with other methanol extracts.
Methanol precipitate 2	0.4	<0.001	N/A.
Methanol extract 3	3.3	0.002	Combined with other methanol extracts.
Methanol precipitate 3	0.5	<0.001	N/A.
Combined methanol	79.2	0.043	Concentrated and partitioned with ACN and hexane.
ACN	50.4	0.027	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 19.6% TRR 0.010 ppm Plus an additional 11 unknowns totaling 30.5% TRR (0.016 ppm), each ≤7.0% TRR (≤0.004 ppm).
Hexane	31.4	0.017	N/A.
Water	5.1	0.003	N/A.
Nonextractable	13.7	0.007	N/A.
Kidney, High Dose (TRR = 0.335 ppm) - 1st extraction			
Methanol extract 1	76.2	0.255	Combined with other methanol extracts.
Methanol extract 2	4.2	0.014	Combined with other methanol extracts.
Methanol extract 3	0.6	0.002	Combined with other methanol extracts.
Combined methanol	73.3	0.246	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 22.1% TRR 0.074 ppm 500M04 4.4% TRR 0.015 ppm 500M05 13.4% TRR 0.045 ppm 500M64 1.0% TRR 0.003 ppm 500M66 1.2% TRR 0.004 ppm 500M67 13.0% TRR 0.043 ppm 500M85 6.5% TRR 0.022 ppm Plus an additional 9 unknowns totaling 11.7% TRR (0.039 ppm), each ≤3.0% TRR (≤0.010 ppm).

Table 14a (chlorophenyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
Nonextractable	18.6	0.062	N/A.
Kidney, High Dose (TRR = 0.335 ppm) - 2nd extraction			
Methanol	80.8	0.271	Subjected to acid (HCl) hydrolysis and partitioned with EtOAc.
EtOAc	75.7	0.254	<u>HPLC analysis resolved:</u> 500M04 32.5% TRR 0.109 ppm 500M85 29.7% TRR 0.100 ppm Plus an additional 5 unknowns totaling 11.2% TRR (0.037 ppm), each ≤4.2% TRR (≤0.014 ppm).
Aqueous	6.3	0.021	N/A.
Water	2.0	0.007	N/A.
Nonextractable	N/R	N/R	Split into two subsamples. SS1 subjected to pronase digestion. SS2 subjected to acid (HCl) hydrolysis.
SS1: pronase digestate	12.2	0.041	Partitioned with EtOAc.
SS1: EtOAc	0.9	0.003	N/A.
SS1: Aqueous	N/R	N/R	Subjected to acid (HCl) hydrolysis and partitioned with EtOAc.
SS1: EtOAc	4.7	0.016	<u>HPLC analysis resolved:</u> 500M04 0.7% TRR 0.002 ppm 500M85 2.2% TRR 0.007 ppm Plus an additional 6 unknowns totaling 1.8% TRR (0.006 ppm), each ≤0.6% TRR (≤0.002 ppm).
SS1: Aqueous	N/R	N/R	N/A.
SS1: Solids	N/R	N/R	N/A.
SS2: Acid hydrolysate	17.2	0.057	Partitioned with EtOAc.
SS2: EtOAc	5.2	0.017	<u>HPLC analysis resolved:</u> 500M04 2.1% TRR 0.007 ppm 500M85 2.3% TRR 0.007 ppm Plus an additional 4 unknowns totaling 0.8% TRR (0.003 ppm), each ≤0.3% TRR (≤0.001 ppm).
SS2: Aqueous	N/R	N/R	N/A.
SS2: Solids	N/R	N/R	N/A.

^a Extraction of the third subsample of kidney did not yield additional information, and is not presented here.

Table 14b. Distribution of total radioactive residues in milk and tissues from lactating goats orally dosed with [tolyl-U-¹⁴C]pyraclostrobin at a feeding level of 12.2 ppm (low dose) or 70 ppm (high dose) in the diet.

Fraction ^a	% TRR	ppm	Characterization/Identification
Milk, Low Dose (TRR = 0.026 ppm)			
ACN	75.8	0.020	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 37.4% TRR 0.010 ppm Plus an additional 3 unknowns totaling 38.4% TRR (0.010 ppm), each ≤29.3 % TRR (≤0.008 ppm).
Hexane	4.5	0.001	Not further analyzed (N/A).
Nonextractable	17.5	0.005	N/A.
Milk, High Dose (TRR = 0.127 ppm)			
Organic extract	91.5	0.116	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 21.4% TRR 0.027 ppm 500M08 0.8% TRR 0.001 ppm 500M45 1.1% TRR 0.001 ppm 500M67 2.8% TRR 0.004 ppm Plus an additional 15 unknowns totaling 65.5% TRR (0.083 ppm), each ≤16.6% TRR (≤0.021 ppm).
Hexane	2.3	0.003	N/A.
Nonextractable	10.7	0.014	N/A.
Muscle, Low Dose (TRR = 0.022 ppm)			
Methanol	77.6	0.017	Partitioned with ACN and hexane.
Hexane	9.4	0.002	N/A.
ACN	65.6	0.014	<u>HPLC analysis resolved:</u> Pyraclostrobin 53.6% TRR 0.011 ppm 500M07 12.0% TRR 0.003 ppm
Methanol precipitate	3.5	<0.001	N/A.
Water	4.7	0.001	N/A.
Nonextractable	15.3	0.003	N/A.
Muscle, High Dose (TRR = 0.063 ppm)			
Methanol	83.4	0.053	<u>HPLC analysis resolved:</u> Pyraclostrobin 76.3% TRR 0.048 ppm 500M07 7.1% TRR 0.005 ppm
Nonextractable	18.9	0.012	N/A.
Fat, Low Dose (TRR = 0.082 ppm)			
ACN	94.2	0.077	<u>HPLC analysis resolved:</u> Pyraclostrobin 74.2% TRR 0.061 ppm 500M07 20.0% TRR 0.016 ppm
Hexane	5.8	0.005	N/A.
Nonextractable	10.5	0.009	N/A.
Fat, High Dose (TRR = 0.380 ppm)			

Table 14b (tolyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
ACN	98.8	0.376	<u>HPLC analysis resolved:</u> Pyraclostrobin 83.4% TRR 0.318 ppm 500M07 15.4% TRR 0.058 ppm
Hexane	1.9	0.007	N/A.
Nonextractable	2.7	0.010	N/A.
Liver, Low Dose (TRR = 0.383 ppm)			
Methanol extract 1	19.2	0.074	Combined with other methanol extracts.
Methanol precipitate 1	1.8	0.007	N/A.
Methanol extract 2	3.3	0.013	Combined with other methanol extracts.
Methanol precipitate 2	0.2	0.001	N/A.
Methanol extract 3	0.8	0.003	Combined with other methanol extracts.
Methanol precipitate 3	0.1	<0.001	N/A.
Combined methanol	23.1	0.088	Concentrated and partitioned with hexane and ACN.
Hexane	8.2	0.032	N/A.
ACN	12.4	0.048	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 1.4% TRR 0.006 ppm Plus an additional 14 unknowns totaling 11.0% TRR (0.042 ppm), each ≤2.3% TRR (≤0.009 ppm).
Water	2.5	0.010	N/A.
Nonextractable	74.6	0.286	N/A.
Liver, High Dose (TRR = 0.828 ppm) - 1st extraction			
Methanol	33.5	0.278	Partitioned with hexane and ACN.
Hexane	6.3	0.052	N/A.
ACN	24.9	0.203	<u>HPLC analysis resolved:</u> Pyraclostrobin 8.4% TRR 0.070 ppm 500M07 2.9% TRR 0.024 ppm 500M39 0.8% TRR 0.007 ppm 500M66 2.5% TRR 0.021 ppm 500M67 2.8% TRR 0.024 ppm Plus an additional 15 unknowns totaling 7.3% TRR (0.061 ppm), each ≤1.9% TRR (≤0.016 ppm).
Water	3.4	0.028	N/A.
Nonextractable	Not reported (N/R)	N/R	Split into two subsamples. SS1 subjected to pronase digestion. SS2 subjected to acid (HCl) hydrolysis.
SS1: pronase digestate	53.9	0.446	Partitioned with EtOAc.
SS1: EtOAc	1.2	0.010	N/A.
SS1: Aqueous	48.8	0.404	N/A.
SS1: Solids	N/R	N/R	N/A.
SS2: Acid hydrolysate	61.0	0.506	Partitioned with EtOAc.

Table 14b (tolyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
SS2: EtOAc	3.1	0.025	N/A.
SS2: Aqueous	54.1	0.448	N/A.
SS2: Solids	N/R	N/R	N/A.
Liver, High Dose (TRR = 1.013 ppm) - 2nd extraction ^b			
Methanol	34.4	0.349	Water added and mixture concentrated to remove methanol. Aqueous phase sequentially partitioned with hexane, DCM, DCM with formic acid, and EtOAc.
Hexane	21.5	0.218	N/A.
DCM	1.4	0.014	N/A.
Acidic DCM	2.3	0.024	N/A.
EtOAc	0.5	0.005	N/A.
Aqueous	3.4	0.035	N/A.
Water	2.9	0.030	N/A.
Nonextractable	67.3	0.381	Subjected to pronase digestion.
Digestate	50.5	0.511	Applied to C18 column which was washed with water and eluted with methanol and methanol with formic acid.
Filtrate	3.3	0.033	N/A.
Water wash	2.7	0.027	N/A.
Methanol	28.2	0.286	HPLC analysis resolved 9 unknowns, each $\leq 7.3\%$ TRR (≤ 0.074 ppm).
Acidic methanol	8.6	0.087	N/A.
Solids	19.8	0.200	N/A.
Kidney, Low Dose (TRR = 0.085 ppm)			
Methanol extract 1	43.3	0.037	Combined with other methanol extracts.
Methanol precipitate 1	1	0.001	N/A.
Methanol extract 2	5.9	0.005	Combined with other methanol extracts.
Methanol precipitate 2	0.2	<0.001	N/A.
Methanol extract 3	2.3	0.002	Combined with other methanol extracts.
Methanol precipitate 3	0.2	<0.001	N/A.
Combined methanol	47.0	0.040	Concentrated and partitioned with ACN and hexane.
ACN	34.2	0.029	HPLC analysis resolved: Pyraclostrobin + 500M07 8.8% TRR 0.007 ppm Plus an additional 6 unknowns totaling 25.4% TRR (0.022 ppm), each $\leq 6.7\%$ TRR (≤ 0.006 ppm).
Hexane	13.9	0.012	N/A.
Water	9.1	0.008	N/A.
Nonextractable	36.7	0.031	N/A.
Kidney, High Dose (TRR = 0.316 ppm) - 1st extraction			

Table 14b (tolyl label; continued).

Fraction ^a	% TRR	ppm	Characterization/Identification
Methanol extract 1	63.5	0.201	Combined with other methanol extracts.
Methanol extract 2	3.8	0.012	Combined with other methanol extracts.
Methanol extract 3	0.8	0.003	Combined with other methanol extracts.
Combined methanol	65.5	0.207	HPLC analysis resolved: Pyraclostrobin + 500M07 23.2% TRR 0.073 ppm 500M51 12.4% TRR 0.039 ppm 500M67 7.8% TRR 0.025 ppm Plus an additional 9 unknowns totaling 22.2% TRR (0.070 ppm), each $\leq 5.1\%$ TRR (≤ 0.016 ppm).
Nonextractable	44.5	0.141	N/A.
Kidney, High Dose (TRR = 0.316 ppm) - 2nd extraction			
Methanol	71.6	0.226	Water added and mixture concentrated to remove methanol. Aqueous phase sequentially partitioned with hexane, DCM, DCM with formic acid, and EtOAc.
Hexane	18.2	0.058	N/A.
DCM	5.2	0.016	N/A.
Acidic DCM	20.1	0.063	N/A.
EtOAc	3.4	0.011	N/A.
Aqueous	16.8	0.053	N/A.
Water	6.0	0.019	N/A.
Nonextractable	24.8	0.079	Subjected to pronase digestion.
Digestate	22.4	0.071	Applied to C18 column which was washed with water and eluted with methanol and methanol with formic acid.
Filtrate	3.3	0.010	N/A.
Water wash	2.2	0.007	N/A.
Methanol	11.1	0.035	HPLC analysis resolved 14 unknowns, each $\leq 1.5\%$ TRR (≤ 0.005 ppm).
Acidic methanol	4.1	0.013	N/A.
Solids	4.9	0.015	N/A.

^a Extraction of the third subsample of kidney did not yield additional information, and is not presented here.

^b The petitioner provided no explanation for the difference in TRR between the second liver extraction sample and the first.

Table 15a. Summary of radioactive residues characterized/identified in milk and edible tissues from a lactating goat dosed with [chlorophenyl-¹⁴C]pyraclostrobin at a feeding level of 78 ppm in the diet.

Fraction	Milk (TRR = 0.382 ppm)		Muscle (TRR = 0.117 ppm)		Fat (TRR = 0.928 ppm)		Liver (TRR = 1.505 ppm)		Kidney (TRR = 0.335 ppm)	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
Identified ^a										
Pyraclostrobin	17.4	0.067	76.2	0.089	88.2	0.819	1.4	0.021	22.1	0.074
500M07			8.1	0.010	8.8	0.082	1.5	0.022		
500M04	16.3	0.062	--	--	--	--	0.9	0.013	4.4	0.015
500M05	14.1	0.054	--	--	--	--	0.1	0.002	13.4	0.045
500M08	1.0	0.004	--	--	--	--	0.3	0.004	--	--
500M39	--	--	--	--	--	--	1.0	0.015	--	--
500M45	1.6	0.006	--	--	--	--	0.2	0.003	--	--
500M64	2.6	0.010	--	--	--	--	--	--	1.0	0.003
500M66	1.5	0.006	--	--	--	--	1.3	0.020	1.2	0.004
500M67	2.1	0.008	--	--	--	--	4.6	0.069	13.0	0.043
500M85	5.5	0.021	--	--	--	--	1.6	0.025	6.5	0.022
500M04 from acid hydrolysate	--	--	--	--	--	--	26.5	0.398	2.1 ^b	0.007
500M85 from acid hydrolysate	--	--	--	--	--	--	13.9	0.207	2.3 ^b	0.007
Total identified	62.1	0.237	84.3	0.099	97.0	0.901	53.3	0.799	66.0	0.217
Characterized										
Minor peaks, each <0.05 ppm	32.9	0.126	--	--	--	--	5.6	0.085	11.7	0.039
Hexane extract	0.9	0.003	--	--	1.5	0.014	6.0	0.091	--	--
Water extract	--	--	--	--	--	--	1.7	0.025	--	--
Hydrolysate aqueous phase	--	--	--	--	--	--	13.1	0.197	N/R	N/R
Total characterized/identified	95.9	0.366	84.3	0.099	98.5	0.915	79.7	1.197	77.7	0.256
Nonextractable	4.4	0.017	11.1	0.013	1.3	0.012	N/R ^c	N/R	N/R	N/R

^a See Figure 2 (Attachment II) for chemical structures of identified metabolites.

- ^b Acid hydrolysate of nonextractable residues from SS2 sample.
- ^c N/R = Not reported.

Table 15b. Summary of radioactive residues characterized/identified in milk and edible tissues from a lactating goat dosed with [tolyl-¹⁴C]pyraclostrobin at a feeding level of 70 ppm in the diet.

Fraction	Milk (TRR = 0.127 ppm)		Muscle (TRR = 0.063 ppm)		Fat (TRR = 0.380 ppm)		Liver (TRR = 0.828 ppm)		Kidney (TRR = 0.316 ppm)	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
Identified ^a										
Pyraclostrobin	21.4	0.027	76.3	0.048	83.4	0.318	8.4	0.070	23.2	0.073
500M07			7.1	0.005	15.4	0.058	2.9	0.024		
500M08	0.8	0.001	--	--	--	--	--	--	--	--
500M39	--	--	--	--	--	--	0.8	0.007	--	--
500M45	1.1	0.001	--	--	--	--	--	--	--	--
500M51	--	--	--	--	--	--	--	--	12.4	0.039
500M66	--	--	--	--	--	--	2.5	0.021	--	--
500M67	2.8	0.004	--	--	--	--	2.8	0.024	7.8	0.025
Total identified	26.0	0.033	83.4	0.053	98.8	0.376	17.4	0.145	43.3	0.137
Characterized										
Minor peaks, each <0.03 ppm	65.5	0.083	--	--	--	--	7.3	0.061	22.2	0.070
Hexane extract	2.3	0.003	--	--	1.9	0.007	6.3	0.052	--	--
Water extract	--	--	--	--	--	--	3.4	0.028	--	--
pronase digest	--	--	--	--	--	--	(53.9 ^b)	(0.446)	22.4 ^c	0.071
Acid hydrolysate	--	--	--	--	--	--	61.0 ^b	0.506	--	--
Total characterized/identified	93.8	0.119	83.4	0.053	100.7	0.383	95.4	0.792	87.9	0.278
Nonextractable	10.7	0.014	18.9	0.012	2.7	0.010	N/R ^d	N/R	4.9	0.015

^a See Figure 2 (Attachment II) for chemical structures of identified metabolites.

^b The nonextractable residues of liver were separately subjected to pronase digestion and acid hydrolysis; the acid hydrolysate is included in the total characterized/identified because it released higher residues than the pronase digestion. For the pronase digestate, only 1.2% TRR partitioned into EtOAc. For the acid hydrolysate, only 3.1% TRR partitioned into EtOAc. The aqueous fractions from the hydrolyses were not analyzed. Nonextractable residues from a second subsample of liver were subjected to pronase digestion, and the digestate was fractionated on a C18 column; the fraction containing the most radioactivity was analyzed by HPLC, however, no metabolites were identified.

- ^c Pronase digestate resulting from a second subsample of kidney. The digestate was fractionated on a C18 column, and the fraction containing the most radioactivity was analyzed by HPLC; however, no metabolites were identified.
- ^d N/R = Not reported.

Storage stability

Milk and tissue sample analyses were completed within 4-7 months of sample collection. Residues in milk from both labels were initially extracted and submitted for HPLC analysis <60 days after collection, and the extract was reanalyzed after ~5 months; HPLC patterns from the two analyses were similar. For high dose tolyl-label kidney, similar HPLC patterns were observed in the methanol extract obtained within 64 days of sampling and in that same extract after ~5 months of storage. In addition, the kidney sample was re-extracted and reanalyzed after 8.5 months of frozen storage; the HPLC analysis of the storage stability extract indicated that the metabolite profile was stable over the 8.5-month storage interval. These data are sufficient to support the storage intervals and conditions of samples from this study.

Proposed metabolic pathway in ruminants

Based on the results of the metabolism study, the petitioner proposed that pyraclostrobin may be metabolized in goats via three steps: (i) loss of the N-methoxy group yielding 500M07 (elsewhere referenced as BF 500-3); (ii) hydroxylation of the chlorophenyl, pyrazole, and/or tolyl ring system (500M08, 500M39, 500M45, 500M64, 500M66, and 500M67); and (iii) cleavage of the ether linkage (500M04 and 500M51) and subsequent oxidation of the resulting components (500M05).

Study summary

The submitted goat metabolism study adequately delineates the nature of the residue in ruminants. Following oral administration of [¹⁴C]pyraclostrobin, labeled in either the chlorophenyl ring or the tolyl ring, to lactating goats for 5 consecutive days at a feeding level of 12.2 ppm (~0.34x the maximum theoretical dietary burden, MTDB, for beef cattle and dairy cattle), the TRR were 0.013-0.058 ppm in milk, 0.018 and 0.022 ppm in muscle, 0.082 and 0.094 ppm in fat, 0.054 and 0.085 ppm in kidney, and 0.241 and 0.383 ppm in liver.

Following oral administration of [¹⁴C]pyraclostrobin to lactating goats for 5 consecutive days at feeding levels of 70 ppm (tolyl label) or 78 ppm (chlorophenyl label) (~2.2x the MTDB for beef cattle and dairy cattle), TRR were 0.051-0.659 ppm in milk, 0.063 and 0.117 ppm in muscle, 0.380 and 0.928 ppm in fat, 0.316 and 0.335 ppm in kidney, and 0.828 and 1.505 ppm in liver. Residue levels were generally comparable for the two labels. Residues in milk plateaued around 36 hours of the first dose (tolyl label).

Approximately 79-101% of the TRR were characterized/identified in the milk and tissues from the high-dose group. The parent, pyraclostrobin, was the major residue identified in muscle and fat, at 76.2-88.2% TRR (0.048-0.819 ppm). The parent was also identified in liver (1.4-8.4% TRR, 0.021-0.070 ppm) and in milk and kidney (17.4-23.2% TRR, 0.027-0.074 ppm). However, in milk and kidney, the parent was not resolved from the desmethoxy metabolite, 500M07 (elsewhere referenced as BF 500-3). Metabolite 500M07 was also identified in muscle, fat, and

liver, at 1.5-15.4% TRR (0.005-0.082 ppm). Additional major metabolites identified were 500M04 (in chlorophenyl-label milk at 16.3% TRR and in chlorophenyl-label kidney at 4.4% TRR), 500M05 (in chlorophenyl-label milk at 14.1% TRR and in chlorophenyl-label kidney at 13.4% TRR), 500M51 (in tolyl-label kidney at 12.4% TRR), and 500M67 (in kidney at 7.8-13.0% TRR and in milk at 2.1-2.8% TRR). Several additional metabolites were identified in milk, kidney, and liver, each at <6% TRR; see Figure 2 (Attachment II) for the chemical structures of identified metabolites.

Nonextractable residues in kidney and liver were further characterized by pronase digestion and acid hydrolysis. Pronase digestion released ~50% TRR in liver and ~20% TRR in kidney. In general, higher levels of residue were released by refluxing with hydrochloric acid. Acid hydrolysis released ~60% TRR in liver and ~17% TRR in kidney. The bound residues in chlorophenyl-label kidney and liver were converted to chlorophenylpyrazole derivatives with acid hydrolysis.

Poultry

BASF has submitted a study (citations listed below) pertaining to the metabolism of [¹⁴C]pyraclostrobin in hens. The in-life phase of the study was performed at BASF Aktiengesellschaft, Department of Toxicology, Ludwigshafen, Germany, and the analytical phase was conducted at BASF Agricultural Center, Limburgerhof, Germany.

45118434 Hafemann, C. and Knoell, K. (1999) Metabolism of ¹⁴C-BAS-500 F in Laying Hens. Laboratory Project Identification No. 35635; 1999/11480. Unpublished study submitted by BASF Corporation. 131 p.

45118435 Leibold, E.; Hoffmann, H.; and Hildebrand, B. (1998) ¹⁴C-BAS-500 F - Absorption, Distribution and Excretion After Repeated Oral Administration to Laying Hens. Laboratory Project Identification No. 02B0363/966023; 1998/10637. Unpublished study submitted by BASF Corporation. 46 p.

The study was conducted using [chlorophenyl-U-¹⁴C]pyraclostrobin [specific activity 4.14 Mbq/mg (248,400 dpm/μg) and radiochemical purity >98%] and [tolyl-U-¹⁴C]pyraclostrobin [specific activity 4.46 Mbq/mg (267,600 dpm/μg) and radiochemical purity >98%]. The test substances were isotopically diluted with non-labeled pyraclostrobin to final specific activities of 45,870 dpm/μg for the chlorophenyl label and 53,652 dpm/μg for the tolyl label. For each label, 11 hens were dosed orally (by gavage) once a day, following morning egg collection, for 7 consecutive days. The dosing rates were equivalent to 12.14 ppm (chlorophenyl label) and 12.72 ppm (tolyl label) in the diet, based on actual feed consumption. The feeding levels are equivalent to 35-36x the maximum theoretical dietary burden (0.30 ppm) to poultry; see "Meat, Milk, Poultry, Eggs" for calculation of dietary burden. The petitioner did not mention establishment of experimental controls (untreated hens) for the study.

During the study, the hens were fed a commercial pelleted feed and received water, containing a vitamin mix, *ad libitum*. The petitioner provided sufficient descriptions of preparation of dose solutions and animal husbandry practices, as well as data concerning daily feed intake, body weights, and egg production.

Eggs were collected twice daily, and were refrigerated for up to 2 days prior to transport to the analytical laboratory. The hens were sacrificed 23 hours after the last dose, and liver, kidney, breast and leg muscle, and fat were sampled. Tissue samples were stored at 0 C during transport to the analytical laboratory. At the laboratory, egg and tissue samples were stored frozen (temperature unspecified) prior to analysis.

Total radioactive residues (TRR)

Egg and tissue samples were homogenized, and total radioactive residues (TRR) were determined by LSC following combustion (all matrices except fat) or tissue solubilization (fat). The TRR in egg and tissues are presented in Table 16. The LODs for the radioassay were 0.00014-0.00015 ppm for fat, 0.00019-0.00021 ppm for eggs, 0.00060-0.00065 ppm for muscle, and 0.00165-0.00178 ppm for liver.

Table 16. Total radioactive residues in eggs and tissues from hens dosed for 7 days with [¹⁴C]pyraclostrobin at 12.14 ppm (chlorophenyl label) or 12.72 ppm (tolyl label).

Matrix	TRR, ppm [¹⁴ C]pyraclostrobin equivalents	
	Chlorophenyl label	Tolyl label
Eggs		
Day 1	0.004	0.002
Day 2	0.007	0.006
Day 3	0.010	0.011
Day 4	0.016	0.017
Day 5	0.022	0.028
Day 6	0.025	0.033
Day 7	0.029	0.037
Composited sample (Days 5-7) used for characterization	0.026	0.031
Liver	0.317	0.474
Muscle	0.007	0.009
Fat	0.083	0.065

TRR in eggs did not reach a plateau during the study. The highest levels of radioactivity were found in liver, at 0.317 and 0.474 ppm, respectively, for the chlorophenyl and tolyl labels. Overall, the TRR concentrations were comparable for the two labels.

Composite samples of excreta were collected during the study. Radioactivity determinations on these samples indicated that a large portion of the dosed radioactivity was excreted: 93.3% for the chlorophenyl label and 86.59% for the tolyl label.

Extraction and characterization of ¹⁴C-residues

Samples of liver, fat, and eggs were subjected to extraction and hydrolysis procedures for residue characterization and identification. Muscle samples were not extracted because the TRR were <0.010 ppm. The petitioner provided adequate descriptions of the fractionation procedures for each matrix. During the extraction and fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for radioactivity by LSC or combustion/LSC. The general extraction and fractionation procedures are summarized below.

Radioactive residues in liver were sequentially extracted with ACN (3x) and water (2x), and centrifuged. The ACN phase was partitioned with hexane, and the resulting hexane phase was back-partitioned with ACN. The ACN phases were combined and reserved for HPLC analysis. Nonextractable residues were subjected to digestion with pronase (in TRIS, pH 7.3, at 37 C for 16.25 h), and the solubilized residues were applied to an XAD-4 column which was sequentially eluted with water, methanol, 1% formic acid in methanol, and methanol:formic acid (1:1, v:v). The water and methanol eluates were separately combined and reserved for HPLC analysis.

Residues in eggs (composite of samples from Days 5-7) were extracted with ACN, and the ACN phase was partitioned (3x) with hexane. The ACN phases were combined and reserved for HPLC analysis.

Residues in fat were sequentially extracted with ACN:hexane (1:1, v:v; 3x), ACN (1x), and water (2x). The ACN, hexane, and water extracts were separately combined, and the ACN extract was reserved for HPLC analysis.

The distribution of ¹⁴C-activity in the extracts and hydrolysates of eggs and tissues is presented in Tables 17a (chlorophenyl label) and 17b (tolyl label).

Characterization and identification of residues

Egg, liver, and fat extracts were analyzed by HPLC using a PRP1 or ODS column and a gradient mobile phase of water, ACN, and formic acid, or water, methanol, and formic acid. Radioactivity was detected and quantified using a radioactivity monitor. Metabolites were identified by comparison of retention times and/or co-chromatography with radioactive standards of pyraclostrobin and 500M07 (elsewhere referenced as BF 500-3) or with components identified

from excreta (500M04, 500M64, 500M66, and 500M77). Residues were extracted from excreta with methanol and ACN and fractionated by HPLC. Radioactive fractions were purified by HPLC, and the structures of the isolated compounds were elucidated using HPLC/MS and HPLC/MS/MS. NMR spectroscopy was used to verify the MS results and to determine the position of hydroxy substituents. Additional elucidation was obtained by NMR analysis of molecular fragments formed during acid reflux of residues in the excreta.

Metabolites 500M39, 500M83, and 500M06 were isolated from liver extracts (tolyl label) and identified by MS. Metabolite 500M32, a glucuronic acid conjugate, was isolated from liver slices incubated with [tolyl-¹⁴C]pyraclostrobin and identified by HPLC/MS and HPLC/MS/MS.

In an attempt to further characterize bound liver residues, nonextractable residues (containing 34.6% TRR, 0.110 ppm) obtained from a second subsample of chlorophenyl-label liver were hydrolyzed with 5 M HCl (at reflux for 2 h). Hydrolysis released 26.3% TRR (0.083 ppm), of which 11.4% TRR (0.036 ppm) could be partitioned into EtOAc. HPLC analysis of the EtOAc extract indicated the presence of 1-(4-hydroxy-3-chlorophenyl)-3-hydroxypyrazol (BF500-9), suggesting residues were covalently linked to proteins.

A summary of the characterized and identified ¹⁴C-residues in poultry matrices is presented in Tables 18a (chlorophenyl label) and 18b (tolyl label).

Table 17a. Distribution of total radioactive residues in egg and tissues from laying hens orally dosed with [chlorophenyl-U-¹⁴C]pyraclostrobin at a feeding level of 12.14 ppm in the diet.

Fraction	% TRR	ppm	Characterization/Identification
Egg, Days 5-7 (TRR = 0.026 ppm)			
ACN	66.2	0.017	Partitioned with hexane.
ACN	62.1	0.016	<u>HPLC analysis resolved:</u> Pyraclostrobin 8.8% TRR 0.002 ppm 500M04 3.1% TRR 0.001 ppm 500M64 2.6% TRR 0.001 ppm 500M07 (BF 500-3) 11.2% TRR 0.003 ppm Plus an additional 7 unknowns totaling 36.5% TRR (0.010 ppm), each ≤ 15.2 % TRR (≤ 0.004 ppm).
Hexane	4.1	0.001	Not further analyzed (N/A).
Nonextractable	38.5	0.010	N/A.
Fat (TRR = 0.083 ppm)			
ACN	69.4	0.057	<u>HPLC analysis resolved:</u> Pyraclostrobin 10.2% TRR 0.008 ppm 500M04 2.7% TRR 0.002 ppm 500M64 10.8% TRR 0.009 ppm 500M77 1.8% TRR 0.001 ppm 500M07 (BF 500-3) 27.3% TRR 0.022 ppm Plus an additional 8 unknowns totaling 16.6% TRR (0.014 ppm), each ≤ 3.9% TRR (≤ 0.003 ppm).
Hexane	26.7	0.022	N/A.
Water	3.3	0.003	N/A.
Nonextractable	1.8	0.002	N/A.
Liver (TRR = 0.317 ppm)			
ACN	42.8	0.136	Partitioned with hexane.
Hexane	0.5	0.002	N/A.
ACN	42.7	0.135	<u>HPLC analysis resolved:</u> 500M39 1.0% TRR 0.003 ppm 500M83 4.5% TRR 0.014 ppm 500M32 10.9% TRR 0.035 ppm 500M06 4.1% TRR 0.013 ppm 500M04 1.4% TRR 0.004 ppm 500M64 2.8% TRR 0.009 ppm 500M77 1.8% TRR 0.006 ppm 500M66 3.8% TRR 0.012 ppm Plus an additional 13 unknowns totaling 12.4% TRR (0.038 ppm), each ≤ 2.7% TRR (≤ 0.008 ppm).
Water	8.7	0.027	N/A.
Nonextractable	42.7	0.136	Subjected to pronase digestion.

Table 17a (*chlorophenyl label; continued*).

Fraction	% TRR	ppm	Characterization/Identification
Digestate	15.1	0.048	Applied to XAD-4 column and sequentially eluted with water, methanol, 1% formic acid in methanol, and methanol:formic acid (1:1, v:v). Water and methanol eluates were separately combined.
Combined water eluates	6.6	0.021	N/A.
Combined methanol eluates	7.9	0.025	HPLC analysis was conducted, which indicated the presence of 5 peaks. Two peaks were tentatively identified as 500M04 and 500M64, however, no quantitative data were provided.
Digested solids	24.5	0.078	N/A.

Table 17b. Distribution of total radioactive residues in egg and tissues from laying hens orally dosed with [tolyl-U-¹⁴C]pyraclostrobin at a feeding level of 12.72 ppm in the diet.

Fraction	% TRR	ppm	Characterization/Identification
Egg, Days 5-7 (TRR = 0.031 ppm)			
ACN	54.0	0.017	Partitioned with hexane.
ACN	50.6	0.016	HPLC analysis resolved: Pyraclostrobin 8.5% TRR 0.003 ppm 500M39 1.3% TRR <0.001 ppm 500M49 0.7% TRR <0.001 ppm 500M06 2.6% TRR 0.001 ppm 500M64 1.9% TRR 0.001 ppm 500M77 0.2% TRR <0.001 ppm 500M07 (BF 500-3) 8.3% TRR 0.003 ppm Plus an additional 11 unknowns totaling 27.0% TRR (0.008 ppm), each ≤8.4 % TRR (≤0.003 ppm).
Hexane	4.8	0.001	Not further analyzed (N/A).
Nonextractable	46.0	0.014	N/A.
Fat (TRR = 0.065 ppm)			
ACN	76.1	0.049	HPLC analysis resolved: Pyraclostrobin 15.2% TRR 0.010 ppm 500M49 1.7% TRR 0.001 ppm 500M64 7.8% TRR 0.005 ppm 500M77 2.3% TRR 0.001 ppm 500M07 (BF 500-3) 38.9% TRR 0.025 ppm Plus an additional 4 unknowns totaling 10.2% TRR (0.005 ppm), each ≤3.8% TRR (≤0.002 ppm).
Hexane	14.2	0.009	N/A.
Water	5.2	0.003	N/A.
Nonextractable	2.8	0.002	N/A.
Liver (TRR = 0.474 ppm)			
ACN	46.0	0.218	Partitioned with hexane.
Hexane	0.6	0.003	N/A.
ACN	47.8	0.227	HPLC analysis resolved: 500M39 0.4% TRR 0.002 ppm 500M49 7.5% TRR 0.036 ppm 500M83 4.2% TRR 0.020 ppm 500M32 13.1% TRR 0.062 ppm 500M06 5.0% TRR 0.024 ppm 500M64 7.3% TRR 0.034 ppm 500M77 1.9% TRR 0.009 ppm 500M66 1.9% TRR 0.009 ppm 500M80 0.6% TRR 0.003 ppm Plus an additional 4 unknowns totaling 6.0% TRR (0.029 ppm), each ≤3.7% TRR (≤0.018 ppm).
Water	5.8	0.028	N/A.

Table 17b (tolyl label; continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable	47.5	0.225	Subjected to pronase digestion.
Digestate	20.7	0.098	The petitioner concluded that these results indicate that a significant portion of the bound residues were protein bound.
Digested solids	7.8	0.037	N/A.

Table 18a. Summary of radioactive residues characterized/identified in eggs and edible tissues from laying hens dosed with [chlorophenyl-¹⁴C]pyraclostrobin at a feeding level of 12.14 ppm in the diet.

Fraction	Eggs (TRR = 0.026 ppm)		Fat (TRR = 0.083 ppm)		Liver (TRR = 0.317 ppm)	
	%TRR	ppm	%TRR	ppm	%TRR	ppm
Identified ^a						
Pyraclostrobin	8.8	0.002	10.2	0.008	--	--
500M04	3.1	0.001	2.7	0.002	1.4	0.004
500M06	--	--	--	--	4.1	0.013
500M07 (BF 500-3)	11.2	0.003	27.3	0.022	--	--
500M32	--	--	--	--	10.9	0.035
500M39	--	--	--	--	1.0	0.003
500M64	2.6	0.001	10.8	0.009	2.8	0.009
500M66	--	--	--	--	3.8	0.012
500M77	--	--	1.8	0.001	1.8	0.006
500M83	--	--	--	--	4.5	0.014
Total identified	25.7	0.007	52.8	0.042	30.3	0.096
Characterized						
Minor peaks, each ≤0.008 ppm	36.5	0.010	16.6	0.014	12.4	0.038
Hexane extract	4.1	0.001	26.7	0.022	0.5	0.002
Water extract	--	--	3.3	0.003	8.7	0.027
Pronase - methanol extract	--	--	--	--	7.9	0.025
Pronase - aqueous extract	--	--	--	--	6.6	0.021
Total characterized/identified	66.3	0.018	99.4	0.081	66.4	0.209
Nonextractable	38.5	0.010	1.8	0.002	24.5	0.078

^a See Figure 2 (Attachment II) for chemical structures of identified metabolites.

Table 18b. Summary of radioactive residues characterized/identified in eggs and edible tissues from laying hens dosed with [tolyl-¹⁴C]pyraclostrobin at a feeding level of 12.72 ppm in the diet.

Fraction	Eggs (TRR = 0.031 ppm)		Fat (TRR = 0.065 ppm)		Liver (TRR = 0.474 ppm)	
	%TRR	ppm	%TRR	ppm	%TRR	ppm
Identified ^a						
Pyraclostrobin	8.5	0.003	15.2	0.010	--	--
500M06	2.6	0.001	--	--	5.0	0.024
500M07 (BF 500-3)	8.3	0.003	38.9	0.025	--	--
500M32	--	--	--	--	13.1	0.062
500M39	1.3	<0.001	--	--	0.4	0.002
500M49	0.7	<0.001	1.7	0.001	7.5	0.036
500M64	1.9	0.001	7.8	0.005	7.3	0.034
500M66	--	--	--	--	1.9	0.009
500M77	0.2	<0.001	2.3	0.001	1.9	0.009
500M80	--	--	--	--	0.6	0.003
500M83	--	--	--	--	4.2	0.020
Total identified	23.5	0.008	65.9	0.042	41.9	0.199
Characterized						
Minor peaks, each ≤0.018 ppm	27.0	0.008	10.2	0.005	6.0	0.029
Hexane extract	4.8	0.001	14.2	0.009	0.6	0.003
Water extract	--	--	5.2	0.003	5.8	0.028
Pronase digest	--	--	--	--	20.7	0.098
Total characterized/identified	55.3	0.017	95.5	0.059	75.0	0.357
Nonextractable	46.0	0.014	2.8	0.002	7.8	0.037

^a See Figure 2 (Attachment II) for chemical structures of identified metabolites.

Storage stability

Liver, fat, and egg samples were stored for 7-8 months prior to extraction, and analyses were completed within 11 months of sample collection. The petitioner stated that samples were subjected to preliminary extraction and analysis procedures within 1 month of collection. To demonstrate storage stability, the petitioner re-extracted and reanalyzed samples of liver that had been stored frozen for 7 months and samples of egg and excreta that had been stored frozen for 21-23 months and compared the results to those for the initial extraction. The percentages of TRR in the extracts and the nonextractable fractions were similar for the two intervals. In addition, HPLC results from extracts of stored samples showed similar metabolite profiles to those from the initial analyses. These results indicate that the metabolite profiles were stable in poultry matrices over the course of the study.

Proposed metabolic pathway in poultry

Based on the results of the metabolism study, the petitioner proposed that pyraclostrobin may be metabolized in poultry via one of five routes: (i) loss of the nitrogen methoxy group (500M07; otherwise known as BF 500-3); (ii) addition of a hydroxy group to the tolyl ring of the demethoxylated parent (500M64) followed by conjugation with glucuronic acid (500M32); (iii) hydroxylation of the demethoxylated parent at the chlorophenyl or pyrazol ring (500M80 or 500M39) followed by conjugation with glucuronic acid (500M06); (iv) hydroxylation of the chlorophenyl ring at the para position and shifting of the chloro substituent to the meta position (500M77); and (v) cleavage of the parent compound at the ether linkage (500M04 and 500M49). In addition, one metabolite (500M83) was observed which indicated metabolism via substitution of the chloro substituent in the demethoxylated parent with glucuronic acid.

Study summary

The submitted hen metabolism study adequately delineates the nature of the residue in poultry. Following oral administration of [¹⁴C]pyraclostrobin, labeled in either the chlorophenyl ring or the tolyl ring, to laying hens for 7 consecutive days at a feeding level of 12-13 ppm (~40x the maximum theoretical dietary burden for poultry), the TRR were 0.002-0.037 ppm in eggs, 0.007 and 0.009 ppm in muscle, 0.065 and 0.083 ppm in fat, and 0.317 and 0.474 ppm in liver. Residue levels were comparable for the two labels. Residues in eggs gradually increased during the study and had not reached a plateau at the time of sacrifice.

Approximately 55-99% of the TRR were characterized/identified in eggs, fat, and liver; muscle samples were not analyzed because TRR levels were <0.010 ppm. The parent, pyraclostrobin, was identified in eggs (8.5-8.8% TRR, 0.002-0.003 ppm) and fat (10.2-15.2% TRR, 0.008-0.010 ppm) but was not identified in liver. Metabolite 500M07 (BF 500-3) was a major metabolite identified in eggs (8.3-11.2% TRR, 0.003 ppm) and fat (27.3-38.9% TRR, 0.022-0.025 ppm); it was not identified in liver. The major metabolite identified in liver was 500M32, a glucuronide conjugate, at 10.9-13.1% TRR (0.035-0.062 ppm); this metabolite was not identified in eggs or

fat. Several additional metabolites were identified in eggs, fat, and liver, each at <10% TRR; see Figure 2 (Attachment II) for the chemical structures of identified metabolites.

In liver, a large portion of the TRR remained bound after initial extractions (43-48% TRR). A significant portion of this radioactivity (15-21% TRR) was released following pronase digestion, indicating that a large portion of the nonextractable residues were protein bound. HPLC analysis of the digestate (chlorophenyl label) indicated the presence of 500M04 and 500M64, however, no quantitative data were provided.

OPPTS GLN 860.1340: Residue Analytical Method - Plant Commodities

Enforcement analytical methods - plant commodities

BASF has proposed two methods, LC/MS/MS method D9808 (U.S.) or 421/0 (Germany), and HPLC/UV method D9904, for the enforcement of tolerances for residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 in/on plant commodities. The LC/MS/MS method was used as the data collection method in the residue field trials. The petitioner has submitted method descriptions and validation data (citations listed below) for the proposed enforcement methods.

45118436 Reinhard, K.; Mackenroth, C. (1999) Validation of BASF Method No. 421/0 (Germany)/D9808 (USA): Determination of BAS 500 F and its Metabolite BF 500-3 in wheat, grape, peanut, and orange matrices. Laboratory Project Identification Number 35509; BASF Registration Document Number 1999/11134. Unpublished study prepared by BASF Corporation. 114 p.

45118437 Abdel-Baky, S.; Riley, M. (2000) Validation of BASF Analytical Method D9904, Method for Determination of BAS 500 F and its Metabolite BF 500-3 Residues in Plant Matrices Using HPLC/UV. BASF Study Number 63770; BASF Registration Document Number 1999/5179. Unpublished study prepared by BASF Corporation. 105 p.

45118504 Wilkinson, D.; Jones, J.; Abdel-Bakey, S. et al. (1999) Technical Procedure: Method for Determination of BAS 500 F and its Metabolite BF 500-3 Residues in Plant Matrices using LC/MS/MS. BASF Method Number D9808 (USA), 421/0 (Germany). BASF Registration Document Number 1999/5106. Unpublished study prepared by BASF Corporation and BASF Aktiengesellschaft. 35 p.

45118505 Jones, J.; Abdel-Bakey, S. (1999) Technical Procedure: Method for Determination of BAS 500 F and its Metabolite BF 500-3 Residues in Plant Matrices using HPLC/UV. BASF Method Number D9904. BASF Registration Document Number 1999/5185. Unpublished study prepared by BASF Corporation. 27 p.

For the **LC/MS/MS** method, homogenized crop samples (except peanut nutmeat and oil samples) are extracted with methanol:water (7:3, v:v) and filtered. An aliquot of the extract is removed, diluted with water, and concentrated to complete dryness. Residues are redissolved in methanol:water (7:3, v:v) and subjected to C18 Polar Plus® micro-column chromatography. Residues are eluted from the C18 micro-column with dichloromethane (DCM) under vacuum and the eluates are evaporated to complete dryness. If further cleanup is required, the dried residues are then reconstituted in DCM:hexane (2:8, v:v) and applied to a micro silica column. Residues are eluted from the micro silica column with ethyl acetate:DCM (2:98, v:v) under vacuum, and the eluate is evaporated to complete dryness. Residues are dissolved in methanol:buffer solution (99.9% 4 mM ammonium formate in water and 0.1% formic acid) (8:2, v:v) for LC/MS/MS analysis.

Peanut nutmeat samples are initially homogenized with acetonitrile (ACN), hexane is added, and the mixture is homogenized again. Following filtration of the extract, the filtrate is transferred to a separatory funnel. The hexane phase is discarded, and the ACN phase is partitioned again with additional hexane. The ACN phase is evaporated to complete dryness and reconstituted in methanol:water (7:3, v:v) for C18 micro-column cleanup as described above.

For oil crop matrices, residues are partitioned between hexane and ACN. The hexane phase is discarded, and the ACN phase is partitioned with additional hexane. The ACN phase is evaporated to complete dryness and reconstituted in methanol:water (7:3, v:v) for C18 micro-column cleanup as described above.

The petitioner recommends that the following matrices be subjected to both C18 and silica micro-column chromatography for cleanup of residues: forage (barley, dry pea, and wheat), hay (barley, peanut, and wheat), straw (barley and wheat), orange, onion, and peanut (nutmeat and oil). All other plant matrices (barley and wheat grain, grape, raisins, grape juice, dry pea and lentil seeds, tomato, potato, cucurbits, sugarcane, and banana) typically only require cleanup using the C18 micro-column. For quantitation, the product/daughter ion for the transition m/z 388 → 194 for pyraclostrobin and m/z 358 → 164 for BAS 500-3 are measured. The reported method LOQs for pyraclostrobin and BF 500-3 are 0.02 ppm each for all plant matrices.

For the **HPLC/UV** method, plant matrices are extracted and cleaned up by C18 micro-column and/or silica micro-column chromatography as described above for the LC/MS/MS method, and residues of pyraclostrobin and its metabolite BF 500-3 are quantitated by HPLC/UV with column switching. HPLC analysis is conducted using a UV detector at 276 nm and one of two systems: a Luna phenyl hexyl column with a gradient mobile phase of ACN:methanol:water, and a Betasil 5 C18 column with an isocratic mobile phase of ACN:methanol:water (45:10:45, v:v:v). The

reported LOQs are 0.02 ppm each for residues of pyraclostrobin and BF 500-3 in plant matrices. The petitioner stated that residues determined using one HPLC system may be confirmed using the other system.

Method validations of the LC/MS/MS and HPLC/UV methods were conducted on six representative plant matrices: grape, orange, peanut (nutmeat), and wheat forage, grain, and straw. Samples of untreated grape, orange, peanut nutmeat, and wheat forage, grain, and straw, obtained commercially for validation of the LC/MS/MS method and obtained from U.S. field trials for validation of the HPLC/UV method, were fortified with pyraclostrobin and BF 500-3 each at 0.02 ppm (LOQ), 0.2 ppm (10x LOQ), and/or 2.0 ppm (100x LOQ). Unfortified and fortified samples were analyzed using either the LC/MS/MS method D9808 (421/0) or HPLC/UV method D9904. Method validation recoveries are reported in Table 19; method recoveries were corrected for interferences from matrix compounds. Apparent residues of pyraclostrobin and BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on two samples each of unfortified grape, orange, peanut nutmeat, and wheat forage, grain, and straw analyzed by the LC/MS/MS method. Apparent residues of pyraclostrobin and BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on two samples each of unfortified grape, orange, peanut nutmeat, and wheat forage, grain, and straw analyzed by the HPLC/UV method. (Inspection of the chromatograms for the controls used in the HPLC/UV and D9808 methods showed negligible background or interfering peaks.)

Table 19. Method validation recoveries of residues of pyraclostrobin and BF 500-3 from fortified samples of plant commodities analyzed using the LC/MS/MS method D9808 (421/0) or HPLC/UV method D9904.

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin	BF 500-3
LC/MS/MS Method D9808 (421/0)				
Grape (45118436)	0.02, 2.0	Average (%)	91.8	90.7
		Recovery range (%)	87.5-99.5	85.4-100.5
		SD (%)	4.4	5.3
		Number of samples	10	10
Orange (45118436)	0.02, 0.2	Average (%)	81.6	78.3
		Recovery range (%)	72.1-92.1	68.0; 73.2-87.6
		SD (%)	6.6	6.3
		Number of samples	10	10
Peanut, nutmeat (45118436)	0.02, 0.2	Average (%)	83.7	80.6
		Recovery range (%)	73.6-95.0	71.7-90.4
		SD (%)	8.4	7.2
		Number of samples	10	10
Wheat, forage (45118436)	0.02, 2.0	Average (%)	93.0	91.2
		Recovery range (%)	88.4-98.9	87.2-97.9
		SD (%)	3.1	3.3
		Number of samples	10	10
Wheat, grain (45118436)	0.02, 0.2	Average (%)	83.4	81.2
		Recovery range (%)	73.7-93.6; 137.2 ^b	73.3-91.3
		SD (%)	8.5	6.5
		Number of samples	10	10
Wheat, straw (45118436)	0.02, 2.0	Average (%)	81.4	74.8
		Recovery range (%)	74.6-90.4	66.8; 73.0-84.9
		SD (%)	4.9	4.5
		Number of samples	10	10
HPLC/UV Method D9904				
Grape (45118437)	0.02, 2.0	Average (%)	105	87
		Recovery range (%)	82-119; 124	56; 77-103
		SD (%)	15	13
		Number of samples	10	10

Table 19 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin	BF 500-3
Orange (45118437)	0.02, 2.0	Average (%)	97	96
		Recovery range (%)	72-115	66; 80-120
		SD (%)	12	14
		Number of samples	10	10
Peanut, nutmeat (45118437)	0.02, 2.0	Average (%)	104	84
		Recovery range (%)	94-113	70-90
		SD (%)	6	7
		Number of samples	10	10
Wheat, forage (45118437)	0.02, 2.0	Average (%)	98	89
		Recovery range (%)	91-103	83-99
		SD (%)	4	5
		Number of samples	10	10
Wheat, grain (45118437)	0.02, 2.0	Average (%)	94	83
		Recovery range (%)	68; 74-119	54, 65; 73-108
		SD (%)	16	16
		Number of samples	9	9
Wheat, straw (45118437)	0.02, 2.0	Average (%)	93	89
		Recovery range (%)	77-104	69; 75-111
		SD (%)	9	15
		Number of samples	10	10

^a Recoveries outside the acceptable 70-120% range are listed separately.

^b The petitioner indicated that high recovery was probably due to contamination; this value was not included in calculation of the mean and standard deviation.

Independent laboratory validation

BASF submitted data (citations listed below) from independent laboratory validation (ILV) trials for both of the proposed tolerance enforcement methods (LC/MS/MS method D9808 (421/0) and HPLC/UV method D9904) for plant matrices.

45118501 Jordan, J. (2000) Independent Method Validation of BASF Analytical Method D9904 Entitled "Method for the Determination of BAS 500 F and its Metabolite BF 500-3 Residues in Plant Matrices Using HPLC-UV." BASF Study No. 64058. BASF Document No. 1999/5184. Unpublished study prepared by BASF Corporation. 68 p.

45118503 Perez, R.; Perez, S. (2000) Independent Method Validation of BASF Method Numbers D9808 (USA) and 421/0 (Germany) Entitled "Method for Determination of BAS 500 F and its Metabolite BF 500-3 Residues in Plant Matrices Using LC/MS/MS." BASF Study No. 63832. Unpublished study prepared by BASF Corporation. 96 p.

The ILV of the LC/MS/MS method was performed by ADPEN Laboratories, Inc. (Jacksonville, FL), and the ILV of the HPLC/UV method was performed by BASF, Agricultural Products Center (APC; Research Triangle Park, NC) by chemists unfamiliar with the method or its development. Untreated homogenized samples of grapes and wheat straw supplied by BASF were used for both studies; grapes and wheat straw were chosen as representative difficult matrices. Five subsamples each of untreated grape and wheat straw were fortified with pyraclostrobin and BF 500-3 each at the LOQ (0.02 ppm) and at the proposed tolerance levels of 2.0 ppm for grapes and 6.0 ppm for wheat straw; we note that the proposed tolerance for wheat straw has since been increased to 8.5 ppm. Fortified and unfortified grape and wheat straw samples were analyzed for residues of pyraclostrobin and BF 500-3 using either the LC/MS/MS method D9808 (421/0) or HPLC/UV method D9904 (described above).

Using the LC/MS/MS method, acceptable validation recoveries were obtained with the first attempt for pyraclostrobin and BF 500-3 in grapes at both fortification levels; however, unacceptable validation recoveries were obtained with the first attempt for pyraclostrobin and BF 500-3 in wheat straw. Following communication between ADPEN Laboratories and BASF, it was concluded that low and variable recoveries were probably due to poor extraction efficiency. Wheat straw samples were subsequently extracted with a larger volume of methanol:water, and two to three methanol:water rinses were made to the pellet remaining following filtration. In addition, because signal suppression had been reported for pyraclostrobin and BF 500-3, the laboratory included a suppression check sample with the second attempt; a control sample was run through the extraction procedure and fortified with standard at the final dilution step. Recoveries were better for both pyraclostrobin and BF 500-3 with the second attempt; however, recoveries were still not acceptable at the LOQ (0.02 ppm) fortification level. Signal suppression effects due to the matrix were determined to be the cause; a 10-fold dilution of the samples and standards eliminated the interference. Acceptable recoveries were obtained from re-injection of the second attempt samples (fortified at the LOQ) following a 10-fold dilution. The results of the ILV study are shown in Table 20. Apparent residues of pyraclostrobin and BF 500-3 were less than the method LOQ (0.006 ppm or less) in control samples of grape and wheat straw from all trials. The laboratory indicated that 8 person hours were required to extract one complete set of 12 samples. Representative sample calculations and chromatograms were provided.

Using the HPLC/UV method, acceptable validation recoveries were obtained with the first attempt for pyraclostrobin and BF 500-3 in grapes and wheat straw at both fortification levels. To represent a worse case, both grape and wheat straw samples were subjected to C18 SPE micro-column and silica SPE micro-column chromatography for clean-up. The laboratory noted that washing down the sides of the flask in the final step to ensure quantitative transfer of residues, and the calibration/adjustment of the column switching window were critical steps of

the method. The results of the ILV study are shown in Table 20. Apparent residues of pyraclostrobin and BF 500-3 were less than the method LOQ (ave of 0.005 ppm or less) in control samples of grape and wheat straw. The laboratory reported that working slowly and methodically as required for an independent validation, one analyst prepared the samples in 8 hours (or 1 day); analysis required 2 additional hours. Representative sample calculations and chromatograms were provided.

Table 20. Independent method validation recoveries of pyraclostrobin and BF 500-3 from fortified grape and wheat straw untreated samples analyzed using the proposed LC/MS/MS or HPLC/UV tolerance enforcement methods.

Matrix	Fortification Level, ppm	Percent Recovery	
		Pyraclostrobin	BF 500-3
LC/MS/MS Method D9808 (421/0)			
Grape Trial #1	0.02	76.6, 86.5, 89.4, 89.9, 90.6	73.9, 78.1, 78.9, 82.4, 82.8
	2.0	98.3, 98.3, 100.9, 104.0, 104.6	91.9, 97.0, 97.2, 97.3, 99.7
	Mean ± s.d.	93.9 ± 8.9	87.9 ± 9.7
Wheat Straw Trial #1	0.02	36.2, 38.1, 41.7, 45.6, 72.7	18.8, 19.2, 22.0, 36.4, 57.2
	6.0	70.0, 70.5, 75.4, 91.7, 116.4	68.0, 68.5, 70.3, 88.4, 121.1
	Mean ± s.d.	65.8 ± 25.9	57.0 ± 33.4
Wheat Straw Trial #2	0.02	60.2, 61.3, 66.3, 67.9, 79.1	41.9, 42.0, 43.3, 51.1, 72.8
	0.02; 10-fold dilution	81.5, 83.6, 88.1, 95.9, 107.3	68.8, 69.4, 71.0, 83.8, 110.4
	6.0	79.6, 85.9, 86.5, 89.0, 89.8	83.7, 84.9, 85.1, 85.9, 89.6
	Mean ± s.d. ^a	81.5 ± 13.0	72.2 ± 20.1
HPLC/UV Method D9904			
Grape Trial #1	0.02	68.8, 75.8, 78.8, 91.8, 108.8	69.0, 70.3, 73.8, 80.8, 82.8
	2.0	84.1, 87.8, 91.7, 93.0, 97.1	76.3, 81.7, 83.2, 85.4, 91.5
	Mean ± s.d. ^b	87.8 ± 11.5	79.5 ± 7.1
Wheat Straw Trial #1	0.02	92.0, 92.9, 97.2, 100.3, 106.6	85.9, 86.2, 92.8, 98.1, 99.2
	6.0	70.8, 73.7, 75.6, 78.0, 89.1	65.6, 71.3, 72.4, 74.5, 82.4
	Mean ± s.d. ^b	87.6 ± 12.4	82.8 ± 11.7

^a Overall mean and standard deviation provided by the petitioner included recoveries from the initial and dilution analyses.

^b Overall mean and standard deviations were calculated by the study reviewer.

Radiovalidation

To demonstrate extraction efficiency of the proposed LC/MS/MS enforcement method for plants, the petitioner submitted radiovalidation data (citation listed below) for LC/MS/MS Method

421/0 using ¹⁴C-labeled samples from the grape and wheat metabolism studies. The radiovalidation study was conducted by BASF Aktiengesellschaft (Germany).

45118502 Reinhard, K.; Mackenroth, C. (1999) Extractability of ¹⁴C-BAS 500 F Residues from Wheat and Grape Matrices with Aqueous Methanol (according to Method No. 421/0). Laboratory Project Identification No. 35512; BASF Registration Document No. 1999/11138. Unpublished study prepared by BASF Corporation. 24 p.

Extraction efficiency data submitted with the potato metabolism study (MRID 45118431) are also reviewed below.

Samples of chlorophenyl-label grapes, chlorophenyl- and tolyl-label potato tubers, and chlorophenyl-label wheat forage, grain, and straw from the plant metabolism studies were used to demonstrate the extraction efficiency of the proposed enforcement method. TRR in these samples were determined in the metabolism studies by LSC or combustion/LSC following extraction with methanol (grapes, potatoes) or methanol followed by water (wheat matrices). For the radiovalidation study and for determination of extraction efficiency in the potato metabolism study, the metabolism samples were extracted with methanol:water (7:3, v:v) as required for the residue method. The TRR were determined by LSC or combustion/LSC for the extractable and nonextractable fractions, and the percent TRR was calculated based on the sum of the extractable and nonextractable residues. Results of the radiovalidation study and the potato extraction efficiency study are presented in Table 21; percent TRR values were similar for grapes, potato tubers, and wheat matrices using the extraction procedures of the metabolism studies and the extraction method of the residue method. We note that these results are applicable to the proposed HPLC/UV enforcement method as well because the extraction and clean-up procedures are identical.

Table 21. Radiolabeled method validation of the LC/MS/MS residue extraction method using samples from grape, potato, and wheat metabolism studies bearing [¹⁴C]pyraclostrobin residues.

Matrix	Metabolism Study ^a			Residue Method ^b		
	TRR, ppm	TRR, ppm, extracted	% TRR extracted	TRR, ppm	TRR, ppm, extracted	% TRR extracted
Grape - chlorophenyl (MRID 45118502)	0.951	0.835	87.8	1.03, 1.13	0.867, 0.994	84.5, 88.1
Potato tuber - chlorophenyl (MRID 45118431)	0.040	0.021	52.2	0.035	0.024	68.8
Potato tuber - tolyl (MRID 45118431)	0.048	0.020	41.6	0.052	0.029	56.9
Wheat, forage - chlorophenyl (MRID 45118502)	6.53	5.56	85.1	5.38, 5.75	4.48, 4.78	83.4, 83.2
Wheat, grain - chlorophenyl (MRID 45118502)	0.098	0.070	71.0	0.088, 0.111	0.053, 0.070	60.1, 63.0
Wheat, straw - chlorophenyl (MRID 45118502)	37.8	31.9	84.5	49.4, 50.6	42.2, 43.7	85.4, 86.4

^a Average TRR as determined in the metabolism study by LSC or combustion/LSC analysis; samples were extracted with methanol (grapes and potato tubers) or water followed by methanol (wheat matrices).

^b Individual TRR and extracted TRR values are listed respectively; samples were extracted with methanol:water (7:3, v:v) as required for the residue method.

The submitted radiovalidation data demonstrate that the extraction efficiency of LC/MS/MS Method D9808 (421/0) is comparable to the extraction procedures used in the metabolism study. These data are sufficient to confirm that the proposed enforcement methods can adequately extract weathered residues of pyraclostrobin and BF 500-3 from plant commodities.

Residue data collection methods - plant commodities

Samples of almond (nutmeat and hulls), banana, barley (hay, grain, and straw), blueberry (highbush), cabbage (with and without wrapper leaves), cantaloupe, carrot, cherry (sweet and tart), cucumber, dry field pea (hay, vine, and seed), grape and grape processed commodities, grapefruit, grass grown for seed (forage, hay, seed screenings, and straw), lemon, lentil (seed), onion (dry bulb and green), orange and orange processed commodities, peach, peanut (nutmeat and hay) and peanut processed commodities, pecan (nutmeat), pepper (bell and chili), pistachios, plum and prune, potato, radish (roots and tops), raspberry (red), rye (grain and straw), squash (summer), strawberry, sugar beet (roots and tops) and sugar beet processed commodities, tomato and tomato processed commodities, and wheat forage, hay, grain, straw, and aspirated grain fractions (1998 studies) from the submitted field trials, field rotational crop, and processing studies were analyzed for residues of pyraclostrobin and BF 500-3 using the proposed

enforcement method (LC/MS/MS BASF Method Number D9808). Samples of wheat grain and straw and wheat processed commodities from the 2000 field trials and processing studies were analyzed for residues of pyraclostrobin and BF 500-3 using a similar LC/MS/MS method, BASF Method Number D9908. Method D9908 used an alternate extraction option: wheat matrices were extracted with methanol:water:2 N HCl (7:2.5:0.5) instead of methanol:water (7:3; v:v). Samples from the European crop field trial studies were analyzed for residues of pyraclostrobin and BF 500-3 using LC/MS/MS 421/0. Only rye, barley, and wheat straw samples from the field trial studies required additional cleanup using micro silica column chromatography. The method limit of quantitation was 0.02 ppm for each analyte (pyraclostrobin and BF 500-3) in/on all crop matrices.

The petitioner included concurrent method recovery data for the LC/MS/MS method. Samples of untreated commodities from the field and processing studies were fortified with pyraclostrobin and BF 500-3 and were analyzed concurrently with the field trial and processing samples. The concurrent method recoveries are presented in Table 22.

Table 22. Concurrent method recoveries of pyraclostrobin and its metabolite BF 500-3 from fortified samples of various crop commodities analyzed using BASF LC/MS/MS Method D9808 (421/0).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Concurrent Method Recovery Data LC/MS/MS (BASF Analytical Method Number D9808)				
Almond, nutmeat (45118521)	0.02, 1.0	Average (%)	81	75.5
		Recovery Range (%)	80, 82	71, 80
		SD (%)	--	--
		Number	2	2
Almond, hulls (45118521)	0.02, 1.0	Average (%)	99	98.5
		Recovery Range (%)	92, 106	95, 102
		SD (%)	--	--
		Number	2	2
Banana (45118532)	0.02, 1.0	Average (%)	92.3	85.5
		Recovery Range (%)	78-117	70-111
		SD (%)	18.0	18.5
		Number	4	4
Barley, hay (45118535)	0.02-25.0	Average (%)	98.5	86.6
		Recovery Range (%) ^a	74-120	65; 70-118
		SD (%)	15.5	17.9
		Number	18	18
Barley, grain (45118535)	0.02, 1.0	Average (%)	90.4	84.3
		Recovery Range (%) ^a	75-106	60, 65; 72-104
		SD (%)	9.6	13.8
		Number	16	16
Barley, straw (45118535)	0.02,1.0	Average (%)	86.8	74.5
		Recovery Range (%) ^a	75-110; 124	60-67; 70-84
		SD (%)	13.9	8.1
		Number	14	14
Bean, dry (45367501)	0.02,1.0	Average (%)	80	79
		Recovery Range (%) ^a	67; 74-99	68; 73-97
		SD (%)	14	13
		Number	4	4
Bean, snap (45367501)	0.02,1.0	Average (%)	88	98
		Recovery Range (%) ^a	75-107	86-117
		SD (%)	11	11
		Number	6	6
Blueberry, highbush (45118605)	0.02, 5.0	Average (%)	90	105
		Recovery Range (%)	82, 98	102, 108
		SD (%)	--	--
		Number	2	2
Cabbage, with wrapper leaves (45118623)	0.02, 1.0	Average (%)	91	89
		Recovery Range (%)	89, 93	85, 93
		SD (%)	--	--

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
		Number	2	2
Cabbage, without wrapper leaves (45118623)	0.02, 1.0	Average (%)	88	87.5
		Recovery Range (%)	85, 91	83, 92
		SD (%)	--	--
		Number	2	2
Cantaloupe (45118603)	0.02, 1.0	Average (%)	87.5	85.0
		Recovery Range (%)	80-94	73-96
		SD (%)	6.4	9.6
		Number	6	6
Cantaloupe (45118613)	0.02, 1.0	Average (%)	89.0	82.0
		Recovery Range (%)	86, 92	75, 89
		SD (%)	--	--
		Number	2	2
Carrot (45118523)	0.02, 1.00	Average (%)	87.5	87.5
		Recovery Range (%)	87, 88	82, 93
		SD (%)	0.7	7.8
		Number	2	2
Cherry, tart (45118607)	0.02, 2.50	Average (%)	87.8	83.0
		Recovery Range (%)	84-93	79-86
		SD (%)	3.9	3.2
		Number	4	4
Cucumber (45118603)	0.02, 1.0	Average (%)	90.9	87.6
		Recovery Range (%)	84-103	75-110
		SD (%)	5.1	8.2
		Number	20	20
Cucumber (45118613)	0.02, 1.0	Average (%)	109.5	105
		Recovery Range (%)	108, 111	105
		SD (%)	--	--
		Number	2	2
Grape (45118529)	0.02-2.0	Average (%)	87.5	83.4
		Recovery Range (%)	73-109	74-99
		SD (%)	9.3	7.6
		Number	13	13
Grape (45118530)	0.02, 1.0	Average (%)	102	88.7
		Recovery Range (%)	86-119	73-115
		SD (%)	16.5	22.9
		Number	3	3
Grape (45118531)	0.02, 1.0	Average (%)	83.6	77.3
		Recovery Range (%) ^a	66; 75-99	59, 69; 74-97
		SD (%)	10.4	11.9
		Number	7	7

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Grape (45118613)	0.02, 1.0	Average (%)	92.5	91.5
		Recovery Range (%)	90, 95	91, 92
		SD (%)	--	--
		Number	2	2
Grape (for processing) (45118616)	0.02, 2.0	Average (%)	102.5	93.8
		Recovery Range (%)	89-117	78-110
		SD (%)	11.9	13.8
		Number	4	4
Grape, juice (45118616)	0.02, 2.0	Average (%)	99.0	93.3
		Recovery Range (%)	88-106	83-97
		SD (%)	7.9	6.8
		Number	4	4
Raisin (45118616)	0.02-10.0	Average (%)	101	89.7
		Recovery Range (%) ^a	90-113	69; 82-103
		SD (%)	9.2	12.2
		Number	6	6
Grapefruit (45118606)	0.02, 1.0	Average (%)	83.2	77.3
		Recovery Range (%) ^a	66; 75-100	57-65; 74-102
		SD (%)	9.6	14.7
		Number	12	12
Grass, forage (45118527)	0.02,1.0	Average (%)	93.8	91.5
		Recovery Range (%)	88-99	81-99
		SD (%)	4.6	7.7
		Number	4	4
Grass, hay (45118527)	0.02, 1.0	Average (%)	77.5	73.0
		Recovery Range (%) ^a	65; 71-98	59, 65; 73, 95
		SD (%)	14.4	15.7
		Number	4	4
Grass, straw (45118527)	0.02-10.0	Average (%)	75.4	75.2
		Recovery Range (%) ^a	67; 72-87	68; 73-90
		SD (%)	7.4	9.1
		Number	5	5
Grass, seed screenings (45118527)	0.02-30.0	Average (%)	83.0	80.2
		Recovery Range (%) ^a	70-92	67; 73-88
		SD (%)	8.5	8.3
		Number	6	6
Lemon (45118606)	0.02, 1.0	Average (%)	76.0	86.5
		Recovery Range (%)	70, 82	79, 94
		SD (%)	--	--
		Number	2	2

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Lentil, seed (45118526)	0.02, 1.00	Average (%)	98	92.5
		Recovery Range (%)	86, 110	81, 104
		SD (%)	--	--
		Number	2	2
Onion, dry bulb (45118525)	0.02, 1.00	Average (%)	86.3	84
		Recovery Range (%)	77-99	71-98
		SD (%)	9.6	12.2
		Number	4	4
Onion, green (45118525)	0.02, 1.00	Average (%)	77.5	78.5
		Recovery Range (%)	68, 87	71, 86
		SD (%)	--	--
		Number	2	2
Orange (45118606)	0.02, 1.0	Average (%)	92.1	96.0
		Recovery Range (%)	76-112	83-115
		SD (%)	9.7	8.8
		Number	12	12
Orange, unwashed (for processing) (45118617)	0.02, 1.0	Average (%)	93.5	87.0
		Recovery Range (%)	89, 98	80, 94
		SD (%)	--	--
		Number	2	2
Orange, washed (for processing) (45118617)	0.02, 1.0	Average (%)	93.5	82.5
		Recovery Range (%)	90, 97	75, 90
		SD (%)	--	--
		Number	2	2
Orange, pulp (45118617)	0.02-20.0	Average (%)	76.8	73.6
		Recovery Range (%) ^a	65, 67; 80-84	65, 67; 70-84
		SD (%)	10.3	8.8
		Number	5	5
Orange, oil (45118617)	0.02-20.0	Average (%)	93.4	75.6
		Recovery Range (%) ^a	79-115	68; 72-90
		SD (%)	16.8	8.4
		Number	5	5
Orange, juice (45118617)	0.02, 1.0	Average (%)	94.5	96.5
		Recovery Range (%)	94, 95	95, 98
		SD (%)	--	--
		Number	2	2
Pea, dry, hay (45118522)	0.02, 1.0	Average (%)	82.7	84
		Recovery Range (%)	78-90	78-91
		SD (%)	6.4	6.6
		Number	3	3

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Pea, dry, vine (45118522)	0.02, 1.0	Average (%)	83	83.8
		Recovery Range (%) ^a	61; 82-99	61; 84-103
		SD (%)	16.2	17.3
		Number	4	4
Pea, dry, seed (45118522)	0.02-10.0	Average (%)	94.8	104.8
		Recovery Range (%) ^a	88-104	88-111; 125
		SD (%)	7.0	16.6
		Number	4	4
Peach (45118607)	0.02-5.0	Average (%)	83.5	79.4
		Recovery Range (%) ^a	72-96	66, 68; 70-96
		SD (%)	7.7	10.3
		Number	11	11
Peanut, hay (45118533)	0.02-50.0	Average (%)	87.5	89.7
		Recovery Range (%) ^a	67; 75-99	50; 71-120
		SD (%)	13.4	26.0
		Number	6	6
Peanut, hay (45118534)	0.02-20.0	Average (%)	95.3	81.8
		Recovery Range (%) ^a	78-94; 121	71-96
		SD (%)	18.4	10.5
		Number	4	4
Peanut, nutmeat (45118533)	0.02, 1.0	Average (%)	80.0	71.5
		Recovery Range (%) ^a	71-105	66, 69; 70-83
		SD (%)	12.6	5.9
		Number	6	6
Peanut, nutmeat (45118534)	0.02, 1.00	Average (%)	97.0	93.0
		Recovery Range (%)	96-98	86-100
		SD (%)	1	7
		Number	3	3
Peanut, nutmeat (for processing) (45118614)	0.02, 1.0	Average (%)	107.5	92.5
		Recovery Range (%)	100, 115	91, 94
		SD (%)	--	--
		Number	2	2
Peanut, meal (45118614)	0.02, 1.0	Average (%)	102	--
		Recovery Range (%) ^a	84, 120	20 ^b ; 120
		SD (%)	--	--
		Number	2	2
Peanut, oil (45118614)	0.02, 1.0	Average (%)	103	96.5
		Recovery Range (%)	99, 107	94, 99
		SD (%)	--	--
		Number	2	2

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Pecan, nutmeat (45118612)	0.02, 1.0	Average (%)	89.0	87.5
		Recovery Range (%)	81, 97	80, 95
		SD (%)	--	--
		Number	2	2
Pepper, bell (45118611)	0.02, 1.0	Average (%)	78.8	74.8
		Recovery Range (%) ^a	73-86	66; 76-79
		SD (%)	5.4	6.0
		Number	4	4
Pepper, chili (45118611)	0.02, 1.0	Average (%)	85	80.5
		Recovery Range (%)	80, 90	75, 86
		SD (%)	--	--
		Number	2	2
Pistachio (45118610)	0.02, 1.00	Average (%)	87.5	87.5
		Recovery Range (%)	82, 93	80, 95
		SD (%)	--	--
		Number	2	2
Plum (45118607)	0.02-5.0	Average (%)	92.0	81.4
		Recovery Range (%)	77-119	74-100
		SD (%)	16.1	10.9
		Number	5	5
Plum, unwashed (for processing) (45118621)	0.02, 1.0	Average (%)	81.5	78.5
		Recovery Range (%)	79, 84	73, 84
		SD (%)	--	--
		Number	2	2
Plum, washed (for processing) (45118621)	0.02, 1.0	Average (%)	81	79.5
		Recovery Range (%)	80, 82	79, 80
		SD (%)	--	--
		Number	2	2
Potato (45118608)	0.02, 1.0	Average (%)	81.8	87.3
		Recovery Range (%) ^a	57-67; 72-109	67, 68; 72-114
		SD (%)	16.1	15.7
		Number	12	12
Potato (45118618)	0.02, 1.0	Average (%)	84.5	86.5
		Recovery Range (%)	81, 88	83, 90
		SD (%)	--	--
		Number	2	2
Prune (45118621)	0.02, 1.0	Average (%)	79	76
		Recovery Range (%)	74, 84	75, 77
		SD (%)	--	--
		Number	2	2

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Radish, roots (45118609)	0.02, 1.00	Average (%)	85.5	85.5
		Recovery Range (%)	84, 87	80, 91
		SD (%)	--	--
		Number	2	2
Radish, roots (45118623)	0.02, 1.00	Average (%)	91	90.5
		Recovery Range (%)	88, 94	87, 94
		SD (%)	--	--
		Number	2	2
Radish, tops (45118609)	0.02, 1.00	Average (%)	86.5	82.5
		Recovery Range (%)	81, 92	79, 86
		SD (%)	--	--
		Number	2	2
Radish, tops (45118623)	0.02, 1.00	Average (%)	96.5	92
		Recovery Range (%)	95, 98	92
		SD (%)	--	--
		Number	2	2
Raspberry, red (45118605)	0.02, 5.0	Average (%)	90.0	84.0
		Recovery Range (%)	75, 105	82, 86
		SD (%)	--	--
		Number	2	2
Rye, grain (45118536)	0.02, 1.0	Average (%)	82	74.5
		Recovery Range (%)	80, 84	65, 84
		SD (%)	--	--
		Number	2	2
Rye, straw (45118536)	0.02, 1.0	Average (%)	75	66
		Recovery Range (%)	73-78	63; 72
		SD (%)	2.6	5.2
		Number	3	3
Squash, summer (45118603)	0.02, 1.0	Average (%)	96.8	93.5
		Recovery Range (%)	88-103	88-99
		SD (%)	5.3	4.2
		Number	8	8
Squash, summer (45118613)	0.02, 1.0	Average (%)	92.0	92.5
		Recovery Range (%)	88, 96	92, 93
		SD (%)	--	--
		Number	2	2
Strawberry (45118604)	0.02-5.0	Average (%)	86.5	85.0
		Recovery Range (%)	80-90	73-93
		SD (%)	4.5	8.6
		Number	4	4

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Sugar beet, roots (45118524)	0.02, 1.0	Average (%)	92.8	88
		Recovery Range (%)	77-110	70-118
		SD (%)	13.7	21.4
		Number	4	4
Sugar beet, roots (for processing) (45118619)	0.02-2.0	Average (%)	97.25	92.5
		Recovery Range (%) ^a	85-112	69; 80-113
		SD (%)	13.8	21.4
		Number	4	4
Sugar beet, dried pulp (45118619)	0.02, 1.0	Average (%)	81.5	80
		Recovery Range (%)	74, 89	70, 90
		SD (%)	--	--
		Number	2	2
Sugar beet, molasses (45118619)	0.02, 1.0	Average (%)	95	101.5
		Recovery Range (%)	74, 116	83, 120
		SD (%)	--	--
		Number	2	2
Sugar beet, refined sugar (45118619)	0.02, 1.00	Average (%)	118.5	125
		Recovery Range (%) ^a	112; 125	120, 130
		SD (%)	--	--
		Number	2	2
Sugar beet, tops (45118524)	0.02-5.0	Average (%)	98	92.5
		Recovery Range (%)	85-110	84-100
		SD (%)	11.5	8.7
		Number	4	4
Tomato (45118528)	0.02, 1.0	Average (%)	94.7	86.3
		Recovery Range (%) ^a	75-116; 121	60-65; 70-106
		SD (%)	12.6	15.0
		Number	18	18
Tomato (45118613)	0.02, 1.0	Average (%)	80.0	81.0
		Recovery Range (%)	63, 97	70, 92
		SD (%)	--	--
		Number	2	2
Tomato, whole (for processing) (45118615)	0.02, 1.0	Average (%)	82.5	75.3
		Recovery Range (%) ^a	77-89	57; 70-88
		SD (%)	5.5	14.6
		Number	4	4
Tomato, paste (45118615)	0.02, 1.0	Average (%)	92.5	93.3
		Recovery Range (%)	83-104	74-113
		SD (%)	8.7	15.9
		Number	4	4

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Tomato, puree (45118615)	0.02, 1.0	Average (%)	90.5	89.5
		Recovery Range (%)	87-95	85-95
		SD (%)	3.7	4.8
		Number	4	4
Wheat, forage (45118623)	0.02, 1.0	Average (%)	87	86
		Recovery Range (%)	84, 90	76, 96
		SD (%)	--	--
		Number	2	2
Wheat, hay (45118537)	0.02-10.0	Average (%)	88	81
		Recovery Range (%) ^a	36; 76-107	36-68; 72-106
		SD (%)	13.9	15.2
		Number	23	23
Wheat, hay (45118623)	0.02, 1.0	Average (%)	79.5	80.5
		Recovery Range (%)	75, 84	71, 90
		SD (%)	--	--
		Number	2	2
Wheat, straw (45118537)	0.02-1.0	Average (%)	80	73
		Recovery Range (%)	68; 71-118	61-68; 70-84
		SD (%)	11.6	6.8
		Number	14	14
Wheat, straw (45118623)	0.02	Recovery (%)	75	73
		Number	1	1
Wheat, straw ^b (45321101)	0.02-10.0	Average (%)	100.9	100.1
		Recovery Range (%) ^a	84-119	76-117; 175 ^c
		SD (%)	12.3	13.7
		Number	14	14
Wheat, grain (45118537)	0.02, 1.0	Average (%)	86	76
		Recovery Range (%) ^a	70-110	65-69; 70-89
		SD (%)	9.4	6.2
		Number	26	26
Wheat, grain (45118623)	0.02, 1.0	Average (%)	95.7	91
		Recovery Range (%)	88-109	83-103
		SD (%)	11.6	10.6
		Number	3	3
Wheat, grain ^b (45321101)	0.02, 1.0	Average (%)	91.8	91.7
		Recovery Range (%)	80-106	70-117
		SD (%)	9.3	14.0
		Number	12	12
Wheat, grain (for processing) (45118620)	0.02, 1.0	Average (%)	80	86
		Recovery Range (%)	80	82, 90
		SD (%)	--	--

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
		Number	2	2
Wheat, grain ^b (for processing) (45321101)	0.02, 1.0	Average (%)	93.5	76
		Recovery Range (%)	86, 101	73, 79
		SD (%)	--	--
		Number	2	2
Wheat, flour (45118620)	0.02, 1.0	Average (%)	80.5	81
		Recovery Range (%)	76, 85	77, 85
		SD (%)	--	--
		Number	2	2
Wheat, flour ^b (45321101)	0.02, 1.0	Average (%)	82.5	88
		Recovery Range (%)	74, 91	86, 90
		SD (%)	--	--
		Number	2	2
Wheat, bran (45118620)	0.02, 1.0	Average (%)	91	88
		Recovery Range (%)	80, 102	80, 96
		SD (%)	--	--
		Number	2	2
Wheat, bran ^b (45321101)	0.04, 1.0	Average (%)	79	81
		Recovery Range (%)	75, 83	81
		SD (%)	--	--
		Number	2	2
Wheat, middlings (45118620)	0.02, 1.0	Average (%)	98.5	95.5
		Recovery Range (%)	92, 105	95, 96
		SD (%)	--	--
		Number	2	2
Wheat, middlings (45321101) ^b	0.02, 1.0	Average (%)	82	80
		Recovery Range (%)	70, 94	77, 83
		SD (%)	--	--
		Number	2	2
Wheat, shorts (45118620)	0.02, 1.0	Average (%)	93	87.5
		Recovery Range (%)	85, 101	80, 95
		SD (%)	--	--
		Number	2	2
Wheat, shorts ^b (45321101)	0.02, 1.0	Average (%)	92	73
		Recovery Range (%) ^a	88, 96	66; 80
		SD (%)	--	--
		Number	2	2
Wheat, germ (45118620)	0.02, 1.0	Average (%)	117.5	110.5
		Recovery Range (%) ^a	95; 140	90; 131
		SD (%)	--	--
		Number	2	2

Table 22 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Pyraclostrobin	BF 500-3
Wheat, germ ^b (45321101)	0.02, 1.0	Average (%)	80.5	77.5
		Recovery Range (%) ^a	74, 87	66; 89
		SD (%)	--	--
		Number	2	2
Wheat, aspirated grain fractions (45118620)	0.02, 1.0	Average (%)	81.7	65
		Recovery Range (%) ^a	75-91	62-68
		SD (%)	8.3	3.0
		Number	3	3
Wheat, aspirated grain fractions ^b (45321101)	0.02, 1.0	Average (%)	75	79
		Recovery Range (%) ^a	62; 88	77, 81
		SD (%)	--	--
		Number	2	2
Concurrent Method Recovery Data (European Trials) - LC/MS/MS BASF Method Number 421/0				
Barley and wheat, plant without roots, ears, haulms, grain, and straw (45118601)	0.02-2.0	Average (%)	85.7	82.7
		Recovery Range (%) ^a	65.5-67.4; 71.9-117.4; 122.0	62.2-67.5; 70.1-119.2
		SD (%)	11.7	11.3
		Number	64	60
Barley and wheat, plant without roots, ears, haulms, grain, and straw (45118602)	0.02-2.0	Average (%)	86.4	83.2
		Recovery Range (%) ^a	66.6-67.4; 71.9-117.4; 122	62.2-67.5; 70.5-119.2
		SD (%)	12.0	11.8
		Number	48	46

^a Recoveries outside the acceptable 70-120% range are listed separately.

^b Samples of wheat RACs and processed commodities from the 2000 field trials were analyzed using LC/MS/MS (BASF Method Number D9908).

^c The petitioner considered this recovery value a data outlier, and it was not included in the average recovery.

Comments:

The petitioner has proposed two tolerance enforcement methods for the determination of residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 in/on plant commodities: LC/MS/MS method D9808 (U.S.) or 421/0 (Germany), and HPLC/UV method D9904. The validated method LOQs for pyraclostrobin and BF 500-3 for both the LC/MS/MS or HPLC/UV methods are 0.02 ppm for each analyte in plant matrices. Adequate independent method validation and radiovalidation data have been submitted for both methods.

Based on the submitted concurrent method validation data, the LC/MS/MS method is adequate for data collection of residues of pyraclostrobin and BF 500-3 in/on almond (nutmeat and hulls); banana; barley (hay, grain, and straw); blueberry (highbush); cabbage (with and without wrapper leaves); dry field pea (hay, vine, and seed); cantaloupe; carrot; cherry (tart); cucumber; grape;

grapefruit; grass (forage, hay, straw, and seed screenings); lemon; lentil (seed); onion (dry bulb and green); orange; peach; peanut (hay and nutmeat); pecan (nutmeat); pepper (bell and chili); pistachio; potato; plum; radish (roots and tops); raspberry (red); rye (grain and straw); squash (summer); strawberry; sugar beet (roots and tops); tomato; and wheat (forage, hay, grain, straw, and aspirated grain fractions), and the processed commodities of grapes, oranges, peanuts, plums, sugar beets, tomatoes, and wheat. Although some recoveries of pyraclostrobin and BF 500-3 were outside the acceptable range, average recoveries were generally within the acceptable range.

LC/MS/MS method D9808 and HPLC/UV method D9904 have been forwarded to ACB/BEAD for petition method validation (D269850, L. Cheng, 11/8/2000). The petitioner must modify the proposed enforcement methods to include any modifications made by the EPA laboratory during the Agency laboratory validation.

OPPTS GLN 860.1340: Residue Analytical Method - Livestock commodities

Enforcement analytical methods - livestock commodities

BASF has proposed three methods, HPLC/UV method 439/0, Method 446 (GC/MS and LC/MS/MS method), and LC/MS/MS method D9902, for the enforcement of tolerances for residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 in/on livestock commodities. The proposed enforcement methods were used as the data collection methods in the ruminant and poultry feeding studies. HPLC/UV method 439/0 is for the determination of the parent *per se* in livestock commodities. Method 446, which consists of GC/MS method 446/0 and LC/MS/MS method 446/1, is a common moiety method for the analysis of ruminant commodities for residues of the parent and its metabolites which are hydrolyzable to BF 500-5 and BF 500-8; see Figure 3 (Attachment III) for the chemical structures of these compounds. LC/MS/MS Method D9902 is a common moiety method for the analysis of poultry commodities for residues of the parent and its metabolites hydrolyzable to BF 500-5 and BF 500-9 (see Figure 3).

The petitioner has submitted method descriptions and validation data (citations listed below) for the proposed enforcement HPLC/UV, GC/MS, and LC/MS/MS methods for livestock commodities.

45118506 Tilting, N.; Lehman, W. (2000) Validation of Analytical Method No. 446: Determination of BAS 500 F (Reg. No. 304428) in Sample Material of Animal Origin. Laboratory Project Identification Number 35636; BASF Registration Document Number 1999/11075. Unpublished study prepared by BASF Corporation. 112 p.

45118508 Malinsky, D.; Riley, M. (2000) Method Validation of BASF Analytical Method D9902, "Method for Determination of Residues of BAS 500 F and its Metabolite BF 500-16 in Hen Tissues Using LC/MS/MS. BASF Study Number 60916; BASF Registration Document Number 2000/5004. Unpublished study prepared by BASF Corporation. 73 p.

45118509 Malinsky, D.; Trumbly, R. (2000) Technical Procedure: Method for Determination of Residues of BAS 500 F and its Metabolite BF 500-16 in Hen Tissues using LC/MS/MS. BASF Method Number D9902. BASF Registration Document Number 2000/5003. Unpublished study prepared by BASF Corporation. 27 p.

45118510 Tilting, N.; Lehmann, W. (1999) LC-MS/MS Method of Determination of Reg. No. 304428 (BAS 500 F) and its Metabolites (BF 500-10) in Matrices of Animal Origin. BASF Registration Document Number 2000/5139. Unpublished study prepared by BASF Corporation. 32 p.

45118511 Kampke-Thiel, K.; Tilting, N. (1999) Method of Determination of Reg. No. 304428 (BAS 500 F) in matrices of animal origin. BASF Registration Document Number 2000/5138. Unpublished study prepared by BASF Corporation. 21 p.

45118513 Kampke-Thiel, K. (1999) Validation of BASF Method 439/0 for the Determination of BAS 500 F (as Parent Compound) in Matrices of Animal Origin. Laboratory Project Identification No. 53018; BASF Registration Document Number 1999/11079. Unpublished study prepared by BASF Corporation. 45 p.

For the **HPLC/UV** method 439/0, animal samples (muscle, fat, liver, kidney, milk, and eggs) are homogenized with ACN:iso-hexane (2:1, v:v) and filtered. After phase separation, the ACN phase is partitioned with iso-hexane; egg and fat samples are partitioned twice. The aqueous phase is extracted (3x) with DCM and filtered. The DCM phase is evaporated to dryness and redissolved in 5% ethyl acetate for micro-silica column cleanup. Residues are eluted from the silica column with 1% ethyl acetate in DCM. The eluate is evaporated to dryness and redissolved in iso-octane:methanol:iso-propanol:water (99:0.5:0.5:0.0025, v:v:v:v) for HPLC analysis. The normal phase HPLC system utilizes two columns; a silica pre-column, with an isocratic mobile phase of iso-octane:methanol:iso-propanol:water (99:0.5:0.5:0.0025, v:v:v:v), and an alumina analytical column, with an isocratic mobile phase of iso-octane:methanol:iso-propanol:water (90:5:5:0.0025, v:v:v:v). Residues of pyraclostrobin are quantitated using a UV detector at 270 nm. The method LOQs for residues of pyraclostrobin were reported as 0.01 ppm for milk and 0.05 ppm for tissue and egg samples. The petitioner stated that a reversed-phase column may be used for confirmation of residues.

Method 446 was initially developed using GC/MS in milk (Method 446/0), but has been replaced with the shorter LC/MS/MS detection method (Method 446/1). For the **GC/MS** method 446/0, milk samples are first homogenized with iso-hexane:ACN (1:1, v:v), filtered, and the ACN phase is collected and evaporated to dryness. Residues are then heated with 2.5 M sodium hydroxide and sodium chloride at reflux to produce the hydroxypyrazole derivatives, BF 500-5 and BF 500-8. The derivatized extracts of milk are cooled, acidified with 5 M HCl, and partitioned with ethyl acetate. Silica gel is added to an aliquot of the ethyl acetate phase, and the mixture is evaporated to dryness. The dried silica gel/residues are subjected to silica gel column chromatography; residues are eluted from the silica gel column with iso-hexane:acetone (7:3, v:v) and evaporated

to dryness. Residues are redissolved in acetone, and powdered potassium carbonate is added. Next, residues are methylated with methyl iodide at reflux, filtered and evaporated to dryness. Residues are then redissolved in iso-hexane and subjected to sequential SPE column (silica and ENV) cleanup; residues are eluted with iso-hexane:DCM (75:25, v:v). The purified residues are concentrated for GC/MS analysis. BF 500-5 residues are determined as its methyl ether, MMP (monitoring m/z 193, 139, 179), and BF 500-8 residues are determined as its methyl ether, DMP (monitoring m/z 238, 179, 126). Each are then converted to parent equivalents using molecular weight ratios. The method LOQs are 0.01 ppm each for BF 500-5 residues and BF 500-8 residues in milk.

For the LC/MS/MS method 446/1, ruminant fat and milk samples are first homogenized with iso-hexane:ACN (1:1, v:v), filtered, and the ACN phase is collected and evaporated to dryness. Milk and fat dried residues and other ruminant tissue samples (muscle, liver, and kidney) are then hydrolyzed with 2.5 M sodium hydroxide and sodium chloride at reflux to produce the hydroxypyrazole derivatives BF 500-5 and BF 500-8). After hydrolysis, 5 N HCl and methanol are added to the hydrolysate. Fat samples require less cleanup than the other matrices; therefore, the hydrolyzed fat extract is extracted (2x) with ethyl acetate, and an aliquot of the organic phase is evaporated to dryness and redissolved in ACN for LC/MS/MS analysis. The derivatized extracts of milk and the remaining tissues are partitioned (3x) with DCM. Silica gel is added to an aliquot of the DCM phase, and the mixture is evaporated to dryness. The dried silica gel/residues are subjected to silica gel column chromatography; residues are eluted from the silica gel column with isohexane:acetone (7:3, v:v) and evaporated to dryness. Residues are redissolved in iso-hexane and partitioned (2x) with HCl. The acid phases are combined, sodium hydroxide is added (pH paper is used to ensure that the mixture remains acidic), and the mixture is partitioned with DCM. The DCM phase is dried with anhydrous sodium sulfate, then evaporated to dryness, and residues are redissolved in ACN for LC/MS/MS analysis. For quantitation, the product/daughter ion for the transition m/z 195 – 153 for BF 500-5 and m/z 211 – 194 for BAS 500-8 are measured. Molecular weight conversion is used to convert all residues to parent equivalents. The reported method LOQs for each analyte are 0.01 ppm for milk and 0.05 ppm for ruminant tissues.

LC/MS/MS method D9902 for poultry eggs and tissues is similar to LC/MS/MS method 446/1 for ruminant commodities. Samples of homogenized egg, and ground poultry liver and muscle are hydrolyzed in 2.5 N sodium hydroxide to produce the hydroxypyrazole derivatives (BF 500-5 or BF 500-9). After hydrolysis, 5 N HCl and methanol are added to the hydrolysate, and the samples are precipitated overnight in a refrigerator and filtered. The extract is mixed with methanol:water (1:1, v:v), and an aliquot is diluted with water for sequential ENV and silica SPE column cleanup. Residues are eluted from the ENV column with DCM:ethyl acetate (1:2, v:v), evaporated to complete dryness, and residues are redissolved in ethyl acetate and hexane for silica column cleanup. Residues are eluted from the silica column with ethyl acetate:hexane (35:65, v:v), evaporated to dryness, and residues are redissolved in methanol:water (9:1, v:v) for LC/MS/MS analysis. As for ruminant fat samples, poultry fat samples are initially extracted with hexane:ACN (1:1, v:v) prior to hydrolysis with 2.5 N sodium hydroxide. Following

hydrolysis, 5 N HCl and water are added to the hydrolysate, and the derivatized extracts are then partitioned with ethyl acetate. The ethyl acetate phase is filtered and evaporated to complete dryness. Residues are redissolved in methanol:water (9:1, v:v) for LC/MS/MS analysis. For quantitation, the product/daughter ion for the transition m/z 195 → 153 for BF 500-5 and m/z 211 → 169 for BAS 500-9 are measured. Molecular weight conversion is used to convert residues to parent equivalents. The reported method LOQs for each analyte are 0.05 ppm for eggs and poultry tissues.

Method validations of the HPLC/UV and LC/MS/MS methods were conducted on representative animal matrices. Untreated samples of cow milk, fat, kidney, liver, and muscle, and hen eggs, obtained commercially for validation of the HPLC/UV method, were fortified with pyraclostrobin at the LOQ (0.01 ppm for milk and 0.05 ppm for tissues and eggs) and 10x the LOQ. Untreated samples of cow milk, fat, kidney, liver, and muscle, obtained commercially for validation of LC/MS/MS method 446/1, were fortified with pyraclostrobin (representative of compounds hydrolyzable to BF 500-5) and compound BF 500-10 (representative of compounds hydrolyzable to BF 500-8; see Figure 3) each at the LOQ (0.01 ppm for milk and 0.05 ppm for tissues) and 10x the LOQ; the fortified milk sample was also analyzed by GC/MS method 446/0. Untreated samples of hen eggs, fat, liver, and muscle, obtained from the hen feeding study for validation of the LC/MS/MS method D9902, were fortified with pyraclostrobin (representative of compounds hydrolyzable to BF 500-5) and metabolite BF 500-16 (representative of compounds hydrolyzable to BF 500-9; see Figure 3) each at the LOQ (0.05 ppm) and 2x the LOQ.

Unfortified and fortified samples were analyzed using either HPLC/UV method 439/0, GC/MS method 446/0, or LC/MS/MS method 446/1 or D9902. Method validation recoveries are reported in Table 23; method recoveries were corrected for interferences from matrix compounds. Apparent residues of pyraclostrobin were not reported for the HPLC/UV method 439/0 and GC/MS method 446/0, but representative chromatograms of the control samples were included demonstrating negligible background or baseline noise. Apparent residues of pyraclostrobin and BF 500-10 using LC/MS/MS method 446/1 were each less than the method LOQ (0.01 ppm for milk and 0.05 ppm for tissues; inspection of the control chromatograms showed negligible background or interfering peaks) in two samples each of untreated cow milk, fat, kidney, liver, and muscle. Apparent residues of pyraclostrobin and BF 500-16 using LC/MS/MS method D9902 were each less than the method LOQ (0.05 ppm; inspection of the control chromatograms showed negligible background or interfering peaks) in four samples each of untreated poultry egg, fat, liver, and muscle.

The petitioner noted that lower recoveries were obtained for residues of BF 500-10 (55.5-85.6%) in ruminant commodities using LC/MS/MS method 446/1 and for residues of BF 500-16 (58-71%) in poultry commodities using LC/MS/MS method D9902, but that the standard deviations

were low within each analytical series demonstrating good repeatability. The petitioner therefore considered the recoveries acceptable for the minor metabolites.

Table 23. Method validation recoveries of residues of pyraclostrobin and BF 500-10 or BF 500-16 from fortified samples of livestock commodities analyzed using the HPLC/UV method 439/0, GC/MS method 446/0, or LC/MS/MS method 446/1 or D9902.

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
HPLC/UV Method 439				
Cow, milk (45118513)	0.01, 0.1	Average (%)	81.9	--
		Recovery range (%)	67.9; 70.1-92.2	--
		SD (%)	8.6	--
		Number of samples	10	--
Cow, fat (45118513)	0.05, 0.5	Average (%)	90.3	--
		Recovery range (%)	56.0 ^d ; 82.4-98.9	--
		SD (%)	6.6	--
		Number of samples	10	--
Cow, kidney (45118513)	0.05, 0.5	Average (%)	86.7	--
		Recovery range (%)	77.9-92.7	--
		SD (%)	4.8	--
		Number of samples	10	--
Cow, liver (45118513)	0.05, 0.5	Average (%)	90.5	--
		Recovery range (%)	76.0-99.9	--
		SD (%)	6.2	--
		Number of samples	10	--
Cow, muscle (45118513)	0.05, 0.5	Average (%)	90.0	--
		Recovery range (%)	80.3-95.1	--
		SD (%)	5.3	--
		Number of samples	10	--
Hen, eggs (45118513)	0.05, 0.5	Average (%)	89.0	--
		Recovery range (%)	67.1; 84.0-100.3	--
		SD (%)	9.1	--
		Number of samples	10	--
GC/MS Method 446/0				
Cow, milk (45118506)	0.01, 0.1	Average (%)	71.7	64.6
		Recovery range (%)	61.3-69.0; 71.5-78.0	55.6-69.3; 70.1
		SD (%)	5.4	4.4
		Number of samples	10	10

Table 23 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
LC/MS/MS Method 446/1				
Cow, milk (45118506)	0.01, 0.1	Average (%)	81.7	67.0
		Recovery range (%)	61.1-67.9; 71.3-110.3	58.4-69.5; 74.9-80.9
		SD (%)	17.9	8.0
		Number of samples	10	10
Cow, fat (45118506)	0.05, 0.5	Average (%)	84.0	85.6
		Recovery range (%)	63.3; 70.8-101.3	54.0, 68.2; 74.1-105.9
		SD (%)	12.2	16.1
		Number of samples	10	10
Cow, kidney (45118506)	0.05, 0.5	Average (%)	76.6	63.2
		Recovery range (%)	61.4-69.7; 70.2-92.9	52.0-67.4; 70.5
		SD (%)	10.6	4.9
		Number of samples	10	10
Cow, liver (45118506)	0.05, 0.5	Average (%)	80.8	74.0
		Recovery range (%)	73.8-87.5	62.3-68.1; 79.8-86.7
		SD (%)	4.5	9.1
		Number of samples	10	10
Cow, muscle (45118506)	0.05, 0.5	Average (%)	80.8	55.5
		Recovery range (%)	76.4-86.1	53.5-60.2
		SD (%)	3.2	1.8
		Number of samples	10	10
LC/MS/MS Method D9902				
Hen, eggs (45118508)	0.05, 0.10	Average (%)	104	62
		Recovery range (%)	79-108; 122, 131	50-67; 71
		SD (%)	17	7
		Number of samples	8	8
Hen, fat (45118508)	0.05, 0.10	Average (%)	93	68
		Recovery range (%)	88-100	42-68; 70-91
		SD (%)	4	15
		Number of samples	8	8

Table 23 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
Hen, liver (45118508)	0.05, 0.10	Average (%)	104	71
		Recovery range (%)	69; 85-117; 152	63-66; 71-78
		SD (%)	25	6
		Number of samples	8	8
Hen, muscle (45118508)	0.05, 0.10	Average (%)	110	58
		Recovery range (%)	90-119; 132	51-62
		SD (%)	13	4
		Number of samples	8	8

^a Recoveries outside the acceptable 70-120% range are listed separately.

^b For LC/MS/MS methods 446/1 and D9902, residues of pyraclostrobin were quantitated as BF 500-5 and calculated using molecular weight conversions

^c For cow commodities, residues of BF 500-10 were determined as BF 500-8, and for hen commodities, residues of BF 500-16 were determined as BF 500-9. BF 500-10 (ruminants) and BF 500-16 (poultry) are reported as parent equivalents.

^d Recovery value was considered an outlier and was not included in calculation of the mean and standard deviation.

Independent Laboratory Validation

BASF submitted data (citations listed below) from ILV trials for two of the proposed tolerance enforcement methods (HPLC/UV method 439/0 and LC/MS/MS method 446/1) for animal matrices.

45118507 Jordan, J. (2000) Independent Method Validation of BASF Analytical Method 446/1 Entitled "LC/MS/MS Method for the Determination of Reg No. 304428 (BAS 500 F) and its Metabolites BF 500-10 in Matrices of Animal Origin." BASF Study No. 62681; BASF Registration Document No. 2000/5002. Unpublished study prepared by BASF Corporation. 58 p.

45118514 Kruppa, J. (1999) Independent Method Validation of BASF Method 439/0 for the Determination of BAS 500 F (as Parent Compound) in Matrices of Animal Origin. Laboratory Project Identification No. 15G99015; BASF Registration Document No. 1999/11369. Unpublished study prepared by BASF Corporation. 19 p.

The ILV of the HPLC/UV method was performed by Fraunhofer Institute of Toxicology and Aerosol Research (Germany), and the ILV of the LC/MS/MS method was performed by BASF, Agricultural Products Center (APC; Research Triangle Park, NC) by chemists unfamiliar with the method or its development.

For independent method validation of **HPLC/UV method 439/0**, untreated homogenized samples of cow milk and muscle supplied by BASF were used. Five subsamples each of untreated milk and muscle were fortified with pyraclostrobin at the LOQ (0.01 ppm for milk and 0.05 ppm for muscle) and 10x the LOQ (0.1 ppm for milk and 0.5 ppm for muscle). Fortified and unfortified milk and muscle samples were analyzed for residues of pyraclostrobin using the HPLC/UV method 439/0 (described above).

Using the **HPLC/UV** method, acceptable validation recoveries were obtained with the first attempt for pyraclostrobin in milk and muscle at both fortification levels. The results of the ILV study are shown in Table 24. Apparent residues of pyraclostrobin were less than the method LOQ in control milk and muscle (inspection of the control chromatograms showed negligible background or interfering peaks). The required time for analysis was not reported by the laboratory. Representative sample calculations and chromatograms were provided.

For independent method validation of the **LC/MS/MS method 446/1**, untreated homogenized samples of cow milk and liver supplied by BASF were used as representative difficult matrices. Two subsamples each of untreated milk and liver were fortified with pyraclostrobin and BF 500-10 at the LOQ (0.01 ppm for milk and 0.05 ppm for liver) and 10x the LOQ (0.1 ppm for milk and 0.5 ppm for liver). Fortified and unfortified milk and liver samples were analyzed for residues of pyraclostrobin and BF 500-10 using the LC/MS/MS method 446/1 (described above).

Using the **LC/MS/MS** method, unacceptable validation recoveries were obtained with the first attempt for pyraclostrobin and BF 500-10 in liver at the higher fortification level. Following communication between APC Laboratory and BASF, it was concluded that the interferences observed in liver samples could be reduced by modifying the chromatographic conditions (mobile phases). Samples from the first attempt were re-injected using an isocratic mobile phase of ACN:water (9:1, v:v) instead of the gradient ACN and water mobile phase suggested in the method, but this system actually enhanced the matrix interference. Samples from the first attempt were then diluted and re-analyzed using the gradient system; acceptable recoveries were obtained, peak shape was slightly better, and less interference was observed. A fourth attempt was also made using a different column and methanol mobile phase, but matrix interferences were not improved with this system. Only the results from the diluted sample (third re-injection) were reported. Acceptable validation recoveries were obtained with the first attempt for pyraclostrobin and BF 500-10 in milk at both fortification levels; however recoveries were low for pyraclostrobin at the higher fortification level. The laboratory noted that milk samples were diluted for analysis to a greater level than specified in the method. The petitioner states that the lower recoveries for pyraclostrobin in milk were comparable to method validation recoveries, and, based on the unsuccessful method variations tried with liver, no additional attempts were made for milk. The results of the ILV study are shown in Table 24. Apparent residues of BF 500-5 and BF 500-8 were each less than the method LOD (50 pg, lowest standard level injected with the analysis set with at least a 10:1 signal:noise ratio) in control milk and liver, except that residues of BF 500-5 were 0.003 ppm in one milk control sample. Milk recoveries reported in Table 24 were corrected for the matrix interferences observed in the control sample for BF 500-

5. The laboratory reported that, working slowly and methodically, as required for an independent validation, one analyst prepared the samples in 18 hours (or 2 days); analysis required 2 additional hours. Representative sample calculations and chromatograms were provided.

Table 24. Independent method validation recoveries of pyraclostrobin and/or BF 500-10 from fortified cow milk and liver or muscle untreated samples analyzed using the proposed HPLC/UV or LC/MS/MS tolerance enforcement methods.

Matrix	Fortification Level, ppm	Percent Recovery	
		Pyraclostrobin ^a	BF 500-10 ^b
HPLC/UV Method 439/0			
Cow, milk	0.01	89.1, 94.5, 96.2, 97.3, 109	--
	0.1	87.0, 91.0, 92.0, 92.0, 93.0	--
	Mean ± s.d. ^c	94.1 ± 6	--
Cow, muscle	0.05	78.0, 83.5, 84.5, 96.0, 101	--
	0.5	93.3, 94.0, 94.5, 94.5, 96.3	--
	Mean ± s.d. ^c	91.6 ± 7	--
LC/MS/MS Method 446/1			
Cow, milk Trial #1	0.01	54.3, 98.6	97.5, 109.4
	0.10	53.4, 60.2	54.5, 108
	Mean ± s.d. ^c	66.6 ± 22	92.4 ± 26
Cow, liver Trial #1; 3rd injection (diluted)	0.05	67.0, 73.0	73.1, 92.4
	0.50	58.4, 75.5	60.9, 67.1
	Mean ± s.d. ^c	68.5 ± 8	73.4 ± 14

^a Residues of pyraclostrobin were quantitated as parent using the HPLC/UV method; residues of pyraclostrobin were quantitated as BF 500-5 and calculated as pyraclostrobin by molecular weight conversion using the LC/MS/MS method.

^b Residues of BF 500-10 were quantitated as BF 500-8 and calculated as BF 500-10 by molecular weight conversion using the LC/MS/MS method.

^c Overall mean and standard deviation were calculated by the study reviewer.

Radiovalidation

To demonstrate extraction efficiency and accountability of the proposed LC/MS/MS and GC/MS enforcement methods for animals, the petitioner submitted radiovalidation data (citation listed below) for LC/MS/MS Method 446/1 and GC/MS method 446/0 using ¹⁴C-labeled samples from the goat metabolism study. The radiovalidation study was conducted by BASF Aktiengesellschaft (Germany).

45118512 Tilting, N.; Knoell, H. (2000) ¹⁴C-Validation of Method 446 for the determination of BAS 500 F (Reg. No. 304428) and its Metabolites in Matrices of Animal Origin.

Samples of milk, liver, and muscle from the goat metabolism study (goat dosed with [¹⁴C-chlorophenyl]pyraclostrobin at 78 ppm for 5 consecutive days) were used for the radiovalidation study. For the radiovalidation study, the metabolism samples were extracted as required for the residue method and quantitated using the residue methods LC/MS/MS (milk, liver and muscle) or GC/MS (milk only), and by HPLC/radiodetection. Residues were converted to parent equivalents.

To verify extractability, TRR were redetermined for the metabolism samples using LSC or combustion/LSC prior to extraction by the residue method and at various points during the extraction and cleanup procedures. Results of the radiovalidation study are presented in Table 25. The radiovalidation data presented in Table 25 indicate that the proposed enforcement methods, GC/MS method 446/0 and LC/MS/MS method 446/1, adequately extract residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 from ruminant commodities.

Table 25. Radiolabeled method validation of the GC/MS and LC/MS/MS residue extraction methods using samples from goat metabolism studies bearing [¹⁴C]pyraclostrobin residues.

Matrix	Residue Method	Metabolism Study	Recovery, %
	Total residues ^a , as parent equivalents, ppm	Total pyraclostrobin and BF 500-10 associated residues, ppm [¹⁴ C]pyraclostrobin equivalents ^b	
GC/MS Method 446/0			
Milk	0.251	0.222	113
LC/MS/MS Method 446/1			
Milk	0.144	0.222	64.9
Liver	0.709	0.757	93.7
Muscle	0.055	0.099	55.6

^a Includes all residues hydrolyzable to BF 500-5 and to BF 500-8.

^b Metabolites from the metabolism which were included in this total are: (i) for milk, parent, 500M04 (BF 500-5), 500M05, 500M07 (BF 500-3), 500M64, 500M67, and 500M85 (BF 500-8); (ii) for liver, parent, 500M04, 500M05, 500M07, 500M67, and 500M85; and (iii) for muscle, parent and 500M07.

Data collection methods - livestock commodities

Whole milk, skim milk, milk fat, and tissue samples from the ruminant feeding study were analyzed for residues of pyraclostrobin *per se* using HPLC/UV method 439/0. Milk and tissue samples were also analyzed by common moiety methods. Milk samples were analyzed for residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 using

GC/MS method 446/0. Tissue samples were analyzed for residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 using LC/MS/MS method 446/1. For all methods, the reported method LOQs for BF 500-5 and BF 500-8 (in parent equivalents) were each 0.01 ppm in milk and 0.05 ppm in tissues.

Egg and tissue samples from the poultry feeding study were analyzed for residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-3 and BF 500-9 using a common moiety method, LC/MS/MS method D9902. The reported method LOQs for BF 500-5 and BF 500-9 (in parent equivalents) were 0.05 ppm each in eggs and tissues.

The analytical methods used in the feeding studies for data collection are the same as those proposed for enforcement purposes and have been described above. Concurrent method validations were performed in conjunction with the ruminant and poultry feeding studies. For the ruminant feeding study, untreated samples of whole and skim milk, milk fat, fat, kidney, liver, and muscle were fortified with pyraclostrobin at the method LOQ (0.01 ppm for milk and 0.05 ppm for tissues) and 10x the LOQ, and analyzed with the treated samples using the HPLC/UV method 439/0. In addition, untreated samples of whole and skim milk, and milk fat were fortified with pyraclostrobin (representative of compounds hydrolyzable to BF 500-5) and BF 500-10 (representative of compounds hydrolyzable to BF 500-8) at the method LOQ (0.01 ppm) and 10x the LOQ, and analyzed with the treated samples using the GC/MS method 446/0. Untreated samples of fat, kidney, liver, and muscle were fortified with pyraclostrobin and BF 500-10 at the method LOQ (0.05 ppm for tissues), 10x the LOQ, and 2.0 ppm (liver only), and analyzed with the treated samples using the LC/MS/MS method 446/1. For the poultry feeding study, untreated samples of eggs, fat, liver, and muscle were fortified with pyraclostrobin and BF 500-16 (representative of compounds hydrolyzable to BF 500-9) at the method LOQ (0.05 ppm each analyte). Fortified poultry samples were analyzed with the treated samples using the LC/MS/MS method D9902. Concurrent method recoveries of fortified ruminant and poultry samples are reported in Table 26.

Table 26. Concurrent method validation recoveries of residues of pyraclostrobin and BF 500-10 or BF 500-16 from fortified samples of livestock commodities analyzed using the HPLC/UV method 439/0, GC/MS method 446/0, or LC/MS/MS method 446/1 or D9902.

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
HPLC/UV Method 439/0				
Cow, whole milk (45118518)	0.01, 0.1	Average (%)	88.5	--
		Recovery range (%)	74.3-109.1	--
		SD (%)	7.4	--
		Number of samples	32	--
Cow, skim milk (45118518)	0.01, 0.1	Average (%)	81.7	--
		Recovery range (%)	72.0-90.5	--
		SD (%)	8.9	--
		Number of samples	4	--
Cow, milk fat (45118518)	0.01, 0.1	Average (%)	87.3	--
		Recovery range (%)	68.8; 71.8-99.2	--
		SD (%)	13.6	--
		Number of samples	6	--
Cow, fat (45118518)	0.05, 0.5	Average (%)	95.2	--
		Recovery range (%)	87.4-102.3	--
		SD (%)	5.4	--
		Number of samples	6	--
Cow, kidney (45118518)	0.05, 0.5	Average (%)	85.5	--
		Recovery range (%)	69.0; 77.2-97.9	--
		SD (%)	12.2	--
		Number of samples	5	--
Cow, liver (45118518)	0.05, 0.5	Average (%)	100.8	--
		Recovery range (%)	97.2-103.3	--
		SD (%)	2.3	--
		Number of samples	6	--
Cow, muscle (45118518)	0.05, 0.5	Average (%)	92.8	--
		Recovery range (%)	81.5-103.8	--
		SD (%)	7.7	--
		Number of samples	6	--

Table 26 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
GC/MS Method 446/0				
Cow, whole milk (45118518)	0.01, 0.1	Average (%)	79.4	73.5
		Recovery range (%)	44.7-69.9; 70.2-114.9	45.0-69.4; 71.0-92.8
		SD (%)	14.5	12.0
		Number of samples	48	48
Cow, skim milk (45118518)	0.01, 0.1	Average (%)	66.4	66.8
		Recovery range (%)	56.2-64.6; 84.6	59.5-66.3; 79.4
		SD (%)	12.6	8.9
		Number of samples	4	4
Cow, milk fat (45118518)	0.01-0.5	Average (%)	68.9	66.6
		Recovery range (%)	56.7, 66.5; 75.0, 77.3	51.0, 65.2; 72.3, 78.0
		SD (%)	9.4	11.7
		Number of samples	4	4
LC/MS/MS Method 446/1				
Cow, fat (45118518)	0.05, 0.5	Average (%)	79.4	83.7
		Recovery range (%)	73.7, 85.2	82.9, 84.6
		SD (%)	--	--
		Number of samples	2	2
Cow, kidney (45118518)	0.05, 0.5	Average (%)	83.0	90.1
		Recovery range (%)	79.8-88.2	75.8-107.7
		SD (%)	3.7	15.7
		Number of samples	4	4
Cow, liver (45118518)	0.05-2.0	Average (%)	81.1	85.3
		Recovery range (%)	70.5-93.9	79.4-91.5
		SD (%)	9.7	5.0
		Number of samples	4	4
Cow, muscle (45118518)	0.05, 0.5	Average (%)	79.4	63.8
		Recovery range (%)	74.7, 84.1	60.8, 66.7
		SD (%)	--	--
		Number of samples	2	2

Table 26 (continued).

Commodity (MRID)	Fortification Level, ppm	Statistic	Method Recoveries ^a	
			Pyraclostrobin ^b	BF 500-10 or BF 500-16 ^c
LC/MS/MS Method D9902				
Hen, eggs (45118520)	0.05	Average (%)	101	68
		Recovery range (%)	75-114; 122	61-69; 70-80
		SD (%)	16	7
		Number of samples	7	7
Hen, fat (45118520)	0.05	Recovery (%)	96	80
		Number of samples	1	1
Hen, liver (45118520)	0.05	Recovery (%)	85	96
		Number of samples	1	1
Hen, muscle (45118520)	0.05	Recovery (%)	112	52
		Number of samples	1	1

^a Recoveries outside the acceptable 70-120% range are listed separately.

^b Residues of pyraclostrobin were quantitated as BF 500-5 and calculated using molecular weight conversions for LC/MS/MS methods 446/1 and D9902.

^c For cow commodities, residues of BF 500-10 were determined (as BF 500-8), and for hen commodities, residues of BF 500-16 were determined (as BF 500-9).

Comments:

The petitioner has proposed two tolerance enforcement methods for ruminant commodities: HPLC/UV method 439/0 and Method 446, consisting of GC/MS method 446/0 and LC/MS/MS method 446/1. The HPLC/UV method determines residues of pyraclostrobin *per se*. Method 446 is a common moiety method that determines residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8. The validated method LOQs for BF 500-5 residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues, and the validated LOQs for BF 500-8 residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues. Independent method validation is adequate for the HPLC/UV method and marginal for the LC/MS/MS method. radiovalidation data are adequate for the GC/MS method, and adequate for liver but marginal for milk and muscle for the LC/MS/MS method.

The petitioner has proposed that the tolerance expression for livestock commodities consist of pyraclostrobin and its desmethoxy metabolite, BF 500-3; pyraclostrobin and BF 500-3 would be hydrolyzed to BF 500-5 using Method 446. The proposed enforcement methods, therefore, include more metabolites than the petitioner has proposed in the tolerance expression. Pending MARC determination of the residues of concern in livestock commodities, the petitioner may have to revise the proposed tolerance expression for livestock commodities to include the compounds that are determined using the enforcement method.

The petitioner has proposed tolerances for eggs and poultry tissues, and has included method validation data for the LC/MS/MS method D9902, a common moiety method which is used to quantitate residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-9 in poultry matrices. No independent laboratory validation or radiovalidation data have been submitted in support of the method. Since Method D9902 is very similar to Method 446, an independent laboratory validation is not required.

The proposed enforcement methods were used for data collection in the ruminant and poultry feeding studies. The concurrent method validation recoveries demonstrate that the methods are adequate for data collection.

Method 446 has been forwarded to ACB/BEAD for petition method validation, because adequate method validation (marginal for ILV and radiovalidation) data have been submitted. The petitioner must modify the proposed enforcement method to include any modifications made by the EPA laboratory during the Agency laboratory validation.

OPPTS GLN 860.1360: Multiresidue Method

The petitioner has submitted data (citation listed below) pertaining to the multiresidue methods testing of pyraclostrobin and its desmethoxy metabolite, BF 500-3.

45118515 Fomenko, J. (2000) Evaluation of BAS 500 F Through the FDA Multiresidue Methods. Lab Project Number: A0080.84. BASF Protocol Number: 97136. BASF Reg. Doc. Number: 2000/5015. Unpublished study prepared by Maxim Technologies, Inc. 106 p.

Pyraclostrobin was successfully evaluated through several of the FDA protocols, while recovery of BF 500-3 was unsuccessful in all protocols. Neither pyraclostrobin nor BF 500-3 were evaluated by Protocol A or B because they do not contain N-methylcarbamate, or carboxylic or phenol structures. Under Protocol C, pyraclostrobin demonstrated good chromatography with DB-1 column/ECD, and was completely recovered through Protocol D (in grape) and E (in grape), and partially recovered through Protocol F (in peanut) with the mixed ether elution system; pyraclostrobin was not recoverable from Florisil using the methylene chloride elution system. Metabolite BF 500-3 had poor peak shape and inadequate sensitivity with Protocol C columns and therefore was not further analyzed under Protocols D, E, and F. The results of the multiresidue testing for pyraclostrobin will be forwarded to FDA for inclusion in PAM Volume I.

OPPTS GLN 860.1380: Storage Stability Data

Plant sample storage conditions and intervals

The RAC samples from the submitted field trial and field rotational crop studies, except bananas, were frozen soon after collection and were shipped frozen to BASF APC for analysis. Samples of bananas from the Central and South American field trials, which were shipped at ambient conditions and were frozen within 3-7 days of harvest once received at APC. Samples were stored under frozen conditions (<-10 C) at the analytical laboratory until preparation for analysis.

Grape samples from a processing study were stored in temperature-monitored coolers, and were shipped at ambient temperature to National Food Laboratories (Dublin, CA) the day for processing. Samples were stored frozen at the National Food Laboratories for 4 days prior to processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

Orange samples from a processing study were collected and shipped the day after harvest at ambient conditions to the Citrus Research and Education Center, University of Florida (Lake Alfred, FL) for processing. Samples were stored under ambient conditions for 3 days at the University of Florida until processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

Whole peanut samples from a processing study were collected, threshed, placed into bags, and stored in an air conditioned room for 5 hours until being shipped at ambient conditions to Texas A&M, Food Protein Research and Development Center (Bryan, TX) for processing. Samples were stored frozen for 8 days until processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

Plums samples from a processing study were collected, placed into bags, and shipped at ambient conditions to National Food Laboratories (Dublin, CA) the same day for processing. Following processing, washed plums and prunes were stored frozen, and RAC and processed samples (washed plums and prunes) were shipped frozen to BASF APC for analysis.

Whole potato samples from a processing study were placed into bags and cardboard boxes for shipment to Englar Food Laboratories, Inc. (Moses Lake, CA). Before delivery to the processor, a RAC subsample was collected from the larger sample and shipped directly to BASF APC for residue screening prior to processing. Upon receipt RAC samples were frozen (<-10 C) prior to analysis.

Sugar beet root samples from a processing study were collected by hand, lightly brushed to remove excess dirt, placed into bags, and shipped at ambient conditions to Englar Food Laboratories, Inc. (Moses Lake, CA) within 24 hours of harvest. Samples were stored frozen for 18-22 days at the Englar Food Laboratories until processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

Whole tomato samples from a processing study were collected and shipped fresh to National Food Laboratories, Inc. (Dublin, CA) on the day of harvest. Samples were stored in a cooler for 1-2 days at the National Food Laboratories until processing. Processed commodities (tomato paste and puree) were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

Wheat grain samples from processing studies were each collected from the 1x and 5x treatment plots. Samples from the 1998 study were shipped at ambient conditions to Englar Food Laboratories, Inc. (Moses Lake, WA) on the day of harvest. Samples were stored frozen at Englar Food Laboratories prior to processing. Samples from the 2000 study were shipped frozen to the Food Protein Research and Development Center (Bryan, TX) within 14 days of harvest. Samples were stored frozen at the processor prior to processing, and processing was completed within 53 days of harvest. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis.

The total storage intervals between harvest and analysis for RAC and processed commodity samples from the submitted field trial, processing, and field rotational crop studies are reported in Table 27.

Table 27. Storage intervals of various crop commodities from harvest to analysis.

Crop Commodity	MRID	Storage Interval
Almond, nutmeat	45118521	~2.5-4 months
Almond, hull		~3-4 months
Banana	45118532	~1-3.5 months
Barley, hay	45118535	~7-10 months
Barley, grain		~4-7 months
Barley, straw		~7-10 months
Bean, dry	45367501	~4-5 months
Bean, snap	45367501	~5-6 months
Blueberry, highbush	45118605	~2-3 months
Cabbage (with wrapper leaves)	45118623	~4-9 months
Cabbage (without wrapper leaves)		~2-9 months
Cantaloupe	45118603	~2-4 months
	45118613	~2 months
Carrot	45118523	~3.5-7.5 months
Cherry, sweet	45118607	~3-4 months
Cherry, tart		~3 months
Cucumber	45118603	~1.5-10.5 months
	45118613	~2.5 months
Grape	45118529	~11-15.5 months
	45118530	~0.5-3.5 months
	45118531	~8-10 months
	45118613	~1.5-2.5 months
Grape (for processing)	45118616	~15 months
Grape juice		~15 months
Raisin		~15-15.5 months
Grapefruit	45118606	~0.5-7 months
Grass, forage	45118527	~1-5.5 months
Grass, hay		~1-5.5 months
Grass, straw		~3.5-6 months
Grass, seed screenings		~3.5-6 months
Lemon	45118606	~1-7 months
Lentil, seed	45118526	~1.5-3 months
Onion, dry bulb	45118525	~2-5.5 months
Onion, green		~3.5-6 months
Orange	45118606	~0.5-7.5 months

Table 27 (continued).

Crop Commodity	MRID	Storage Interval
Orange, unwashed (for processing)	45118617	~2 months
Orange, washed (for processing)		~2 months
Dried orange pulp		~2-3 months
Orange oil		~2-3.5 months
Orange juice		~2 months
Pea, dry, hay	45118522	~3-5 months
Pea, dry, vines		~3-5 months
Pea, dry, seed		~3-4 months
Peach	45118607	~2-4.5 months
Peanut, hay	45118533	~12-15 months
	45118534	~6.5-8 months
Peanut, nutmeat	45118533	~12-15.5 months
	45118534	~6.5-8 months
Peanut, nutmeat (for processing)	45118614	~19 months
Peanut, meal		~18 months
Peanut, oil		~17 months
Pecan, nutmeat	45118612	~1-2 months
Pepper, bell	45118611	~3-5 months
Pepper, chili		~2-4 months
Pistachio	45118610	~3.5-4 months
Plum	45118607	~2-3 months
Plum, unwashed (for processing)	45118621	~3 months
Plum, washed (for processing)		~3 months
Prune		~3 months
Potato	45118608	~1-6 months
	45118618	5 days
Radish, roots	45118609	~1-5 months
Radish, tops		~1-5 months
Radish, roots	45118623	~5-11 months
Radish, tops		~5-10 months
Raspberry, red	45118605	~2-3 months
Rye, grain	45118536	~12-13.5 months
Rye, straw		~12-14 months
Squash, summer	45118603	~4-5.5 months
	45118613	~1.5 months
Strawberry	45118604	~3-5 months

Table 27 (continued).

Crop Commodity	MRID	Storage Interval	
Sugar beet, roots	45118524	~1-2.5 months	
Sugar beet, tops		~1-2.5 months	
Sugar beet, roots (for processing)	45118619	~1.5 months	
Dried sugar beet pulp		~1.5 months	
Molasses		~1.5 months	
Refined sugar		~1.5 months	
Tomato		~3-6 months	
	45118613	~1-2 months	
Tomato, whole, unwashed (for processing)	45118615	~4 months	
Tomato, paste		~4 months	
Tomato, puree		~4 months	
Wheat, hay		~6-9 months	
Wheat, grain	45118537	~4-7 months	
Wheat, straw		~10-13 months	
Wheat, forage		~5-8 months	
Wheat, hay	45118623	~5-7 months	
Wheat, grain		~3-7 months	
Wheat, straw		~1-4 months	
Wheat, grain (for processing)		~12 months	
Wheat, flour	45118620	~12 months	
Wheat, bran		~12 months	
Wheat, middlings		~12 months	
Wheat, shorts		~12 months	
Wheat, germ		~12 months	
Wheat, aspirated grain fractions		~15 months	
Wheat, grain		45321101	~1.5-7 months
Wheat, straw			~1.5-7.5 months
Wheat, grain (for processing)	~3 months		
Wheat, flour	~3.5 months		
Wheat, bran	~3.5 months		
Wheat, middlings	~3 months		
Wheat, shorts	~3 months		
Wheat, germ	~3 months		
Wheat, aspirated grain fractions	~3 months		

Plant storage stability data

In support of the storage intervals and conditions of samples from the field trial and processing studies, BASF has submitted storage stability data (citations listed below) for various plant commodities. Diverse plant commodities were chosen to represent all crops: an oilseed (peanut nutmeat), a non-oily grain (wheat grain), a leafy vegetable (sugar beet tops), a root crop (sugar beet roots), a fruit/fruited vegetable (tomatoes), a dry feed (wheat straw), and processed oil (peanut) and juice (grape) commodities.

45118516 Abdel-Baky, S.; Riley, M. (1999) Freezer Storage Stability of BAS 500 F and BF 500-3 in Various Plant Commodities Including Processed Commodities: Interim Report for up to 6 Months of Freezer Storage. BASF Study No. 90001419; BASF Registration Document No. 1999/5064. Unpublished study prepared by BASF Corporation. 80 p.

45272801 Abdel-Baky, S. (2000) Storage Stability of BAS 500 F and BF 500-3 in Various Plant Commodities Including Processed Commodities For Up to 19 Months of Freezer Storage. BASF Study No. 90001419; BASF Registration Document No. 2000/5248. Unpublished study prepared by BASF Corporation. 96 p.

45429901 Abdel-Baky, S. (2001) FINAL REPORT Freezer Storage Stability of BAS 500 F and BF 500-3 in Plant Matrices Including Processed Commodities. BASF Study No. 66414; BASF Registration Document No. 2001/5000232. Unpublished study prepared by BASF Corporation. 62 p.

Untreated samples of grape juice, peanut nutmeat and processed oil, sugar beet tops and roots, tomatoes, and wheat grain and straw from field trial and processing studies were fortified with pyraclostrobin and its metabolite BF 500-3 each at 0.5-2.0 ppm (typically 1.0 ppm), and stored frozen (≤ -10 C). Samples were analyzed at the 0-, 1-, 3-, 6-, 14-, 18- or 19-, and 25-month storage intervals. The 18-19 month storage stability data support the longest storage intervals incurred in the field trial, processing, and field rotational crop studies.

Residues of pyraclostrobin and BF 500-3 were determined using the LC/MS/MS method D9808. Control samples were fortified with pyraclostrobin and BF 500-3, each at 1.0 ppm, at the time of analysis for concurrent recoveries; control samples of peanut nutmeat, sugar beet roots, and wheat grain at the 3-month interval were fortified with pyraclostrobin and BF 500-3, each at 0.50 ppm, and control samples of peanut oil were fortified with each analyte at 2.0 ppm at the 1-month interval. Apparent residues of pyraclostrobin and BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on six untreated samples each of grape juice, peanut nutmeat and refined oil, sugar beet tops and roots, tomatoes, and wheat grain and straw. The results of the storage stability studies are presented in Table 28.

Table 28. Frozen storage stability and concurrent method recoveries (fresh fortification recovery) of residues of pyraclostrobin and its metabolite BF 500-3 from samples of fortified plant commodities.

Matrix	Fresh Fortification Level, ppm	Storage Period, months	Pyraclostrobin			BF 500-3		
			Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b	Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b
Grape, juice	1.0	0	106, 117, 121, 133	--	--	97, 104, 104, 115	--	--
		1	79, 83 (81)	76, 79	94, 98	72, 74 (73)	68, 70	93, 96
		3	96, 107 (102)	95, 96	93, 94	98, 103 (101)	92, 93	91, 92
		6	74, 75 (75)	71, 72	95, 96	78, 79 (79)	73, 74	92, 94
		14	73, 85 (79)	42, 67	53, 85	65, 77 (71)	56, 58	79, 82
		18	96, 99 (98)	76, 95	78, 97	92, 101 (97)	84, 95	87, 98
		25	91, 79 (85)	71, 65 (68)	84, 76 (80)	97, 90 (94)	87, 80 (84)	93, 85 (89)
Peanut, nutmeat	1.0	0	57, 75, 80, 86	--	--	51, 67, 75, 82	--	--
	1.0	1	83, 118 (101)	90, 103	89, 102	80, 127 (104)	92, 106	88, 102
	0.5	3	91	78, 85	86, 93	79	82, 95	104, 120
	1.0	6	53, 84 (69)	57, 67	83, 97	64, 80 (72)	66, 66	92, 92
	1.0	14	58, 71 (65)	59, 63	91, 98	55, 63 (59)	52, 56	88, 95
	1.0	19	85, 89 (87)	70, 83	80, 95	85, 86 (86)	61, 82	71, 96
Peanut, refined oil	1.0	0	79, 84, 87, 90	--	--	75, 75, 78, 84	--	--
	2.0	1	105, 109 (107)	97, 100	91, 93	104, 109 (107)	96, 100	90, 93
	1.0	3	106, 107 (107)	108, 109	101, 102	91, 92 (92)	91, 96	99, 104
	1.0	6	75, 79 (77)	88, 94	114, 122	73, 76 (75)	88, 93	117, 124
	1.0	14	89	89, 91	100, 102	75	76, 78	101, 104
	1.0	19	86, 89 (88)	89, 95	102, 109	65, 78 (72)	83, 89	116, 124

Table 28 (continued).

Matrix	Fortification Level, ppm	Storage Period, months	Pyraclostrobin			BF 500-3		
			Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b	Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b
Sugar beet, tops	1.0	0	96, 107, 109, 114	--	114, 122, 122, 124	--	--	--
		1	92, 96 (94)	91, 97	97, 103	91, 92 (92)	92, 93	100, 101
		3	99, 102 (101)	94, 100	93, 99	85, 93 (89)	86, 90	97, 101
		6	85, 88 (87)	85, 88	98, 101	85, 86 (86)	83, 87	97, 101
		14	72, 78 (75)	67, 70	89, 93	63, 64 (64)	57, 61	90, 96
		18	84, 90 (87)	83, 88	95, 101	79, 90 (85)	82, 85	97, 101
		25	73, 87 (80)	73, 85 (79)	91, 106 (99)	70, 78 (74)	76, 81 (79)	103, 109 (107)
		0	99, 101, 106, 111	--	--	119, 119, 135, 139	--	--
		1	95, 97 (96)	90, 90	94, 94	92, 94 (93)	88, 93	95, 100
		0.5	97, 97 (97)	86, 92	89, 95	90, 91 (91)	88, 88	97, 97
Sugar beet, roots	1.0	1	98, 98 (98)	96, 97	98, 99	97, 98 (98)	95, 96	97, 98
		3	106, 108 (107)	102, 103	95, 96	99, 103 (101)	96, 100	95, 99
		6	84, 101 (93)	79, 88	85, 95	84, 95 (90)	74, 79	82, 88
		14	79, 81 (80)	69, 76	86, 95	71, 73 (72)	58, 65	81, 90
		18	93, 95 (94)	88, 92	94, 98	92, 96 (94)	85, 88	90, 94
		25	94, 84 (89)	70	79	92, 87 (90)	68	76
Tomato	1.0	0	93, 99, 101, 101	--	--	89, 96, 97, 98	--	--
		1	98, 98 (98)	96, 97	98, 99	97, 98 (98)	95, 96	97, 98
		3	106, 108 (107)	102, 103	95, 96	99, 103 (101)	96, 100	95, 99
		6	84, 101 (93)	79, 88	85, 95	84, 95 (90)	74, 79	82, 88
		14	79, 81 (80)	69, 76	86, 95	71, 73 (72)	58, 65	81, 90
		18	93, 95 (94)	88, 92	94, 98	92, 96 (94)	85, 88	90, 94

Table 28 (continued).

Matrix	Fresh Fortification Level, ppm	Storage Period, months	Pyraclostrobin			BF 500-3		
			Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b	Fresh Fortification Recovery, % ^a	Apparent Recovery in Stored Samples, %	Corrected Recovery in Stored Samples, % ^b
		25	84, 82 (83)	79, 78 (79)	95, 94 (95)	80, 83 (82)	75, 71 (73)	91, 87 (89)
Wheat, grain	1.0	0	82, 89, 90, 91	--	--	82, 87, 89, 93	--	--
	1.0	1	96, 97 (97)	87, 91	90, 94	89, 94 (92)	79, 85	86, 92
	0.5	3	89, 95 (92)	80, 80	87, 87	78, 82 (80)	68, 69	85, 86
	1.0	6	91, 93 (92)	83, 85	90, 92	88, 95 (92)	78, 79	85, 86
	1.0	14	73, 75 (74)	60, 61	81, 82	64, 67 (66)	51, 52	78, 79
	1.0	18	94, 106 (100)	87, 88	87, 88	91, 106 (99)	88, 88	89, 89
	1.0	25	91, 89 (90)	80, 81 (81)	89, 90 (90)	85, 82 (84)	67, 73 (70)	80, 87 (83)
Wheat, straw	1.0	0	75, 81, 85, 91	--	--	93, 95, 102, 122	--	--
		1	107, 117 (112)	100, 115	89, 103	105, 116 (111)	89, 112	80, 101
		3	77, 81 (79)	75, 76	95, 96	66, 69 (68)	65, 69	96, 101
		6	80, 85 (83)	93	112	76, 85 (81)	84	104
		14	49, 53 (51)	32, 40	63, 78	48, 56 (52)	31, 35	60, 67
		18	89, 92 (91)	84, 96	93, 106	89, 90 (90)	82, 92	92, 103
		25	82, 81 (82)	82, 81 (82)	101, 99 (100)	71, 74 (73)	76, 68 (72)	105, 94 (100)

^a Average fresh fortification recoveries are presented in parentheses.

^b The petitioner calculated the corrected recovery values using the average fresh fortification recovery value.

Comments:

The submitted storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-3 are 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 plant commodities chosen for the storage stability study are representative of all crops: an oilseed (peanut nutmeat), a non-oily grain (wheat grain), a leafy vegetable (sugar beet tops), a root crop (sugar beet roots), a fruit/fruited vegetable (tomatoes), a dry feed (wheat straw), and processed oil (peanut) and juice (grape) commodities.

The available storage stability data support the storage intervals (≤ 19 months) of the samples of almond nutmeat and hull, banana, barley hay, straw, and grain, blueberry, cabbage, cantaloupe, carrot, cherry (sweet and tart), cucumber, grape, grape juice, raisin, grapefruit, grass forage, hay, straw, and seed screenings, lemon, lentils, onion (bulb and green), orange, orange processed commodities, dry pea hay, vine, and seed, peach, peanut hay and nutmeat, peanut processed commodities, pecan, pepper (bell and chili), pistachio, plum and its processed commodity prune, potato, radish roots and tops, raspberry (red), rye grain and straw, squash (summer), strawberry, sugar beet (roots and tops), sugar beet processed commodities, tomato, tomato processed commodities, wheat forage, hay, grain, aspirated grain fractions, and straw; and wheat processed commodities from the submitted field trial, field rotational crop, and processing studies.

Animal sample storage conditions and intervals

Samples of cow milk from the ruminant feeding study were composited by day (a.m. and p.m.) and frozen. Subsamples of milk collected on Day 26 were separated into milk fat and skim milk by centrifugation and frozen. Milk samples were shipped twice during the study by freezer van to BASF for analysis. Tissue samples (liver, kidney, fat, and muscle) were chopped, frozen, and shipped to BASF for analysis. Milk and tissue samples were stored frozen (-18 C) at BASF prior to analysis. The maximum storage intervals from collection until analysis were 92 days (3 months) for whole milk, 81 days (2.7 months) for skim milk, 185 days (~ 6 months) for milk fat, 197 days (6.5 months) for fat, 172 days (5.7 months) for liver, 165 days (5.4 months) for kidney, and 153 days (5 months) for muscle.

Egg and tissue samples from the poultry feeding study were frozen after collection; tissue samples were homogenized with liquid nitrogen and frozen. Egg and tissue samples were shipped frozen via express mail to BASF for analysis, where all egg and tissue samples were stored frozen ($< -10\text{ C}$) prior to analysis. The maximum storage intervals from collection until analysis were 149 days (~ 5 months) for eggs, 126 days (~ 4 months) for fat, 92 days (~ 3 months) for liver, 174 days (~ 6 months) for muscle.

Animal storage stability data

In support of the storage intervals and conditions of samples from the ruminant and poultry feeding studies, BASF has submitted interim storage stability data for ruminant commodities and final storage stability data for eggs (citations listed below).

45118517 Tilting, N.; Knoell, H. (2000) Investigation of the Stability of Residues of BAS 500 F (Reg. No. 304428) in Sample Materials of Animal Origin Under Usual Storage Conditions. Laboratory Project Identification No. 35913; BASF Registration Document No. 2000/1000002. Unpublished study prepared by BASF Corporation. 41 p.

45274901 Malinsky, D. (2000) Freezer Storage Stability of BAS 500 F and its Metabolite BF 500-16 in Eggs. Laboratory Project Identification No. 61117; BASF Registration Document No. 2000/5047. Unpublished study prepared by BASF Corporation. 47 p.

Untreated samples of cow milk, liver, and muscle from the feeding study were fortified with pyraclostrobin and/or its metabolite BF 500-10 each at 0.5 ppm (liver and muscle) or 0.1 ppm (milk) and stored frozen (-20 C). Samples were analyzed at 0-, 30-, 60-, and 90-day storage intervals (MRID 45118517); a final report will be submitted to include data from the 240-day (~8 month) storage interval.

For ruminant samples fortified with only the parent, residues of pyraclostrobin were determined using HPLC/UV method 439/0. For samples fortified with both the parent and BF 500-10, residues of pyraclostrobin and BF 500-10 were determined as BF 500-5 and BF 500-8, respectively, using LC/MS/MS method 446/1. Control samples were fortified with pyraclostrobin and/or BF 500-10 at the same level as the stored samples at the time of analysis for concurrent recoveries. Apparent residues of pyraclostrobin were less than the method LOQ (<0.01 ppm for milk and <0.05 ppm for tissues) in/on one untreated sample each of cow milk, liver, and muscle using HPLC/UV method 439/0. Apparent residues of pyraclostrobin and BF 500-10 were each less than the method LOQ (<0.01 ppm for milk and <0.05 ppm for tissues) in/on one untreated sample each of cow milk, liver, and muscle using LC/MS/MS method 446/1. The results of the storage stability studies are presented in Table 29.

Untreated samples of eggs obtained from a local grocery were fortified with pyraclostrobin and BF 500-16 each at 0.10 ppm and stored frozen (<-10 C). Samples were analyzed at 0-, 1-, 3-, and 7-month storage intervals (MRID 45274901).

For egg samples, residues of pyraclostrobin and BF 500-16 were determined as BF 500-5 and BF 500-9, respectively, using LC/MS/MS method D9902. Control samples were fortified with pyraclostrobin and/or BF 500-16 at the same level (0.10 ppm) as the stored samples at the time of analysis for concurrent recoveries; the 1-month fresh recovery samples were mistakenly fortified at the 0.05 ppm level. Apparent residues of pyraclostrobin and BF 500-16 were each

less than the method LOQ (<0.05 ppm) in/on four untreated samples of eggs using LC/MS/MS method D9902. The results of the storage stability studies are presented in Table 29.

Table 29. Frozen storage stability and concurrent method recoveries (fresh fortification recovery) of residues of pyraclostrobin and/or its metabolite BF 500-10 (milk and ruminant tissues) or BF 500-16 (eggs) from samples of fortified livestock commodities.

Matrix	Fresh Fortification Level, ppm	Storage Period, months	Pyraclostrobin			BF 500-10 or BF 500-16 ^a		
			Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d	Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d
HPLC/UV Method 439/0								
Cow, milk	0.1	0	91.6, 94.5	--	--	--	--	--
		1	89.2, 90.4 (89.8)	87, 91	96.9, 101	--	--	--
		2	92.3, 104 (98.2)	93, 97	94.7, 98.8	--	--	--
		3	84.8, 85.5 (85.2)	95, 95	112, 112	--	--	--
Cow, liver	0.5	0	80.0, 91.6	--	--	--	--	--
		1	83.5, 92.0 (87.8)	87.8, 89.6	100, 102	--	--	--
		2	94.3, 98.9 (96.6)	93.6, 94.4	96.9, 97.7	--	--	--
		3	71.5, 79.8 (75.7)	82.4, 87.6	109, 116	--	--	--
Cow, muscle	0.5	0	78.7, 87.1	--	--	--	--	--
		1	88.0, 92.9 (90.5)	79.2, 84.2	87.5, 93.0	--	--	--
		2	90.9, 94.5 (92.7)	88.0, 90.6	94.9, 97.7	--	--	--
		3	87.6, 93.0 (90.3)	82.6, 83.4	91.5, 92.4	--	--	--

Table 29 (continued).

Matrix	Fresh Fortification Level, ppm	Storage Period, months	Pyraclostrobin				BF 500-10 or BF 500-16 ^a			
			Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d	Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d		
LC/MS/MS Method 446/1										
Cow, milk	0.1	0	71.9, 75.5	--	--	65.2, 67.9	--	--	--	--
		1	90.2, 90.9 (90.6)	74, 80	81.7, 88.3	86.6, 92.7 (89.7)	87, 88	97.0, 98.1		
		2	63.1, 64.7 (63.9)	79, 80	124, 125	63.7, 74.8 (69.3)	86, 89	124, 128		
		3	86.8	78, 91	89.9, 105	89.9	89, 97	99.0, 108		
Cow, liver	0.5	0	78.9, 82.0	--	--	74.2, 76.6	--	--	--	--
		1	80.7, 84.4 (82.6)	76.6, 80.2	92.7, 97.1	88.5, 93.4 (91.0)	93.4, 96.4	103, 106		
		2	64.6, 68.0 (66.3)	69.0, 70.2	104, 106	78.7, 83.2 (81.0)	74.4, 80.6	91.9, 99.5		
		3	68.3, 78.1 (73.2)	68.2, 75.8	93.2, 104	70.9, 76.5 (73.7)	68.6, 73.6	93.1, 99.9		
Cow, muscle	0.5	0	68.3, 75.8	--	--	62.3, 74.2	--	--	--	--
		1	75.0, 80.2 (77.6)	61.2, 67.4	78.9, 86.9	64.4, 66.0 (65.2)	54.8, 58.2	84.0, 89.3		
		2	76.1, 82.6 (79.4)	74.8, 76.8	94.2, 96.7	76.3, 78.5 (77.4)	72.6, 76.6	93.8, 99.0		
		3	61.4, 74.1 (67.8)	64.8, 74.6	95.6, 110	66.1, 87.0 (76.6)	64.6, 70.4	84.3, 91.9		

Table 29 (continued).

Matrix	Fresh Fortification Level, ppm	Storage Period, months	Pyraclostrobin			BF 500-10 or BF 500-16 ^a		
			Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d	Fresh Fortification Recovery, % ^b	Apparent Recovery in Stored Samples, % ^c	Corrected Recovery in Stored Samples, % ^d
LC/MS/MS Method D9902								
Eggs	0.10	0	78, 80	--	--	55, 56	--	--
		1	98, 107 (103)	87, 91	84, 88	58, 86 (72)	78, 81	108, 113
		3	76, 93 (85)	84, 97	99, 114	68, 86 (77)	67, 69	87, 90
		7	112, 114 (113)	86, 99	76, 88	78, 84 (81)	81, 87	100, 107

^a For milk and ruminant tissues, BF 500-10 was determined as BF 500-8; for eggs, BF 500-16 was determined as BF 500-9.

^b Average fresh fortification recoveries are presented in parentheses.

^c The corrected recovery values were calculated using the average fresh fortification recovery value.

Comments:

Cow commodity samples from the submitted ruminant feeding studies were stored frozen from collection to analysis for up to 3 months for whole and skim milk, 6.1 months for milk fat, 6.5 months for fat, 5.7 months for liver, 5.4 months for kidney, and 5 months for muscle. The submitted interim storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-10 are stable under frozen storage conditions in/on fortified samples of cow milk, liver, and muscle for up to 90 days (~3 months). The submitted storage stability data are adequate to support the storage conditions and intervals of the whole and skim milk samples from the ruminant feeding study; however, additional storage stability data are required to support the storage conditions and intervals of the milk fat and tissue samples from the ruminant feeding study. When the final report of the ruminant storage stability study becomes available, RAB3 will validate the stability of pyraclostrobin and its metabolites in milk and cow tissues stored under the conditions and intervals of the ruminant feeding study.

Hen commodity samples from the submitted poultry feeding study were stored frozen from collection until analysis up to 5 months for eggs, 4 months for fat, 3 months for liver, and 6 months for muscle. The submitted storage stability data indicate that residues of pyraclostrobin and its metabolite BF 500-16 are relatively stable under frozen storage conditions in/on fortified samples of eggs for up to 7 months. The submitted storage stability data for eggs are adequate to support the storage conditions and intervals of the egg samples from the poultry feeding study. The petitioner has referenced ruminant storage stability data to support the storage conditions and intervals of the remaining poultry matrices. The storage stability data for ruminant commodities may be translated to poultry commodities, pending MARC's decision on the residues of concern in livestock commodities.

OPPTS GLN 860.1500: Crop Field Trials

Root and Tuber Vegetables

Root Vegetables (Except Sugar Beet) - Crop Subgroup 1-B

BASF Corporation submitted carrot and radish field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Root Vegetables (Crop Subgroup 1-B) at 0.4 ppm. Data pertaining to radish tops are presented in the Leaves of Root and Tuber Vegetables section.

45118523 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of BAS 500 F Residues in Carrots: Lab Project Number: 1999/5155: 46743:99180. Unpublished study prepared by BASF Corporation. 61 p.

45118609 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Radishes: Lab Project Number: 1999/5149: 61658. Unpublished study prepared by Florida Pesticide Research, Inc., Crop Management Strategies, Inc. and California Agricultural Research, Inc. 59 p.

Carrot

A total of eight field trials were conducted during the 1999 growing season in CA(4), FL(1), ID(1), MN(1), and TX(1). In six trials conducted in CA(4), ID(1), and MN(1), mature carrots were harvested on the day of the last of three broadcast foliar applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application, made at 5- to 8-day retreatment intervals. The total seasonal application rates were 0.60-0.61 lb ai/A (~1x the maximum proposed seasonal application rate). In two trials conducted in FL(1) and TX(1), mature carrots were harvested on the day of the last of six broadcast foliar applications of the 20% WDG formulation at 0.08-0.09 lb ai/A/application, made at 6- to 7-day retreatment intervals. The total seasonal application rates were 0.49 lb ai/A (0.8x the maximum proposed seasonal application rate). The petitioner stated that these trials had commenced before the decision was made to pursue a crop subgroup tolerance for root vegetables. Applications were made in 13.17-40.07 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (CA), additional carrot samples were collected at 5, 9, 15, and 20 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature carrots were collected from each test site. The carrot tops were removed, and the collected samples were then frozen. All samples were shipped frozen to the BASF Agricultural Products Center (APC; Research Triangle Park, NC) where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02

ppm) in/on eight samples of untreated carrots. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 30.

Table 30. Residues of pyraclostrobin and its metabolite BF 500-3 in/on carrots harvested on the day of the last of either three applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate) or six applications of the 20% WDG formulation at 0.08-0.09 lb ai/A/application (0.8x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Tulare, CA/10	3	0.60	0	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
Tulare, CA/10	3	0.60	0	0.03, 0.04	<0.02, <0.02	<0.05, <0.06
Madera, CA/10	3	0.60	0	0.11, 0.12	<0.02, <0.02	<0.13, <0.14
			5	0.07, 0.08	<0.02, <0.02	<0.09, <0.10
			9	0.07, 0.08	<0.02, <0.02	<0.09, <0.10
			15	0.07, 0.08	<0.02, <0.02	<0.09, <0.10
			20	0.06, 0.08	<0.02, <0.02	<0.08, <0.10
Madera, CA/10	3	0.60	0	0.15, 0.15	<0.02, <0.02	<0.17, <0.17
Jerome, ID/11	3	0.61	0	0.23, 0.24	<0.02, <0.02	<0.25, <0.26
Freeborn, MN/5	3	0.60	0	0.10, 0.13	<0.02, <0.02	<0.12, <0.15
Hamilton, FL/3	6	0.49	0	0.05, 0.06	<0.02, <0.02	<0.07, <0.08
Uvalde, TX/6	6	0.49	0	0.03, 0.03	<0.02, <0.02	<0.05, <0.05

Radish

Five field trials were conducted during the 1999 growing season in CA(1), FL(2), IA(1), and PA(1). Mature radishes were harvested on the day of the last of three broadcast foliar applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application, made at 6- to 7-day retreatment intervals. The total seasonal application rates were 0.59-0.62 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 9.9-31.06 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature radishes (roots and tops) were collected from each test site. The collected samples were bagged separately, labeled, and then frozen. All samples were shipped frozen to the BASF APC for analysis. Samples of radish roots and tops were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples of untreated radish roots. Residues of pyraclostrobin and BF 500-3 in/on

treated root samples are presented in Table 31; residues in treated tops samples are presented in Table 33.

Table 31. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **radish roots** harvested on the day of the last of three applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Lehigh, PA/1	3	0.62	0	0.21, 0.24	<0.02, <0.02	<0.23, <0.26
Orange, FL/3	3	0.60	0	0.07, 0.09	<0.02, <0.02	<0.09, <0.11
Seminole, FL/3	3	0.60	0	0.29, 0.31	<0.02, <0.02	<0.31, <0.33
Jefferson, IA/5	3	0.59	0	0.04, 0.05	<0.02, <0.02	<0.06, <0.07
Fresno, CA/10	3	0.61	0	0.06, 0.07	<0.02, <0.02	<0.08, <0.09

Geographic representation of data for the establishment of a crop subgroup tolerance for the root vegetables (except sugar beets) subgroup (Crop Subgroup 1-B) is adequate. According to Table 3 of OPPTS GLN 860.1500, a total of 11 trials are required for this subgroup; six trials for carrot and five trials for radish. A total of six field trials were conducted with carrots in Regions 5 (1 trial), 10 (4 trials), and 11 (1 trial) and a total of five field trials were conducted with radishes in Regions 1 (1 trial), 3 (2 trials), 5 (1 trial), and 10 (1 trial) at the maximum proposed use rate. Two additional trials were conducted with carrots in Regions 3 (1 trial) and 6 (1 trial) at 0.8x the proposed maximum use rate.

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern for pyraclostrobin on carrots and radishes, the representative commodities of the root vegetables (except sugar beet) subgroup. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on carrots and radish roots harvested immediately (0-day PHI) following the last of three foliar applications of the WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.59-0.62 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-<0.26 ppm in/on 12 treated samples of carrots and <0.06-<0.33 ppm in/on 10 treated samples of radish roots; residues of BF 500-3 were below the LOQ in/on all samples.

The residue decline data for carrots showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.11-0.12 ppm at a 0-day PHI and declined to 0.06-0.08 ppm at a 20-day PHI. Residues of the metabolite BF 500-3 were below the LOQ in/on each treated sample.

Tuberous and Corm Vegetable - Crop Subgroup 1-C

Potato

BASF Corporation submitted potato field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Tuberous and Corm Vegetables (Crop Subgroup 1-C) at 0.04 ppm.

45118608 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Potatoes: Lab Project Number: 1999/5148: 46325. Unpublished study prepared by Southeast Ag Research, Inc., Ag-Quest, Inc. and Marbicon, Inc. 97 p.

A total of 23 field trials were conducted during the 1999 growing season. Seventeen of these field trials were conducted in the U.S. in CA(1), CO(1), FL(1), ID(5), MN(3), NJ(1), OR(1), PA(2), VA(1), and WI(1). Six field trials were conducted in Canada in AB(1), BC(1), MB(1), NS(1), PE(1), and QC(1). In the U.S. trials, potatoes were harvested 3 and 13-14 days following the last of six foliar applications, made at 6- to 9-day retreatment intervals, of the 20% WDG formulation at 0.18-0.22 lb ai/A/application. Total seasonal application rates were 1.18-1.24 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 16.27-40.7 gal/A of water using ground equipment with a spray adjuvant added to the spray solution. In two trials (MN and PA), additional potato samples were harvested 23, 33, and 43 days following treatment to evaluate residue decline.

In the Canadian trials, potatoes were harvested 3 and 13-14 days following the last of four foliar applications, made at 6- to 9-day retreatment intervals, of the 20% WDG formulation at 0.20-0.21 lb ai/A/application. Total seasonal application rates were 0.80-0.82 lb ai/A. Applications were made in 21.1-33.4 gal/A of water using ground equipment with a spray adjuvant added to the spray solution.

In two Canadian trials (MB and NS), three additional treatment plots were established in support of formulation bridging and to include metiram as a tankmix partner. For the bridging study, potatoes were harvested 3 and 14 days following the last of four foliar applications, made at 6- to 9-day retreatment intervals, of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application. Total seasonal application rates were 0.80-0.81 lb ai/A. For the tankmix study, potatoes were harvested 3 and 14 days following the last of four foliar applications, made at 6- to 9-day retreatment intervals, of either a tank mix of pyraclostrobin (20% WDG) at 0.19-0.21 lb ai/A/application plus metiram (72.1% WDG) at 1.55-1.66 lb ai/A/application or metiram (72.1% WDG) alone at 1.52-1.67 lb ai/A/application. Total seasonal application rates were 0.79-0.81 lb ai/A for pyraclostrobin and 6.337-6.495 lb ai/A for metiram. All applications were made in 20.4-23.9 gal/A of water using ground equipment with a spray adjuvant added to the spray solution.

A single untreated sample and duplicate treated samples of mature potatoes were collected from each test site. The collected samples were bagged separately, labeled, and then frozen. All

samples were shipped frozen to the BASF APC for analysis. Samples of potatoes from the 3-day PHI were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808; samples from the tank mix study were not analyzed for metiram. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 23 untreated samples of potato tubers. Residues of pyraclostrobin and BF 500-3 were each less than the LOQ in/on all treated potato tuber samples: 3-day PHI samples treated with the WDG formulation from the U.S. and Canadian trials (n=46), treated samples collected to evaluate residue decline (n=20), and 3-day PHI samples from the Canadian trials treated with the EC formulation or the WDG formulation as a tank mix with metiram (n=8). Since residues were below the LOQ at the 3-day PHI, samples collected at the 13- to 14-day PHI were not analyzed.

Geographic representation of potato data is adequate for the purposes of this petition. According to Table 3 of OPPTS 860.1500, a total of 16 potato trials are required for this subgroup. Seventeen potato field trials were conducted in the U.S. in Regions 1 (3 trials), 2 (1 trial), 3 (1 trial), 5 (4 trials), 9 (1 trial), 10 (1 trial), and 11 (6 trials). In addition, six potato field trials were conducted in Canada in Regions 1A (2 trials), 5B (1 trial), 7A (1 trial), 12 (1 trial), and 14 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on potato, the representative commodity of the tuberous and corm vegetables subgroup. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tuberous and corm vegetables (crop subgroup 1-C) tolerance level of 0.04 ppm in/on potatoes harvested 3 days following the last of six foliar applications of the WDG formulation at 0.18-0.22 lb ai/A/application for a total seasonal application rate of 1.24 lb ai/A (~1x the maximum proposed seasonal rate). The combined residues were <0.04 ppm (below the LOQ) in/on all samples of potatoes grown in the U.S., including residue decline samples.

In the Canadian trials, the combined residues of pyraclostrobin and BF 500-3 were <0.04 ppm in/on all samples of potatoes harvested 3 days following the last of: (i) four foliar applications of the WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.80-0.82 lb ai/A; (ii) four foliar applications of the EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.80-0.81 lb ai/A; or (iii) four foliar applications of a tank mix of pyraclostrobin (WDG) at 0.19-0.21 lb ai/A/application plus metiram (WDG) at 1.55-1.66 lb ai/A/application for total seasonal application rates of 0.79-0.81 lb ai/A pyraclostrobin and 6.34-6.50 lb ai/A metiram.

Sugar Beet

BASF Corporation submitted sugar beet field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on sugar beet (root) at 0.2 ppm. Data pertaining to sugar beet tops are presented in the Leaves of Root and Tuber Vegetables section.

45118524 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Sugarbeets: Lab Project Number: 1999/5157: 55185:99229. Unpublished study prepared by BASF Corporation. 74 p.

Twelve field trials were conducted during the 1999 growing season in CA(2), CO(1), ID(2), MI(1), MN(2), ND(2), TX(1), and WI(1). Mature sugar beets were harvested 7-8 days following the last of four broadcast foliar applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application, made at 13- to 15-day retreatment intervals. The total seasonal application rates were 0.75-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 14.9-30.4 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (MN), additional sugar beet samples were collected at 0, 14, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature sugar beets (roots and tops) were collected from each test site. The collected samples were then bagged separately, labeled, and frozen. All samples were shipped frozen to the BASF APC for analysis. Samples of sugar beet roots and tops were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 12 samples of untreated sugar beet roots. Residues of pyraclostrobin and BF 500-3 in/on treated root samples are presented in Table 32; residues in treated tops samples are presented in Table 34.

Table 32. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **sugar beet roots** harvested 7-8 days following the last of four applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application (~ 1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Ingham, MI/5	4	0.80	7	0.06, 0.10	<0.02, 0.02	<0.08, 0.12
Freeborn, MN/5	4	0.80	0	0.04, 0.07	<0.02, <0.02	<0.06, <0.09
			7	0.04, 0.07	<0.02, <0.02	<0.04, <0.04
			14	0.08, 0.08	<0.02, <0.02	<0.10, <0.10
			21	0.04, 0.05	<0.02, <0.02	<0.06, <0.07
			28	<0.02, 0.04	<0.02, <0.02	<0.04, <0.06
Wilkin, MN/5	4	0.80	7	0.03, 0.04	<0.02, <0.02	<0.05, <0.06
Grand Forks, ND/5	4	0.75	7	0.03, 0.09	<0.02, 0.02	<0.05, 0.11
Pepin, WI/5	4	0.80	7	0.07, 0.08	0.02, 0.02	0.09, 0.10
McHenry, ND/7	4	0.81	8	0.09, 0.12	0.03, 0.03	0.12, 0.15 HAFT = 0.135
Hockley, TX/8	4	0.81	7	0.02, 0.02	0.02, 0.02	0.04, 0.04
Mesa, CO/9	4	0.80	7	0.03, 0.03	<0.02, 0.02	<0.05, 0.05
Butte, CA/10	4	0.80	7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Madera, CA/10	4	0.80	7	<0.02, 0.03	<0.02, <0.02	<0.04, 0.05
Jerome, ID/11	4	0.79	7	0.03, 0.04	<0.02, <0.02	<0.05, <0.06
Payette, ID/11	4	0.79	7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Geographic representation of sugar beet data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 5), 12 trials were conducted on sugar beets in Regions 5 (5 trials), 7 (1 trial), 8 (1 trial), 9 (1 trial), 10 (2 trials), and 11 (2 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on sugar beet roots. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.2 ppm in/on sugar beet roots harvested 7-8 days following the last of four foliar applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application for a total seasonal application rate of 0.75-0.81 lb ai/A (~ 1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.15 ppm in/on 24 samples of sugar beet roots.

The residue decline data for sugar beets did not demonstrate any conclusive trends in pyraclostrobin residues at longer posttreatment intervals.

Leaves of Root and Tuber Vegetables

Radish

BASF Corporation submitted radish field trial data (2000; MRID 45118609) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on radish (tops) at 16.0 ppm. These data were submitted in conjunction with the root vegetable data; details of the study, including sample handling, storage intervals, and analytical method, are presented in the “Root and Tuber Vegetables” section.

Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples of untreated radish tops. Residues of pyraclostrobin and BF 500-3 in/on treated samples of radish tops are presented in Table 33.

Table 33. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **radish tops** harvested on the day of the last of three applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Lehigh, PA/1	3	0.62	0	14.60, 15.44	0.29, 0.40	14.86, 15.84
Orange, FL/3	3	0.60	0	8.74, 11.14	0.09, 0.12	8.83, 11.26
Seminole, FL/3	3	0.60	0	11.69, 12.68	0.14, 0.13	11.83, 12.81
Jefferson, IA/5	3	0.59	0	9.34, 10.03	0.16, 0.16	9.50, 10.19
Fresno, CA/10	3	0.61	0	6.99, 7.97	0.18, 0.19	7.17, 8.16

Geographic representation of data, for the establishment of a tolerance on radish tops is adequate. As required by OPPTS GLN 860.1500 (Table 5), a total of 5 trials were conducted on radish tops in Regions 1 (1 trial), 3 (2 trials), 5 (1 trial), and 10 (1 trial).

Study summary:

The petitioner has submitted adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on radish tops. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 16.0 ppm in/on radish tops harvested immediately (0-day PHI) following the last of three foliar applications of the 20% WDG formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.59-0.62 lb

ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 7.17-15.84 ppm in/on 10 samples of radish tops.

Sugar Beet

BASF Corporation submitted sugar beet field trial data (2000; MRID 45118524) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on sugar beet (top) at 8.0 ppm. These data were submitted in conjunction with the root vegetable data; details of the study, including sample handling, storage intervals, and analytical method, are presented in the "Root and Tuber Vegetables" section.

Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 12 samples of untreated sugar beet tops. Residues of pyraclostrobin and BF 500-3 in/on treated samples of sugar beet tops are presented in Table 34.

Table 34. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **sugar beet tops** harvested 7-8 days following the last of four applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Ingham, MI/5	4	0.80	7	1.11, 1.60	0.42, 0.60	1.53, 2.20
Freeborn, MN/5	4	0.80	0	3.61, 4.19	0.49, 0.52	4.10, 4.71
			7	2.53, 2.71	0.74, 0.91	3.27, 3.62
			14	1.45, 1.57	0.06, 0.64	1.51, 2.21
			21	1.18, 1.34	0.57, 0.60	1.75, 1.94
			28	0.73, 0.94	0.39, 0.50	1.12, 1.44
Wilkin, MN/5	4	0.80	7	1.79, 2.24	0.50, 0.46	2.29, 2.70
Grand Forks, ND/5	4	0.75	7	1.17, 1.99	0.13, 0.34	1.30, 2.33
Pepin, WI/5	4	0.80	7	2.05, 2.52	0.52, 0.52	2.57, 3.04
McHenry, ND/7	4	0.81	8	1.23, 1.43	0.32, 0.31	1.55, 1.74
Hockley, TX/8	4	0.81	7	1.42, 1.51	0.42, 0.49	1.84, 2.00
Mesa, CO/9	4	0.80	7	1.41, 1.95	0.36, 0.50	1.77, 2.45
Butte, CA/10	4	0.80	7	4.92, 5.68	1.55, 1.69	6.47, 7.37
Madera, CA/10	4	0.80	7	2.90, 3.27	0.92, 0.97	3.82, 4.24
Jerome, ID/11	4	0.79	7	0.27, 0.28	0.15, 0.17	0.42, 0.45
Payette, ID/11	4	0.79	7	1.35, 1.57	0.44, 0.51	1.79, 2.08

Geographic representation of sugar beet data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 5), a total of 12 trials were conducted on sugar beet tops in Regions 5 (5 trials), 7 (1 trial), 8 (1 trial), 9 (1 trial), 10 (2 trials), and 11 (2 trials).

Study summary:

The petitioner has submitted adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on sugar beet tops. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 8.0 ppm in/on sugar beet tops harvested 7-8 days following the last of four foliar applications of the 2 lb/gal EC formulation at 0.16-0.21 lb ai/A/application for a total seasonal application rate of 0.75-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.42-7.37 ppm in/on 24 samples of sugar beet tops.

The residue decline data for sugar beet tops showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 3.61-4.19 ppm at the 0-day PHI and declined to 0.73-0.94 ppm at the 28-day PHI. Residues of the metabolite BF 500-3 were 0.49-0.52 ppm at the 0-day PHI and declined to 0.39-0.50 ppm at the 28-day PHI.

Bulb Vegetables

BASF Corporation submitted dry bulb and green onion field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Bulb vegetables (crop group) at 0.7 ppm.

45118525 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Dry Bulb and Green Onions: Lab Project Number: 1999/5158: 46694:99171. Unpublished study prepared by BASF Corporation. 64 p.

Dry Bulb and Green Onion

A total of nine field trials were conducted during the 1999 growing season. Six trials were conducted on dry bulb onions grown in CA(2), PA(1), OR(1), and TX(2) and three trials were conducted on green onions grown in CA(2) and TX(1). Mature onions (dry bulb and green) were harvested seven days following the last of six broadcast foliar applications of the 20% WDG formulation at 0.15-0.16 lb ai/A/application, made at 13- to 15-day retreatment intervals. The total seasonal application rates were 0.90-0.91 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 21.4-31.3 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (CA), additional dry bulb onion samples were collected at 0, 14, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature dry bulb and green onions were collected from each test site. The roots were removed from the green onions, and the collected samples were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples of untreated dry bulb onions and three samples of untreated green onions. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 35.

Table 35. Residues of pyraclostrobin and its metabolite BF 500-3 in/on onions (dry bulb and green) harvested seven days following the last of six applications of the 20% WDG formulation at 0.15-0.16 lb ai/A/application (~ 1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Dry bulb onion						
Lehigh, PA/1	6	0.91	7	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
Uvalde, TX/6	6	0.90	7	0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Armstrong, TX/8	6	0.90	7	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Tulare, CA/10	6	0.90	0	0.10, 0.11	<0.02, <0.02	<0.12, <0.13
			7	0.02, 0.02	<0.02, <0.02	<0.04, <0.04
			14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			28	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Madera, CA/10	6	0.91	7	0.04, 0.13	<0.02, <0.02	<0.06, <0.15
Jefferson, OR/11	6	0.90	7	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Green onion						
Uvalde, TX/6	6	0.91	7	0.31, 0.52	0.06, 0.11	0.37, 0.63
Tulare, CA/10	6	0.90	7	0.47, 0.59	0.05, 0.06	0.52, 0.65
Madera, CA/10	6	0.91	7	0.03, 0.07	<0.02, <0.02	<0.052, <0.093

Geographic representation of data for bulb vegetables is adequate for the purposes of this petition. According to Tables 2 and 5 of OPPTS 860.1500, a minimum of nine trials, six for bulb onions and three for green onions, are required for the establishment of a crop group tolerance for bulb vegetables. As required, six bulb onion field trials were conducted in Regions 1 (1 trial), 6 (1 trial), 8 (1 trial), 10 (2 trials), and 11 (1 trial); and three green onion trials were conducted in Regions 6 (1 trial) and 10 (2 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin and its metabolite BF 500-3 on dry bulb onions and green onions, the representative commodities of the bulb vegetable crop group. The combined residues of pyraclostrobin and BF 500-3 in/on dry bulb and green onions harvested seven days following the last of six broadcast foliar applications of the WDG formulation at 0.15-0.16 lb ai/A/application for a total seasonal application rates of 0.90-0.91 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.04-0.15 ppm in/on bulb onions and <0.05-0.65 ppm in/on green onions treated with the WDG formulation. RAB3 recommends that the bulb vegetables (crop group) tolerance be proposed at 0.9 ppm.

The residue decline data for dry bulb onions showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.10-0.11 ppm at the 0-day PHI and declined to <0.02 ppm at the 28-day PHI. Residues of the metabolite BF 500-3 were below the LOQ in/on each treated sample.

Legume Vegetables (Succulent or Dried)

Dried Shelled Pea and Bean (Except Soybean) - Subgroup 6C

BASF Corporation submitted dry field pea, lentil, and dry bean (and snap bean) field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on the dried shelled pea and bean crop group (except soybean) at 0.5 ppm. Data pertaining to pea hay and vines are presented in the "Foliage of Legume Vegetables" section.

45118522 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of BAS 500 F Residues in Dry Field Peas: Lab Project Number: 1999/5154: 46591: 99216. Unpublished study prepared by BASF Corporation. 76 p.

45118526 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of BAS 500 F Residues in Lentils: Lab Project Number: 1999/5159: 46590: 99224. Unpublished study prepared by BASF Corporation. 55 p.

45367501 Haughey, D.; Abdel-Baky, S. (2001) Magnitude of BAS 500 F Residues in Dry Beans and Snap Beans: Lab Project Number: 2001/5000906: 77915. Unpublished study prepared by BASF Corporation. 73 p.

Pea, dry, seed

A total of eight dry pea field trials were conducted during the 1999 growing season. Two trials were conducted in the U.S. in MN; and six trials were conducted in Canada in AB(2), MB(2),

and SK(2). Pea vines and hay were cut 0-2 days (when pods began forming), and dry field pea seed was harvested 29-34 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application, made at 6- to 8-day retreatment intervals. Total seasonal application rates were 0.40-0.41 lb ai/A (~1.5x the maximum proposed seasonal rate). Applications were made in 10.6-99.1 gal/A of water using ground equipment with a spray adjuvant added to the spray solution. In one trial (MN), additional pea vine and hay samples were cut at 3, 6, 9, and 12 days, and dry pea seed samples were harvested 25, 30, 40, and 46 days following treatment to evaluate residue decline. A separate plot at each trial site was not treated for control samples.

Samples of treated and untreated dry field pea vine, hay, and mature seed were collected from each test site; hay samples were dried in the field for 4-7 days before collection. The moisture content of hay, vines, and seed was determined to be 29-70%, 77-93%, and 14-35%, respectively. All samples were transferred to freezers as soon as possible after collection and then shipped frozen to the BASF APC for analysis. All samples remained frozen during shipment except for pea seed samples from one test site (AB), which were received very cold but not frozen. Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on eight samples of untreated dry field pea seed. Residues of pyraclostrobin and BF 500-3 in/on treated dry field pea seed samples are presented in Table 36a; residues in field pea vines and hay are presented in Table 38.

Table 36a. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **dry field pea seed** harvested 29-34 days following two applications of the 2 lb/gal EC formulation at 0.40-0.41 lb ai/A (~1.5x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Dry field pea, seed						
U.S. Trials						
Wilkin, MN/5	2	0.40	25	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			30	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			35	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			46	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Ottertail, MN/5	2	0.40	30	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Canada Trials						
Red Deer, AB/14	2	0.40	30	0.10, 0.18	0.07, 0.13	0.17, 0.31
Lancombe, AB/14	2	0.40	34	0.07, 0.18	0.06, 0.18	0.13, 0.36
Blaine Lake, SK/14	2	0.41	30	0.03, 0.06	0.02, 0.03	0.05, 0.09
Hoodoo, SK/14	2	0.40	29	0.06, 0.11	0.05, 0.09	0.11, 0.20
Whitewater, MB/14	2	0.41	30	0.03, 0.04	0.04, 0.04	0.07, 0.09
Morton, MB/14	2	0.41	30	0.19, 0.21	0.11, 0.16	0.30, 0.37

Geographic representation of dry field pea seed data from the U.S. is inadequate. According to Tables 1 and 6 of OPPTS GLN 860.1500, a total of three trials are required in Region 11, which accounts for ≥97% of the U.S. production of dry peas. Two field pea field trials were conducted in the U.S. in Region 5 (MN). In addition, six dry field pea field trials conducted in Canada in Region/Zone 14 (AB, SK, and MB).

Study summary:

The petitioner has not provided adequate residue data for field pea in support of the subgroup crop tolerance. Three field pea seed trials must be conducted in Region 11 reflecting application of the 2 lb/gal WDG formulation according to the maximum proposed use pattern. Because Canadian trials were conducted in Region/Zone 14 which does not border Region 11, these data cannot be translated to the U.S. registration.

The submitted U.S. field pea field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 are <0.04 ppm in/on dry field pea seed harvested 30 days following the last of two foliar applications of the EC formulation at 0.2 lb ai/A/application for a total seasonal

application rate of ~0.4 lb ai/A (~1.5x the maximum proposed seasonal rate). The combined residues were 0.05-0.37 ppm in/on dry field pea seed grown in Canada treated with the EC formulation at 1.5x the maximum proposed use pattern.

The residue decline data for dry field pea seed did not demonstrate any conclusive trends in pyraclostrobin residues at longer posttreatment intervals; the combined residues of pyraclostrobin and BF 500-3 are <0.04 ppm at each harvest interval.

Lentil

A total of five field trials were conducted during the 1999 growing season. Three field trials were conducted in the U.S. in MT(1) and ND(2), and two field trials were conducted in Canada in AB(1) and MB(1). Mature dry lentil seeds were harvested 29-33 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.20 lb ai/A/application, made at 6- to 8-day retreatment intervals. Total seasonal application rates were 0.39-0.41 lb ai/A (~2x the maximum proposed seasonal rate). Applications were made in 11.2-20.4 gal/A of water using ground equipment with a spray adjuvant added to the spray solution. In one trial (ND), additional lentil seed samples were harvested 26, 35, 40, and 45 days following treatment to evaluate residue decline. A separate plot at each trial site was not treated for control samples.

A single untreated sample and duplicate treated samples of mature lentil seed were collected from each test site and were frozen. The moisture content of lentil seed was determined to be 13-46%. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples of untreated lentil seed. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 36b.

Table 36b. Residues of pyraclostrobin and its metabolite BF 500-3 in/on lentil seed harvested 29-33 days following two applications of the 2 lb/gal EC formulation at 0.39-0.41 lb ai/A (~2x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
U.S. Trials						
Cass, ND/5	2	0.41	26	0.04	<0.02	<0.06
			30	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
			35	0.05	<0.02	<0.07
			40	0.06	<0.02	<0.08
			45	0.04	<0.02	<0.06
McHenry, ND/7	2	0.40	29	0.07, 0.09	<0.02, <0.02	<0.09, <0.11
Sheridan, MT/7	2	0.40	29	0.12, 0.21	0.04, 0.07	0.16, 0.28
Canada Trials						
Strathcona, AB/14	2	0.40	33	0.15, 0.15	0.08, 0.09	0.23, 0.24
Hamiota, MB/14	2	0.39	30	0.11, 0.39	0.03, 0.09	0.13, 0.48

Geographic representation of lentil seed data is inadequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 1), three trials were conducted on lentil seed in the U.S. in Regions 5 (1 trial) and 7 (2 trials). In addition, two lentil field trials were conducted in Canada in Region/Zone 14. However, we note that all trials were conducted at 2x the maximum proposed use rate.

Study summary:

The petitioner has not provided adequate residue data on lentil seed because the submitted field trials were conducted at twice the proposed maximum application rate. The petitioner must conduct trials at the 1x rate to support the proposed subgroup crop tolerance for dry shelled pea and bean (except soybean).

The combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.05-0.28 ppm in/on six samples of lentil seed grown in the U.S. and 0.13-0.48 ppm in/on four samples of lentil seed grown in Canada harvested 29-33 days following the last of two foliar applications of the EC formulation at 0.19-0.20 lb ai/A/application for a total seasonal application rate of 0.39-0.41 lb ai/A (~2x the maximum proposed seasonal application rate).

The residue decline data for lentil seed did not demonstrate any conclusive trends in pyraclostrobin residues at longer posttreatment intervals. Residues of pyraclostrobin in lentil

seed remained low ranging 0.03-0.06 ppm at the 26- to 45-day PHIs; residues of BF 500-3 were less than the LOQ in all samples.

Dry Beans and Snap Beans

A total of nineteen field trials were conducted during the 2000 growing season. Ten trials were conducted on dry beans grown in the CA, CO, ID, MN, ND (3), TX, WI, and AB (Canada); and nine trials were conducted on snap beans in CA, GA, ID, MN, PA, WI in the US, and NS, QC (2) in Canada. Mature dry bean plants were cut at 21 days after the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application (and then allowed to dry in the field or at the test facility for 0-15 days), made at 4- to 8-day retreatment intervals, and snap beans were harvested 7 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application, made at 6- to 8-day retreatment intervals. Total seasonal application rates were 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 11-38 gal/A of water using ground equipment with a spray adjuvant added to the spray solution. At the WI site, additional bean plant samples were cut at 0, 7, 14, and 28 days and allowed to dry for 2-4 days, and snap bean samples were harvested 0, 3, 10, and 14 days following treatment to evaluate residue decline. A separate plot at each trial site was not treated for control samples.

Samples of treated and untreated dry bean and snap bean were collected from each test site. All samples were transferred to freezers as soon as possible after collection and then shipped frozen to the BASF APC for analysis. All samples remained frozen during shipment. Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9908 (identical to D9808 using methanol:water:2N HCl instead of methanol:water for extraction). Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on untreated samples. Residues of pyraclostrobin and BF 500-3 in/on treated dry bean and snap bean samples are presented in Table 37.

Table 37. Residues of pyraclostrobin and its metabolite BF 500-3 in/on dry bean and snap bean harvested 7 or 21 days following two applications of the 2 lb/gal EC formulation at 0.39-0.42 lb ai/A (~1.5x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Dry bean						
Northwood, ND/5	2	0.41	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Gardner, ND/5	2	0.41	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Geneva, MN/5	2	0.40	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Arkansaw, WI/5	2	0.40	0	<0.02, 0.03	<0.02, <0.02	<0.04, 0.05
			7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			28	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Velva, ND/7	2	0.40	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Levelland, TX/8	2	0.41	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Eaton, CO/8	2	0.39	21	0.15, 0.04	0.06, <0.02	0.21, <0.06
Chico, CA/10	2	0.40	21	0.04, 0.04	<0.02, <0.02	<0.06, <0.06
Payette, ID/11	2	0.40	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Lethbride, AB/7A	2	0.40	21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Snap bean						
Germansville, PA/1	2	0.42	7	0.10, 0.09	0.03, 0.05	0.13, 0.14
Athens, GA/2	2	0.40	7	0.09, 0.10	0.05, 0.03	0.14, 0.13
Geneva, MN/5	2	0.40	7	0.14, 0.11	0.03, <0.02	0.17, 0.13
Arkansaw, WI/5	2	0.40	0	0.13, 0.14	<0.02, <0.02	<0.15, <0.16
			3	0.08, 0.11	<0.02, <0.02	<0.10, <0.13
			7	0.02, 0.05	<0.02, <0.02	<0.04, <0.07
			10	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fresno, CA/10	2	0.40	7	0.06, 0.09	0.05, 0.06	0.11, 0.15
Jerome, ID/11	2	0.40	7	0.05, 0.03	0.02, 0.03	0.07, 0.06
Berwick, NS/1A	2	0.41	7	0.14, 0.07	0.02, <0.02	0.16, <0.09
St. Paul D', QC/5B	2	0.40	7	0.12, 0.12	0.03, 0.02	0.15, 0.14
St. Paul D', QC/5B	2	0.41	7	0.16, 0.16	0.03, 0.03	0.19, 0.19

Geographic representation of dry bean and snap bean data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 1), nine trials were conducted on dry bean in the U.S. in Regions 5 (4 trials), and 7, 8, 9, 10 and 11 (1 trial in each region), and one dry bean field trial was conducted in Canada in Region/Zone 7A. In addition, six trials were conducted on snap bean in the U.S. in Regions 1, 2, 10, and 11 (1 trial in each region) and 5 (two trials), and three snap bean field trials were conducted in Canada in Region/Zone 1A and 5B (two trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on dry bean (and may be adequate for snap bean pending submission of a proposed label/Section B). The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed 0.21 ppm in/on dry bean and snap bean harvested 21 and 7 days following the last of two foliar applications of the EC formulation at 0.19-0.20 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1.5x the maximum proposed seasonal application rate for dry bean).

The residue decline data for dry bean did not demonstrate any conclusive trends in pyraclostrobin residues at longer posttreatment intervals; those in snap bean declined at longer posttreatment intervals. Residues of pyraclostrobin in dry bean and snap bean remained low ranging <0.02 to 0.16 ppm at the 21- and 7-day PHIs; residues of BF 500-3 were less than 0.02 to 0.06 ppm in all samples.

To establish a tolerance for the dried shelled pea and bean (except soybean) subgroup, the petitioner should conduct the five field pea trials or side-by-side lentil field trials as described above. The submitted residue data support a tolerance of 0.3 ppm for the combined residues of pyraclostrobin and its metabolite BF 500-3 in/on dry bean.

Pending submission of a proposed label, the residue data may support the proposed tolerance of 0.3 ppm in/on snap bean (bean, succulent).

Foliage of Legume Vegetables Except Soybeans

BASF Corporation submitted field trial data (2000; MRID 45118522) for field pea hay and vines in conjunction with the dry field pea seed data to support the establishment of tolerances for residues of pyraclostrobin and BF 500-3 in/on field pea hay at 26.0 ppm and vines at 10.0 ppm. Details of the study, including sample handling, storage intervals, and analytical method, are presented in the "Legume Vegetables" section.

Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on eight samples each of untreated field pea hay and vines. Residues of pyraclostrobin and BF 500-3 in/on treated samples of field pea hay and vines are presented in Table 38.

Table 38. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **field pea hay and vines** harvested 0-2 days following two applications of the 2 lb/gal EC formulation at 0.40-0.41 lb ai/A (~1.5x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Field pea, hay						
U.S. Trials						
Wilkin, MN/5	2	0.40	0 (+6)	5.10, 9.28	1.60, 2.88	6.70, 12.16
			3 (+6)	5.44, 5.81	3.24, 3.79	8.67, 9.60
			6 (+6)	3.59, 4.07	2.73, 3.11	6.32, 7.18
			9 (+5)	3.02, 3.27	2.27, 2.74	5.29, 6.01
			12 (+6)	2.73, 2.63	2.17, 2.30	4.90, 4.93
Ottertail, MN/5	2	0.40	0 (+5)	17.01, 18.99	5.47, 6.19	22.48, 25.18
Canada Trials						
Red Deer, AB/14	2	0.40	0 (+7)	6.02, 6.86	0.90, 1.30	6.92, 8.16
Lancombe, AB/14	2	0.40	0 (+6)	7.84, 16.20	1.21, 5.42	9.05, 21.62
Blaine Lake, SK/14	2	0.41	2 (+6)	5.01, 4.72	2.97, 3.26	7.98, 7.99
Hoodoo, SK/14	2	0.40	2 (+4)	4.56, 5.97	2.45, 2.86	7.01, 8.83
Whitewater, MB/14	2	0.41	1 (+7)	8.83, 9.49	2.63, 3.03	11.46, 12.52
Morton, MB/14	2	0.41	2 (+7)	7.22, 7.82	3.50, 3.89	10.73, 11.71
Field pea, vines						
U.S. Trials						
Wilkin, MN/5	2	0.40	0	3.70, 6.46	0.59, 0.78	4.28, 7.24
			3	1.43, 4.48	0.73, 1.94	2.16, 6.42
			6	0.21, 2.57	0.16, 2.01	0.37, 4.58
			9	1.64, 1.37	0.14, 1.17	1.78, 2.54
			12	1.55, 2.08	1.20, 1.81	2.75, 3.90
Ottertail, MN/5	2	0.40	0	6.20, 7.86	1.55, 1.64	7.75, 9.50
Canada Trials						
Red Deer, AB/14	2	0.40	0	3.82, 3.85	0.51, 0.50	4.33, 4.35
Lancombe, AB/14	2	0.40	0	3.87, 4.56	0.41, 0.49	4.28, 5.05
Blaine Lake, SK/14	2	0.41	2	4.93, 5.18	2.06, 2.22	6.99, 7.40
Hoodoo, SK/14	2	0.40	2	4.99, 5.92	1.70, 1.83	6.69, 7.75
Whitewater, MB/14	2	0.41	1	5.44, 5.53	1.61, 1.63	7.05, 7.16
Morton, MB/14	2	0.41	2	3.09, 3.44	1.39, 1.54	4.48, 4.98

^a For hay, the drying time is reported in parentheses.

Geographic representation of field pea hay and vine data is inadequate for the purposes of this petition. According to Table 3 of OPPTS GLN 860.1500, a total of six trials of which three are for field pea in Region 11 are required; Region 11 accounts for $\geq 97\%$ of the U.S. production of field pea. Two field pea field trials were conducted in the U.S. in Region 5 (MN). In addition, six field pea field trials were conducted in Canada in Region/Zone 14 (AB, SK, and MB).

Study summary:

The petitioner has not provided adequate residue data on field pea vines and hay because geographic representation of data is inadequate. Five additional pea hay and vine trials must be conducted in Region 11 reflecting application of the 2 lb/gal WDG formulation according to the maximum proposed use pattern. Because Canadian trials were conducted in Region/Zone 14 which does not border Region 11, these data cannot be translated to the U.S. registration.

The submitted U.S. field pea field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 were 4.90-25.18 ppm in/on field pea hay and 0.37-9.50 ppm in/on pea vines harvested 0-2 days following the last of two foliar applications of the EC formulation at 0.2 lb ai/A/application for a total seasonal application rate of 0.4 lb ai/A (~1.5x the maximum proposed seasonal rate). The combined residues were 6.92-21.62 ppm in/on field pea hay and 4.28-7.75 ppm in/on field pea vines grown in Canada treated with the EC formulation according to 1.5x the maximum proposed use pattern.

The residue decline data for field pea hay and vines showed trends in decreasing residues at longer posttreatment intervals in pea hay and vines. For hay, the combined residues were 6.70-12.16 ppm at the 0-day PHI and declined to 4.90-4.93 ppm at the 12-day PHI. For vines, the combined residues were 4.28-7.24 ppm at the 0-day PHI and declined to 2.75-3.90 ppm at the 12-day PHI.

Based on the proposed use of the 2 lb/gal EC formulation on dried shelled peas and beans (except soybeans), establishment of a tolerance for the foliage of legume vegetables except soybeans subgroup (7A) would be appropriate. For establishment of the subgroup tolerance, the petitioner would be required to conduct three field pea trials and three field trials on a cultivar of bean (cowpea is the preferred commodity) reflecting the maximum proposed use pattern for the 2 lb/gal WDG formulation.

Fruiting Vegetables (Except Cucurbits)

BASF Corporation submitted pepper (bell and chili) and tomato field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Fruiting vegetables (crop group) at 1.0 ppm.

45118611 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Bell and Chili Peppers: Lab Project Number: 61659: 1999/5151. Unpublished study prepared by BASF Corporation. 64 p.

45118528 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Tomatoes: Lab Project Number: 1999/5084: 98023. Unpublished study prepared by BASF Corporation. 79 p.

Pepper (Bell and Chili)

A total of nine field trials were conducted during the 1999 growing season. Six trials were conducted on bell peppers grown in CA(2), FL(1), GA(1), IA(1), and OK(1) and three trials were conducted on chili peppers grown in NM(1), OK(1) and TX(1). Mature peppers (bell and chili) were harvested on the day of the last of six broadcast foliar applications of the 20% WDG formulation at 0.19-0.22 lb ai/A/application, made at 6- to 9-day retreatment intervals. The total seasonal application rates were 1.19-1.24 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 14.2-40.8 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature bell and chili peppers were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples of untreated bell peppers and three samples of untreated chili peppers. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 39.

Table 39. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **peppers (bell and chili)** harvested on the day following the last of six applications of the 20% WDG formulation at 0.19-0.22 lb ai/A/application (~ 1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Bell peppers						
Tift, GA/2	6	1.23	0	0.08, 0.11	<0.02, <0.02	<0.10, <0.13
Seminole, FL/3	6	1.21	0	0.15, 0.18	<0.02, <0.02	<0.17, <0.20
Jefferson, IA/5	6	1.24	0	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Caddo, OK/6	6	1.19	0	0.13, 0.14	<0.02, <0.02	<0.15, <0.16
Madera, CA/10	6	1.21	0	0.19, 0.28	<0.02, <0.02	<0.21, <0.30
Madera, CA/10	6	1.20	0	0.06, 0.09	<0.02, <0.02	<0.08, <0.11
Chili peppers						
Washita, OK/8	6	1.20	0	0.69, 0.94	0.03, 0.04	0.72, 0.99
Armstrong, TX/8	6	1.20	0	0.16, 0.27	<0.02, <0.02	<0.18, <0.29
Luna, NM/9	6	1.20	0	0.12, 0.15	<0.02, <0.02	<0.14, <0.17

Tomato

A total of 15 field trials were conducted during the 1998 growing season in CA(10), FL(2), MI(1), NC(1), and PA(1). Mature tomatoes were harvested on the day of the last of six broadcast foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application, made at 6- to 8-day retreatment intervals. The total seasonal application rates were 1.19-1.22 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 19.4-39.5 gal/A using ground equipment with a spreader-sticker added to the spray mixture. In two trials (CA and PA), additional tomato samples were collected at 3, 7, 10, and 15 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature tomatoes were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 15 samples of untreated tomatoes. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 40.

Table 40. Residues of pyraclostrobin and its metabolite BF 500-3 in/on tomatoes harvested on the day following the last of six applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Lehigh, PA/1	6	1.22	0	0.20, 0.22	<0.02, 0.03	<0.22, 0.25 HAFT = 0.235
			3	0.13, 0.16	0.02, <0.02	0.15, <0.18
			7	0.09, 0.13	<0.02, 0.02	<0.11, 0.15
			10	0.07, 0.13	<0.02, 0.02	<0.09, 0.15
			15	0.09, 0.09	<0.02, 0.02	<0.11, 0.11
Sampson, NC/2	6	1.20	0	0.13, 0.21	<0.02, <0.02	<0.15, <0.23
Martin, FL/3	6	1.22	0	0.10, 0.11	<0.02, 0.020	<0.12, 0.13
Jackson, FL/3	6	1.21	0	0.10, 0.13	<0.02, <0.02	<0.12, <0.15
Ottawa, MI/5	6	1.20	0	0.09, 0.10	<0.02, <0.02	<0.11, <0.12
Tulare, CA/10	6	1.20	0	0.18, 0.21	0.03, 0.04	0.20, 0.25
			3	0.15, 0.18	0.03, 0.03	0.18, 0.21
			7	0.11, 0.17	<0.02, 0.04	<0.13, 0.21
			10	0.12, 0.17	0.03, 0.04	0.14, 0.21
			15	0.08, 0.11	<0.02, 0.02	<0.10, 0.13
Tulare, CA/10	6	1.20	0	0.12, 0.17	<0.02, 0.02	<0.14, 0.20
Monterey, CA/10	6	1.20	0	0.12, 0.19	<0.02, 0.02	<0.14, 0.21
Fresno, CA/10	6	1.19	0	0.04, 0.19	<0.02, 0.02	<0.06, 0.22
Fresno, CA/10	6	1.21	0	0.06, 0.09	<0.02, <0.02	<0.08, <0.11
Merced, CA/10	6	1.21	0	0.14, 0.19	0.02, 0.03	0.17, 0.22
Glenn, CA/10	6	1.20	0	0.15, 0.18	<0.02, <0.02	<0.17, <0.20
Madera, CA/10	6	1.20	0	0.06, 0.08	<0.02, <0.02	<0.08, <0.10
Fresno, CA/10	6	1.21	0	0.11, 0.13	<0.02, 0.020	<0.13, 0.15
Merced, CA/10	6	1.20	0	0.12, 0.14	0.02, 0.03	0.14, 0.17

Geographic representation of data for fruiting vegetables is adequate for the purposes of this petition. According to Tables 2 and 5 of OPPTS 860.1500, a minimum of 21 trials [9 trials for pepper (6 trials for bell and 3 trials for a cultivar other than bell) and 12 trials for tomato] are required for the establishment of a crop group tolerance for fruiting vegetables. A total of 9 pepper field trials were conducted (6 bell pepper trial conducted in Regions 2 (1 trial), 3 (1 trial), 5 (1 trial), 6 (1 trial), and 10 (2 trials) and 3 chili pepper trials conducted in Regions 8 (2

trials) and 9 (1 trial)]. Fifteen tomato trials were conducted in Regions 1 (1 trial), 2 (1 trial), 3 (2 trials), 5 (1 trial), and 10 (10 trials).

Bridging Study

BASF Corporation submitted a bridging study (citation listed below) comparing the use of the WDG and EC formulations of pyraclostrobin on tomato, cucurbits, and grape.

45118613 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) A Bridging Study Comparing Two Formulations of BAS 500 F in Tomatoes, Cucurbits, and Grapes: Lab Project Number: 1999/5145: 59472. Unpublished study prepared by Crop Management Strategies, Excel Research Services, Inc. and Agriscope, LLC. 74 p.

A total of nine field trials were conducted during the 1999 growing season in CA(3), GA(1), NC(1), NY(1), PA(1), and WA(1). Three trials each were conducted on tomatoes grown in CA, NC, and PA, cucurbits (cantaloupe, cucumber, and summer squash) grown in CA, GA, and PA, respectively, and grapes grown in CA, NY, and WA. Each trial site consisted of three plots: (i) an untreated control plot; (ii) a treatment plot reflecting use of the 2 lb/gal EC formulation; and (iii) a treatment plot reflecting use of the 20% WDG formulation. Mature tomatoes and cucurbits were harvested on the day of the last of six broadcast foliar applications of either the 2 lb/gal EC formulation or the 20% WDG formulation at 0.19-0.21 lb ai/A/application, made at 6- to 8-day retreatment intervals. The total seasonal application rates were 1.18-1.22 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 19.9-41.2 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. Mature grapes were harvested 14-15 days following the last of three broadcast foliar applications of either the 2 lb/gal EC formulation or the 20% WDG formulation at 0.18 lb ai/A/application, made at 14-day retreatment intervals. The total seasonal application rates were 0.54 lb ai/A (~0.6x the maximum proposed seasonal application rate). Applications were made in 100.0-184.6 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture.

A single untreated sample and duplicate treated samples of mature cucurbits, grapes, and tomatoes were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on three samples of untreated tomatoes. Residues of pyraclostrobin and BF 500-3 in/on treated tomato samples are presented in Table 41; bridging data for the cucurbits (cantaloupe, cucumber, and summer squash) and grapes are presented in the respective sections "Cucurbit Vegetables" and "Grape."

Table 41. Residues of pyraclostrobin and its metabolite BF 500-3 in/on tomatoes harvested on the day following the last of six applications of either the 2 lb/gal EC or 20% WDG formulation at 0.19-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
2 lb/gal EC formulation						
Lehigh, PA/1	6	1.21	0	0.06, 0.07	<0.02, <0.02	<0.08, <0.09
Sampson, NC/2	6	1.21	0	0.08, 0.11	<0.02, <0.02	<0.10, <0.13
Madera, CA/10	6	1.18	0	0.11, 0.17	0.02, 0.03	0.13, 0.20
20% WDG formulation						
Lehigh, PA/1	6	1.22	0	0.10, 0.12	<0.02, <0.02	<0.12, <0.14
Sampson, NC/2	6	1.20	0	0.06, 0.06	<0.02, <0.02	<0.08, <0.08
Madera, CA/10	6	1.19	0	0.10, 0.13	<0.02, <0.02	<0.12, <0.15

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on peppers (bell and non-bell) and tomatoes, representative commodities of the fruiting vegetables crop group. The results of the pepper and tomato field trials indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 in/on peppers and tomatoes harvested on the day (0-day PHI) of the last of six foliar applications of either the WDG (peppers) or EC (tomatoes) formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.04-<0.30 ppm in/on bell peppers, <0.14-0.99 ppm in/on non-bell (chili) peppers, and <0.08-<0.25 ppm in/on tomatoes. RAB3 recommends that a fruiting vegetables (crop group) tolerance of 1.4 ppm be proposed.

In side-by-side tomato field trials conducted to compare the use of the EC and WDG formulations, tomatoes were harvested on the day (0-day PHI) of the last of six foliar applications of either the EC or WDG formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.08-0.20 ppm following applications of the EC formulation and <0.08-<0.15 ppm following applications of the WDG formulation. These data indicate that there were no significant differences in residue levels between tomato samples treated with the EC formulation and the WDG formulation.

The residue decline data for tomatoes showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.18-0.22 ppm at the 0-day PHI and declined to 0.08-0.11 ppm at the 15-day PHI. Residues of the metabolite BF 500-3 were <0.02-0.04 ppm at the 0-day PHI and declined to <0.02-0.02 ppm at the 15-day PHI.

Cucurbit Vegetables

BASF Corporation submitted cantaloupe, cucumber, and summer squash field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Cucurbit vegetables (crop group) at 0.5 ppm.

45118603 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Cucurbits: Lab Project Number: 98022: 1999/5083. Unpublished study prepared by BASF Corporation. 92 p.

A total of 19 field trials were conducted during the 1998 growing season. Six trials were conducted on cantaloupe grown in AL(1), CA(3), MI(1), and OK(1), eight trials were conducted on cucumber grown in CA(1), FL(1), GA(2), MI(1), SC(1), TX(1), and WI(1), and five trials were conducted on summer squash grown in CA(1), FL(1), NC(1), PA(1) and WI(1). Mature cantaloupe, cucumber, and summer squash were harvested on the day (0-day PHI) of the last of six broadcast foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application, made at 6- to 10-day retreatment intervals. The total seasonal application rates were 1.19-1.23 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 12.1-30.1 gal/A using ground equipment with a spreader sticker added to the spray mixture. In two cucumber trials (CA and GA), additional samples were collected at 3, 7, 10, and 15 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature cantaloupe, cucumber, and squash were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples of untreated cantaloupe, eight samples of untreated cucumber, and five samples of untreated summer squash. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 42.

Table 42. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **cucurbits (cantaloupe, cucumber, and summer squash)** harvested on the day following the last of six applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application (~ 1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Cantaloupe						
Henry, AL/2	6	1.20	0	0.10, 0.11	<0.02, <0.02	<0.12, <0.130
Ottawa, MI/5	6	1.20	0	0.10, 0.10	<0.02, <0.02	<0.12, <0.120
Caddo, OK/6	6	1.19	0	0.06, 0.08	<0.02, <0.02	<0.08, <0.10
Tulare, CA/10	6	1.20	0	0.12, 0.13	0.02, 0.03	0.14, 0.16
Glenn, CA/10	6	1.21	0	0.08, 0.12	<0.02, <0.02	<0.10, <0.14
Fresno, CA/10	6	1.21	0	0.09, 0.09	<0.02, <0.02	<0.11, <0.11
Cucumber						
Macon, GA/2	6	1.20	0	0.36, 0.41	<0.02, <0.02	<0.38, <0.43
Barnwell, SC/2	6	1.23	0	0.05, 0.06	<0.02, <0.02	<0.07, <0.08
Tift, GA/2	6	1.203	0	<0.02, 0.05	<0.02, <0.02	<0.04, <0.07
			3	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			10	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			15	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Seminole, FL/3	6	1.22	0	0.08, 0.09	<0.02, <0.02	<0.10, <0.11
Ottawa, MI/5	6	1.20	0	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
Pepin, WI/5	6	1.22	0	0.06, 0.07	<0.02, <0.02	<0.08, <0.09
Uvalde, TX/6	6	1.19	0	0.11, 0.14	<0.02, <0.02	<0.13, <0.16
Tulare, CA/10	6	1.20	0	0.09, 0.12	<0.02, <0.02	<0.11, <0.14
			3	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
			7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			10	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			15	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Summer squash						
Lehigh, PA/1	6	1.21	0	0.14, 0.20	<0.02, <0.02	<0.16, <0.22
Sampson, NC/2	6	1.20	0	0.05, 0.09	<0.02, <0.02	<0.07, <0.11
Seminole, FL/3	6	1.19	0	0.14, 0.14	<0.02, <0.02	<0.16, <0.16
Pepin, WI/5	6	1.23	0	0.13, 0.17	<0.02, <0.02	<0.15, <0.19
Fresno, CA/10	6	1.21	0	0.17, 0.19	<0.02, <0.02	<0.19, <0.21

Geographic representation of data for cucurbit vegetables is adequate for the purposes of this petition. According to Tables 2 and 5 of OPPTS 860.1500, a minimum of 17 trials (6 trials for cucumber, 6 trials for muskmelon, and 5 trials for summer squash) are required for the establishment of a crop group tolerance for cucurbit vegetables. A total of 19 cucurbit field trials were conducted on cucumbers in Regions 2 (3 trials), 3 (1 trial), 5 (2 trials), 6 (1 trial), and 10 (1 trial); cantaloupes in Regions 2 (1 trial), 5 (1 trial), 6 (1 trial), and 10 (3 trials); and summer squash in Regions 1 (1 trial), 2 (1 trial), 3 (1 trial), 5 (1 trial), and 10 (1 trial).

Bridging Study

BASF Corporation submitted a bridging study (MRID 45118613) comparing the WDG and EC formulations of pyraclostrobin in cucurbits, grape, and tomato. Details of this study, including sample handling, storage intervals, and analytical method, are presented in the “Fruiting Vegetables” section.

Apparent residues of pyraclostrobin and its metabolite BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of cantaloupe, cucumber, and summer squash. Residues of pyraclostrobin and BF 500-3 in/on treated cucurbit samples are presented in Table 43; bridging data for tomato and grape are presented in the respective sections “Fruiting Vegetables” and “Grape.”

Table 43. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **cucurbits (cantaloupe, cucumber, and summer squash)** harvested on the day following the last of six applications of either the 2 lb/gal EC or 20% WDG formulation at 0.19-0.21 lb ai/A/application (~1x the maximum proposed seasonal rate).

Commodity	Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
2 lb/gal EC formulation							
Cantaloupe	Madera, CA/10	6	1.20	0	0.13, 0.14	<0.02, 0.02	<0.15, <0.16
Cucumber	Clarke, GA/2	6	1.20	0	0.12, 0.13	<0.02, <0.02	<0.14, <0.15
Squash, summer	Lehigh, PA/1	6	1.22	0	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
20% WDG formulation							
Cantaloupe	Madera, CA/10	6	1.19	0	0.06, 0.10	<0.02, <0.02	<0.08, <0.12
Cucumber	Clarke, GA/2	6	1.21	0	0.13, 0.14	<0.02, ,0.02	<0.15, <0.16
Squash, summer	Lehigh, PA/1	6	1.22	0	0.02, 0.04	<0.02, <0.02	<0.04, <0.06

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on cucumber, muskmelon (cantaloupe), and summer squash, the representative commodities of the cucurbit vegetables crop group. The results of the cucurbit field trials indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed cucurbit vegetables (crop group) tolerance level of 0.5 ppm in/on cantaloupe, cucumber, and summer squash harvested on the day (0-day PHI) of the last of six foliar applications of the EC formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.08-0.16 ppm in/on cantaloupe, <0.04-<0.43 ppm in/on cucumber, and <0.07-<0.22 ppm in/on summer squash.

In side-by-side cucurbit field trials conducted to compare the use of the EC and WDG formulations, cantaloupes, cucumbers, and summer squash were harvested on the day (0-day PHI) of the last of six foliar applications of either the EC or WDG formulation at ~0.2 lb ai/A/application for a total seasonal application rate of ~1.2 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.15-<0.16 ppm in/on cantaloupe, <0.14-<0.15 ppm in/on cucumber, and <0.04-<0.05 ppm in/on summer squash following applications of the EC formulation and <0.08-<0.12 ppm in/on cantaloupe, <0.15-<0.16 ppm in/on cucumber, and <0.04-<0.06 ppm in/on summer squash following applications of the WDG formulation. These data indicate that there were no significant differences in residues levels in/on cucurbit vegetable samples treated with the EC formulation or the WDG formulation.

The residue decline data for cucumbers showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were <0.02-0.12 ppm at the 0-day PHI and declined to <0.02 ppm at the 15-day PHI. Residues of the metabolite BF 500-3 were below the LOQ in/on each treated sample.

Citrus Fruits (Citrus Spp., *Fortunella* Spp.)

BASF Corporation submitted grapefruit, lemon, and orange field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Citrus fruits (crop group) at 0.7 ppm.

45118606 Wofford, J.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of BAS 500 F Residues in Citrus: Lab Project Number: 54766: 1999/5144. Unpublished study prepared by BASF Corporation. 106 p.

Only the specimen label for the 2 lb/gal EC formulation lists proposed uses on citrus fruits; however, all the citrus field trial data submitted in support of this petition reflect application of the 20% WDG formulation. The guidelines for conducting field trials (OPPTS GLN 860.1500) state that for pesticides used in late-season foliar applications (as is the case with pyraclostrobin)

separate residue trials or bridging data are needed to support registration of different formulations.

A total of 24 citrus fruit field trials were conducted during the 1999 growing season. Six trials were conducted on grapefruit grown in CA(2), FL(3), and TX(1), five trials were conducted on lemons grown in CA(4) and FL(1), and thirteen trials were conducted on oranges grown in CA(4), FL(8), and TX(1). Samples of grapefruit, lemons, and oranges were harvested 13-14 days following the last of four broadcast foliar applications of the 20% WDG formulation at 0.14-0.16 lb ai/A/application (first and second applications) and 0.25-0.26 lb ai/A/application (third and fourth applications), were made at 9- to 11-day retreatment intervals. The total seasonal application rates were 0.79-0.83 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in either 63.2-95.8 gal/A (concentrate spray volume) or 133-356.6 gal/A (dilute spray volume) using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (FL), additional orange samples were collected at 0 and 7 days following treatment to evaluate residue decline; however, these samples were not analyzed. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated whole fruit samples of mature grapefruit, lemons, and oranges were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC for analysis. A portion of the whole fruit samples from six sites was separated into peel and pulp samples. Whole fruit, peel, and pulp samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples of untreated grapefruit, five samples of untreated lemons, and thirteen samples of untreated oranges. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 44.

Table 44. Residues of pyraclostrobin and its metabolite BF 500-3 in/on citrus fruits (grapefruit, lemon, and orange) harvested 13-14 days following the last of four applications of the 20% WDG formulation at ~0.15 lb ai/A/application (first and second applications) and ~0.25 lb ai/A/application (third and fourth applications) [~1x the maximum proposed seasonal rate].

Test Site/Region	PHI, days	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	Matrix	Residues, ppm		
						Pyraclostrobin	BF 500-3	Total
Grapefruit								
Brevard, FL/3	14	290.2-294.2	4	0.80	Whole fruit	0.12, 0.12	<0.02, <0.02	<0.14, <0.14
Palm Beach, FL/3	13	65.9-67.5	4	0.82	Whole fruit	0.15, 0.22	<0.02, <0.02	<0.17, <0.24
Palm Beach, FL/3	14	140-147.5	4	0.81	Whole fruit	0.24, 0.25	0.02, 0.03	0.26, 0.28
Willacy, TX/6	14	73.3-76.7	4	0.81	Whole fruit	0.06, 0.07	<0.02, <0.02	<0.08, <0.09
Tulare, CA/10	14	227.8-254.3	4	0.80	Whole fruit	0.07, 0.09	<0.02, <0.02	<0.09, <0.10
Tulare, CA/10	14	67.4-74.6	4	0.79	Whole fruit	0.11 ^a , 0.13 ^a	<0.02 ^a , <0.02 ^a	<0.13, <0.15
					Peel	0.06 ^a , 0.16 ^a	<0.02 ^a , <0.02 ^a	<0.08, <0.18
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Lemon								
Hendry, FL/3	13	63.2-69.4	4	0.80	Whole fruit	0.19, 0.19	0.04, 0.04	0.23, 0.23
Tulare, CA/10	14	72.4-74.1	4	0.80	Whole fruit	0.12, 0.19	<0.02, <0.02	<0.13, <0.21
Kern, CA/10	14	201.8-206.5	4	0.80	Whole fruit	0.19, 0.21	<0.02, <0.02	<0.21, <0.23
Tulare, CA/10	14	88.0-95.8	4	0.80	Whole fruit	0.24, 0.39	0.04, 0.06	0.28, 0.45
Ventura, CA/10	14	197.3-200.4	4	0.80	Whole fruit	0.24, 0.31	0.04, 0.04	0.28, 0.35
Orange								
Lake, FL/3	14	73.5-76.9	4	0.80	Whole fruit	0.15, 0.19	0.05, 0.06	0.20, 0.25
Palm Beach, FL/3	14	140.6-144.6	4	0.80	Whole fruit	0.36, 0.38	0.06, 0.08	0.42, 0.46
Collier, FL/3	14	66.3-68.2	4	0.81	Whole fruit	0.47, 0.54	0.08, 0.07	0.55, 0.61 HAFT= 0.58
Hendry, FL/3	14	143.5-155.2	4	0.80	Whole fruit	0.31, 0.40	0.03, 0.05	0.34, 0.45

Table 44 (continued).

Test Site/Region	PHI, days	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	Matrix	Residues, ppm		
						Pyraclostrobin	BF 500-3	Total
Palm Beach, FL/3	14	66.8-69.5	4	0.83	Whole fruit	0.23, 0.25	0.08, 0.08	0.31, 0.33
Collier, FL/3	14	133-141.6	4	0.79	Whole fruit	0.30, 0.37	0.05, 0.06	0.35, 0.43
Martin, FL/3	13	64.6-69.0	4	0.81	Whole fruit	0.23, 0.26	0.09, 0.10	0.32, 0.36
Seminole, FL/3	14	227-237	4	0.80	Whole fruit	0.16, 0.19	0.05, 0.06	0.21, 0.25
Willacy, TX/6	14	250.3-258.9	4	0.81	Whole fruit	0.22, 0.24	0.02, 0.02	0.24, 0.26
					Peel	0.47, 0.47	0.02, 0.05	0.49, 0.52
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tulare, CA/10	14	75.2-77.4	4	0.80	Whole fruit	0.10, 0.15	<0.02, <0.02	<0.12, <0.17
					Peel	0.39, 0.40	<0.02, <0.02	<0.41, <0.42
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tulare, CA/10	14	345.3-356.6	4	0.80	Whole fruit	0.24, 0.26	0.02, <0.02	0.26, 0.27
					Peel	0.44, 0.52	<0.02, 0.02	<0.46, 0.54
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Kern, CA/10	14	74.1-77.5	4	0.80	Whole fruit	0.09, 0.14	<0.02, <0.02	<0.11, <0.16
					Peel	0.18, 0.20	<0.02, <0.02	<0.20, <0.22
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tulare, CA/10	14	347.1-353.3	4	0.80	Whole fruit	0.17, 0.18	<0.02, <0.02	<0.19, <0.20
					Peel	0.16, 0.45	<0.02, <0.02	<0.18, <0.47
					Pulp	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

^a Reported residue is the highest of replicate analyses of a single sample.

Geographic representation of citrus fruit data is adequate for the purposes of this petition. The Agency (Tables 2 and 5 of OPPTS 860.1500) requires a total of 23 trials for the establishment of a crop group tolerance on citrus fruits; 12 trials on oranges, 5 trials on lemons, and 6 trials on grapefruit. Twenty-four citrus field trials were conducted on grapefruit in Regions 3 (3 trials), 6 (1 trial), and 10 (2 trials); on lemons in Regions 3 (1 trial) and 10 (4 trials); and on oranges in Regions 3 (8 trials), 6 (1 trial), and 10 (4 trials).

Study summary:

The available citrus field trial data are adequate to support the proposed crop group tolerance because the three bridging studies (conducted with tomato, cucurbits, and grape) indicated no significant difference in the residue levels between the use of the WDG formulation or the EC formulation. The field trial data reflecting application of the WDG formulation can be extrapolated to project the residue levels for the EC formulation for which use on citrus is proposed.

The combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.08-0.28 ppm in/on grapefruit, <0.13-0.45 ppm in/on lemons, and <0.11-0.61 ppm in/on oranges harvested 13-14 days following the last of four foliar applications of the WDG formulation at ~0.15 lb ai/A/application (first and second applications) and ~0.25 lb ai/A/application (third and fourth applications) for a total seasonal application rate of ~0.8 lb ai/A (~1x the maximum proposed seasonal application rate). These residue levels did not exceed the proposed tolerance level of 0.7 ppm in/on citrus.

In addition, the pulp and peel were analyzed separately in selected samples of grapefruit and oranges. These data indicate that combined residues were <0.04 ppm in/on citrus pulp samples (n = 6) and <0.08-0.54 ppm in/on citrus peel samples (n = 6).

Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues for concentrate and dilute spray applications were, respectively, <0.08-<0.24 ppm and <0.09-0.28 ppm in/on grapefruit; <0.13-0.45 ppm and <0.21-0.35 ppm in/on lemons; and <0.11-0.61 ppm and <0.19-0.46 ppm in/on oranges.

Stone Fruits

BASF Corporation submitted cherry (sweet and tart), peach, and plum field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Stone fruits (crop group) at 0.7 ppm.

45118607 Wofford, J.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Stonefruit: Lab Project Number: 46867: 1999/5146. Unpublished study prepared by BASF Corporation. 92 p.

A total of 21 stone fruit field trials were conducted during the 1999 growing season. Six trials were conducted on cherries grown in CA(1), MI(3), NY(1), and WA(1), nine trials were conducted on peaches grown in CA(3), GA(2), MI(1), PA(1), SC(1), and TX(1), and six trials were conducted on plums grown in CA(4), MI(1), and OR(1). Samples of cherries (sweet and tart), peaches, and plums were harvested immediately (0-day PHI) following the last of five broadcast foliar applications of the 20% WDG formulation at 0.12 lb ai/A/application, made at 6- to 8-day retreatment intervals. The total seasonal application rates were 0.59-0.60 lb ai/A (~1x the maximum proposed seasonal application rate). Two separate plots at each site were treated with concentrated (20-100 gal/A) or dilute (100-400 gal/A) spray volumes. Applications were made in either 49.4-101.5 gal/A (concentrate spray volume) or 107.2-282.3 gal/A (dilute spray volume) using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In two trials (GA and MI), additional peach and plum samples were collected at 7, 14, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and a single treated sample from each treatment group (concentrate spray volume and dilute spray volume) of mature cherries (sweet and tart), peaches, and plums were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples each of untreated cherries and plums and ten samples of untreated peaches. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 45.

Table 45. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **stone fruits (cherry, peach, and plum)** harvested on the day of the last of five applications of the 20% WDG formulation at ~0.12 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Cherry (sweet)							
Ottawa, MI/5	73.0-75.6	5	0.60	0	0.25	0.02	0.27
	212.9-224.3	5	0.60		0.27	<0.02	<0.29
Tulare, CA/10	60.9-63.1	5	0.60	0	0.25	<0.02	<0.27
	241.7-263.9	5	0.60		0.38	<0.02	<0.41
Grant, WA/11	49.5-50.0	5	0.60	0	0.42	<0.02	<0.44
	199.6-202.5	5	0.60		0.34	<0.02	<0.36
Cherry (tart)							
Wayne, NY/1	80.1-80.6	5	0.60	0	0.48	0.04	0.52
	149.6-150.6	5	0.60		0.51	0.05	0.55
Ottawa, MI/5	64.8-68.3	5	0.60	0	0.50	0.03	0.53
	192.4-201.3	5	0.60		0.63	0.03	0.67
Kent, MI/5	65.2-68.5	5	0.60	0	0.43	0.03	0.45
	194.0-202.0	5	0.60		0.50	0.02	0.52
Peach							
Berrs, PA/1	54.4-55.6	5	0.60	0	0.26	<0.02	<0.28
	213.8-217	5	0.60		0.28	<0.02	<0.30
Aiken, SC/2	51.5-53.4	5	0.59	0	0.07	<0.02	<0.09
	209.1-217.4	5	0.59		0.08	<0.02	<0.10
Oglethorpe, GA/2	58.3-73.6	5	0.60	0	0.15	<0.02	<0.17
	117.6-152.5	5	0.60		0.14	<0.02	<0.16
Tift, GA/2	52.0-55.5	5	0.60	0	0.21	<0.02	<0.23
				7	0.12	<0.02	<0.14
				14	0.08	<0.02	<0.10
				21	0.06	<0.02	<0.08
				28	0.07	<0.02	<0.09
	263-269	5	0.60	0	0.20	<0.02	<0.22
				7	0.07	<0.02	<0.09
				14	0.08	<0.02	<0.10
				21	0.06	<0.02	<0.08
				28	0.11	<0.02	<0.13

Table 45 (continued).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Ottawa, MI/5	65.7-68.5	5	0.60	0	0.15	<0.02	<0.17
	194.0-200.6	5	0.60		0.13	<0.02	<0.15
Wilaberge, TX/6	49.4-62.3	5	0.60	0	0.23	<0.02	<0.25
	107.2-131.8	5	0.60		0.31	<0.02	<0.33
Tulare, CA/10	71.1-77.1	5	0.60	0	0.16	<0.02	<0.18
	264.3-282.3	5	0.60		0.10	<0.02	<0.12
Fresno, CA/10	97.7-100.4	5	0.60	0	0.16	<0.02	<0.18
	196.6-202.0	5	0.60		0.08	<0.02	<0.10
Butte, CA/10	55.5-58	5	0.60	0	0.11	<0.02	<0.13
	132.4-135	5	0.60		0.10	<0.02	<0.12
Plum							
Ottawa, MI/5	73.2-76.8	5	0.60	0	0.19	<0.02	<0.21 = HAFT
				7	0.15	<0.02	<0.17
				14	0.09	<0.02	<0.11
				21	0.06	<0.02	<0.08
				28	0.06	<0.02	<0.08
	216.0-227.7	5	0.60	0	0.13	<0.02	<0.15
				7	0.05	<0.02	<0.07
				14	0.07	<0.02	<0.09
				21	0.05	<0.02	<0.07
				28	0.07	<0.02	<0.09
Tulare, CA/10	54.4-56.3	5	0.60	0	0.04	<0.02	<0.06
	215.1-227.7	5	0.60		0.05	<0.02	<0.07
Tulare, CA/10	58.8-62.9	5	0.60	0	0.06	<0.02	<0.08
	239.0-246.7	5	0.60		0.12	<0.02	<0.14
Butte, CA/10	90.3-92.5	5	0.60	0	0.02	<0.02	<0.04
	169-181	5	0.59		0.02	<0.02	<0.04
Fresno, CA/10	96.5-101.5	5	0.60	0	0.06	<0.02	<0.08
	200.0-205.6	5	0.60		0.06	<0.02	<0.08
Polk, OR/12	63.7-65.9	5	0.60	0	0.03	<0.02	<0.05
	188.9-200.5	5	0.60		0.04	<0.02	<0.06

Geographic representation of stone fruit data is adequate for the purposes of this petition. The Agency (Tables 2 and 5 of OPPTS 860.1500) requires a total of 21 trials for the establishment of a crop group tolerance on stone fruits; six trials on cherries (sweet or tart), nine trials on peaches, and six trials on plums. As required, twenty-one stone fruit field trials were conducted on cherries in Regions 1 (1 trial), 5 (3 trials), 10 (1 trial), and 11 (1 trial); on peaches in Regions 1 (1 trial), 2 (3 trials), 5 (1 trial), 6 (1 trial), and 10 (3 trials); and on plums in Regions 5 (1 trial), 10 (4 trials), and 11 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on cherries (sweet and tart), peaches, and plums, the representative commodities of the stone fruits crop group. The combined residues of pyraclostrobin and its metabolite BF 500-3 in/on cherries (sweet and tart), peaches, and plums harvested immediately (0-day PHI) following the last of five foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.6 lb ai/A (~1x the maximum proposed seasonal application rate) were <0.27-<0.44 ppm in/on sweet cherries, 0.45-0.67 ppm in/on tart cherries, <0.09-<0.33 ppm in/on peaches, and <0.04-<0.21 ppm in/on plums. RAB3 recommends that a stone fruits (crop group) tolerance of 0.9 ppm be proposed.

Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.27-0.53 ppm and <0.29-0.67 ppm in/on cherries, <0.09-<0.28 ppm and <0.10-<0.33 ppm in/on peaches, and <0.04-<0.21 ppm and <0.04-<0.15 ppm in/on plums treated with concentrated or dilute spray volumes, respectively.

The residue decline data for peaches and plums showed that residues decreased gradually at longer posttreatment intervals. For peaches, residues of pyraclostrobin were 0.20-0.21 ppm at the 0-day PHI and declined to 0.07-0.11 ppm at the 28-day PHI. For plums, residues of pyraclostrobin were 0.13-0.19 ppm at the 0-day PHI and declined to 0.06-0.07 ppm at the 28-day PHI. For both peaches and plums, residues of the metabolite BF 500-3 were below the LOQ in/on each treated sample.

Berries

BASF Corporation submitted blueberry and raspberry field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Berries (crop group) at 1.0 ppm.

45118605 Versoi, P.; Abdel-Baky, S.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Red Raspberries and Highbush Blueberries: Lab Project Number: 46911: 1999/5143. Unpublished study prepared by BASF Corporation. 64 p.

A total of nine berry field trials were conducted during the 1999 growing season. Three trials were conducted on red raspberries grown in NY(1 trial) and OR(2), and six trials were conducted on highbush blueberries grown in GA(2), NY(1), OR(1), and WI(2). Samples of blueberries and raspberries were harvested immediately (0-day PHI) following the last of four broadcast foliar applications of the 20% WDG formulation at 0.18-0.19 lb ai/A/application at 6- to 7-day retreatment intervals. The total seasonal application rates were 0.72-0.74 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 49.6-102.2 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (NY), additional raspberry samples were collected at 2, 4, 6, and 8 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature blueberries and raspberries were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on six samples of untreated blueberries and three samples of untreated raspberries. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 46.

Table 46. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **berries (blueberry and raspberry)** harvested on the day of the last of four applications of the 20% WDG formulation at ~0.18 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Blueberry						
Yates, NY/1	4	0.74	0	0.30, 0.35	<0.02, 0.02	<0.32, 0.38
Tift, GA/2	4	0.72	0	0.44, 0.52	0.03, 0.04	0.47, 0.56
Colquitt, GA/2	4	0.73	0	0.52, 0.62	0.05, 0.07	0.57, 0.69
Piencce, WI/5	4	0.72	0	0.28, 0.42	<0.02, 0.02	<0.30, 0.44
Jackson, WI/5	4	0.73	0	0.27, 0.34	0.02, 0.03	0.29, 0.37
Benton, OR/12	4	0.73	0	0.10, 0.27	<0.02, 0.02	<0.12, 0.29
Raspberry						
Yates, NY/1	4	0.74	0	0.62, 0.94	<0.02, 0.03	<0.64, 0.97
			2	0.52, 0.54	0.02, 0.02	0.54, 0.57
			4	0.44, 0.61	0.02, 0.03	0.46, 0.64
			6	0.32, 0.50	0.02, 0.03	0.34, 0.53
			8	0.21, 0.38	<0.02, 0.03	<0.23, 0.40
Washington, OR/12	4	0.73	0	0.44, 0.51	<0.02, <0.02	<0.46, <0.53
Washington, OR/12	4	0.72	0	0.47, 0.78	<0.02, 0.04	<0.49, 0.82

Geographic representation of berry data is adequate for the purposes of this petition. The Agency (Tables 2 and 5 of OPPTS 860.1500) requires a total of nine trials for the establishment of a crop group tolerance on berries; 6 trials on highbush blueberry and 3 trials on any one blackberry or any one raspberry. As required, nine berry field trials were conducted on highbush blueberry in Regions 1 (1 trial), 2 (2 trials), 5 (2 trials), and 12 (1 trial), and on red raspberry in Regions 1 (1 trial) and 12 (2 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on blueberries and raspberries, the representative commodities of the berries crop group. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed berries (crop group) tolerance level of 1.0 ppm in/on highbush blueberries and red raspberries harvested immediately (0-day PHI) following the last of four foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.72 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues

were <0.12-0.69 ppm in/on highbush blueberries and <0.46-0.97 ppm in/on red raspberries. RAB3 recommends that the tolerance in berry crop group be proposed at 1.3 ppm.

The residue decline data for raspberries showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.62-0.94 ppm at the 0-day PHI and declined to 0.21-0.38 ppm at the 8-day PHI. Residues of the metabolite BF 500-3 were below the LOQ (<0.02 ppm) to 0.03 ppm at each interval.

Tree Nuts

BASF Corporation submitted almond and pecan field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on Tree nuts (crop group) at 0.04 ppm and almond hulls at 1.6 ppm.

45118521 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Almonds: Lab Project Number: 47727: 1999/5161. Unpublished study prepared by BASF Corporation. 64 p.

45118612 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Pecans: Lab Project Number: 61660: 1999/5152. Unpublished study prepared by BASF Corporation. 56 p.

Almond

A total of five almond field trials were conducted in CA during the 1999 growing season. Samples of almond nutmeat and hulls were harvested 108-148 days following the last of four broadcast foliar applications of the 20% WDG formulation at 0.12 lb ai/A/application made at 6- to 8-day retreatment intervals. Total seasonal application rates were 0.47-0.48 lb ai/A (~1x the maximum proposed seasonal application rate). Two separate plots at each site were treated with concentrated (50-100 gal/A) or dilute (100-400 gal/A) spray volumes. Applications were made in either 67.5-100.8 gal/A (concentrate spray volume) or 157.9-256.9 gal/A (dilute spray volume) using ground equipment with a spray adjuvant added to the spray mixture. In one trial, additional almond nutmeat and hull samples were collected at 127, 134, 148, and 155 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and a single treated sample from each treatment group (concentrate spray volume and dilute spray volume) of mature almond (nutmeat and hulls) were collected from each test site and were frozen. The moisture content of hulls was determined to be 24-83%. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples of untreated almond nutmeat and four samples of untreated almond hulls. Residues of pyraclostrobin and BF 500-3 were each

less than the LOQ in/on almond nutmeat samples treated with a concentrate spray volume (n=5), almond nutmeat samples treated with a dilute spray volume (n=5), and treated almond nutmeat samples collected to evaluate residue decline (n=8). Residues of pyraclostrobin and BF 500-3 in/on treated samples of almond hulls are presented in Table 47.

Table 47. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **almond hulls** harvested 108-148 days following the last of four applications of the 20% WDG formulation at ~0.12 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Almond, hulls							
Tulare, CA/10	82.6-88.0	4	0.48	148	<0.02	<0.02	<0.04
	209.4-230.1	4	0.48		<0.02	<0.02	<0.04
Kern, CA/10	74.8-77.9	4	0.48	108	0.47	0.09	0.56
	196.2-202.1	4	0.48		0.55	0.10	0.65
Fresno, CA/10	97.1-99.1	4	0.47	116	0.16	0.04	0.20
	246.9-251.6	4	0.48		0.19	0.06	0.25
Madera, CA/10	96.7-100.8	4	0.48	115	0.11	0.02	0.13
	247.9-256.9	4	0.48		0.21	0.03	0.24
Butte, CA/10	67.5-70.6	4	0.48	120	0.33	0.08	0.41
				127	0.58	0.11	0.70
				134	0.61	0.12	0.73
				148	0.87	0.15	1.02
				155	0.46	0.11	0.57
	157.9-162.2	4	0.48	120	0.55	0.12	0.67
				127	0.88	0.17	1.04
				134	0.86	0.16	1.03
				148	1.34	0.25	1.59
				155	1.06	0.22	1.27

Pecan

A total of five pecan field trials were conducted in GA(2), MS(1), and OK(2) during the 1999 growing season. Samples of pecan nutmeat were harvested 14 days following the last of four broadcast foliar applications of the 20% WDG formulation at 0.12-0.13 lb ai/A/application, made at 6- to 8-day retreatment intervals. Total seasonal application rates were 0.47-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). Two separate plots at each site were treated

with concentrate (50-100 gal/A) or dilute (100-400 gal/A) spray volumes. Applications were made in either 63.6-88.6 gal/A (concentrate spray volume) or 136.2-205 gal/A (dilute spray volume) using ground equipment with a non-silicone spray adjuvant added to the spray mixture. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and a single treated sample from each treatment group (concentrate spray volume and dilute spray volume) of mature pecan nutmeat were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples of untreated pecan nutmeat. Residues of pyraclostrobin and BF 500-3 were each less than the LOQ in/on five samples each of pecan nutmeat treated with a concentrate spray volume and pecan nutmeat treated with a dilute spray volume.

Geographic representation of tree nuts data is adequate for the purposes of this petition. The Agency (Tables 2 and 5 of OPPTS 860.1500) requires a total of 10 trials for the establishment of a crop group tolerance on tree nuts; 5 trials each on almonds and pecans. As required, five trials were conducted on almonds in Region 10, and five trials were conducted on pecans in Regions 2 (2 trials), 4 (1 trial), 6 (1 trial), and 8 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on almonds and pecans, the representative commodities of the tree nuts crop group.

Almond and pecan nutmeat: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tree nuts (crop group) tolerance level of 0.04 ppm in/on almonds harvested 108-148 days and pecans harvested 14 days following the last of four foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.48 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm in/on all samples of almond and pecan nutmeat.

Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues in/on almond and pecan nutmeat were <0.04 ppm in all samples whether treated with concentrate or dilute spray volumes.

The residue decline data for almond nutmeat did not demonstrate any conclusive trends in pyraclostrobin residues at longer posttreatment intervals. Residues were less than the LOQ in all nutmeat samples.

Almond hulls: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 1.6 ppm in/on almond hulls harvested 108-148 days following the

last of four foliar applications of the WDG formulation at ~0.12 lb ai/A/application for a total seasonal application rate of ~0.48 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm to 0.67 ppm in/on almond hulls sampled at normal harvest. The maximum combined residue (1.59 ppm) was detected in an almond hull sample from the decline study harvested 148 days following the last application.

Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.04-0.56 ppm in/on almond hulls treated with concentrate spray volumes, and <0.04-0.67 ppm in/on almond hulls treated with dilute spray volumes.

The residue decline data for almond hulls did not demonstrate any conclusive trends in decreasing residues at longer posttreatment intervals. The petitioner indicated that the higher residues detected in the almond hull samples from the decline study were possibly due to dusty field conditions that worsened at each sampling interval.

Pistachio

BASF Corporation submitted pistachio field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on pistachio at 0.5 ppm.

45118610 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Pistachios: Lab Project Number: 61661: 1999/5150. Unpublished study prepared by BASF Corporation. 54 p.

Three pistachio field trials were conducted in CA during the 1999 growing season. Samples of pistachios were harvested 14-15 days following the last of four broadcast foliar applications of the 20% WDG (formulation at 0.12-0.21 lb ai/A/application at 6- to 8-day retreatment intervals for a total seasonal application rate of 0.72-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). Two separate plots at each site were treated with concentrated (50-100 gal/A) or dilute (100-400 gal/A) spray volumes. Applications were made in either 61.3-102.4 gal/A (concentrate spray volume) or 144-199.9 gal/A (dilute spray volume) using ground equipment with a non-silicone spray adjuvant added to the spray mixture. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and a single treated sample from each treatment group (concentrate and dilute spray volumes) of mature pistachios were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on three samples of untreated pistachios. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 48.

Table 48. Residues of pyraclostrobin and its metabolite BF 500-3 in/on pistachios harvested 14-15 days following the last of four applications of the 20% WDG formulation at ~0.2 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Glenn, CA/10	66.7-69.5	4	0.72	14	0.16	<0.02	<0.18
	159.7-162	4	0.80		0.27	<0.02	<0.29
Butte, CA/10	61.3-62.9	4	0.80	14	0.44	<0.02	<0.46
	144-148	4	0.80		0.45	0.03	0.48
Fresno, CA/10	99.7-102.4	4	0.81	15	<0.02	<0.02	<0.04
	197.9-199.9	4	0.80		<0.02	<0.02	<0.04

Geographic representation of pistachio data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Tables 1 and 6), three trials were conducted on pistachios in Region 10, which accounts for 100% of the U.S. production of pistachios.

Study summary:

The petitioner has provided adequate data reflecting the maximum proposed use pattern of pyraclostrobin on pistachios. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.5 ppm in/on pistachios harvested 14-15 days following the last of four foliar applications of the WDG formulation at 0.12-0.21 lb ai/A/application for a total seasonal application rate of 0.72-0.81 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.48 ppm in/on pistachios. RAB3 recommends that the tolerance in pistachio be proposed at 0.7 ppm.

Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were <0.04-<0.46 ppm in/on pistachios treated with concentrate spray volumes, and <0.04-0.48 ppm in/on pistachios treated with dilute spray volumes.

Small Grains

Barley

BASF Corporation submitted barley field trial data (citation listed below) to support the establishment of tolerances for residues of pyraclostrobin and BF 500-3 in/on barley (grain) at 0.4 ppm, barley (hay) at 25.0 ppm, and barley straw at 6.0 ppm.

45118535 Versoi, P.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Barley: Lab Project Number: 1999/5079: 98209. Unpublished study prepared by BASF Corporation. 117 p.

A total of 25 field trials were conducted during the 1998 growing season. Twelve of these field trials were conducted in the U.S. in CA(1), CO(1), ID(1), MN(3), ND(3), PA(1), SD(1), and WA(1). Thirteen field trials were conducted in Canada in AB(6), SK(2), MB(4), and QC(1). Barley hay was cut 9-16 days (allowed to dry for 3-7 days before collection) and barley grain and straw were harvested 38-70 days following the last of two foliar applications, made at 3- to 17-day retreatment intervals, of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application. The first application was made when the flag leaf was just visible, and the second application was applied at 50-100% head emergence, inflorescence completely emerged, head fully extended, or early head emergence, not less than 40 days prior to grain/straw harvest. Total seasonal application rates were 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 10.0-32.9 gal/A using ground equipment with a spray adjuvant added to the spray solution. In two trials (MN and SK), additional barley hay samples were cut at 18-19, 23-24, 28-29, and 32-34 days, and additional barley grain and straw samples were harvested 47-49, 54-57, 61-63, and 68-70 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

Samples of treated and untreated barley hay, grain, and straw were collected from each test site; hay samples were allowed to dry in the field for 3-7 days (12-47% moisture) before collection. All samples were frozen and then shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 25 samples each of untreated barley hay, grain, and straw. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 49.

Table 49. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **barley (hay, grain, and straw)** harvested 9-16 days (hay) or 38-70 days (grain and straw) following two applications of the 2 lb/gal EC formulation at 0.40-0.49 lb ai/A (~ 1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^b
Barley hay						
U.S. Trials						
Lehigh, PA/1	2	0.41	9 (+ 4)	15.20, 19.05	2.25, 3.39	17.72, 22.44
Wabasha, MN/5	2	0.41	14 (+ 3)	15.86, 22.36	2.12, 2.65	17.98, 25.01
Freeborn, MN/5	2	0.40	14 (+ 3)	10.71, 13.66	1.58, 2.06	12.29, 15.72
Wilkin, MN/5 decline study	2	0.40	14 (+ 6)	9.89, 13.08	1.79, 2.29	11.68, 15.37
			19 (+ 5)	7.41, 8.81	1.26, 1.36	8.67, 10.17
			24 (+ 5)	7.19, 7.65	1.26, 1.17	8.45, 8.82
			29 (+ 5)	5.63, 6.73	0.95, 1.08	6.58, 7.81
			34 (+ 3)	4.87, 5.06	0.93, 0.98	5.80, 6.04
Brown, SD/7	2	0.40	14 (+ 3)	2.52, 2.57	0.45, 0.41	2.97, 2.98
Stutsman, ND/7	2	0.40	14 (+ 5)	0.96, 1.40	0.17, 0.22	1.13, 1.62
Eddy, ND/7	2	0.40	14 (+ 5)	0.87, 1.13	0.19, 0.25	1.06, 1.38
McHenry, ND/7	2	0.40	14 (+ 4)	1.10, 1.16	0.16, 0.18	1.25, 1.34
Delta, CO/9	2	0.40	14 (+ 7)	1.22, 1.82	0.21, 0.33	1.43, 2.15
Tulare, CA/10	2	0.40	14 (+ 5)	1.31, 1.89	0.32, 0.47	1.63, 2.36
Jerome, ID/11	2	0.40	13 (+ 5)	0.96, 1.12	0.20, 0.23	1.16, 1.35
Grant, WA/11	2	0.40	14 (+ 3)	1.48, 1.64	0.34, 0.38	1.82, 2.02
Canada Trials						
St-Cesaire, QC/ 5B	2	0.42	14 (+ 4)	1.44, 1.74	0.15, 0.20	1.59, 1.94
Bagot, MB/14	2	0.40	16 (+ 7)	1.39 ^c , 1.43 ^c	0.32 ^c , 0.37 ^c	1.71, 1.80
Gladstone, MB/14	2	0.40	14 (+ 7)	0.84, 1.02	0.22, 0.28	1.06, 1.30
Minto, MB/14	2	0.40	14 (+ 5)	3.49, 3.90	0.59, 0.63	4.08, 4.53
Boissevain, MB/14	2	0.40	14 (+6)	3.15, 4.07	1.16, 1.44	4.31, 5.51
Aberdeen, SK/14	2	0.40	14 (+ 5)	3.17, 3.31	0.90, 0.86	4.07, 4.17
Hague, SK/14 decline study	2	0.40	14 (+ 4)	1.97, 2.33	0.20, 0.19	2.17, 2.52
			18 (+ 5)	1.63, 2.20	0.15, 0.18	1.81, 2.35
			23 (+ 5)	0.69, 0.96	0.11, 0.13	0.80, 1.09
			28 (+ 3)	0.99, 1.11	0.19, 0.14	1.18, 1.25
			32 (+ 4)	0.98, 1.04	0.16, 0.13	1.14, 1.17

Table 49 (continued).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^b
Beaumont, AB/14	2	0.40	16 (+ 5)	2.74, 2.84	0.60, 0.63	3.34, 3.47
Ferintosh, AB/14	2	0.41	14 (+ 3)	2.10, 2.29	0.07, 0.37	2.17, 2.66
Lancombe, AB/14	2	0.40	14 (+ 8)	3.18, 3.12	0.07, 0.40	3.25, 3.52
Red Deer, AB/14	2	0.40	14 (+ 4)	0.88, 1.04	0.10, 0.12	0.98, 1.16
Fairview, AB/14	2	0.41	12 (+ 5)	1.71, 2.03	0.51, 1.02	2.22, 3.05
Fairview, AB/14	2	0.49	12 (+ 5)	1.96, 2.24	1.02, 1.03	2.98, 3.27
Barley Grain						
U.S. Trials						
Lehigh, PA/1	2	0.41	47	0.14 ^c , 0.14 ^c	0.05 ^c , 0.05 ^c	0.19, 0.19
Wabasha, MN/5	2	0.41	42	0.04, 0.05	<0.02, <0.02	<0.06, <0.07
Freeborn, MN/5	2	0.40	43	<0.02, <0.02 ^d	<0.02, <0.02 ^d	<0.04, <0.04
Wilkin, MN/5 decline study	2	0.40	40	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
			47	0.02, 0.03	<0.02, <0.02	<0.04, <0.05
			54	0.02, 0.04	<0.02, <0.02	<0.04, <0.06
			61	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
			68	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Brown, SD/7	2	0.40	45	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Stutsman, ND/7	2	0.40	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Eddy, ND/7	2	0.40	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
McHenry, ND/7	2	0.40	45	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Delta, CO/9	2	0.40	63	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tulare, CA/10	2	0.41	43	0.06, 0.07	<0.02, 0.02	<0.08, 0.09
Jerome, ID/11	2	0.40	53	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Grant, WA/11	2	0.40	52	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Canada Trials						
St-Cesaire, QC/ 5B	2	0.42	42	0.05, 0.05	<0.02, <0.02	<0.07, <0.07
Bagot, MB/14	2	0.40	55	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Gladstone, MB/14	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Minto, MB/14	2	0.40	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Boissevain, MB/14	2	0.40	40	0.03, 0.03	<0.02, 0.02	<0.05, 0.05
Aberdeen, SK/14	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Table 49 (continued).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^b
Hague, SK/14 decline study	2	0.40	42	0.03, 0.04	<0.02, 0.02	<0.05, 0.06
			49	0.02, 0.02	<0.02, <0.02	<0.04, <0.04
			57	<0.02, 0.03	<0.02, <0.02	<0.04, <0.05
			63	<0.02, 0.03	<0.02, <0.02	<0.04, <0.05
			70	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
Beaumont, AB/14	2	0.40	70	0.02 ^c , 0.25 ^c	<0.02 ^c , 0.08 ^c	<0.04, 0.33
Ferintosh, AB/14	2	0.41	38	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Lancombe, AB/14	2	0.40	43	0.04, 0.04	<0.02, <0.02	<0.06, <0.06
Red Deer, AB/14	2	0.40	50	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fairview, AB/14	2	0.41	44	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fairview, AB/14	2	0.49	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Barley straw						
U.S. Trials						
Lehigh, PA/1	2	0.41	47	0.78, 0.86	0.15, 0.16	0.93, 1.02
Wabasha, MN/5	2	0.41	42	<0.02 ^c , 0.22	<0.02 ^c , 0.03	<0.04, 0.24
Freeborn, MN/5	2	0.40	43	0.44, 0.46	0.10, 0.10	0.55, 0.56
Wilkin, MN/5 decline study	2	0.40	40	0.94 ^c , 1.08 ^c	0.16 ^c , 0.17 ^c	1.10, 1.25
			47	1.63 ^c , 2.14 ^c	0.30 ^c , 0.40 ^c	1.93, 2.54
			54	0.83 ^c , 1.66 ^c	0.17 ^c , 0.31 ^c	1.00, 1.97
			61	1.21 ^c , 1.38 ^c	0.26 ^c , 0.29 ^c	1.47, 1.67
			68	1.42 ^c , 1.82 ^c	0.37 ^c , 0.39 ^c	1.79, 2.21
Brown, SD/7	2	0.40	45	0.50, 0.54	0.12, 0.13	0.62, 0.67
Stutsman, ND/7	2	0.40	43	1.10, 1.17	0.26, 0.28	1.36, 1.45
Eddy, ND/7	2	0.40	43	0.12, 0.13	0.02, 0.02	0.14, 0.16
McHenry, ND/7	2	0.40	45	0.23, 0.28	0.03, 0.04	0.26, 0.32
Delta, CO/9	2	0.40	63	0.31, 0.33	0.08, 0.08	0.38, 0.42
Tulare, CA/10	2	0.40	43	2.43, 2.38	0.62, 0.79	3.05, 3.17
Jerome, ID/11	2	0.40	53	0.25, 0.38	0.07, 0.09	0.32, 0.47
Grant, WA/11	2	0.40	52	0.08, 0.09 ^c	0.03, 0.03 ^c	0.11, 0.12

Table 49 (continued).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^b
Canada Trials						
St-Cesaire, QC/ 5B	2	0.42	42	0.30, 0.32	0.05, 0.04	0.35, 0.36
Bagot, MB/14	2	0.40	55	1.46, 1.49	0.53, 0.52	1.99, 2.01
Gladstone, MB/14	2	0.40	41	0.84, 0.90	0.26, 0.29	1.10, 1.19
Minto, MB/14	2	0.40	40	1.80, 2.05	0.46, 0.61	2.26, 2.66
Boissevain, MB/14	2	0.40	40	1.26, 1.26	0.56, 0.59	1.82, 1.85
Aberdeen, SK/14	2	0.40	41	2.81 ^c , 3.14 ^c	1.05 ^c , 1.11 ^c	3.86, 4.25
Hague, SK/14 decline study	2	0.40	42	1.40 ^c , 1.66 ^c	0.36 ^c , 0.38 ^c	1.76, 2.04
			49	1.65 ^c , 1.83 ^c	0.42 ^c , 0.48 ^c	2.07, 2.31
			57	1.44 ^c , 1.71 ^c	0.38 ^c , 0.47 ^c	1.82, 2.18
			63	1.15 ^c , 1.46 ^c	0.33 ^c , 0.39 ^c	1.48, 1.85
			70	1.27 ^c , 1.40 ^c	0.40 ^c , 0.41 ^c	1.66, 1.80
Beaumont, AB/14	2	0.40	70	4.00 ^c , 4.53 ^c	0.83 ^c , 1.02 ^c	4.83, 5.55
Ferintosh, AB/14	2	0.41	38	0.22, 0.38	0.04, 0.06	0.26, 0.44
Lancombe, AB/14	2	0.40	43	0.47, 0.66	0.11, 0.18	0.58, 0.84
Red Deer, AB/14	2	0.40	50	0.27, 0.31	0.03, 0.04	0.30, 0.35
Fairview, AB/14	2	0.41	44	0.28, 0.32	0.23, 0.27	0.51, 0.59
Fairview, AB/14	2	0.49	43	0.35, 0.42	0.42, 0.47	0.77, 0.89

^a For hay, the drying time is reported in parentheses.

^b Total pyraclostrobin and BF 500-3 residue values provided by the petitioner may vary slightly due to rounding.

^c Reported residue is the highest of replicate analyses of a single sample.

^d Reported residue is the lower of duplicate analyses of a single sample because the higher data point was considered an outlier.

Geographic representation of barley data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 5) a total of 12 trials were conducted on barley in Regions 1 (1 trial), 5 (3 trials), 7 (4 trials), 9 (1 trial), 10(1 trial), and 11 (2 trials). In addition, 13 barley field trials were conducted in Canada in Regions 5B (1 trial) and 14 (12 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on barley.

Barley hay: The combined residues of pyraclostrobin and BF 500-3 support the proposed tolerance level of 25.0 ppm in/on barley hay harvested 9-16 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 1.06-25.01 ppm in/on 24 samples of barley hay grown in the U.S. and 0.80-5.51 ppm in/on 26 samples of barley hay grown in Canada. The petitioner must modify the proposed label to add a 14-day PHI for barley hay.

Barley grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on barley grain harvested 38-70 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-0.19 ppm in/on 24 samples of barley grain grown in the U.S. and <0.04-0.33 ppm in/on 26 samples of barley grain grown in Canada.

Barley straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 6.0 ppm in/on barley straw harvested 38-70 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.29 lb ai/A/application for a total seasonal application rate of 0.40-0.49 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-3.17 ppm in/on 24 samples of barley straw grown in the U.S. and 0.26-5.55 ppm in/on 26 samples of barley straw grown in Canada.

The residue decline data for barley hay, grain and straw did not demonstrate any conclusive trends in decreasing residues at longer posttreatment intervals. Residues in hay decreased slightly with increased harvest intervals; residues in grain remained consistent at or near the LOQ, and residues in straw were variable and most likely dependent on the moisture content of the straw.

Rye

BASF Corporation submitted rye field trial data (citation listed below) to support the establishment of tolerances for residues of pyraclostrobin and BF 500-3 in/on rye grain at 0.04 ppm and rye straw at 0.5 ppm.

45118536 Haughey, D.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Rye: Lab Project Number: 1999/5107: 98010. Unpublished study prepared by BASF Corporation. 63 p.

A total of five field trials were conducted during the 1998 growing season in KS(1), ND(2), SD(1), and VA(1). Rye grain and straw were harvested 55-66 days following the last of two foliar applications, made at 9- to 19-day retreatment intervals, of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application. The first application was made when the flag leaf was just visible

to 25% head emergence, and the second application was applied at $\leq 50\%$ head emergence, no less than 40 days prior to grain/straw harvest. Total seasonal application rates were 0.40-0.41 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 9.9-31.1 gal/A using ground equipment with a spreader/sticker added to the spray solution. A separate plot at each trial site was left untreated to provide control samples.

Samples of treated and untreated mature rye grain and straw were collected from each test site. The petitioner indicated that rye forage was not sampled because it was unavailable at the late spray schedule of the proposed use pattern. All samples were transferred to freezers as soon as possible after collection, and then shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on five samples each of untreated rye grain and straw. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 50.

Table 50. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **rye (grain and straw)** harvested 55-66 days following two applications of the 2 lb/gal EC formulation at 0.40-0.41 lb ai/A (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Rye Grain						
Pulaski, VA/2 ^b	2	0.41	66	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Marshall, SD/5	2	0.40	58	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Stafford, KS/5	2	0.41	55	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Ward, ND/7	2	0.40	59	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
McHenry, ND/7	2	0.40	59	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Rye straw						
Pulaski, VA/2 ^b	2	0.41	66	0.12, 0.15	0.02, 0.03	0.14, 0.18
Marshall, SD/5	2	0.40	58	0.27, 0.34	0.08, 0.09	0.34, 0.43
Stafford, KS/5	2	0.41	55	0.09, 0.13	0.05, 0.06	0.13, 0.19
Ward, ND/7	2	0.40	59	0.25, 0.29	0.10, 0.12	0.35, 0.41
McHenry, ND/7	2	0.40	59	0.16, 0.17	0.09, 0.08	0.25, 0.26

^a Total pyraclostrobin and BF 500-3 residue values provided by the petitioner may vary slightly due to rounding.

^b The test site was located 6 miles NW of Region 2 (in Region 1), but still meets the EPA guideline requirements for Region 2.

Geographic representation of rye data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Table 5) a total of 5 trials were conducted on rye in Regions 2 (1 trial), 5 (2 trials), and 7 (2 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on rye.

Rye grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.04 ppm in/on rye grain harvested 58-66 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.40-0.414 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04 ppm in/on 10 samples of rye grain.

Rye straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 0.5 ppm in/on rye straw harvested 55-66 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.20-0.21 lb ai/A/application for a total seasonal application rate of 0.40-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.13-0.43 ppm in/on 10 samples of rye straw.

Rye forage: The petitioner did not provide residue data or propose a tolerance for rye forage because applications are made after the growth stages at which rye is foraged. Based on the proposed use pattern, the Agency will not require residue data or a tolerance for rye forage.

Wheat

BASF Corporation submitted wheat field trial data (citations listed below) to support the establishment of tolerances for residues of pyraclostrobin and BF 500-3 in/on wheat (grain) at 0.20 ppm, wheat (hay) at 6.0 ppm, and wheat (straw) at 8.5 ppm. Data pertaining to aspirated grain fractions submitted in conjunction with the 2000 field trial data will be addressed in the "Processed Food/Feed" section.

45118537 Versoi, P.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Wheat: Lab Project Number: 1999/5096: 98032: 98175. Unpublished study prepared by BASF Corporation. 173 p.

45321101 Versoi, P.; Abdel-Baky, S. (2001) The Magnitude of BAS 500 F Residues in Wheat and Wheat Processed Fractions - Year 2000 Field Project (Data Supporting a Later Spray Schedule for Fusarium Control). Lab Project Number: 2000/5283: 64146. Unpublished study prepared by BASF Corporation. 167 p.

Field trials conducted in 1998 provided data supporting foliar applications made at earlier growth stages, when the flag leaf was visible and at 50% head emergence. The petitioner subsequently expanded the proposed use of pyraclostrobin to target control of Fusarium head scab, a later-onset disease in wheat. The petitioner indicated that the expanded use requires a later spray schedule. The first spray is made at 100% grain head emergence and the second spray is made at the end of anthesis, with the result that the preharvest interval (PHI) may decrease from ~14-15 days to possibly ~3-14 days for wheat hay, and from ~40-57 days to approximately ~25-40 days for wheat grain and straw. Additional field trials were conducted in 2000 reflecting application of pyraclostrobin to wheat according to the expanded use pattern.

In support of the 2000 wheat field trials, BASF Corporation submitted a report (citation listed below) requesting a reduction in the number of field trials required for the expanded use pattern (later applications with a shorter PHI) on wheat.

45118624 Versoi, P.; Burkey, J. (2000) Request for Reduced Count of Magnitude of the Residue Field Trials with BAS 500 F Fungicide for NAFTA Registration on Wheat: Lab Project Number: 2000/5105. Unpublished study prepared by BASF Corporation. 8 p.

In the Request for Reduced Count of Magnitude of the Residue Field Trials, the petitioner proposed to conduct a total of 20 wheat field trials distributed within the U.S. (15 trials) and Canada (5 trials). The petitioner indicated that the proposed distribution of the 20 field trials was based on the acreage data (1991 Census), and that the regions represented within the 20 field trials represented 96% of the total production acres in the NAFTA area. The proposed and actual distribution of the 2000 wheat field trials conducted according to region is presented in Table 51.

The request for a reduced number of wheat field trials was evaluated by R. Loranger of HED (e-mail communication dated 6/22/2000; MRID 45321101) who agreed that data from the 15 U.S. trials, together with data from three Canadian trials conducted in southern Alberta (Region 7A, 1 trial) and southern Manitoba (Region 14, 2 trials), should be sufficient to support the new use pattern, provided residue levels in wheat grain were consistently low.

Following review of the subject report by EPA and PMRA, the petitioner added two U.S. trials (Region 7) and six Canadian trials (Region 14) to the 2000 study to bring the total number of trials relevant to U.S. application to 20.

Table 51. Field trial distribution proposed for pyraclostrobin in an EPA/PMRA harmonized wheat study.

Wheat Production Region	Number of Field Trials Required by PMRA ^a	Number of Field Trials Required by EPA ^b	1998 Trials Conducted (MRID 45118537)	No. Field Trials Proposed for Expanded Use	2000 Trials Conducted Expanded Use (MRID 45321101)
2	--	1	1	1	1
4	--	1	1	--	--
5	2	5	5	4	4
6	--	1	1	1	1
7	7	5	7	5	7
7A	1	--	1	1	1
8	--	6	6	3	3
11	--	1	1	1	1
14	10	--	10	4	10
Site Total	20	20	33	20	28

^a Suggested distribution of field trials by region (PMRA).

^b Suggested distribution of field trials by region (Table 5 of OPPTS 860.1500).

1998 Field Trials - Earlier growth stage applications (MRID 45118537)

A total of 33 wheat field trials were conducted during the 1998 growing season. Twenty-two trials were conducted in the U.S. in ID(1), KS(1), MN(3), MO(1), NC(1), ND(6), NE(1), OK(2), SD(2), and TX(4). Eleven field trials were conducted in Canada in AB(5), SK(3), and MB(3). Wheat hay was cut 12-19 days and wheat grain and straw were harvested 40-57 days following the last of two foliar applications, made at 4- to 21-day retreatment intervals, of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application. The first application was made when the flag leaf was just visible, and the second application was applied at 50% head emergence. Total seasonal application rates were 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 7.2-39.1 gal/A using ground equipment with a spray adjuvant added to the spray solution. In three trials (KS, MN, and SK), additional wheat hay samples were cut at 24, 29, and 34 days, and additional wheat grain and straw samples were harvested 54, 61, and 68 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

Samples of treated and untreated wheat hay, grain, and straw were collected from each test site. Hay samples were allowed to dry in the field for 3-8 days (21-70% moisture) before collection, except that hay from one of the AB trials was collected the day it was cut without field drying. Wheat forage was not sampled because it was unavailable at the late spray schedule of this use pattern. All samples were transferred to freezers soon after collection (within 3.8 hours), with the exception of wheat grain and straw samples from one AB trial site which were frozen within 6.8 hours of collection. All samples were shipped frozen to the BASF APC where they were

analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 33 samples each of untreated wheat hay and wheat grain, and 32 samples of untreated wheat straw. Detectable pyraclostrobin residues were found in one sample of untreated wheat straw (duplicate analyses; 0.069 and 0.103 ppm); BF 500-3 residues were 0.021 ppm and less than the LOQ in this sample. No explanation for detectable residues in the untreated sample was provided by the petitioner. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 52.

Table 52. Residues of pyraclostrobin and its metabolite BF 500-3 in/on wheat (hay, grain, and straw) harvested 14-19 days (hay) or 40-57 days (grain and straw) following two applications of the 2 lb/gal EC formulation at 0.39-0.43 lb ai/A (~ 1x the maximum proposed seasonal rate).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Wheat hay						
U.S. Trials						
Sampson, NC/2 (winter)	2	0.40	14 (+ 5)	0.55, 0.90	0.11, 0.15	0.66, 1.06
Pemiscot, MO/4 (winter)	2	0.42	14 (+ 3)	0.67, 0.84	0.13, 0.17	0.79, 1.02
Caddo, OK/6 (winter)	2	0.40	14 (+ 5)	1.72, 1.89	0.64, 0.79	2.36, 2.68
Washita, OK/8 (winter)	2	0.40	14 (+ 5)	1.92, 2.61	0.75, 0.75	2.66, 3.35
Armstrong, TX/8 (winter)	2	0.40	14 (+ 7)	1.55, 1.65	0.69, 0.77	2.24, 2.42
Carson, TX/8 (winter)	2	0.40	14 (+ 7)	1.02, 1.01	0.37, 0.43	1.39, 1.44
Hockley, TX/8 (winter)	2	0.41	14 (+ 5)	1.97, 2.51	0.81, 1.04	2.78, 3.55
Lamb, TX/8 (winter)	2	0.41	14 (+ 5)	2.70, 3.44	1.17, 1.29	3.87, 4.73
Pawnee, KS/8 (winter) decline study	2	0.40	15 (+ 4)	1.48, 1.49	0.58, 0.58	2.06, 2.07
			19 (+ 5)	1.20, 1.26	0.52, 0.53	1.73, 1.78
			24 (+ 6)	1.27, 1.28	0.51, 0.53	1.78, 1.81
			29 (+ 5)	1.34, 1.47	0.53, 0.63	1.87, 2.10
			34 (+ 3)	1.42, 1.49	0.59, 0.60	2.01, 2.09
Hall, NE/7 (winter)	2	0.40	14 (+ 4)	0.46, 0.46	0.06, 0.08	0.52, 0.54
Wabasha, MN/5 (spring)	2	0.41	14 (+ 3)	0.90 ^c , 1.01 ^c	0.10 ^c , 0.16 ^c	1.01, 1.17
Freeborn, MN/5 (spring)	2	0.40	14 (+ 4)	0.89, 0.92	0.20, 0.24	1.09, 1.15
Wilkin, MN/5 (spring) decline study	2	0.40	14 (+ 6)	0.48, 0.59	0.13, 0.18	0.61, 0.77
			19 (+ 5)	0.37, 0.68 ^c	0.12, 0.21 ^c	0.49, 0.89
			24 (+ 5)	0.32, 0.45 ^c	0.11, 0.12 ^c	0.44, 0.57
			29 (+ 5)	0.37, 0.40	0.12, 0.13	0.49, 0.51
			34 (+ 3)	0.18 ^c , 0.24 ^c	0.06 ^c , 0.08 ^c	0.24, 0.32
Cass, ND/5 (spring)	2	0.40	14 (+ 4)	4.18, 4.92	0.80, 1.03	4.98, 5.95
Stutsman, ND/7 (durum)	2	0.41	14 (+ 4)	1.79, 2.26	0.51, 0.57	2.30, 2.83
Grand Forks, ND/5 (spring)	2	0.39	15 (+ 3)	0.34, 0.52	0.07, 0.11	0.40, 0.63

Table 52 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Eddy, ND/7 (durum)	2	0.40	19 (+ 3)	0.24, 0.24	0.09, 0.10	0.32, 0.34
McHenry, ND/7 (durum)	2	0.40	14 (+ 8)	0.69 ^c , 1.62 ^c	0.09 ^c , 0.34 ^c	0.79, 1.96
Ward, ND/7 (durum)	2	0.40	14 (+ 7)	0.83, 1.26	0.14, 0.33	0.97, 1.59
Brown, SD/7 (spring)	2	0.40	14 (+ 3)	0.24, 0.29	0.05, 0.06	0.29, 0.34
McPherson, SD/7 (spring)	2	0.40	14 (+ 3)	0.19, 0.22	0.02, 0.03	0.21, 0.25
Jerome, ID/11 (spring)	2	0.40	14 (+ 7)	0.49, 0.48	0.10, 0.12	0.59, 0.60
Canada Trials						
Bamwell, AB/7A (spring)	2	0.41	14 (+ 0)	1.36, 1.55	0.34, 0.30	1.70, 1.85
Lancombe, AB/14 (spring)	2	0.40	14 (+ 7)	0.72, 1.31	0.27, 0.50	0.99, 1.81
Red Deer, AB/14 (spring)	2	0.40	14 (+ 7)	0.64, 1.24	0.26, 0.45	0.90, 1.69
Fairview, AB/14 (spring)	2	0.42	12 (+ 3)	1.61, 1.92	0.90, 1.10	2.51, 3.01
Fairview, AB/14 (spring)	2	0.43	12 (+ 3)	1.74, 2.59	1.09, 1.62	2.83, 4.21
Aberdeen, SK/14 (spring) decline study	2	0.40	14 (+ 5)	2.83, 3.16	1.06, 1.13	3.89, 4.30
			19 (+ 5)	2.86, 2.86	1.01, 1.05	3.86, 3.91
			24 (+ 5)	2.41, 2.71	0.93, 0.10	3.33, 3.71
			29 (+ 5)	1.68, 2.78	0.78, 1.15	2.46, 3.93
			34 (+ 6)	1.85, 1.98	0.80, 0.85	2.65, 2.83
Hague, SK/14 (spring)	2	0.39	14 (+ 4)	1.11, 1.36	0.33, 0.43	1.44, 1.78
Duck Lake, SK/14 (spring)	2	0.40	14 (+ 3)	1.77, 1.97	0.65, 0.69	2.42, 2.65
Minto, MB/14 (spring)	2	0.40	14 (+ 5)	0.89, 1.02	0.23, 0.24	1.12, 1.25
Boissevain, MB/14 (spring)	2	0.40	14 (+ 5)	1.18, 1.58	0.66, 0.86	1.84, 2.44
Bagot, MB/14 (spring)	2	0.40	14 (+ 5)	1.30, 1.45	0.34, 0.38	1.65, 1.83

Table 52 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Wheat Grain						
U.S. Trials						
Sampson, NC/2 (winter)	2	0.40	53	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Pemiscot, MO/4 (winter)	2	0.42	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Caddo, OK/6 (winter)	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Washita, OK/8 (winter)	2	0.40	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Armstrong, TX/8 (winter)	2	0.40	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Carson, TX/8 (winter)	2	0.40	44	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Hockley, TX/8 (winter)	2	0.41	51	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Lamb, TX/8 (winter)	2	0.41	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Pawnee, KS/8 (winter) decline study	2	0.40	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			54	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			61	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			68	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Hall, NE/7 (winter)	2	0.40	45	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Wabasha, MN/5 (spring)	2	0.41	42	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Freeborn, MN/5 (spring)	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Wilkin, MN/5 (spring) decline study	2	0.40	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			54	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			61	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			68	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Cass, ND/5 (spring)	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Stutsman, ND/7 (durum)	2	0.41	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Grand Forks, ND/5 (spring)	2	0.39	49	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Eddy, ND/7 (durum)	2	0.40	47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Table 52 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
McHenry, ND/7 (durum)	2	0.40	50	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Ward, ND/7 (durum)	2	0.40	46	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Brown, SD/7 (spring)	2	0.40	41	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
McPherson, SD/7 (spring)	2	0.40	47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Jerome, ID/11 (spring)	2	0.40	46	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Canada Trials						
Barnwell, AB/7A (spring)	2	0.41	49	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
Lancombe, AB/14 (spring)	2	0.40	53	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Red Deer, AB/14 (spring)	2	0.40	57	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fairview, AB/14 (spring)	2	0.42	50	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fairview, AB/14 (spring)	2	0.43	51	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Aberdeen, SK/14 (spring) decline study	2	0.397	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			54	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			61	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			68	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Hague, SK/14 (spring)	2	0.394	46	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Duck Lake, SK/14 (spring)	2	0.404	45	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Minto, MB/14 (spring)	2	0.399	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Boissevain, MB/14 (spring)	2	0.402	40	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Bagot, MB/14 (spring)	2	0.401	47	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Table 52 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Wheat straw						
U.S. Trials						
Sampson, NC/2 (winter)	2	0.40	53	0.20, 0.26	0.08, 0.10	0.28, 0.36
Pemiscot, MO/4 (winter)	2	0.42	40	0.54, 0.58	0.22, 0.23	0.76, 0.81
Caddo, OK/6 (winter)	2	0.40	41	0.85, 0.94	0.47, 0.54	1.32, 1.48
Washita, OK/8 (winter)	2	0.40	43	0.65, 0.83	0.43, 0.53	1.08, 1.36
Armstrong, TX/8 (winter)	2	0.40	43	1.26, 1.83	0.67, 0.97	1.92, 2.80
Carson, TX/8 (winter)	2	0.40	44	1.06 °, 1.20 °	0.63 °, 0.59 °	1.66, 1.83
Hockley, TX/8 (winter)	2	0.41	51	1.44 °, 1.75 °	0.83 °, 1.04 °	2.27, 2.79
Lamb, TX/8 (winter)	2	0.41	41	3.61, 4.08	1.53, 1.62	5.15, 5.70
Pawnee, KS/8 (winter) decline study	2	0.40	40	1.56, 2.26	0.69, 0.94	2.26, 3.20
			47	1.73, 2.67	0.87, 1.08	2.59, 3.75
			54	1.63 °, 2.71 °	0.75 °, 1.16 °	2.37, 3.86
			61	1.02, 1.59	0.57, 0.87	1.58, 2.46
			68	0.66, 1.08	0.40, 0.59	1.05, 1.67
Hall, NE/7 (winter)	2	0.40	45	0.05, 0.07	<0.02, 0.02	0.07, 0.09
Wabasha, MN/5 (spring)	2	0.41	42	0.10, 0.16	0.02, 0.03	0.12, 0.19
Freeborn, MN/5 (spring)	2	0.40	41	0.16, 0.235	0.07, 0.09	0.23, 0.33
Wilkin, MN/5 (spring) decline study	2	0.40	40	0.10 °, 0.13 °	0.05 °, 0.05 °	0.15, 0.18
			47	0.13, 0.15	0.07, 0.07	0.20, 0.22
			54	0.13, 0.17	0.08, 0.09	0.21, 0.26
			61	0.09, 0.10	0.07, 0.06	0.16, 0.16
			68	0.09, 0.12	0.07, 0.08	0.16, 0.20
Cass, ND/5 (spring)	2	0.40	41	4.03, 4.16	0.82, 0.96	4.85, 5.12
Stutsman, ND/7 (durum)	2	0.41	43	0.81, 0.88	0.29, 0.33	1.10, 1.20
Grand Forks, ND/5 (spring)	2	0.39	49	0.06, 0.11	0.02, 0.03	0.08, 0.14
Eddy, ND/7 (durum)	2	0.40	47	0.10, 0.11	0.05, 0.05	0.14, 0.16

Table 52 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
McHenry, ND/7 (durum)	2	0.40	50	0.21, 0.22	0.07, 0.06	0.28, 0.28
Ward, ND/7 (durum)	2	0.40	46	0.13, 0.13	0.03, 0.03	0.16, 0.16
Brown, SD/7 (spring)	2	0.40	41	0.06, 0.07	<0.02, 0.02	<0.08, 0.09
McPherson, SD/7 (spring)	2	0.40	47	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
Jerome, ID/11 (spring)	2	0.40	46	0.11, 0.13	0.05, 0.06	0.16, 0.19
Canada Trials						
Barnwell, AB/7A (spring)	2	0.41	49	1.48, 1.61	0.34, 0.38	1.82, 1.99
Lancombe, AB/14 (spring)	2	0.40	53	0.07, 0.14	0.04, 0.10	0.11, 0.25
Red Deer, AB/14 (spring)	2	0.40	57	0.10, 0.11	0.08, 0.08	0.17, 0.19
Fairview, AB/14 (spring)	2	0.42	50	0.28, 0.39	0.19, 0.27	0.47, 0.66
Fairview, AB/14 (spring)	2	0.43	51	0.23, 0.25	0.18, 0.20	0.41, 0.44
Aberdeen, SK/14 (spring) decline study	2	0.40	40	0.90, 1.44	0.52, 0.74	1.42, 2.18
			47	2.75, 4.27	1.32, 1.90	4.07, 6.16
			54	1.33, 2.00	0.90, 1.25	2.23, 3.24
			61	1.20, 1.47	0.83, 0.94	2.03, 2.41
			68	0.80, 2.14 ^c	1.34, 1.18 ^c	1.34, 3.32
Hague, SK/14 (spring)	2	0.39	46	0.93, 0.97	0.45, 0.42	1.38, 1.38
Duck Lake, SK/14 (spring)	2	0.40	45	1.65, 1.72	0.79, 0.84	2.44, 2.56
Minto, MB/14 (spring)	2	0.40	40	0.36, 0.37	0.10, 0.12	0.46, 0.48
Boissevain, MB/14 (spring)	2	0.40	40	0.41, 0.62	0.27, 0.43	0.68, 1.05
Bagot, MB/14 (spring)	2	0.40	47	0.30, 0.33	0.14, 0.14	0.44, 0.47

^a For hay, the drying time is reported in parentheses.

^b Total pyraclostrobin and BF 500-3 residue values provided by the petitioner may vary slightly due to rounding.

^c Reported residue is the highest of replicate analyses of a single sample.

2000 Field Trials - Later growth stage applications (MRID 45321101)

A total of 28 wheat field trials were conducted during the 2000 growing season. Seventeen trials were conducted in the U.S. in ID(1), MN(2), NC(1), ND(6), NE(2), OK(2), TX(2), and WI(1). Eleven field trials were conducted in Canada in AB(5), SK(2), and MB(4). Mature wheat grain and straw were harvested 24-60 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application, made at 5- to 14-day retreatment intervals. The first application was made at full head emergence and the second application was made at the end of anthesis. Total seasonal application rates were 0.39-0.41 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 10-31 gal/A using ground equipment with a spray adjuvant added to the spray solution. In two trials (MN and NE), additional wheat grain and straw samples were harvested 35-42, 42-48, 49-55, and 56-62 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

Exaggerated rates were applied to a separate plot of wheat in one of the ND trials to obtain samples for processing. Mature wheat grain was harvested 39 days following the last of two foliar applications of the 2 lb/gal EC formulation at 1.0 lb ai/A/application, for a total rate of 2.0 lb ai/A (~5x the maximum proposed seasonal application rate). Bulk samples of 1x and 5x treated wheat grain were collected from the ND trial site for generation of aspirated grain fractions (AGF) and processed commodities, respectively. These data will be addressed in the "Processed Food/Feed" section with the 1998 AGF and processed commodity data.

A single untreated and duplicate treated samples of wheat grain and straw were collected from each test site. Wheat forage and hay were not sampled because forage was unavailable at the late spray schedule of this use pattern, and data were available for hay harvested at a 14-day PHI from the 1998 field trials. All samples were transferred to freezers soon after collection (time unspecified) and were shipped frozen to the BASF APC for analysis. Bulk grain samples for processing were shipped frozen directly to the Food Protein Research and Development Center (Bryan, TX). Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9908. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 28 samples each of untreated wheat grain and straw. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 53.

Table 53. Residues of pyraclostrobin and its metabolite BF 500-3 in/on wheat grain and straw harvested 24-60 days following two applications of the 2 lb/gal EC formulation at 0.39-0.41 lb ai/A (~ 1x the maximum proposed seasonal rate).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Wheat Grain						
U.S. Trials						
Wake, NC/2 (winter)	2	0.40	36	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Pepin, WI/5 (spring)	2	0.41	35	0.022, 0.024	<0.02, <0.02	<0.04, <0.04
Wabasha, MN/5 (spring)	2	0.40	28	0.040, 0.046	<0.02, <0.02	<0.06, <0.07
Freeborn, MN/5 (spring) decline study	2	0.40	35	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
			42	<0.02, 0.023	<0.02, <0.02	<0.04, <0.04
			48	0.027, 0.031	<0.02, <0.02	<0.05, <0.05
			55	0.024, 0.043	<0.02, <0.02	<0.04, <0.06
			62	<0.02, 0.024	<0.02, <0.02	<0.04, <0.04
Cass, ND/5 (spring)	2	0.41	39	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Stutsman, ND/7 (durum)	2	0.41	33	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
McHenry, ND/7 (durum)	2	0.40	38	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Ward, ND/7 (durum)	2	0.40	38	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Eddy, ND/7 (spring)	2	0.40	42	0.022, 0.028	<0.02, <0.02	<0.04, <0.05
Eddy, ND/7 (spring)	2	0.40	57	0.064, 0.074	0.039, 0.041	0.10, 0.12
Hall, NE/7 (winter) decline study	2	0.40	29	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			35	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			42	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			49	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			56	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Perkins, NE/7 (winter)	2	0.40	24	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Caddo, OK/6 (winter)	2	0.39	35	<0.02, 0.021	<0.02, <0.02	<0.04, <0.04
Washita, OK/8 (winter)	2	0.40	41	0.020, 0.021	<0.02, <0.02	<0.04, <0.04
Armstrong, TX/8 (winter)	2	0.40	36	0.056, 0.104	<0.02, 0.043	<0.08, 0.15
Carson, TX/8 (winter)	2	0.40	36	0.096, 0.109	0.035, 0.048	0.13, 0.16 HAFT=0.145
Payette, ID/11 (spring)	2	0.41	43	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Table 53 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Canada Trials						
Taber, AB/7A (spring)	2	0.41	37	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Lancombe, AB/14 (spring)	2	0.41	57	0.020, 0.027	<0.02, 0.063	<0.04, 0.09
Red Deer, AB/14 (spring)	2	0.40	48	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Morton, MB/14 (spring)	2	0.41	41	<0.02, 0.048	<0.02, 0.033	<0.04, 0.08
Whitewater, MB/14 (durum)	2	0.40	43	0.031, 0.032	0.018, 0.020	0.05, 0.05
North Cypress, MB/14 (spring)	2	0.40	34	<0.02, 0.022	<0.02, <0.02	<0.04, <0.04
Minto, MB/14 (spring)	2	0.40	48	<0.02, 0.022	<0.02, <0.02	<0.04, <0.04
Wakaw, SK/14 (spring)	2	0.40	50	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Rosthern, SK/14 (spring)	2	0.40	52	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Leduc, AB/14 (spring)	2	0.41	51	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Edmonton, AB/14 (spring)	2	0.40	60	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Wheat straw						
U.S. Trials						
Wake, NC/2 (winter)	2	0.40	36	1.457, 1.590	1.026, 1.068	2.48, 2.66
Pepin, WI/5 (spring)	2	0.41	35	3.487, 4.633	1.865, 1.784	5.35, 6.42
Wabasha, MN/5 (spring)	2	0.40	28	1.593, 1.659	0.209, 0.229	1.80, 1.89
Freeborn, MN/5 (spring) decline study	2	0.40	35	1.154, 1.168	0.384, 0.371	1.54, 1.54
			42	1.227, 1.359	0.430, 0.381	1.66, 1.74
			48	1.279, 1.617	0.364, 0.527	1.64, 2.14
			55	1.204, 1.441	0.379, 0.550	1.58, 1.99
			62	1.495, 1.739	0.542, 0.584	2.04, 2.32
Cass, ND/5 (spring)	2	0.41	39	1.646, 1.656	0.522, 0.780	2.17, 2.44
Stutsman, ND/7 (durum)	2	0.41	33	1.979, 2.222	0.539, 0.581	2.52, 2.80
McHenry, ND/7 (durum)	2	0.40	38	0.529, 0.588	0.118, 0.120	0.65, 0.71
Ward, ND/7 (durum)	2	0.40	38	1.071, 1.176	0.312, 0.429	1.38, 1.61
Eddy, ND/7 (spring)	2	0.40	42	2.082, 1.961	0.513, 0.685	2.60, 2.65
Eddy, ND/7 (spring)	2	0.40	57	1.185, 1.345	0.520, 0.603	1.71, 1.95

Table 53 (continued).

Test Site/Region (wheat type)	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total ^a
Hall, NE/7 (winter) decline study	2	0.40	29	1.476, 1.595	0.425, 0.475	1.90, 2.07
			35	0.754, 1.366	0.307, 0.464	1.06, 1.83
			42	0.839, 0.905	0.322, 0.352	1.16, 1.26
			49	0.876, 1.665	0.341, 0.482	1.22, 2.15
			56	1.007, 1.821	0.216, 0.546	1.22, 2.37
Perkins, NE/7 (winter)	2	0.40	24	2.879, 3.108	0.771, 1.021	3.65, 4.13
Caddo, OK/6 (winter)	2	0.39	35	2.009, 2.194	1.143, 0.980	3.15, 3.17
Washita, OK/8 (winter)	2	0.40	41	2.474, 2.560	1.105, 1.132	3.58, 3.69
Armstrong, TX/8 (winter)	2	0.40	36	5.919, 5.776	1.872, 2.453	7.79, 8.23
Carson, TX/8 (winter)	2	0.40	36	5.569, 5.917	1.996, 1.967	7.57, 7.88
Payette, ID/11 (spring)	2	0.41	43	0.596, 0.604	0.207, 0.195	0.80, 0.80
Canada Trials						
Taber, AB/7A (spring)	2	0.41	37	0.172, 0.751	0.037, 0.275	0.21, 1.03
Lancombe, AB/14 (spring)	2	0.41	57	1.164, 1.681	0.625, 0.851	1.79, 2.53
Red Deer, AB/14 (spring)	2	0.40	48	0.687, 0.756	0.307, 0.368	0.99, 1.12
Morton, MB/14 (spring)	2	0.41	41	3.387, 4.001	1.468, 1.599	4.86, 5.60
Whitewater, MB/14 (durum)	2	0.40	43	3.163, 3.137	0.851, 0.896	4.01, 4.03
North Cypress, MB/14 (spring)	2	0.40	34	1.185, 1.345	0.520, 0.603	1.71, 1.95
Minto, MB/14 (spring)	2	0.40	48	3.696, 3.927	2.178, 2.379	5.87, 6.31
Wakaw, SK/14 (spring)	2	0.40	50	4.061, 4.337	1.904, 1.975	5.96, 6.31
Rosthern, SK/14 (spring)	2	0.40	52	2.327, 4.384	1.093, 1.792	3.42, 6.18
Leduc, AB/14 (spring)	2	0.41	51	1.000, 1.008	0.503, 0.513	1.50, 1.52
Edmonton, AB/14 (spring)	2	0.40	60	0.745, 0.947	0.321, 0.324	1.07, 1.27

^a Total pyraclostrobin and BF 500-3 residue values provided by the petitioner may vary slightly due to rounding.

Geographic representation of wheat data is adequate for the purposes of this petition. The Agency (OPPTS 860.1500 Table 5) requires a total of 20 field trials for wheat to be conducted in Regions 2 (1 trial), 4 (1 trial), 5 (5 trials), 6 (1 trial), 7 (5 trials), 8 (6 trials), and 11 (1 trial). For the earlier growth stage use pattern, field trials were conducted in 1998 in the U.S. as required,

with two additional field trials conducted in Region 7. In addition, 11 wheat field trials were conducted in Canada in 1998 in Regions 7A (1 trial) and 14 (10 trials). For the later growth stage use pattern, 17 trials were conducted in 2000 in the U.S. in Regions 1 (1 trial), 5 (4 trials), 6 (1 trial), 7 (7 trials), 8 (3 trials), and 11 (1 trial), and 11 wheat trials were conducted in Canada in Regions 7A (1 trial) and 14 (10 trials). The Agency had previously concluded that data from the 2000 U.S. trials, together with data from three Canadian trials conducted in southern Alberta (Region 7A, 1 trial) and southern Manitoba (Region 14, 2 trials), should be sufficient to support the new use pattern.

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on wheat in the U.S. Adequate field trial data were submitted supporting applications made to wheat at the earlier growth stage (applications made at flag leaf and 50% head emergence) and applications made to wheat at later growth stages with a shorter PHI (applications made at full head emergence and the end of anthesis) for control of Fusarium head blight.

Wheat grain: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.2 ppm in/on wheat grain following earlier and later (expanded use) application schedules to wheat. In the early treatment schedule, wheat grain was harvested 40-57 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following the earlier application schedule were <0.04 ppm in/on 44 samples of wheat grain grown in the U.S. and <0.04-<0.05 ppm in/on 22 samples of wheat grain grown in Canada. In the later application schedule, wheat grain was harvested 24-60 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.39-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following later application schedules were <0.04-0.16 ppm in/on 34 samples of wheat grain grown in the U.S. and <0.04-0.09 ppm in/on 22 samples of wheat grain grown in Canada.

Wheat hay: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 6.0 ppm in/on wheat hay following earlier application schedules to wheat. In the early treatment schedule, wheat hay was harvested 12-19 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following early application schedules were 0.21-5.95 ppm in/on 44 samples of wheat hay grown in the U.S. and 0.90-4.3 ppm in/on 22 samples of wheat hay grown in Canada. The petitioner indicated that wheat hay was not sampled from the later treatment schedule study because hay was harvested at a 14-day PHI in the 1998 study. The petitioner must modify the proposed label to add a 14-day PHI for wheat hay.

Wheat straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 8.5 ppm in/on wheat straw following earlier and later (expanded use) application schedules to wheat. In the early treatment schedule, wheat straw was harvested 40-57 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.43 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following early application schedules were <0.05-5.70 ppm in/on 44 samples of wheat straw grown in the U.S. and 0.11-6.17 ppm in/on 22 samples of wheat straw grown in Canada. In the later treatment schedule, wheat straw was harvested 24-60 days following the last of two foliar applications of the 2 lb/gal EC formulation at 0.19-0.21 lb ai/A/application for a total seasonal application rate of 0.39-0.41 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues following later application schedules were 0.65-8.23 ppm in/on 34 samples of wheat straw grown in the U.S. and 0.21-6.31 ppm in/on 22 samples of wheat straw grown in Canada.

The residue decline data for wheat hay, grain, and straw did not demonstrate any conclusive trends in decreasing residues at longer posttreatment intervals. Residues were variable in hay and straw, and residues in grain were consistently near or below the LOQ.

Wheat forage: The petitioner did not provide residue data or propose a tolerance for wheat forage because applications are made after the growth stages at which wheat is foraged. Based on the current proposed use patterns, the Agency will not require residue data or a tolerance for wheat forage.

Small grains - European trials

BASF Corporation submitted two volumes of European small grain field trial data (citations listed below) to support the establishment of the proposed tolerance for residues of pyraclostrobin and BF 500-3 in/on wheat grain at 0.20 ppm. These data will not be considered in the assessment of the proposed U.S. tolerance, but are presented for informational purposes.

45118601 Beck, J. (1999) Study on the Residue Behavior of BAS 500 F, Epoxiconazole and Kresoxim-methyl in Cereals after Treatment with BAS 512 00F under Field Conditions in Belgium, France, Germany, Great Britain, Spain, Sweden and the Netherlands, 1998: Lab Project Number: 1999/11509: EU/FR/01/98. Unpublished study prepared by BASF Aktiengesellschaft. 57 p.

45118602 Meumann, H.; Benz, A.; Mackenroth, C. (1999) Evaluation of the Residue Behavior of BAS 500 F after Application of BASF 500 01 F in Cereals under Field Conditions in Germany, France, and Sweden, 1998: Lab Project Number: NEU/FR/06/98: 1999/11825. Unpublished study prepared by BASF Aktiengesellschaft. 25 p.

In the first study (MRID 45118601), 13 field trials were conducted on barley (5 trials) and wheat (8 trials) during the 1998 growing season in Belgium(1 trial), France(2), Germany(2), Great

Britain(3), Spain(3), Sweden(1), and the Netherlands(1). At each site, three separate plots were treated as follows: (i) pyraclostrobin (250 g/L) was formulated as an EC formulation and was applied to barley and wheat plants as two spray applications at 193.9-265.1 g ai/ha/application (0.17-0.24 lb ai/A/application for a total rate of 0.37-0.45 lb ai/A); (ii) pyraclostrobin (133 g/L) and epoxiconazole (50 g/L) were formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 211.3-284.8 g ai/ha/application (0.19-0.25 lb ai/A/application for a total rate of 0.39-0.46 lb ai/A); or (iii) pyraclostrobin (133 g/L), epoxiconazole (50 g/L), and kresoxim-methyl (67 g/L) were formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 231.3-265.6 g ai/ha/application (0.21-0.24 lb ai/A/application for a total rate of 0.42-0.45 lb ai/A). Applications were made at BBCH growth stages 37-47 and 59-72 (early-dough stage; beginning of ripening); retreatment intervals were 11-50 days. Applications were made in 235-332 L/ha (25-35 gal/A) using ground equipment.

Samples of barley and wheat (whole plant without roots) were collected within 3 hours of the second application. In addition, samples of ears and haulms were collected 20-22 and 32-37 days posttreatment, and samples of grain and straw were collected 33-35, 40-44, and 49-51 days posttreatment. Samples were frozen (within 6 hours of collection) and either shipped directly to the analytical laboratory (BASF Agricultural Center Limburgerhof, Germany) or placed in intermediate frozen storage prior to being sent to Limburgerhof.

Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method 421/0. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on all collected samples of untreated barley plant without roots (1 sample), wheat plant without roots (3 samples), barley grain (1 sample), wheat grain (1 sample), barley straw (3 samples), wheat straw (2 samples), barley ears (1 sample), wheat ears (4 samples), barley haulms (plant stems) (3 samples), and wheat haulms (2 samples). Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 54.

In the second study (MRID 45118602), five field trials were conducted on barley (2 trials) and wheat (3 trials) during the 1998 growing season in France, Germany, and Sweden. Field trials were conducted using pyraclostrobin (250 g/L) formulated as an EC formulation which was applied to barley and wheat plants as two spray applications at 232.0-261.4 g ai/ha/application (0.21-0.23 lb ai/A/application; total rate of 0.43-0.46 lb ai/A). Applications were made at BBCH growth stages 37-39 and 59-69; retreatment intervals were 12-23 days. Applications were made in 281-317 L/ha (30-34 gal/A) using ground equipment.

Samples of barley and wheat (whole plant without roots) were collected within 3 hours of the second application. In addition, samples of ears and haulms were collected 21-22, 35-36, and 41-42 days posttreatment, and samples of grain and straw were collected 35, 41-43, and 64 days posttreatment. Samples were frozen (within 6 hours of collection) and either shipped within 48 hours to the analytical laboratory (BASF Agricultural Center Limburgerhof, Germany) or placed in intermediate frozen storage prior to being sent to Limburgerhof.

Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method 421/0. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on all collected samples of untreated barley plant without roots (1 sample), wheat plant without roots (1 sample), barley grain (1 sample), wheat grain (1 sample), barley straw (1 sample), wheat straw (2 samples), barley ears (1 sample), wheat ears (2 samples), barley haulms (1 sample), and wheat haulms (2 samples). Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 54.

Table 54. Residues of pyraclostrobin and its metabolite BF 500-3 in/on small grain commodities from European field trials.

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
1998 Trials -250 g/L pyraclostrobin EC formulation									
Limburg, Netherlands (45118601)	wheat (winter)	0.213, 0.224 (238.9, 250.8)	2	0.437 (489.7)	plant	0	4.27	0.06	4.33
					ears	20	0.45	0.09	0.54
					haulms	20	0.84	0.09	0.93
					grain	35	0.04	<0.02	<0.06
						44	<0.02	<0.02	<0.04
						51	<0.02	<0.02	<0.04
					straw	35	1.96	0.24	2.20
						44	2.24	0.59	2.83
						51	1.03	0.24	1.27
Brabant, Belgium (45118601)	barley (spring)	0.218, 0.228 (244.2, 255.4)	2	0.446 (499.6)	plant	0	5.68	0.12	5.80
					ears	20	0.26	0.10	0.36
					haulms	20	0.88	0.10	0.98
					grain	34	0.04	0.03	0.07
						40	0.05	0.02	0.07
					straw	34	1.85	0.39	2.24
						40	1.81	0.42	2.23
Andalucia, Seville, Spain (45118601)	wheat (winter)	0.205, 0.217 (229.9, 243.4)	2	0.422 (473.3)	plant	0	9.07	0.76	9.83
					ears	21	0.34	0.11	0.45
						33	0.33	0.10	0.43
					haulms	21	3.20	0.74	3.94
						33	2.43	0.71	3.14
					grain	42	<0.02	<0.02	<0.04
					straw	42	5.53	1.80	7.33

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Andalucia, Seville, Spain (45118601)	wheat (winter)	0.221, 0.223 (248.1, 249.3)	2	0.444 (497.4)	plant	0	4.18	0.12	4.30
					ears	22	0.48	0.26	0.74
						37	0.15	0.08	0.23
					haulms	22	0.74	0.17	0.91
						37	0.44	0.12	0.56
					grain	42	<0.02	<0.02	<0.04
straw	42	1.53	0.61	2.14					
Andalucia, Seville, Spain (45118601)	wheat (Durum)	0.209, 0.210 (234.6, 235.8)	2	0.420 (470.4)	plant	0	7.79	0.30	8.09
					ears	22	0.60	0.28	0.88
						36	0.17	0.10	0.27
					haulms	22	0.92	0.27	1.19
						36	0.67	0.17	0.84
					grain	42	<0.02	<0.02	<0.04
straw	42	1.44	0.52	1.96					
Schleswig-Holstein, Germany (45118601)	wheat (winter)	0.206, 0.237 (231.3, 265.1)	2	0.443 (496.4)	plant	0	5.35	0.15	5.50
					ears	21	0.27	0.08	0.35
						36	0.32	0.08	0.40
					haulms	21	0.93	0.12	1.05
						36	1.42	0.16	1.58
					grain	42	<0.02	<0.02	<0.04
49	<0.02	<0.02	<0.04						
straw	42	2.23	0.52	2.75					
	49	1.45	0.47	1.92					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Rheinland-Pfalz, Germany (45118601)	barley (spring)	0.201, 0.218 (224.8, 244.4)	2	0.419 (469.2)	plant	0	6.44	0.25	6.69
					ears	20	0.18	0.05	0.23
					haulms	20	1.50	0.18	1.68
					grain	35	<0.02	<0.02	<0.04
						41	0.02	<0.02	<0.04
					straw	35	2.59	0.43	3.02
41	0.68	0.18	0.86						
Pas de Calais, France (45118601)	wheat (winter)	0.221, 0.227 (247.5, 254.3)	2	0.448 (501.8)	plant	0	4.92	0.12	5.04
					ears	22	0.36	0.08	0.44
						32	0.19	0.05	0.24
					haulms	22	0.52	0.11	0.63
						32	0.25	0.08	0.33
					grain	42	<0.02	<0.02	<0.04
50	<0.02	<0.02	<0.04						
straw	42	3.14	0.24	3.38					
	50	2.47	0.20	2.67					
Gard, France (45118601)	wheat (Durum)	0.209, 0.220 (234.0, 246.4)	2	0.429 (480.4)	plant	0	5.75	0.21	5.96
					ears	21	0.29	0.12	0.41
						35	0.14	0.05	0.19
					haulms	21	1.21	0.54	1.75
35	1.93	0.64	2.57						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Skåne, Sweden (45118601)	barley (spring)	0.218, 0.223 (244.7, 250.2)	2	0.442 (494.9)	plant	0	5.99	0.14	6.13
					ears	22	0.11	0.05	0.16
						35	0.06	0.04	0.10
					haulms	22	0.46	0.07	0.53
						35	0.53	0.09	0.62
					grain	42	<0.02	<0.02	<0.04
straw	42	0.78	0.16	0.94					
Grampian, UK (45118601)	wheat (winter)	0.173, 0.201 (193.9, 225.5)	2	0.374 (419.4)	plant	0	3.32	0.06	3.38
					ears	20	0.29	0.05	0.34
					haulms	20	0.79	0.09	0.88
						grain	33	0.04	<0.02
					47		<0.02	<0.02	<0.04
					straw	33	1.19	0.26	1.45
47	1.89	0.76	2.65						
Northhamptonshire, UK (45118601)	barley (winter)	0.216, 0.226 (242.5, 253.0)	2	0.442 (495.5)	plant	0	6.89	0.20	7.09
					ears	22	0.39	0.14	0.53
					haulms	22	1.81	0.52	2.33
						grain	35	0.04	<0.02
					42		0.04	0.02	0.06
					straw	35	2.15	0.79	2.94
42	2.82	1.07	3.89						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Warwickshire, UK (45118601)	barley (winter)	0.220, 0.228 (246.9, 255.3)	2	0.448 (502.2)	plant	0	3.35	0.12	3.47
					ears	21	0.37	0.08	0.45
					haulms	21	1.18	0.13	1.31
					grain	35	0.06	<0.02	<0.08
						42	0.07	<0.02	<0.09
					straw	35	4.42	0.52	4.94
42	3.83	0.65	4.48						
Brandenburg, Germany (45118602)	wheat (winter)	0.219, 0.226 (245.4, 253.0)	2	0.445 (498.4)	plant	0	8.93	0.18	9.11
					ears	21	0.26	0.06	0.32
						35	0.15	0.03	0.18
						42	0.10	0.03	0.13
					haulms	21	0.77	0.21	0.98
						35	0.94	0.31	1.25
						42	0.66	0.27	0.93
					grain	64	<0.02	<0.02	<0.04
straw	64	0.67	0.21	0.88					
Rheinland-Pfalz, Germany (45118602)	barley (spring)	0.207, 0.222 (232.0, 248.5)	2	0.429 (480.5)	plant	0	4.88	0.19	5.07
					ears	22	0.21	0.05	0.26
					haulms	22	2.54	0.20	2.74
					grain	35	0.04	<0.02	<0.06
						41	0.03	<0.02	<0.05
					straw	35	4.38	0.39	4.77
41	2.58	0.50	3.08						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Gard, France (45118602)	wheat (hard)	0.212, 0.228 (237.6, 255.7)	2	0.440 (493.3)	plant	0	7.77	0.53	8.30
					ears	21	0.10	0.02	0.12
						35	0.03	<0.02	<0.05
					haulms	21	0.81	0.19	1.00
						35	0.40	0.10	0.50
					grain	43	<0.02	<0.02	<0.04
straw	43	0.75	0.26	1.01					
Skåne, Sweden (45118602)	wheat (winter)	0.218, 0.227 (244.7, 254.3)	2	0.445 (499.0)	plant	0	5.21	0.13	5.34
					ears	22	0.15	0.06	0.21
						36	0.09	0.04	0.13
					haulms	22	0.50	0.18	0.68
						36	1.81	0.52	2.33
					grain	42	<0.02	<0.02	<0.04
straw	42	2.50	1.20	3.70					
Skåne, Sweden (45118602)	barley (spring)	0.228, 0.233 (255.7, 261.4)	2	0.462 (517.1)	plant	0	4.46	0.14	4.60
					ears	22	0.10	0.05	0.15
						36	0.08	0.04	0.12
					haulms	22	0.35	0.07	0.42
						36	0.54	0.12	0.66
					grain	42	0.03	<0.02	<0.05
straw	42	0.78	0.23	1.01					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
1998 Trials - 133 g/L pyraclostrobin and 50 g/L epoxiconazole SE formulation ^a									
Limburg, Netherlands (45118601)	wheat (winter)	0.210, 0.221 (235.8, 247.3)	2	0.431 (483.1)	plant	0	4.04	0.07	4.11
					ears	20	0.34	0.08	0.42
					haulms	20	0.98	0.09	1.07
					grain	35	<0.02	<0.02	<0.04
						44	<0.02	<0.02	<0.04
						51	<0.02	<0.02	<0.04
					straw	35	1.65	0.21	1.86
						44	2.18	0.25	2.43
						51	0.81	0.20	1.01
Brabant, Belgium (45118601)	barley (spring)	0.217, 0.218 (243.5, 244.1)	2	0.435 (487.6)	plant	0	4.80	0.13	4.93
					ears	20	0.29	0.11	0.40
					haulms	20	0.73	0.08	0.81
					grain	34	<0.02	<0.02	<0.04
						40	<0.02	<0.02	<0.04
					straw	34	2.04	0.42	2.46
						40	1.44	0.27	1.71
					Andalucia, Seville, Spain (45118601)	wheat (winter)	0.213, 0.225 (239.1, 251.7)	2	0.438 (490.8)
ears	21	0.39	0.13	0.52					
	33	0.20	0.07	0.27					
haulms	21	2.66	0.80	3.46					
	33	1.99	0.64	2.63					
grain	42	<0.02	<0.02	<0.04					
straw	42	4.95	1.77	6.72					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Andalucia, Seville, Spain (45118601)	wheat (winter)	0.215, 0.218 (241.4, 243.7)	2	0.433 (485.1)	plant	0	6.22	0.19	6.41
					ears	22	0.38	0.21	0.59
						37	0.13	0.09	0.22
					haulms	22	0.85	0.21	1.06
						37	0.64	0.19	0.83
					grain	42	<0.02	<0.02	<0.04
straw	42	1.67	0.61	2.28					
Andalucia, Seville, Spain (45118601)	wheat (Durum)	0.218, 0.221 (243.7, 247.7)	2	0.439 (491.4)	plant	0	6.70	0.34	7.04
					ears	22	0.53	0.29	0.82
						36	0.35	0.18	0.53
					haulms	22	1.38	0.56	1.94
						36	1.30	0.54	1.84
					grain	42	<0.02	<0.02	<0.04
straw	42	2.20	0.99	3.19					
Schleswig-Holstein, Germany (45118601)	wheat (winter)	0.213, 0.218 (238.7, 243.9)	2	0.431 (482.6)	plant	0	5.75	0.12	5.87
					ears	21	0.21	0.06	0.27
						36	0.46	0.10	0.56
					haulms	21	0.87	0.10	0.97
						36	1.17	0.12	1.29
					grain	42	<0.02	<0.02	<0.04
49	<0.02	<0.02	<0.04						
straw	42	1.40	0.34	1.74					
	49	1.73	0.44	2.17					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Rheinland-Pfalz, Germany (45118601)	barley (spring)	0.201, 0.216 (225.3, 242.3)	2	0.417 (467.6)	plant	0	6.01	0.26	6.27
					ears	20	0.18	0.06	0.24
					haulms	20	1.39	0.14	1.53
					grain	35	0.03	<0.02	<0.05
						41	0.03	<0.02	<0.05
					straw	35	2.55	0.36	2.91
41	1.48	0.25	1.73						
Pas de Calais, France (45118601)	wheat (winter)	0.217, 0.218 (242.9, 244.3)	2	0.435 (487.2)	plant	0	6.49	0.12	6.61
					ears	22	0.26	0.07	0.33
						32	0.14	0.04	0.18
					haulms	22	0.62	0.11	0.73
						32	0.23	0.07	0.30
					grain	42	<0.02	<0.02	<0.04
						50	<0.02	<0.02	<0.04
					straw	42	1.00	0.22	1.22
50	1.91	0.88	2.79						
Gard, France (45118601)	wheat (Durum)	0.189, 0.205 (211.3, 229.7)	2	0.394 (441.0)	plant	0	4.69	0.14	4.83
					ears	21	0.21	0.07	0.28
						35	0.06	0.02	0.08
					haulms	21	0.96	0.21	1.17
35	0.76	0.21	0.97						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Skåne, Sweden (45118601)	barley (spring)	0.214, 0.223 (240.3, 249.6)	2	0.437 (489.9)	plant	0	6.22	0.16	6.38
					ears	22	0.12	0.06	0.18
						35	0.06	0.04	0.10
					haulms	22	0.36	0.06	0.42
						35	0.58	0.10	0.68
					grain	42	0.03	<0.02	<0.05
straw	42	0.99	0.23	1.22					
Grampian, UK (45118601)	wheat (winter)	0.201, 0.207 (225.5, 231.5)	2	0.408 (457.0)	plant	0	3.10	0.04	3.14
					ears	20	0.29	0.05	0.34
					haulms	20	1.12	0.15	1.27
						grain	33	0.05	<0.02
					47		0.03	<0.02	<0.05
					straw	33	1.90	0.87	2.77
47	2.23	0.85	3.08						
Northhamptonshire, UK (45118601)	barley (winter)	0.207, 0.213 (231.7, 238.1)	2	0.419 (469.8)	plant	0	6.83	0.14	6.97
					ears	22	0.40	0.15	0.55
					haulms	22	1.73	0.44	2.17
						grain	35	0.07	0.03
					42		0.05	0.02	0.07
					straw	35	3.20	1.02	4.22
42	3.58	1.29	4.87						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Warwickshire, UK (45118601)	barley (winter)	0.210, 0.254 (235.3, 284.8)	2	0.464 (520.1)	plant	0	5.68	0.11	5.79
					ears	21	0.42	0.12	0.54
					haulms	21	1.21	0.15	1.36
					grain	35	0.12	0.03	0.15
						42	0.12	0.03	0.15
					straw	35	6.01	0.64	6.65
42	5.18	0.63	5.81						
1998 Trials - 133 g/L pyraclostrobin, 50 g/L epoxiconazole, and 67 g/L kresoxim-methyl SE formulation ^b									
Limburg, Netherlands (45118601)	wheat (winter)	0.206, 0.212 (231.3, 237.7)	2	0.419 (469.0)	plant	0	2.80	0.02	2.82
					ears	20	0.35	0.06	0.41
					haulms	20	0.92	0.07	0.99
					grain	35	0.02	<0.02	<0.04
						44	<0.02	<0.02	<0.04
						51	<0.02	<0.02	<0.04
					straw	35	1.31	0.15	1.46
						44	1.48	0.17	1.65
51	0.93	0.19	1.12						
Brabant, Belgium (45118601)	barley (spring)	0.217, 0.218 (242.8, 244.1)	2	0.435 (486.9)	plant	0	3.61	0.05	3.66
					ears	20	0.28	0.08	0.36
					haulms	20	0.97	0.08	1.05
					grain	34	<0.02	<0.02	<0.04
						40	<0.02	<0.02	<0.04
					straw	34	1.57	0.25	1.82
40	2.69	0.29	2.98						

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Andalucia, Seville, Spain (45118601)	wheat (winter)	0.213, 0.217 (239.1, 243.1)	2	0.430 (482.2)	plant	0	10.90	0.59	11.49
					ears	21	0.40	0.10	0.50
						33	0.26	0.07	0.33
					haulms	21	2.71	0.55	3.26
						33	2.01	0.53	2.54
					grain	42	<0.02	<0.02	<0.04
straw	42	5.68	1.54	7.22					
Andalucia, Seville, Spain (45118601)	wheat (winter)	0.214, 0.220 (240.3, 246.0)	2	0.434 (486.3)	plant	0	6.34	0.10	6.44
					ears	22	0.26	0.14	0.40
						37	0.12	0.06	0.18
					haulms	22	0.89	0.14	1.03
						37	0.63	0.11	0.74
					grain	42	<0.02	<0.02	<0.04
straw	42	1.73	0.56	2.29					
Andalucia, Seville, Spain (45118601)	wheat (Durum)	0.213, 0.215 (239.1, 241.4)	2	0.429 (480.5)	plant	0	6.62	0.19	6.81
					ears	22	0.48	0.22	0.70
						36	0.29	0.14	0.43
					haulms	22	1.54	0.63	2.17
						36	1.12	0.46	1.58
					grain	42	<0.02	<0.02	<0.04
straw	42	1.85	0.87	2.72					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Schleswig-Holstein, Germany (45118601)	wheat (winter)	0.214, 0.217 (239.4, 242.6)	2	0.430 (482.0)	plant	0	8.23	0.07	8.30
					ears	21	0.22	0.06	0.28
						36	0.43	0.08	0.51
					haulms	21	0.68	0.08	0.76
						36	1.00	0.10	1.10
					grain	42	<0.02	<0.02	<0.04
						49	<0.02	<0.02	<0.04
					straw	42	1.95	0.38	2.33
49	1.57	0.36	1.93						
Rheinland-Pfalz, Germany (45118601)	barley (spring)	0.208, 0.216 (233.3, 242.3)	2	0.425 (475.6)	plant	0	6.70	0.10	6.80
					ears	20	0.23	0.05	0.28
					haulms	20	1.68	0.13	1.81
					grain	35	0.05	<0.02	<0.07
						41	0.04	<0.02	<0.06
					straw	35	2.94	0.24	3.18
						41	1.97	0.23	2.20
					Pas de Calais, France (45118601)	wheat (winter)	0.212, 0.225 (237.6, 252.3)	2	0.437 (489.9)
ears	22	0.19	0.05	0.24					
	32	0.14	0.04	0.18					
haulms	22	0.56	0.10	0.66					
	32	0.23	0.06	0.29					
grain	42	<0.02	<0.02	<0.04					
	50	<0.02	<0.02	<0.04					
straw	42	1.22	0.21	1.43					
	50	2.05	0.25	2.30					

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Gard, France (45118601)	wheat (Durum)	0.209, 0.216 (233.7, 241.7)	2	0.424 (475.5)	plant	0	3.85	0.09	3.94
					ears	21	0.18	0.06	0.24
					haulms	35	0.06	0.02	0.08
					haulms	21	0.75	0.14	0.89
Skåne, Sweden (45118601)	barley (spring)	0.212, 0.237 (237.6, 265.6)	2	0.449 (503.2)	plant	35	0.59	0.10	0.69
					plant	0	3.01	0.05	3.06
					ears	22	0.09	0.38	0.47
					ears	35	0.06	0.03	0.09
					haulms	22	0.39	0.05	0.44
					haulms	35	0.34	0.05	0.39
					grain	42	0.03	<0.02	<0.05
					straw	42	0.52	0.14	0.66
Grampian, UK (45118601)	wheat (winter)	0.210, 0.219 (235.5, 245.5)	2	0.429 (481.0)	plant	42	3.93	0.02	3.95
					ears	0	0.37	0.07	0.44
					haulms	20	0.89	0.07	0.96
					grain	33	0.05	<0.02	<0.07
					grain	47	0.02	<0.02	<0.04
					straw	33	2.13	0.88	3.01
Northamptonshire, UK (45118601)	barley (winter)	0.208, 0.217 (232.9, 242.9)	2	0.425 (475.8)	straw	47	2.73	0.90	3.63
					plant	0	7.51	0.13	7.64
					ears	22	0.52	0.15	0.67
					haulms	22	1.58	0.28	1.86
					grain	35	0.06	0.03	0.09
					grain	42	0.07	0.03	0.10
	straw	35	4.56	1.65	6.21				

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	
						42	2.78	0.69	Total 3.47

Table 54 (continued).

Test Site (MRID)	Crop	Application rate, lb ai/A (g ai/ha)	Number of applications	Total application rate, lb ai/A (g ai/ha)	Commodity	PHI, days	Residues, ppm		
							Pyraclostrobin	BF 500-3	Total
Warwickshire, UK (45118601)	barley (winter)	0.211, 0.217 (236.0, 243.5)	2	0.428 (479.5)	plant	0	5.10	0.10	5.20
					ears	21	0.38	0.80	1.18
					haulms	21	0.86	0.09	0.95
					grain	35	0.09	<0.02	<0.11
						42	0.10	<0.02	<0.12
					straw	35	3.14	0.67	3.81
42	3.26	0.32	3.58						

^a Application rates for pyraclostrobin and epoxiconazole were provided, however, for purposes of this petition, only application rates for pyraclostrobin are reported.

^b Application rates for pyraclostrobin, epoxiconazole, and kresoxim-methyl were provided, however, for purposes of this petition, only application rates for pyraclostrobin are reported.

Study summary:

The submitted European field trial data indicate that combined residues of pyraclostrobin and its metabolite BF 500-3 were <0.04 ppm to 0.15 ppm in/on barley and wheat grain and 0.66-7.33 ppm in/on barley and wheat straw harvested 33-64 days following treatment according to one of the following application patterns: (i) pyraclostrobin (250 g/L) formulated as an EC formulation and applied to barley and wheat plants as two spray applications at 193.9-265.1 g ai/ha/application (0.17-0.24 lb ai/A/application for a total rate of 0.37-0.45 lb ai/A); (ii) pyraclostrobin (133 g/L) and epoxiconazole (50 g/L) formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 211.3-284.8 g ai/ha/application (0.19-0.25 lb ai/A/application for a total rate of 0.39-0.46 lb ai/A); or (iii) pyraclostrobin (133 g/L), epoxiconazole (50 g/L), and kresoxim-methyl (67 g/L) formulated as an "SE" formulation and applied to barley and wheat plants as two spray applications at 231.3-265.6 g ai/ha/application (0.21-0.24 lb ai/A/application for a total rate of 0.42-0.45 lb ai/A).

Although small grain data from Europe are not required to support the subject petition, the submitted European field trial data are useful in demonstrating that combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed U.S. tolerance levels of 0.2 ppm for wheat grain, 0.4 ppm for barley grain, 6.0 ppm for barley, and 8.5 ppm for wheat straw following treatment according to the use patterns utilized in the studies.

Grass Forage, Fodder, and Hay

Grass (Grown for Seed)

BASF Corporation submitted field trial data (citation listed below) for grass grown for seed to support the establishment of tolerances for residues of pyraclostrobin and BF 500-3 in/on grass (seed screenings) at 27 ppm, grass (straw) at 14 ppm, grass (forage) at 10 ppm, and grass (hay) at 4.5 ppm.

45118527 Versoi, P.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of BAS 500 F Residues in Cool Season Grasses Grown For Seed: Lab Project Number: 1999/5160: 59473.
Unpublished study prepared by BASF Corporation. 94 p.

A total of 12 field trials were conducted during the 1999 growing season in/on grass grown for seed; grass varieties included Kentucky bluegrass, bromegrass, chewing fescue, tall fescue, perennial ryegrass, timothy, and wheatgrass. Field trials were conducted in ID(1 trial), MN(2), MT(1), NE(2), OR(5), and WA(1). Grass seed screenings and straw were harvested 13-15 days and grass forage and hay were cut from regrowth 27-115 days following the last of two foliar applications of the 2.12 lb/gal EC formulation at 0.19-0.22 lb ai/A/application, made at 13- to 15-day retreatment intervals. Total seasonal application rates were 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal rate). Applications were made in 8.9-46.1 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray solution. In one trial (OR), additional grass seed screenings and straw samples were collected 4, 8, 19, and 24 days

following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

Samples of treated and untreated grass forage, hay, straw, and seed screenings were collected from each test site. Grass straw and seed screening samples were collected 13-15 days after the last application. Grass forage and hay samples were collected 27-115 days after the last application, when the postharvest regrowth was approximately 2 to 5 inches in height. Hay samples were allowed to dry in the field for 2-7 days before collection. The moisture content in grass samples was determined to be 14-32% in straw, 25-81% in forage, and 18-68% in dried hay. All samples were transferred to freezers as soon as possible after collection and then shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 12 samples each of untreated grass forage, hay, straw, and seed screenings. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 55.

Table 55. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **grass grown for seed** harvested 13-15 days (straw and seed screenings) or from regrowth 27-115 days (forage and hay) following two applications of the 2 lb/gal EC formulation at 0.19-0.22 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region (Crop Variety)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Grass straw						
Washington, OR/12 (Tall Fescue)	2	0.42	14	3.95, 4.12	0.91, 0.80	4.86, 4.92
Washington, OR/12 (Perennial Ryegrass)	2	0.40	14	5.17, 9.90	1.18, 1.94	6.35, 11.84
Marian, OR/12 (Chewing Fescue)	2	0.40	14	2.81, 3.32	1.26, 1.33	4.07, 4.65
Linn, OR/12 (Perennial Ryegrass)	2	0.40	14	3.84, 4.79	1.37, 1.73	5.21, 6.52
Jefferson, OR/11 (Kentucky Bluegrass)	2	0.40	4	5.27, 6.91	0.75, 0.87	6.02, 7.78
			8	4.14, 5.09	0.64, 0.76	4.78, 5.85
			13	4.20, 4.67	0.48, 0.75	4.68, 5.42
			19	4.92, 5.21	1.02, 1.27	5.94, 6.48
			24	5.41, 6.63	0.91, 1.30	6.32, 7.93
Grant, WA/11 (Wheatgrass)	2	0.40	15	5.42, 6.23	1.05, 1.33	6.47, 7.56
Bingham, ID/11 (Kentucky Bluegrass)	2	0.40	14	9.20, 10.40	2.94, 3.37	12.14, 13.77
Fergus, MT/9 (Bromegrass)	2	0.40	13	6.95, 7.62	3.44, 3.43	10.39, 11.05
Hall, NE/7 (Tall Fescue)	2	0.39	15	1.82, 2.49	0.28, 0.40	2.10, 2.89
York, NE/5 (Bromegrass)	2	0.40	13	1.52, 1.84	0.39, 0.36	1.91, 2.20
Roseau, MN/5 (Kentucky Bluegrass)	2	0.40	15	2.10, 5.18	0.62, 1.31	2.72, 6.49
Marshall, MN/5 (Timothy)	2	0.40	14	1.65, 1.79	0.47, 0.52	2.12, 2.31
Grass seed screenings						
Washington, OR/12 (Tall Fescue)	2	0.42	14	10.45, 12.01	2.47, 2.89	12.92, 14.90
Washington, OR/12 (Perennial Ryegrass)	2	0.40	14	6.73, 12.28	1.66, 2.73	8.39, 15.01

Table 55 (continued).

Test Site/Region (Crop Variety)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Marian, OR/12 (Chewing Fescue)	2	0.40	14	10.94, 11.69	3.32, 3.46	14.26, 15.15
Linn, OR/12 (Perennial Ryegrass)	2	0.40	14	18.82, 20.23	6.24, 6.32	25.06, 26.55
Jefferson, OR/11 (Kentucky Bluegrass)	2	0.40	4	15.22, 18.80	2.29, 2.38	17.51, 21.18
			8	7.23, 15.07	1.23, 2.08	8.45, 17.16
			13	15.44, 15.65	2.37, 2.72	17.81, 18.37
			19	11.24, 14.75	2.19, 1.73	13.42, 16.48
			24	14.19, 16.40	2.53, 2.60	16.72, 19.00
Grant, WA/11 (Wheatgrass)	2	0.40	15	2.68, 2.80	0.88, 0.88	3.56, 3.68
Bingham, ID/11 (Kentucky Bluegrass)	2	0.40	14	3.54, 8.07	1.60, 3.17	5.14, 11.24
Fergus, MT/9 (Bromegrass)	2	0.40	13	4.41, 6.70	2.11, 2.90	6.52, 9.60
Hall, NE/7 (Tall Fescue)	2	0.39	15	1.82, 1.95	0.51, 0.59	2.33, 2.54
York, NE/5 (Bromegrass)	2	0.40	13	1.42, 3.08	0.28, 0.69	1.69, 3.77
Roseau, MN/5 (Kentucky Bluegrass)	2	0.40	15	8.72, 11.43	1.84, 2.07	10.56, 13.50
Marshall, MN/5 (Timothy)	2	0.40	14	1.26, 2.42	0.34, 0.66	1.60, 3.08
Grass forage						
Washington, OR/12 (Tall Fescue)	2	0.42	78	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Washington, OR/12 (Perennial Ryegrass)	2	0.40	99	0.05, 0.06	0.04, 0.04	0.09, 0.10
Marian, OR/12 (Chewing Fescue)	2	0.40	112	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Linn, OR/12 (Perennial Ryegrass)	2	0.40	115	<0.02, 0.02	<0.02, 0.02	<0.04, 0.04
Jefferson, OR/11 (Kentucky Bluegrass)	2	0.40	63	0.15, 0.16	0.06, 0.06	0.21, 0.22
Grant, WA/11 (Wheatgrass)	2	0.40	77	0.43, 0.45	0.14, 0.14	0.57, 0.59

Table 55 (continued).

Test Site/Region (Crop Variety)	No. of apps.	Total application rate, lb ai/A	PHI ^a , days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Bingham, ID/11 (Kentucky Bluegrass)	2	0.40	92	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fergus, MT/9 (Bromegrass)	2	0.40	69	7.45, 7.66	1.58, 1.63	9.03, 9.29
Hall, NE/7 (Tall Fescue)	2	0.39	27	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
York, NE/5 (Bromegrass)	2	0.40	27	<0.02, 0.03	<0.02, <0.02	<0.04, <0.05
Roseau, MN/5 (Kentucky Bluegrass)	2	0.40	40	0.08, 0.20	0.03, 0.09	0.11, 0.29
Marshall, MN/5 (Timothy)	2	0.40	41	0.14, 0.16	0.05, 0.06	0.19, 0.22
Grass hay						
Washington, OR/12 (Tall Fescue)	2	0.42	78 (+3)	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Washington, OR/12 (Perennial Ryegrass)	2	0.40	99 (+3)	0.07, 0.12	0.05, 0.08	0.12, 0.20
Marian, OR/12 (Chewing Fescue)	2	0.40	112 (+3)	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Linn, OR/12 (Perennial Ryegrass)	2	0.40	112 (+3)	0.17, 0.18	0.13, 0.13	0.30, 0.31
Jefferson, OR/11 (Kentucky Bluegrass)	2	0.40	63 (+4)	0.23, 0.30	0.09, 0.12	0.32, 0.42
Grant, WA/11 (Wheatgrass)	2	0.40	77 (+2)	0.18, 0.36	0.06, 0.11	0.24, 0.47
Bingham, ID/11 (Kentucky Bluegrass)	2	0.40	92 (+2)	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Fergus, MT/9 (Bromegrass)	2	0.40	69 (+4)	2.33, 2.61	1.47, 1.69	3.80, 4.30
Hall, NE/7 (Tall Fescue)	2	0.39	27 (+4)	0.31, 0.41	0.05, 0.06	0.36, 0.47
York, NE/5 (Bromegrass)	2	0.40	27 (+2)	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04
Roseau, MN/5 (Kentucky Bluegrass)	2	0.40	40 (+4)	0.88, 1.01	0.32, 0.37	1.21, 1.37
Marshall, MN/5 (Timothy)	2	0.40	41 (+7)	0.36, 0.42	0.12, 0.14	0.48, 0.55

^a For hay, the drying time is reported in parentheses.

Geographic representation of residue data for grass grown for seed is adequate. The Agency (Tables 1, 2, and 5 of OPPTS 860.1500) requires a total of 12 trials for the establishment of tolerances on grasses. As required, a total of 12 field trials were conducted on grasses grown for seed including Kentucky bluegrass (3 trials), bromegrass (2 trials), chewing fescue (1 trial), tall fescue (2 trials), perennial ryegrass (2 trials), timothy (1 trial), and wheatgrass (1 trial); trials were conducted across the country in Regions 5 (3 trials), 7 (1 trial), 9 (1 trial), 11 (3 trials), and 12 (4 trials).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on grasses grown for seed.

Grass straw: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 14.0 ppm in/on grass straw harvested 13-15 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were 1.91-13.77 ppm in/on grass straw.

Grass seed screenings: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 27.0 ppm in/on grass seed screenings harvested 13-15 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were 1.60-26.55 ppm in/on grass seed screenings.

Grass forage: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 10.0 ppm in/on grass forage harvested 27-115 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were <0.04-9.29 ppm in/on grass forage cut when the postharvest regrowth was approximately 2 to 5 inches in height.

Grass hay: The combined residues of pyraclostrobin and BF 500-3 did not exceed the proposed tolerance level of 4.5 ppm in/on grass hay harvested 27-115 days and field dried for 2-7 days following the last of two foliar applications of the EC formulation at 0.19-0.22 lb ai/A/application for a total seasonal application rate of 0.39-0.42 lb ai/A (~1x the maximum proposed seasonal application rate). Combined residues were <0.04-4.30 ppm in/on grass forage cut when the postharvest regrowth was approximately 2 to 5 inches in height.

Based on the submitted data for grass forage and hay, a pregrazing and prehay interval of 27 days must be added to the label for the 2 lb/gal EC formulation.

The residue decline data for grass straw did not demonstrate any conclusive trends in decreasing residues at longer posttreatment intervals. Combined residues were 4.68-7.93 ppm in/on grass straw and 8.45-21.18 ppm in/on grass seed screenings over the various sampling intervals.

Miscellaneous Commodities

Banana

BASF Corporation submitted field trial data (citation listed below) for bananas to support the establishment of an import tolerance for residues of pyraclostrobin and BF 500-3 in/on bananas at 0.04 ppm.

45118532 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Bananas For Import Tolerance: Lab Project Number: 1999/5095: 98027. Unpublished study prepared by BASF Corporation. 74 p.

A total of 12 banana field trials were conducted during the 1998 and 1999 growing season in Colombia (2 trials), Costa Rica (3), Ecuador (3), Guatemala (1), Martinique (2), and Mexico (1). Mature whole bagged and unbagged bananas were harvested immediately (0-day PHI) following the last of eight foliar applications of a 250 g/L EC formulation at 0.08-0.13 lb ai/A/application (90.0-141.2 g ai/ha), made at 12- to 14-day retreatment intervals. Total seasonal application rates were 0.66-0.80 lb ai/A (742.6-901.9 g ai/ha; the petitioner stated that the maximum seasonal rate is 800 g ai/ha). Applications were made in 2.1-3.6 gal/A (19.6-34.3 L/ha) using ground equipment to simulate aerial application; a spreader sticker was added to the spray solution, except in the two trials in Martinique, where applications were made using spray oil as a carrier.

A single treated and untreated samples of whole bagged and unbagged mature bananas were collected from each test site and shipped at ambient temperature by air to the BASF APC for analysis. Samples arrived within 3-7 days of collection. Upon arrival samples were placed in cardboard boxes and frozen (<-10 C) until analysis. Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 12 samples of untreated bananas. In treated banana samples, residues of pyraclostrobin and BF 500-3 were each less than the LOQ in/on 12 samples each of unbagged and bagged bananas.

The geographic representation and number of field trials are adequate for the establishment of an import tolerance for bananas. A total of 12 banana field trials reflecting application at 1x the stated maximum proposed seasonal application rate were conducted in Colombia (2), Costa Rica (3), Ecuador (3), Guatemala (1), Martinique (2), and Mexico (1). The current Agency guidance on import tolerances (65 FR 35069-35090, 6/1/00) requires that 12 banana field trials be conducted in Colombia (2), Costa Rica (3), Ecuador (3), Guatemala (1), Honduras (2) and

Mexico (1). No field trials were conducted in Honduras; however, the petitioner noted that the two trials conducted in Martinique would also satisfy European Import Tolerance requirements.

Study summary:

The petitioner has provided adequate residue data reflecting the stated maximum proposed use pattern for pyraclostrobin on imported bananas. The petitioner has indicated that the maximum seasonal rate is 800 g ai/ha; however, specimen labels were not included to confirm the proposed use patterns for pyraclostrobin on imported bananas. A sufficient number of field trials, reflecting the stated maximum proposed use pattern, were conducted in the major banana-growing regions of Central and South America. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance of 0.04 ppm in/on imported bagged or unbagged bananas (whole fruit including peel) harvested immediately (0-day PHI) following the last of eight foliar applications of an EC formulation at 0.08-0.13 lb ai/A/application (90.0-141.2 g ai/ha) for a total seasonal application rate of 0.66-0.80 lb ai/A (742.6-901.9 g ai/ha; ~1x the stated proposed maximum seasonal rate). The combined residues were <0.04 ppm in/on all samples of bagged and unbagged bananas.

Grape

BASF Corporation submitted grape field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on grapes at 2.0 ppm.

45118529 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Grapes, 1997 Field Trials: Lab Project Number: 97044: 1999/5010. Unpublished study prepared by BASF Corporation. 67 p.

45118530 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Grapes: Lab Project Number: 46649: 1999/5153. Unpublished study prepared by BASF Corporation. 66 p.

45118531 Wofford, J.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Grapes, 1998 Field Trials: Lab Project Number: 98025: 1999/5092. Unpublished study prepared by BASF Corporation. 69 p.

We note that only the specimen label for the 20% WDG formulation lists proposed use on grapes; however, 1997 and 1998 grape field trials were conducted using the 2 lb/gal EC formulation at 1x the maximum proposed use rate, and 1999 grape field trials were conducted using the 20% WDG formulation at 0.6x the maximum proposed use rate.

A total of 13 field trials were conducted on grapes. Six grape field trials (MRID 45118529) were conducted during the 1997 growing season in CA(4), NY(1), and OR(1), and seven grape field trials (MRID 45118531) were conducted during the 1998 growing season in CA(4), NY(1), OR(1), and WA(1). Samples of grapes were harvested 14 days following the last of six

broadcast foliar applications of the 2 lb/gal EC formulation at 0.15-0.16 lb ai/A/application, made at 6- to 15-day retreatment intervals. The total seasonal application rates were 0.90-0.91 lb ai/A (~1x the maximum proposed seasonal application rate). Two separate plots at each site were treated using concentrated (~50 gal/A) or dilute (~250 gal/A) spray volumes. Applications were made in either 45.2-53.4 gal/A (concentrate spray volume) or 234.7-294.0 gal/A (dilute spray volume) using ground equipment with a spreader sticker added to the spray mixture. In two trials (one 1997 and 1998 CA), additional grape samples were collected at 0, 7, 21, and 28 (1998 only) days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

In a third study (MRID 45118530), twelve grape field trials were conducted during the 1999 growing season in CA(8), NY(2), and WA(2). Samples of grapes were harvested 14 days following the last of three broadcast foliar applications of the 20% WDG formulation at 0.18-0.19 lb ai/A/application at 13- to 14-day retreatment intervals. The total seasonal application rates were 0.53-0.55 lb ai/A (~0.6x the maximum proposed seasonal application rate). Applications were made in either 50.2-78.8 gal/A (concentrate spray volume) or 100.3-159 gal/A (dilute spray volume) using ground equipment with a non-silicone spray adjuvant added to the spray mixture. In one trial (CA), additional grape samples were collected at 0, 7, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

For the 1997/1998 EC trials, a single untreated sample and a single treated sample from each treatment group (concentrate spray volume and dilute spray volume) of mature grapes were collected from each test site and placed in coolers with blue ice, then transferred to freezers. For the 1999 WDG trials, a single untreated sample and duplicate treated samples of mature grapes were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on 16 samples of untreated grapes from the 1997/1998 EC trials, and in/on 12 samples of untreated grapes from the 1999 WDG trials. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 56.

Table 56. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **grapes** harvested 14 days following the last of either six applications of the 2 lb/gal EC formulation at ~0.15 lb ai/A/application (~1x the maximum proposed seasonal rate) or three applications of the 20% WDG formulation at ~0.18 lb ai/A/application (~0.6x the maximum proposed seasonal rate).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
1997 grape field trials (MRID 45118529) - 2 lb/gal EC formulation							
Yates, NY/1	49.9-50.5	6	0.90	14	1.11 ^a	0.11 ^a	1.22
	247.9-252.2	6	0.90		1.15	0.05	1.20
Tulare, CA/10	50.7-52.1	6	0.90	0	0.62	0.10	0.72
				7	0.33	0.06	0.39
				14	0.33	0.08	0.41
				21	0.08	0.02	0.11
	284.9-294.0	6	0.90	0	0.80	0.11	0.91
				7	0.37	0.09	0.46
				14	0.39 ^a	0.09 ^a	0.49
				21	0.33	0.10	0.43
Fresno, CA/10	50.0-51.1	6	0.91	14	0.49	0.11	0.60
	249.6-257.6	6	0.91		1.71 ^a	0.21 ^a	1.92 = HAFT
Fresno, CA/10	50.1-51.0	6	0.91	14	0.66	0.09	0.75
	249.1-251.7	6	0.90		0.41	0.05	0.46
Fresno, CA/10	49.8-51.3	6	0.90	14	0.21	0.04	0.25
	247.3-260.2	6	0.90		0.32	0.03	0.35
Hood River, OR/11	45.2-49.5	6	0.91	14	1.49 ^a	0.17 ^a	1.66
	249.1-264.3	6	0.91		0.84	0.12	0.96
1998 grape field trials (MRID 45118531) - 2 lb/gal EC formulation							
Yates, NY/1	49.9-50.8	6	0.90	14	1.11	0.06	1.17
	251-252.6	6	0.91		1.43	0.04	1.47

Table 56 (continued).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Tulare, CA/10	48.9-50.1	6	0.90	0	0.39	0.02	0.41
				7	0.22	<0.02	<0.24
				14	0.22	<0.02	<0.24
				21	0.08	<0.02	<0.10
				28	0.12 ^a	<0.02 ^a	<0.14 ^a
	283.8-291.3	6	0.90	0	0.62	0.02	0.64
				7	0.49	0.02	0.51
				14	0.43	<0.02	<0.45
				21	0.40	0.03	0.43
				28	0.56 ^a	0.02 ^a	0.58 ^a
Fresno, CA/10	49.4-50.5	6	0.90	14	0.30 ^a	0.02 ^a	0.32 ^a
	249.6-260	6	0.90		0.67 ^a	0.03 ^a	0.70
Madera, CA/10	48.9-50.8	6	0.91	14	0.45	<0.02	<0.47
	246.6-261	6	0.90		0.38	<0.02	<0.40
Fresno, CA/10	48.8-51.7	6	0.90	14	0.29	0.023	0.31
	248.4-259	6	0.90		0.33	<0.02	<0.35
Grant, WA/11	50.1-50.8	6	0.90	14	0.78	0.04	0.82
	247.0-251.2	6	0.90		0.86	0.07	0.92
Marion, OR/12	50.1-53.4	6	0.90	14	0.20 ^a	0.03 ^a	0.23
	234.7-247.3	6	0.90		1.69 ^a	0.15 ^a	1.84
1999 grape field trials (MRID 45118530) - 20% WDG formulation							
Yates, NY/1	50.2-50.4	3	0.54	14	1.08, 1.21	0.11, 0.10	1.18, 1.31
Yates, NY/1	100.3-100.7	3	0.54	14	0.84, 0.95	0.06, 0.05	0.90, 1.00
Kern, CA/10	75.0-75.9	3	0.54	0	0.10, 0.22	<0.02, <0.02	<0.12, <0.24
				7	0.15, 0.19	<0.02, <0.02	<0.17, <0.21
				14	0.09, 0.11	<0.02, <0.02	<0.11, <0.13
				21	0.11, 0.12	<0.02, <0.02	<0.13, <0.14
				28	0.09, 0.09	<0.02, <0.02	<0.11, <0.11
Tulare, CA/10	152.9-154.9	3	0.54	14	0.11, 0.12	<0.02, <0.02	<0.13, <0.14
Tulare, CA/10	76.7-78.8	3	0.54	14	0.10, 0.10	<0.02, <0.02	<0.12, <0.12
Colusa, CA/10	51.3-53.3	3	0.54	14	0.41, 0.70	<0.02, 0.03	<0.43, 0.74
Glenn, CA/10	154-159	3	0.54	14	0.43, 0.54	<0.02, 0.02	<0.45, 0.56

Table 56 (continued).

Test Site/Region	Spray volume, GPA	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
					Pyraclostrobin	BF 500-3	Total
Fresno, CA/10	73.5-74.2	3	0.53	14	0.21, 0.22	<0.02, <0.02	<0.23, <0.24
Fresno, CA/10	148.2-153.6	3	0.54	14	0.38, 0.48	0.020, 0.03	0.40, 0.51
Madera, CA/10	150.1-153.9	3	0.55	14	0.23, 0.24	<0.02, <0.02	<0.25, <0.26
Grant, WA/11	74.5	3	0.54	14	0.08, 0.09	<0.02, <0.02	<0.10, <0.11
Grant, WA/11	149.4-152.0	3	0.54	14	0.10, 0.13	<0.02, <0.02	<0.12, <0.15

^a Reported residue is the highest of replicate analyses of a single sample.

Geographic representation of grape data is adequate for the purposes of this petition. The Agency (Tables 1 and 5 of OPPTS 860.1500) requires a total of 12 trials for the establishment of a tolerance on grapes. Thirteen grape field trials (1997 and 1998) reflecting the use of the EC formulation were conducted in Regions 1 (2 trials), 10 (8 trials), 11 (2 trials), and 12 (1 trial). Twelve grape field trials (1999) reflecting the use of the WDG formulation were conducted in Regions 1 (2 trials), 10 (8 trials), and 11 (2 trials).

Bridging Study

BASF Corporation submitted a bridging study (MRID 45118613) comparing the WDG and EC formulations of pyraclostrobin in cucurbits, grape, and tomato. Details of this study, including sample handling, storage intervals, and analytical method, are presented in the "Fruiting Vegetables" section. Applications to grapes were made using the EC and WDG formulations at 0.6x the maximum proposed seasonal rate.

Apparent residues of pyraclostrobin and its metabolite BF 500-3 were each less than the LOQ (<0.02 ppm) in/on three samples of untreated grapes. Residues of pyraclostrobin and BF 500-3 in/on treated grape samples are presented in Table 57; bridging data for cucurbits and tomatoes are presented in the respective sections "Cucurbit Vegetables" and "Fruiting Vegetables."

Table 57. Residues of pyraclostrobin and its metabolite BF 500-3 in/on grapes harvested 14-15 days following the last of three applications of either the 2 lb/gal EC or 20% WDG formulation at 0.18-0.19 lb ai/A/application (~0.6x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
2 lb/gal EC formulation						
Grant, WA/11	3	0.54	14	0.22, 0.27	0.02, 0.02	0.24, 0.29
Yates, NY/1	3	0.54	15	0.79, 0.86	0.14, 0.15	0.93, 1.01
Fresno, CA/10	3	0.54	14	0.41, 0.50	0.02, 0.03	0.43, 0.56
20% WDG formulation						
Grant, WA/11	3	0.54	14	0.30, 0.39	0.02, 0.02	0.32, 0.42
Yates, NY/1	3	0.54	15	0.60, 0.73	0.09, 0.10	0.69, 0.83
Fresno, CA/10	3	0.54	14	0.48, 0.50	0.02, 0.02	0.50, 0.52

Study summary:

The available grape field trial data are adequate to support the proposed tolerance because the grape bridging study (as well as those conducted with tomato and cucurbits) indicated no significant difference in the residue levels between the use of the WDG formulation or the EC formulation. The field trial data reflecting application of the EC formulation can be extrapolated to project the residue levels for the WDG formulation for which use on grape is proposed.

The petitioner has provided residue data reflecting the maximum proposed use pattern of pyraclostrobin (for the WDG formulation) following application of the 2 lb/gal EC formulation at 1x on grapes. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 2.0 ppm in/on grapes harvested 14 days following the last of six foliar applications of the EC formulation at ~0.15 lb ai/A/application for a total seasonal application rate of ~0.9 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were 0.23-1.92 ppm in/on grapes. Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined residues were 0.23-1.66 ppm in/on grapes treated with a concentrated spray volume and <0.35-1.92 ppm in/on grapes treated with a dilute spray volume.

The petitioner also provided residue data reflecting application of the 20% WDG formulation at 0.6x on grapes. The combined residues did not exceed the proposed grapes tolerance level of 2.0 ppm in/on grapes harvested 14 days following the last of three foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.54 lb ai/A (~0.6x the maximum proposed seasonal application rate). The combined residues were 0.10-1.31 ppm in/on grapes treated with the WDG formulation at 0.6x the maximum proposed seasonal application rate. Trials conducted with dilute and concentrate spray volumes did not indicate that higher residues were likely to result from either type of application. Combined

residues were 0.10-1.31 ppm in/on grapes treated with a concentrated spray volume and <0.12-1.00 ppm in/on grapes treated with a dilute spray volume.

In side-by-side bridging trials conducted to compare the use of the EC and WDG formulations, grapes were harvested 14-15 days following the last of three foliar applications of either the EC or WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.54 lb ai/A (~0.6x the maximum proposed seasonal application rate). The combined residues were 0.24-1.01 ppm in/on grapes following applications of the EC formulation and 0.32-0.83 ppm in/on grapes following applications of the WDG formulation. These data indicate that there were no significant differences in residues levels between grape samples treated with the EC formulation and the WDG formulation.

The residue decline data for grapes showed that residues decreased gradually at longer posttreatment intervals. For grapes from the 1997 trials, combined residues were 0.72-0.91 ppm at the 0-day PHI and declined to 0.11-0.43 ppm at the 21-day PHI. For grapes from the 1998 trials, combined residues were 0.41-0.64 ppm at the 0-day PHI and declined to <0.14-0.58 ppm at the 28-day PHI. For grapes from the 1999 trials, residues of pyraclostrobin were 0.10-0.22 ppm at the 0-day PHI and declined to 0.09 ppm at the 28-day PHI. For grapes from the 1999 trials, residues of the metabolite BF 500-3 were below the LOQ in/on each treated sample.

Peanut

BASF Corporation submitted peanut field trial data (citations listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on peanut (nutmeat) at 0.05 ppm. No tolerance was proposed for peanut hay.

45118533 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Peanuts: Lab Project Number: 97042: 1999/5071. Unpublished study prepared by BASF Corporation. 73 p.

45118534 Wofford, J.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Peanuts: Lab Project Number: 98026: 1999/5078. Unpublished study prepared by BASF Corporation. 62 p.

A total of twelve peanut field trials were conducted. Seven peanut field trials (MRID 45118533) were conducted during the 1997 growing season in FL(1), GA(2), NC(1), OK(1), SC(1), and TX(1), and five peanut field trials (MRID 45118534) were conducted during the 1998 growing season in AL, GA, NC, SC, and TX. Samples of peanut nutmeat and hay were harvested 14 days (18 days for the 1997 OK trial) following the last of five broadcast foliar applications of the 2 lb/gal EC formulation at 0.24-0.27 lb ai/A/application made at 13- to 15-day retreatment intervals. The total seasonal application rates were 1.24-1.28 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 9.4-40.0 gal/A using ground equipment with a spreader sticker or spray adjuvant added to the spray mixture. In two trials (1997 and 1998 NC), additional peanut nutmeat and hay samples were collected at 0 (1998 only),

7, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature peanut nutmeat and hay were collected from each test site and were either placed in coolers with blue ice and transferred to freezers (within 2.5 hours) or placed directly in transport freezers and then storage freezers. All samples were shipped frozen to the BASF APC for analysis. The moisture content in 1998 peanut hay samples was determined to be 22.5-45.2%; the petitioner did not indicate if the moisture content in peanut hay samples was determined for the 1997 trials. Samples were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on fifteen samples each of untreated peanut nutmeat and hay. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 58.

Table 58. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **peanut nutmeat and hay** harvested 14-18 days following the last of five applications of the 2 lb/gal EC formulation at ~0.25 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Peanut hay						
1997 peanut field trials (MRID 45118533)						
Wayne, NC/2	5	1.25	7	4.49, 7.16	1.04, 1.13	5.53, 8.29
			14	4.01, 5.83	0.70, 1.47	4.71, 7.30
			21	4.67, 4.95	0.87, 0.92	5.55, 5.89
			28	3.80, 6.27	0.65, 0.95	4.45, 7.22
Barnwell, SC/2	5	1.27	14	17.35, 20.03	3.26, 3.41	20.61, 23.44
Macon, GA/2	5	1.28	14	4.62, 4.91	1.04, 1.08	5.66, 5.99
Tift, GA/2	5	1.25	14	1.87, 4.77	0.08, 1.65	1.95, 6.42
Jackson, FL/3	5	1.26	14	3.45, 4.62	1.15, 1.60	4.60, 6.22
Caddo, OK/6	5	1.25	18	25.48 ^a , 26.25 ^a	8.15 ^a , 8.02 ^a	33.63, 34.27
Hockley, TX/8	5	1.24	14	1.39, 1.65	0.06, 0.07	1.45, 1.72
1998 peanut field trials (MRID 45118534)						
Sampson, NC/2	5	1.24	0	14.06, 15.18	1.43, 1.60	15.49, 16.78
			7	12.12, 14.60	2.40, 3.07	14.52, 17.67
			14	9.20, 11.30	1.90, 2.65	11.10, 13.95
			21	18.12, 20.76	4.32, 4.99	22.44, 25.75
			28	5.64, 6.24	1.49, 1.56	7.13, 7.80
Barnwell, SC/2	5	1.27	14	14.78, 15.05	3.53, 3.44	18.31, 18.49
Tift, GA/2	5	1.26	14	7.07, 11.02	1.78, 2.92	8.85, 13.94
Henry, AL/2	5	1.25	14	18.30, 18.42	4.02, 4.18	22.32, 22.60
Wilbarger, TX/6	5	1.26	14	12.01, 17.04	4.57, 5.28	16.58, 22.32
Peanut nutmeat						
1997 peanut field trials (MRID 45118533)						
Wayne, NC/2	5	1.25	7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			28	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Barnwell, SC/2	5	1.27	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Macon, GA/2	5	1.28	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tift, GA/2	5	1.25	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

Table 58 (continued).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Jackson, FL/3	5	1.26	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Caddo, OK/6	5	1.25	18	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Hockley, TX/8	5	1.24	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
1998 peanut field trials (MRID 45118534)						
Sampson, NC/2	5	1.24	0	<0.02, 0.026	<0.02, <0.02	<0.04, <0.046
			7	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			14	<0.02, 0.025	<0.02, <0.02	<0.04, <0.045 HAFT = 0.0425
			21	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
			28	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Barnwell, SC/2	5	1.27	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Tift, GA/2	5	1.26	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Henry, AL/2	5	1.25	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04
Wilbarger, TX/6	5	1.26	14	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04

^a Reported residue is the highest of replicate analyses of a single sample.

Geographic representation of peanut data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Tables 1 and 5), a total of twelve field trials were conducted on peanuts in Regions 2 (8 trials), 3 (1 trial), 6 (2 trials), and 8 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on peanuts.

Peanut nutmeat: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.05 ppm in/on peanut nutmeat harvested 14-18 days following the last of five foliar applications of the EC formulation at 0.24-0.27 lb ai/A/application for a total seasonal application rate of 1.24-1.28 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.04-<0.045 ppm in/on 24 samples of peanut nutmeat.

Peanut hay: The submitted peanut hay field trial data indicate that combined residues of pyraclostrobin and BF 500-3 were 1.45-34.27 ppm in/on peanut hay harvested 14-18 days following the last of five foliar applications of the EC formulation at 0.24-0.27 lb ai/A/application for a total seasonal application rate of 1.24-1.28 lb ai/A (~1x the maximum

proposed seasonal application rate). These data are not adequate to support a tolerance for peanut hay because the moisture content was not provided for the peanut hay samples from the 1997 field trials and ranged from 22.5-45.2% in peanut hay samples from the 1998 peanut field trials. According to Table 1 of OPPTS 860.1000, peanut hay consists of vines and leaves that have been sun-dried to a moisture content of 10 to 20 percent.

A tolerance for peanut hay will not be required if the label for the EC formulation is amended to include the following feeding restriction: "Do not feed green immature growing plants to livestock or do not harvest for livestock feed." Alternatively, additional field trials will be required depicting residues of pyraclostrobin in peanut hay dried to <20% following application of the EC formulation at 1x the maximum proposed use pattern.

The residue decline data for peanut nutmeat did not demonstrate any conclusive trends in decreasing residues at longer posttreatment intervals because the residues were at or below the LOQ. The residue decline data for peanut hay showed trends that residues decreased gradually at longer posttreatment intervals. For peanut hay from the 1997 trials, combined residues were 5.53-8.29 ppm at the 7-day PHI and declined to 4.45-7.22 ppm at the 28-day PHI. For peanut hay from the 1998 trials, combined residues were 15.49-16.78 ppm at the 0-day PHI and declined to 7.13-7.80 ppm at the 28-day PHI. One exception occurred at the 21-day PHI where combined residues (22.44-25.75 ppm) exceeded residues at the 0-day PHI. The petitioner indicated that moisture determinations were performed and the moisture levels were not a contributing factor to the higher residues found in the peanut hay samples from the 21-day PHI.

Strawberry

BASF Corporation submitted strawberry field trial data (citation listed below) to support the establishment of a tolerance for residues of pyraclostrobin and BF 500-3 in/on strawberry at 0.4 ppm.

45118604 Haughey, D.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Strawberries: Lab Project Number: 55223: 1999/5140. Unpublished study prepared by BASF Corporation. 67 p.

A total of eight strawberry field trials were conducted during the 1999 growing season in CA(3), FL(1), MI(1), NC(1), OR(1), and PA(1). Samples of strawberries were harvested immediately (0-day PHI) or one day (OR trial only) following the last of five broadcast foliar applications of the 20% WDG formulation at 0.17-0.19 lb ai/A/application, made at 6- to 8-day retreatment intervals. The total seasonal application rates were 0.88-0.92 lb ai/A (~1x the maximum proposed seasonal application rate). Applications were made in 24.8-100.4 gal/A using ground equipment with a spreader-sticker added to the spray mixture. In one trial (CA), additional strawberry samples were collected at 7, 14, 21, and 28 days following treatment to evaluate residue decline. A separate plot at each trial site was left untreated to provide control samples.

A single untreated sample and duplicate treated samples of mature strawberries were collected from each test site and were frozen. All samples were shipped frozen to the BASF APC where they were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on eight samples of untreated strawberries. Residues of pyraclostrobin and BF 500-3 in/on treated samples are presented in Table 59.

Table 59. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **strawberries** harvested 0-1 days following the last of five applications of the 20% WDG formulation at ~0.18 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Montgomery, PA/1	5	0.89	0	0.05, 0.07	<0.02, <0.02	<0.07, <0.09
Wayne, NC/2	5	0.89	0	0.14, 0.17	<0.02, <0.02	<0.16, <0.19
Alachua, FL/3	5	0.90	0	0.18, 0.21	<0.02, <0.02	<0.20, <0.23
Ottawa, MI/5	5	0.90	0	0.09, 0.14	<0.02, <0.02	<0.11, <0.16
San Diego, CA/10	5	0.89	0	0.24, 0.37	<0.02, <0.02	<0.26, <0.39
			7	0.14, 0.18	<0.02, <0.02	<0.16, <0.20
			14	0.10, 0.11	<0.02, <0.02	<0.12, <0.13
			21	0.05, 0.05	<0.02, <0.02	<0.07, <0.07
			28	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
Stanislaus, CA/10	5	0.88	0	0.20, 0.28	<0.02, <0.02	<0.22, <0.30
Tulare, CA/10	5	0.90	0	0.13, 0.17	<0.02, <0.02	<0.15, <0.19
Marion, OR/12	5	0.92	1	0.11, 0.14	<0.02, <0.02	<0.13, <0.16

Geographic representation of strawberry data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Tables 1 and 5), eight field trials were conducted on strawberries in Regions 1 (1 trial), 2 (1 trial), 3 (1 trial), 5 (1 trial), 10 (3 trials), and 12 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on strawberries. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on strawberries harvested immediately (0-day PHI) or one day following the last of five foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.9 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.07-<0.39 ppm in/on strawberries.

The residue decline data for strawberries showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.24 and 0.37 ppm at the 0-day PHI and declined to 0.03 ppm at the 28-day PHI. Residues of the metabolite BF 500-3 were below the LOQ (<0.02 ppm) at all sampling intervals.

Table 59. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **strawberries** harvested 0-1 days following the last of five applications of the 20% WDG formulation at ~0.18 lb ai/A/application (~1x the maximum proposed seasonal rate).

Test Site/Region	No. of apps.	Total application rate, lb ai/A	PHI, days	Residues, ppm		
				Pyraclostrobin	BF 500-3	Total
Montgomery, PA/1	5	0.89	0	0.05, 0.07	<0.02, <0.02	<0.07, <0.09
Wayne, NC/2	5	0.89	0	0.14, 0.17	<0.02, <0.02	<0.16, <0.19
Alachua, FL/3	5	0.90	0	0.18, 0.21	<0.02, <0.02	<0.20, <0.23
Ottawa, MI/5	5	0.90	0	0.09, 0.14	<0.02, <0.02	<0.11, <0.16
San Diego, CA/10	5	0.89	0	0.24, 0.37	<0.02, <0.02	<0.26, <0.39
			7	0.14, 0.18	<0.02, <0.02	<0.16, <0.20
			14	0.10, 0.11	<0.02, <0.02	<0.12, <0.13
			21	0.05, 0.05	<0.02, <0.02	<0.07, <0.07
			28	0.03, 0.03	<0.02, <0.02	<0.05, <0.05
Stanislaus, CA/10	5	0.88	0	0.20, 0.28	<0.02, <0.02	<0.22, <0.30
Tulare, CA/10	5	0.90	0	0.13, 0.17	<0.02, <0.02	<0.15, <0.19
Marion, OR/12	5	0.92	1	0.11, 0.14	<0.02, <0.02	<0.13, <0.16

Geographic representation of strawberry data is adequate for the purposes of this petition. As required under OPPTS 860.1500 (Tables 1 and 5), eight field trials were conducted on strawberries in Regions 1 (1 trial), 2 (1 trial), 3 (1 trial), 5 (1 trial), 10 (3 trials), and 12 (1 trial).

Study summary:

The petitioner has provided adequate residue data reflecting the maximum proposed use pattern of pyraclostrobin on strawberries. The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 0.4 ppm in/on strawberries harvested immediately (0-day PHI) or one day following the last of five foliar applications of the WDG formulation at ~0.18 lb ai/A/application for a total seasonal application rate of ~0.9 lb ai/A (~1x the maximum proposed seasonal application rate). The combined residues were <0.07-<0.39 ppm in/on strawberries.

The residue decline data for strawberries showed that residues decreased gradually at longer posttreatment intervals. Residues of pyraclostrobin were 0.24 and 0.37 ppm at the 0-day PHI and declined to 0.03 ppm at the 28-day PHI. Residues of the metabolite BF 500-3 were below the LOQ (<0.02 ppm) at all sampling intervals.

OPPTS GLN 860.1520: Processed Food/Feed

Citrus Fruits

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of oranges.

45118617 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Orange Process Fractions: Lab Project Number: 55165: 1999/5120. Unpublished study prepared by BASF Corporation. 119 p.

A single orange field trial was conducted during the 1999 growing season in Palm Beach County, FL using Valencia oranges. The trial consisted of three treated plots in which treatments differed according to application rates. Four broadcast foliar applications of the 2 lb/gal EC formulation were made to orange trees, with 10- to 11-day retreatment intervals. For the three treatment plots, the application rates were as follows: (i) two applications at 0.16 lb ai/A/application plus two applications at 0.25-0.26 lb ai/A/application for a total rate of 0.83 lb ai/A (~1x the maximum proposed seasonal rate); (ii) two applications at 0.48 lb ai/A/application plus two applications at 0.75-0.76 lb ai/A/application for a total rate of 2.47 lb ai/A (~3x the maximum proposed seasonal rate); or (iii) two applications at 0.80 lb ai/A/application plus two applications at 1.24-1.25 lb ai/A/application for a total rate of 4.09 lb ai/A (~5x the maximum proposed seasonal rate). Applications were made in 140.1-146.7 gal/A using ground equipment with a non-silicone spray adjuvant (Latron B-1956) added to the spray solution. A separate plot was left untreated for control samples. Since no phytotoxicity was observed at the 5x rate, oranges treated at the 1x and 3x rates were not harvested, processed, or analyzed. Mature oranges treated at the 5x rate were harvested by hand 14 days following the final application; untreated samples were harvested 11 days following the final application.

One sample of untreated and two samples of treated mature oranges were collected and shipped the day after harvest at ambient conditions to the Citrus Research and Education Center, University of Florida (Lake Alfred, FL) for processing. Samples were stored under ambient conditions for 3 days at the University of Florida until processing. Oranges were processed into washed oranges, dried pulp, oil, and juice using simulated commercial processing procedures. A subsample of whole, unwashed oranges (RAC) was placed in frozen storage prior to processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of oranges and orange processed commodities were analyzed for residues of pyraclostrobin and BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated oranges (unwashed), oranges (washed), and processed dried pulp, juice, and oil. The results of the orange processing study are presented in Table 60.

Table 60. Residues of pyraclostrobin and its metabolite BF 500-3 in/on oranges and processed commodities treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Orange, unwashed (RAC)	1.43, 1.82	0.17, 0.25	1.60, 2.07	--
Orange, washed	1.00, 1.48	0.12, 0.19	1.12, 1.67	--
Dried pulp	13.46, 15.61	1.67, 1.81	15.13, 17.42	8.2x, 9.5x average = 8.9x
Oil	8.99, 11.35	0.80, 1.05	9.79, 12.40	5.3x, 6.8x average = 6.1x
Juice	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.02x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (1.835 ppm) of the unwashed RAC samples.

Study summary:

The submitted orange processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in juice processed from oranges bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 may concentrate 8.2-9.5x in dried pulp and 5.3-6.8x in oil processed from oranges bearing detectable residues.

The HAFT residue of citrus treated at 1x the maximum seasonal rate (0.8 lb ai/A/season; 14-day PHI) from the submitted citrus field trial studies was 0.505 ppm pyraclostrobin and 0.075 ppm BF 500-3 (0.58 ppm combined residues). Based on the HAFT (0.58 ppm) and average concentration factors of 8.9x in dried pulp and 6.1x in citrus oil, the maximum expected pyraclostrobin and BF 500-3 residues would be 5.16 ppm in dried pulp and 3.54 ppm in citrus oil. Data from the processing study indicate that the proposed tolerances of 6.3 ppm for dried orange pulp and 4.2 ppm for orange oil are too high. The RAB3 recommends that the petitioner propose tolerances of 5.5 ppm for citrus, dry pulp and 4 ppm for citrus, oil. We note that the tolerances will have to be revised to be expressed for citrus commodities instead of orange commodities.

Grapes

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of grapes.

45118616 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Grape Process Fractions: Lab Project Number: 97045: 1999/5011. Unpublished study prepared by BASF Corporation. 84 p.

A single grape field trial was conducted during the 1997 growing season in Tulare County, CA using Thompson seedless grapes. The trial consisted of three treated plots in which treatments differed according to application rates. Six broadcast foliar applications of the 2 lb/gal EC formulation were made to grape vines, with a 7-day retreatment interval, at: (i) 0.15 lb ai/A/application for a total rate of 0.90 lb ai/A (~1x the maximum proposed seasonal rate); (ii) 0.30 lb ai/A/application for a total rate of 1.80 lb ai/A (~2x the maximum proposed seasonal rate); or (iii) 0.74-0.75 lb ai/A/application for a total rate of 4.50 lb ai/A (~5x the maximum proposed seasonal rate). Applications were made in 247.6-256.4 gal/A using ground equipment with a non-silicone spray adjuvant (Latron B-1956) added to the spray solution. A separate plot was left untreated for control samples. Since no phytotoxicity was observed at the 5x rate, grapes treated at the 1x and 2x rates were not harvested, processed, or analyzed. Mature grapes treated at the 5x rate were harvested by hand 14 days following the final application.

One sample of untreated and two samples of treated mature grapes were collected. Samples were stored in temperature-monitored coolers and shipped at ambient conditions to National Food Laboratories (Dublin, CA) the same day as harvest for processing. Samples were stored frozen at the National Food Laboratories for 4 days prior to processing. Grapes were processed according to simulated commercial procedures into grape juice and raisins. A subsample of whole, unwashed grapes (RAC) was placed in frozen storage prior to processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of grapes and grape processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated grapes, grape juice, and raisins. The results of the grape processing study are presented in Table 61.

Table 61. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **grapes and processed commodities** treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Grape (RAC)	2.37, 3.60	0.08, 0.15	2.45, 3.75	--
Juice	<0.02, 0.02	<0.02, <0.02	<0.04, <0.04	<0.01x
Raisin	9.00 ^b , 9.07 ^b	1.40 ^b , 1.38 ^b	10.40, 10.45	3.4x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (3.1 ppm) of the RAC samples.

^b Reported residue is the highest of duplicate analyses of a single sample.

Study summary:

The submitted grape processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in juice processed from grapes bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrated in raisins at 3.4x.

The HAFT residue of grape treated at 1x the maximum seasonal rate (0.9 lb ai/A/season; 14-day PHI) from the submitted field trial studies was 1.71 ppm pyraclostrobin and 0.21 ppm BF 500-3 (1.92 ppm combined residues). Based on the HAFT (1.92 ppm) and a concentration factor of 3.4x in raisin, the maximum expected pyraclostrobin and BF 500-3 residues would be 6.53 ppm in raisin. Data from the processing study indicate that the proposed tolerances of 6.0 ppm for raisin is too low. RAB3 recommends that the petitioner propose a tolerance of 7 ppm for raisin.

Peanut

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of peanuts.

45118614 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Peanut Process Fractions: Lab Project Number: 97043: 1999/5072.
Unpublished study prepared by BASF Corporation. 72 p.

A single peanut field trial was conducted during the 1997 growing season in Wayne County, NC. The trial consisted of three treated plots in which treatments differed according to application rates. Five broadcast foliar applications of the 2 lb/gal EC formulation were made to peanut plants, with 14-day retreatment intervals, at: (i) 0.25 lb ai/A/application for a total rate of 1.25 lb ai/A (~1x the maximum proposed seasonal rate); (ii) 0.74-0.76 lb ai/A/application for a total rate of 3.75 lb ai/A (~3x the maximum proposed seasonal rate); or (iii) 1.25-1.26 lb ai/A/application for a total rate of 6.26 lb ai/A (~5x the maximum proposed seasonal rate). Applications were made in 9.9-10.2 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray solution. A separate plot was left untreated for control samples. Since no phytotoxicity was observed at the 5x rate, peanuts treated at the 1x and 3x rates were not harvested, processed, or analyzed. Peanut plants treated at the 5x rate were dug and inverted 7 days following the last application and were allowed to dry in the field for 7 days prior to collection (14-day PHI).

One sample of untreated and two samples of treated whole mature peanuts were collected. Samples of whole peanuts were threshed, placed into bags, and shipped at ambient conditions to Texas A&M, Food Protein Research and Development Center (Bryan, TX) on the day of collection for processing. Samples were stored frozen for 8 days until processing. Samples were processed according to simulated commercial procedures into peanut meal and oil. Processed commodities were stored frozen following processing, and RAC and processed samples were

shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of peanut nutmeat and peanut processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated peanut nutmeat, meal, and oil. The results of the peanut processing study are presented in Table 62.

Table 62. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **peanut nutmeat and processed commodities** treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Peanut nutmeat (RAC)	<0.02, 0.03	<0.02, <0.02	<0.04, <0.05	--
Meal	<0.02, 0.03	<0.02, <0.02	<0.04, <0.05	0.9x, 1.1x average = 1x
Oil	0.05, 0.08	<0.02, <0.02	<0.07, <0.10	1.6x, 2.2x average = 1.9x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (<0.045 ppm) of the RAC samples.

Study summary:

The submitted peanut processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in peanut meal processed from peanut nutmeat bearing detectable residues of pyraclostrobin. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrated in peanut oil at 1.6x and 2.2x (average concentration factor of 1.9x).

The HAFT residue of peanut nutmeat treated at 1x the maximum seasonal rate (1.25 lb ai/A/season; 14-day PHI) from the submitted peanut field trial studies was 0.0225 ppm pyraclostrobin and <0.02 ppm BF 500-3 (<0.0425 ppm combined residues). Based on the HAFT (<0.0425 ppm) and an average concentration factor of 1.9x, the maximum expected pyraclostrobin and BF 500-3 residues in peanut oil would be 0.081 ppm. Data from the peanut processing study indicate that the proposed tolerance of 0.1 ppm for peanut oil is appropriate.

Plum

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in prunes, the only processed commodity of plums.

45118621 Wofford, J.; Abdel-Baky, S.; Riley, M. (2000) Magnitude of the Residues of BAS 500 F in Plum Processed Fractions: Lab Project Number: 55359: 1999/5147. Unpublished study prepared by BASF Corporation. 77 p.

A single plum field trial was conducted during the 1999 growing season in Tulare County, CA. The trial consisted of three treated plots in which treatments differed according to application rates. Four or five broadcast foliar applications of the 2 lb/gal EC formulation were made to plum trees with a 7-day retreatment interval. For the three treatment plots, the application rates were as follows: (i) five applications at 0.12 lb ai/A/application for a total rate of 0.6 lb ai/A (~1x the maximum proposed seasonal rate); (ii) four applications at 0.35-0.36 lb ai/A/application for a total rate of 1.43 lb ai/A (~2.4x the maximum proposed seasonal rate); or (iii) five applications at 0.59-0.60 lb ai/A/application for a total rate of 2.99 lb ai/A (~5x the maximum proposed seasonal rate). Applications were made in 240.5-251.7 gal/A using ground equipment with a non-silicone spray adjuvant (Latron B-1956) added to the spray solution. A separate plot was left untreated for control samples. Since no phytotoxicity was observed at the 5x rate, plums treated at the 1x and 3x rates were not harvested, processed, or analyzed. Mature plums treated at the 5x rate were harvested by hand immediately (0-day PHI) following the final application.

One sample of untreated and two samples of treated mature plums were collected, placed into bags, and shipped at ambient conditions to National Food Laboratories (Dublin, CA) the same day for processing. Samples were processed according to simulated commercial procedures into prunes. A subsample of whole, unwashed plums (RAC) was placed in frozen storage prior to processing. Following processing, washed plums and prunes were stored frozen, and RAC and processed samples (washed plums and prunes) were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of plums (unwashed and washed) and prunes were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated unwashed plums, washed plums, and prunes. The results of the plum processing study are presented in Table 63.

Table 63. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **plums (unwashed and washed) and prunes** treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Plum, unwashed (RAC)	0.20, 0.39	<0.02, <0.02	<0.22, <0.41	--
Plum, washed	0.28, 0.59	<0.02, 0.03	<0.30, 0.62	--
Prune	0.36, 0.39	0.02, 0.03	0.38, 0.42	1.2x, 1.3x average = 1.3x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (0.315 ppm) of the unwashed RAC samples.

Study summary:

The submitted plum processing data are adequate for the purposes of this petition. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrated slightly in prunes at 1.2x and 1.3x.

The HAFT residue of plums treated at 1x the maximum seasonal rate (0.6 lb ai/A/season; 0-day PHI) from the submitted plum field trial studies was 0.19 ppm pyraclostrobin and <0.02 ppm BF 500-3 (<0.21 ppm combined residues). Based on the HAFT (<0.21 ppm) and an average concentration factor of 1.3x, the maximum expected pyraclostrobin and BF 500-3 residues in prunes would be 0.273 ppm, which is lower than the proposed RAC tolerance of 0.7 ppm for the stone fruits crop group. Based on these data, a tolerance for pyraclostrobin residues in prunes is not warranted.

Potato

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of potatoes.

45118618 Versoi, P.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of the Residues of BAS 500 F in Potato Processed Fractions: Lab Project Number: 52239: 1999/5123. Unpublished study prepared by BASF Corporation. 50 p.

A single potato field trial was conducted during the 1999 growing season in Grant County, WA. The trial consisted of three treated plots in which treatments differed according to application rates. Six broadcast foliar applications of the 2 lb/gal EC formulation were made to potato plants, with 7-day retreatment intervals, at: (i) 0.2 lb ai/A/application for a total rate of 1.2 lb ai/A (1x the maximum proposed seasonal rate); (ii) 0.6 lb ai/A/application for a total rate of 3.6 lb ai/A (3x the maximum proposed seasonal rate); or (iii) 0.98-1.0 lb ai/A/application for a total

rate of 5.98 lb ai/A (5x the maximum proposed seasonal rate). Applications were made in 35.0-35.9 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray solution. A separate plot was left untreated for control samples. Since phytotoxicity was not observed at the 5x rate, potatoes treated at the 1x and 3x rates were not harvested, processed, or analyzed. Mature potatoes treated at the 5x rate were harvested by hand three days following the final application.

One sample of untreated and two samples of treated mature potatoes were collected, and placed into bags and cardboard boxes for shipment to Englar Food Laboratories, Inc. (Moses Lake, CA) for processing. A RAC subsample was also shipped directly to BASF APC for residue screening prior to processing. Samples of potato RAC were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample of untreated potato tuber. Combined residues were below the analytical method LOQ (<0.04 ppm) in/on two samples treated potato tuber samples. Because residues of pyraclostrobin and BF 500-3 were below the LOQ in whole potato RAC samples treated at an exaggerated rate (5x), potato samples were not processed and no further analyses were required.

Study summary:

The submitted potato processing data are adequate for the purposes of this petition. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 were below the LOQ (<0.04 ppm) in/on potato samples following treatment at 5x the maximum proposed rate. Therefore, no potato processing study or tolerances for potato processed commodities are required.

Sugar Beet

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of sugar beets.

45118619 Haughey, D.; Abdel-Baky, S.; Riley, M. (2000) The Magnitude of BAS 500 F Residues in Sugar Beet Process Fractions: Lab Project Number: 55187: 1999/5156. Unpublished study prepared by BASF Corporation. 81 p.

A single sugar beet field trial was conducted during the 1999 growing season in Payette County, ID. The trial consisted of three treated plots in which treatments differed according to application rates. Four broadcast foliar applications of the 2 lb/gal EC formulation were made to sugar beet plants, with 14-day retreatment intervals, at: (i) 0.20 lb ai/A/application for a total rate of 0.80 lb ai/A (~1x the maximum proposed seasonal rate); (ii) 0.60-0.61 lb ai/A/application for a total rate of 2.41 lb ai/A (~3x the maximum proposed seasonal rate); or (iii) 1.00-1.02 lb ai/A/application for a total rate of 4.04 lb ai/A (~5x the maximum proposed seasonal rate). Applications were made in 29.8-30.8 gal/A using ground equipment with a non-silicone spray

adjuvant added to the spray solution. A separate plot was left untreated for control samples. Since no phytotoxicity was observed at the 5x rate, sugar beets treated at the 1x and 3x rates were not harvested, processed, or analyzed. Mature sugar beets treated at the 5x rate were harvested by hand 7 days following the final application.

One sample of untreated and duplicate samples of treated mature sugar beet roots were collected by hand, lightly brushed to remove excess dirt, and placed into bags. Samples were shipped at ambient conditions to Englar Food Laboratories, Inc. (Moses Lake, CA) within 24 hours of harvest. Samples were stored frozen for 18-22 days at the Englar Food Laboratories prior to processing. Sugar beet roots were processed according to simulated commercial procedures into dried pulp, molasses, and refined sugar. A subsample of whole, unwashed sugar beet root (RAC) was placed in frozen storage prior to processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of sugar beet roots and sugar beet processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated sugar beet root, dried pulp, molasses, and refined sugar. The results of the sugar beet processing study are presented in Table 64.

Table 64. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **sugar beet roots and processed commodities** treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Sugar Beet Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Roots (RAC)	0.07 ^b , 0.07 ^b	<0.02, <0.02	<0.09, <0.09	--
Dried pulp	0.51, 0.55	0.11, 0.13	0.62, 0.68	6.9x, 7.5x
Molasses	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.4x
Refined sugar	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.4x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (<0.09 ppm) of the RAC samples.

^b Reported residue is the highest of replicate analyses of a single sample.

Study summary:

The submitted sugar beet processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in molasses and refined sugar processed from sugar beet roots bearing detectable residues of pyraclostrobin. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrated in dried pulp at 6.9x and 7.5x (average concentration factor = 7.2x).

The HAFT residue of sugar beet roots treated at 1x the maximum seasonal rate (0.8 lb ai/A/season; 7-day PHI) from the submitted sugar beet field trial studies was 0.105 ppm pyraclostrobin and 0.03 ppm BF 500-3 (0.135 ppm combined residues). Based on the HAFT (0.135 ppm) and an average concentration factor of 7.2x, the maximum expected pyraclostrobin and BF 500-3 residues in dried pulp would be 0.972 ppm. Data from the sugar beet processing study indicate that the proposed tolerance of 1.6 ppm for dried sugar beet pulp is too high. RAB3 recommends that the petitioner propose a tolerance of 1.0 ppm for beet, sugar, dried pulp.

Tomato

BASF Corporation submitted data from a study (citation listed below) depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of tomatoes.

45118615 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) The Magnitude of BAS 500 F Residues in Tomato Process Fractions: Lab Project Number: 98024: 1999/5085.
Unpublished study prepared by BASF Corporation. 77 p.

A single tomato field trial was conducted during the 1998 growing season in Kings County, CA. The trial consisted of three treated plots in which treatments differed according to application rates. Six broadcast foliar applications of the 2 lb/gal EC formulation were made to tomato plants, with 7-day retreatment intervals, at: (i) 0.2 lb ai/A/application for a total rate of 1.2 lb ai/A (1x the maximum proposed seasonal rate); (ii) 0.6 lb ai/A/application for a total rate of 3.6 lb ai/A (3x the maximum proposed seasonal rate); or (iii) 0.99-1.01 lb ai/A/application for a total rate of 6.00 lb ai/A (5x the maximum proposed seasonal rate). We note that details of the field trial information were provided for the 5x treatment only. Applications were made in 24.4-25.3 gal/A using ground equipment with a non-silicone spray adjuvant added to the spray solution. A separate plot was left untreated for control samples. Since phytotoxicity was not observed at the 5x rate, tomatoes treated at the 1x and 3x rates were not harvested, processed, or analyzed. Mature tomatoes treated at the 5x rate were harvested immediately (0-day PHI) following the final application.

One sample of untreated and two samples of treated mature tomatoes were collected and shipped fresh to National Food Laboratories, Inc. (Dublin, CA) on the day of harvest. Samples were stored in a cooler for 1-2 days at the National Food Laboratories until processing. Samples were processed according to simulated commercial procedures into paste and puree. A subsample of whole, unwashed tomatoes (RAC) was placed in frozen storage prior to processing. Processed

commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

Samples of tomatoes and tomato processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using Method D9808. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on one sample each of untreated whole tomato, paste, and puree. The results of the tomato processing study are presented in Table 65.

Table 65. Residues of pyraclostrobin and its metabolite BF 500-3 in/on tomatoes and processed commodities treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Tomato, whole	0.54, 0.72	0.04, 0.06	0.58, 0.78	--
Paste	0.77, 1.28	0.22, 0.51	0.99, 1.79	1.5x, 2.6x average = 2.1x
Puree	0.30, 0.37	0.04, 0.06	0.35, 0.43	0.5x, 0.6x

^a Concentration factors were calculated for the total residues by the study reviewer using the mean residue value (0.68 ppm) of the RAC samples.

Study summary:

The submitted tomato processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in tomato puree processed from whole tomatoes bearing detectable residues. The data indicate that the combined residues of pyraclostrobin and its metabolite BF 500-3 concentrated in tomato paste at 1.5x and 2.6x (average concentration factor = 2.1x).

The HAFT residue of tomatoes treated at 1x the maximum seasonal rate (1.2 lb ai/A/season; 0-day PHI) from the submitted tomato field trial studies was 0.21 ppm pyraclostrobin and <0.025 ppm BF 500-3 (0.235 ppm combined residues). Based on the HAFT (0.235 ppm) and an average concentration factor of 2.1x, the maximum expected pyraclostrobin and BF 500-3 residues in tomato paste would be 0.4935 ppm, which is lower than the proposed RAC tolerance of 1.0 ppm for the fruiting vegetables crop group. Based on these data, a tolerance for pyraclostrobin residues in tomato paste is not warranted.

Wheat

BASF Corporation submitted data from studies depicting the potential for concentration of residues of pyraclostrobin in the processed commodities of wheat. A 1998 study (citation listed below) was submitted demonstrating concentration of residues in processed commodities following earlier treatment schedules.

45118620 Versoi, P.; Abdel-Baky, S.; Riley, M. (1999) Magnitude of BAS 500 F Residues in Wheat Process Fractions and Aspirated Grain Fraction: Lab Project Number: 98033: 1999/5122. Unpublished study prepared by BASF Corporation. 98 p.

In addition, data were submitted in conjunction with the 2000 wheat field trials (MRID 45321101) demonstrating concentration of residues in processed commodities following expanded use (treatment at later growth stages closer to grain harvest) for control of fusarium head blight.

Early growth stage applications (MRID 45118620)

A single wheat field trial was conducted during the 1998 growing season in Grant County, WA. The trial consisted of three treated plots in which treatments differed according to application rates. Two broadcast foliar applications of the 2 lb/gal EC formulation were made to wheat plants, with a 10-day retreatment interval, at: (i) 0.2 lb ai/A/application for a total rate of 0.4 lb ai/A (~1x the maximum proposed seasonal rate); (ii) 0.6 lb ai/A/application for a total rate of 1.2 lb ai/A (~3x the maximum proposed seasonal rate); or (iii) 1.0 lb ai/A/application for a total rate of 2.0 lb ai/A (~5x the maximum proposed seasonal rate). The first application was made when the flag leaf was just visible, and the second application was made at 50% head emergence. Applications were made in 19.9-20.2 gal/A using ground equipment with a spray adjuvant added to the spray solution. A separate plot was left untreated for control samples. Mature wheat grain treated at the 1x and 5x rate was harvested 52 days following the final application; wheat grain treated at the 3x rate was not harvested, processed, or analyzed. Wheat grain from the 1x rate plot was harvested to produce RAC samples to process into aspirated grain fractions and grain from the 5x rate plot was harvested to produce RAC samples for processing into wheat flour, bran, middlings, shorts, and germ.

One sample of untreated and duplicate samples of treated mature wheat grain were each collected from the 1x and 5x treatment plots and shipped at ambient conditions to Englar Food Laboratories, Inc. (Moses Lake, WA) on the day of harvest. Samples were stored frozen at the Englar Food Laboratories prior to processing and processing was completed within 41-42 days of harvest. Wheat grain samples from the 5x treatment plot were processed according to simulated industrial procedures into flour, bran, middlings, shorts, and germ. A subsample of wheat grain (RAC) was placed in frozen storage prior to processing. Processed commodities were stored frozen following processing, and RAC and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

In addition, wheat grain samples from the 1x treatment plot were processed according to simulated industrial procedures into aspirated grain fractions. Processing was completed within 41 days of harvest. Briefly, grain was abraded and cleaned to remove grain dust and small debris using a seed cleaner and aspirator. The aspirated material was collected and screened. The aspirated grain fractions were separated by a sieving process into four fractions based on particle size using 2000- to 2380- μm , 1190- to 2000- μm , 841- to 1190- μm , and 420- to 841- μm mesh screens. Samples were frozen following generation and shipped frozen to BASF APC. The aspirated grain fractions were combined at BASF APC to generate one sample for analysis.

Later growth stage applications (MRID 45321101)

A single wheat field trial was conducted during the 2000 growing season in Cass County, ND. The trial consisted of two treated plots in which treatments differed according to application rates. Two broadcast foliar applications of the 2 lb/gal EC formulation were made to wheat plants, with a 6-day retreatment interval, at 0.20-0.21 lb ai/A/application for a total rate of 0.41 lb ai/A (~1x the maximum proposed seasonal rate) or at 0.99-1.01 lb ai/A/application for a total rate of 2.00 lb ai/A (~5x the maximum proposed seasonal rate). The first application was made at full head emergence and the second application at the end of anthesis. Applications were made in 9.9-10.3 gal/A using ground equipment with a spray adjuvant supplied by BASF added to the spray solution. A separate plot was left untreated for control samples. Mature wheat grain treated at the 1x and 5x rate was harvested 39 days following the final application. Wheat grain from the 1x rate plot was harvested to produce RAC samples to process into aspirated grain fractions, and grain from the 5x rate plot was harvested for processing into wheat flour, bran, middlings, shorts, and germ.

Bulk samples of untreated and treated mature wheat grain were each collected from the 1x and 5x treatment plots and frozen. Samples were shipped frozen to the Food Protein Research and Development Center (Bryan, TX) within 14 days of harvest. Samples were stored frozen at the processor prior to processing and processing was completed within 53 days of harvest. Wheat grain samples from the 5x treatment plot were processed according to simulated commercial procedures into flour, bran, middlings, shorts, and germ. A subsample of wheat grain (RAC) was placed in frozen storage prior to processing. Processed commodities were stored frozen following processing, and RAC, and processed samples were shipped frozen to BASF APC for analysis. The petitioner submitted adequate descriptions of the processing procedures and material balance information.

In addition, wheat grain samples from the 1x treatment plot were processed according to simulated industrial procedures into aspirated grain fractions as described above. The ASPIRATED GRAIN FRACTIONS were separated by a sieving process into six fractions based on particle size using 425, 850, 1180, 2030, and 2540 μm mesh screens; aspirated grain fractions less than 2540 μm were recombined to generate one sample for analysis. Samples were frozen following generation and were shipped frozen to BASF APC for analysis.

Samples of wheat grain, aspirated grain fractions, and wheat processed commodities were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using BASF Analytical Method Number D9908. Apparent residues of pyraclostrobin and BF 500-3 were each less than the LOQ (<0.02 ppm) in/on two samples each of untreated wheat grain, flour, bran, middlings, shorts, and germ, and aspirated grain fractions. The results of the wheat processing studies are presented in Table 66, and residues in/on treated aspirated grain fractions are presented in Table 67.

Table 66. Residues of pyraclostrobin and its metabolite BF 500-3 in/on **wheat grain and processed commodities** treated with the 2 lb/gal EC formulation at 5x the maximum application and seasonal rate.

Wheat Matrix	Residues, ppm			Concentration Factor ^a
	Pyraclostrobin	BF 500-3	Total	
Earlier Application Treatments (MRID 45118620)				
Grain (RAC)	0.034, 0.036	0.020, 0.021	0.054, 0.057	--
Flour	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Bran	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Middlings	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Shorts	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Germ	0.024, 0.029	<0.02, <0.02	<0.044, <0.049	<0.8x, <0.9x
Expanded Use: Later Application Treatments (MRID 45321101)				
Grain (RAC)	0.035, 0.045	<0.02, <0.02	<0.055, <0.065	--
Flour	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Bran	0.048, 0.050	0.031, 0.026	0.079, 0.076	1.3x
Middlings	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x
Shorts	<0.02, 0.021	<0.02, <0.02	<0.04, <0.041	<0.7x
Germ	<0.02, <0.02	<0.02, <0.02	<0.04, <0.04	<0.7x

^a Concentration factors were calculated for the total residues using the mean residue value of the RAC samples (0.056 ppm for MRID 45118620 samples and 0.06 ppm for MRID 45321101 samples).

Table 67. Residues of pyraclostrobin and its metabolite BF 500-3 in/on wheat aspirated grain fractions treated with the 2 lb/gal EC formulation at 1x the maximum application and seasonal rate.

Wheat Matrix	Residues, ppm		
	Pyraclostrobin	BF 500-3	Total
Earlier Application Treatments (MRID 45118620)			
Aspirated grain fractions ^a	0.047, 0.050	<0.02, <0.02	<0.067, <0.070
	0.190, 0.323	0.095, 0.122	0.285, 0.445
Expanded Use: Later Application Treatments (MRID 45321101)			
Aspirated grain fractions	1.463, 1.675	0.409, 0.491	1.87, 2.17

^a Results from duplicate analyses of two separate samples are reported.

Study summary:

The submitted wheat processing data are adequate for the purposes of this petition. No concentration of residues of pyraclostrobin and BF 500-3 was observed in flour, bran, middlings, shorts, and germ processed from wheat grain bearing detectable residues, except in bran from the expanded use application schedule. However, based on the HAFT (0.145 ppm) in wheat grain treated at 1x the maximum proposed seasonal rate (expanded use; 36-day PHI) and a concentration factor of 1.3x, residues in processed wheat bran (0.1885 ppm) are not expected to exceed the proposed tolerance for wheat grain (0.2 ppm). Based on the results of the processing studies, tolerances for residues of pyraclostrobin in the processed commodities of wheat are not required.

ASPIRATED GRAIN FRACTIONS: The combined residues of pyraclostrobin and its metabolite BF 500-3 did not exceed the proposed tolerance level of 2.5 ppm in/on wheat aspirated grain fractions following application of pyraclostrobin at 1x to wheat according to the earlier and later (expanded use) application schedules. Combined residues of pyraclostrobin and BF 500-3 were <0.067-0.445 ppm and 1.87-2.17 ppm in/on aspirated grain fractions from wheat treated at the earlier and the expanded use application schedules, respectively.

The petitioner must submit a revised Section F to change the proposed commodity definition from “Wheat (aspirated grain fractions)” to “Aspirated grain fractions.” The Agency does not set tolerances for the aspirated grain fractions of individual crops.

OPPTS GLN 860.1480: Meat/Milk/Poultry/Eggs

Ruminant Feeding Study.

BASF has submitted a cow feeding study (citations shown below) depicting secondary residues of pyraclostrobin in cow tissues and milk.

45118518 Tilting, N. (2000) Investigation of Residues of BAS 500F (Reg. No. 304428) in Tissues and Milk of Dairy Cows. Laboratory Project Identification No. 35639: BASF Registration Document No. 2000/1000003. Unpublished study prepared by BASF Corporation. 113 p.

45118519 Schat, B., Beelen, G. (1999) Feeding Study with BAS 500 F (Reg. No. 304428) in Lactating Dairy Cows. Laboratory Project Identification No. 010.20504: BASF Registration Document No. 1999/11895. Unpublished study prepared by BASF Corporation. 63 p.

Maximum theoretical dietary burden of pyraclostrobin for beef and dairy cattle

The plant commodities which may be used by beef and dairy cattle as feed items include barley grain, hay, and straw; citrus dried pulp; grass forage, hay, and straw; peanut meal; rye grain and straw; sugar beet tops and pulp; and wheat grain, hay, and straw. The maximum theoretical dietary burden, based on ingestion of these pyraclostrobin-treated feed items by beef and dairy cattle, is presented below in Table 68.

Table 68. Estimation (based on U.S. feeding practices as reflected in Table 1 of OPPTS 860.1000) of the maximum theoretical dietary burden of pyraclostrobin to beef and dairy cattle.

Commodity	%DM	Tolerance (ppm)	% diet beef	% diet dairy	Burden beef (ppm)	Burden dairy (ppm)
Grass forage	25	10	60	60	24	24
Barley hay	88	25	25	40	7.1	11.4
Sugar beet tops	23	8.0	15		5.2	
Total			100	100	36.3	35.4

Discussion of data

The in-life phase of the study was conducted at The Netherlands Organization for Applied Scientific Research (TNO) Voeding (Zeist, The Netherlands) and the analytical phase was conducted by BASF Aktiengesellschaft (Limburgerhof, Germany). Three groups of Friesian crossbred dairy cows (3 cows each in the low and mid dose groups, and 5 cows in the high dose group) were dosed orally (twice per day) for 28 consecutive days with pyraclostrobin at a target rate of 7, 21, and 70 ppm; the dose rate was calculated using standard bodyweights (550 kg/animal) and feed intake (20 kg dry matter/day/animal). An additional group of 3 cows served as controls. The actual administered doses (average) of 8.8, 27.2, and 89.6 ppm are equivalent to $\approx 0.25x$, $\approx 0.75x$, and $2.5x$, respectively, the beef or dairy cattle dietary burden.

Following an acclimation period of 7 days, lactating cows (individually stalled indoors) were dosed twice daily with a feed concentrate soaked with corn oil containing pyraclostrobin (97.1% a.i.). The treated feed was consumed on all occasions except for the evening feeding on Day 11,

in which one cow from the low-dose group which did not eat all of the offered feed. During the treatment period, cows were additionally fed grass silage (41.3% dry matter) and water was provided *ad libitum*. The petitioner submitted adequate information pertaining to body weights, daily food consumption, milk production, and general health of the test animals.

Cows were milked twice daily; a.m. and subsequent p.m. samples were composited for each animal for each sampling day and stored frozen. Subsamples of milk collected on Day 26 were separated into milk fat and skim milk by centrifugation and frozen. Milk samples were shipped twice during the study by freezer van to BASF for analysis. Animals were sacrificed within 23 hours of the final dose; two cows from the high-dose group were sacrificed 2 and 7 days after the final dose to determine residue levels post dosing (residue depletion). Samples of liver, kidney, fat, and muscle (left thigh) were collected after sacrifice. Tissue samples were chopped, frozen, and shipped to BASF for analysis. Tissue samples were ground with dry ice; all milk and tissue samples were stored frozen (-18 C) at BASF prior to analysis. The maximum storage intervals from collection until analysis were 92 days (3 months) for whole milk, 81 days (2.7 months) for skim milk, 185 days (6.1 months) for milk fat, 197 days (6.5 months) for fat, 172 days (5.7 months) for liver, 165 days (5.4 months) for kidney, and 153 days (5 months) for muscle.

Whole milk, skim milk, milk fat, and tissue samples were analyzed for residues of pyraclostrobin *per se* using the HPLC/UV method 439, with LOQs of 0.01 ppm for milk and 0.05 ppm for tissues. Milk and tissue samples were also analyzed by the common moiety methods GC/MS method 446/0 and LC/MS/MS method 446/1. For these methods, the reported LOQs were 0.01 ppm in milk and 0.05 ppm in tissues for pyraclostrobin compounds hydrolyzable to BF 500-5 and 0.01 ppm in milk and 0.05 ppm in tissues for pyraclostrobin compounds hydrolyzable to BF 500-8.

Apparent residues of pyraclostrobin were below the respective LOQ (0.01 ppm for milk and 0.05 ppm for tissues) in all untreated samples of whole milk (n= 16), skim milk (n=2), milk fat (n=3), fat (n=3), liver (n=3), kidney (n=3), and muscle (n=3) analyzed using HPLC/UV. Apparent residues of pyraclostrobin compounds hydrolyzable to BF 500-5 and BF 500-8 were each below the LOQ (0.01 ppm) in untreated whole milk (n=24), skim milk (n=2), and milk fat (n=2) samples analyzed by GC/MS. Apparent residues of pyraclostrobin compounds hydrolyzable to BF 500-5 and BF 500-8 were each below the LOQ (0.05 ppm) in all untreated liver (n=2), kidney (n=1), muscle (n=1), and fat (n=1) samples analyzed by the LC/MS/MS method. Residues of pyraclostrobin and/or its metabolites in milk and tissue samples from the mid and high dose groups are presented in Tables 69 (mid dose) and 70 (high dose); residues of pyraclostrobin and its metabolites were less than the method LOQs in all milk and tissue samples from the low dosing level. Residue values were not corrected or adjusted for method recoveries.

Table 69. Residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 in milk and tissues from cows dosed twice daily with pyraclostrobin at levels equivalent to 27.2 ppm for 28 consecutive days.

Dosing or Sampling Day	Mid Dose (27.2 ppm)			
	HPLC/UV Method 439	GC/MS (milk) Method 446/0 or LC/MS/MS (tissues) Method 446/1		
	Pyraclostrobin <i>per se</i> (ppm)	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-8, ppm pyraclostrobin equivalents ^b	Total residues, ppm pyraclostrobin equivalents ^c
Whole Milk				
1	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.02, <0.02, <0.02
4	--	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.02, <0.02, <0.02
7	--	<0.01, <0.01, <0.01	<0.01, <0.01, 0.0124	<0.02, <0.02, <0.0224
10	--	<0.01, <0.01, <0.01	<0.01, <0.01, 0.011	<0.02, <0.02, <0.021
12	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.01, <0.01, 0.0119	<0.02, <0.02, <0.0219
15	--	<0.01, <0.01, <0.01	<0.01, 0.0126, 0.0135	<0.02, <0.0226, <0.0235
18	--	<0.01, <0.01, <0.01	<0.01, 0.0104, 0.0130	<0.02, <0.0204, <0.0230
21	--	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.02, <0.02, <0.02
24	--	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.02, <0.02, <0.02
27	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.01, <0.01, 0.0108	<0.02, <0.02, <0.0208
Skim Milk				
26	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.02, <0.02, <0.02
Milk Fat				
26	<0.01, <0.01, <0.01	<0.01, <0.01, <0.01	<0.01, 0.0368, 0.0461	<0.02, <0.0468, <0.0561
Fat				
29	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.1, <0.1, <0.1
Kidney				
29	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.1, <0.1, <0.1

Table 69 (continued).

Dosing or Sampling Day	Mid Dose (27.2 ppm)			
	HPLC/UV Method 439	GC/MS (milk) Method 446/0 or LC/MS/MS (tissues) Method 446/1		
	Pyraclostrobin <i>per se</i> (ppm)	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-8, ppm pyraclostrobin equivalents ^b	Total residues, ppm pyraclostrobin equivalents ^c
Liver				
29	<0.05, <0.05, <0.05	0.0645, 0.0761, 0.0973	0.399, 0.426, 0.510	0.464, 0.502, 0.607
Muscle				
29	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.1, <0.1, <0.1

^a Pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were determined in milk using the GC/MS method and in tissues using the LC/MS/MS method.

^b Metabolites hydrolyzable to BF 500-8 were determined in milk using the GC/MS method and in tissues using the LC/MS/MS method.

^c Total BF 500-5 and BF 500-8 residues, expressed as pyraclostrobin equivalents.

Table 70. Residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 in milk and tissues from cows dosed twice daily with pyraclostrobin at levels equivalent to 89.6 ppm for 28 consecutive days.

Dosing or Sampling Day	High Dose (89.6 ppm)			
	HPLC/UV Method 439	GC/MS (milk) Method 446/0 or LC/MS/MS (tissues) Method 446/1		
	Pyraclostrobin <i>per se</i> (ppm)	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-8, ppm pyraclostrobin equivalents ^b	Total residues, ppm pyraclostrobin equivalents ^c
Whole Milk				
1	<0.01, <0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01, <0.01	<0.01, <0.01, <0.01, <0.01, <0.01	<0.02, <0.02, <0.02, <0.02, <0.02
4	<0.01, <0.01, <0.01, <0.01, <0.01	0.0211, 0.0260, 0.0321, 0.0358, 0.0431	0.0211, 0.0528, 0.0777, 0.0631, 0.0914	0.0422, 0.0788, 0.1098, 0.0989, 0.1345
7	<0.01, <0.01, <0.01, <0.01, <0.01	0.0195, 0.0269, 0.0300, 0.0335, 0.0444	0.0296, 0.0576, 0.0625, 0.0907, 0.105	0.0491, 0.0845, 0.0925, 0.1242, 0.1494
10	<0.01, <0.01, <0.01, <0.01, <0.01	0.0170, 0.0196, 0.0275, 0.0286, 0.0325	0.0394, 0.0273, 0.0504, 0.0757, 0.0934	0.0564, 0.0469, 0.0779, 0.1043, 0.1259
12	<0.01, <0.01, <0.01, <0.01, <0.01	0.0199, 0.0212, 0.0272, 0.0341, 0.0437	0.0275, 0.0441, 0.0482, 0.0929, 0.1171	0.0474, 0.0653, 0.0754, 0.1270, 0.1608
15	<0.01, <0.01, <0.01, <0.01, <0.01	0.0122, 0.0231, 0.0289, 0.0306, 0.0438	0.0254, 0.0447, 0.0560, 0.0857, 0.1315	0.0376, 0.0678, 0.0849, 0.1163, 0.1753
18	<0.01, <0.01, <0.01, <0.01, <0.01	0.0210, 0.0212, 0.0301, 0.0320, 0.0453	0.0519, 0.0339, 0.0549, 0.0960, 0.1142	0.0729, 0.0551, 0.0850, 0.1280, 0.1595
21	<0.01, <0.01, <0.01, <0.01, <0.01	0.0234, 0.0237, 0.0248, 0.0290, 0.0368	0.0641, 0.0593, 0.0380, 0.0616, 0.0989	0.0875, 0.0830, 0.0628, 0.0906, 0.1357
24	<0.01, <0.01, <0.01, <0.01, <0.01	0.0173, 0.0181, 0.0249, 0.0270, 0.0347	0.0254, 0.0499, 0.0516, 0.0804, 0.0875	0.0427, 0.0680, 0.0765, 0.1074, 0.1222
27	<0.01, <0.01, <0.01, <0.01, <0.01	0.0195, 0.0208, 0.0280, 0.0280, 0.0361	0.0516, 0.0307, 0.0505, 0.0638, 0.1027	0.0711, 0.0515, 0.0785, 0.0912, 0.1388
30 ^{d,e}	<0.01, <0.01	<0.01, 0.010	<0.01, 0.0441	<0.02, 0.0541
33 ^d	<0.01	<0.01	<0.01	<0.02

Table 70 (continued).

Dosing or Sampling Day	High Dose (89.6 ppm)			
	HPLC/UV Method 439	GC/MS (milk) Method 446/0 or LC/MS/MS (tissues) Method 446/1		
	Pyraclostrobin <i>per se</i> (ppm)	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-8, ppm pyraclostrobin equivalents ^b	Total residues, ppm pyraclostrobin equivalents ^c
35 ^e	<0.01	<0.01	<0.01	<0.02
Skim Milk				
26	<0.01, <0.01, <0.01, <0.01, <0.01	0.0165, 0.0174, 0.0225, 0.0231, 0.0308	0.0368, 0.0219, 0.0563, 0.0459, 0.0713	0.0533, 0.0393, 0.0788, 0.0690, 0.102
Milk Fat				
26	0.0163, 0.0323, 0.0323, 0.0410, 0.0442	0.024, 0.0572, 0.0679, 0.0716, 0.0797	0.1258, 0.0741, 0.1901, 0.1814, 0.1037	0.1498, 0.1313, 0.2580, 0.2530, 0.1834
Fat				
29	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.1, <0.1, <0.1
31 ^d	<0.05	<0.05	<0.05	<0.1
36 ^e	<0.05	<0.05	<0.05	<0.1
Kidney				
29	<0.05, <0.05, <0.05	0.1, 0.118, 0.122	0.267, 0.261, 0.274	0.367, 0.379, 0.396
31 ^d	<0.05	<0.05	0.057	<0.107
36 ^e	<0.05	<0.05	<0.05	<0.1
Liver				
29	<0.05, <0.05, <0.05	0.242, 0.246, 0.281	1.814, 2.37, 2.5	2.056, 2.616, 2.781
31 ^d	<0.05	0.142	1.334	1.476
36 ^e	<0.05	0.0515	0.443	0.495
Muscle				

Table 70 (continued).

Dosing or Sampling Day	High Dose (89.6 ppm)			
	HPLC/UV Method 439	GC/MS (milk) Method 446/0 or LC/MS/MS (tissues) Method 446/1		
	Pyraclostrobin <i>per se</i> (ppm)	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-8, ppm pyraclostrobin equivalents ^b	Total residues, ppm pyraclostrobin equivalents ^c
29	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.1, <0.1, <0.1
31 ^d	<0.05	<0.05	<0.05	<0.1
36 ^e	<0.05	<0.05	<0.05	<0.1

^a Pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were determined in milk using the GC/MS method and in tissues using the LC/MS/MS method.

^b Metabolites hydrolyzable to BF 500-8 were determined in milk using the GC/MS method and in tissues using the LC/MS/MS method.

^c Total BF 500-5 and BF 500-8 residues, expressed as pyraclostrobin equivalents.

^d Samples from one cow sacrificed following 2 days of withdrawal (no treatment).

^e Samples from one cow sacrificed following 7 days of withdrawal (no treatment).

Study summary:

The submitted dairy cattle feeding data are adequate for the purpose of establishing tolerances for pyraclostrobin residues of concern in livestock commodities. Dairy cows were orally dosed twice daily for 28 consecutive days with pyraclostrobin at dose levels equivalent to 8.8 ppm, 27.2 ppm, and 89.6 ppm. The anticipated maximum dietary burdens of pyraclostrobin for beef and dairy cattle are tentatively estimated to be 36.3 ppm and 35.4 ppm, respectively. Assuming that pyraclostrobin residues of concern in ruminant commodities are pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8, RAB3 offers the following conclusions and recommendations based on the maximum residues found at the feeding level of 27.2 ppm (mid dose) and 89.6 ppm (high dose) ($\approx 0.75x$ and $2.5x$ the anticipated maximum dietary burden for beef or dairy cattle).

Maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were <0.02 - <0.0235 ppm and <0.02 - 0.175 ppm, respectively for the mid dose and the high dose groups in whole milk, <0.02 ppm and 0.0393 - 0.102 ppm in skim milk, and <0.02 - <0.0561 ppm and 0.131 - 0.258 ppm in milk fat. These data suggest that the proposed tolerance of 0.1 ppm for milk is adequate.

Maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were 0.464 - 0.607 ppm and 2.06 - 2.78 ppm in liver, respectively for mid dose and high dose groups. These data suggest that the proposed tolerance of 1.5 ppm for liver is adequate.

Maximum combined residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-8 were (for respective mid dose and high dose groups) <0.1 ppm and 0.396 ppm in kidney, and <0.1 ppm and <0.1 ppm in fat and muscle. These data suggest that the proposed tolerance levels of 0.1 ppm for muscle and fat are adequate. However, the proposed tolerance of 0.1 ppm for kidney is not adequate; we recommend a tolerance of 0.2 ppm instead.

The petitioner needs to submit a revised Section F for livestock commodity tolerances. The tolerance expression must be revised to reflect the compounds that are determined using the proposed enforcement methods. In addition, tolerances for ruminant commodities in addition to cattle are required. Tolerances must be proposed for the fat, meat, and meat byproducts of cattle, goats, hogs, horses, and sheep.

Overall, residues of pyraclostrobin increased in milk and tissues with the increase in the dose level. Residues in whole milk appeared to plateau at Day 15 and did not significantly increase with subsequent doses (mid dose data). In tissues, residues were highest in liver. The depletion study (cows sacrificed 2 and 7 days following withdrawal from treatment) demonstrated that residues declined in milk and tissues once exposure was discontinued.

Poultry Feeding Study

BASF has submitted a poultry feeding study (citation shown below) depicting secondary residues of pyraclostrobin in hen eggs and tissues.

45118520 Malinsky, S., Riley, M. (2000) A Meat and Egg Magnitude of the Residue Study with BAS 500 F in Laying Hens. BASF Study No. 60917: BASF Registration Document No. 2000/5005. Unpublished study prepared by BASF Corporation. 213 p.

Maximum theoretical dietary burden of pyraclostrobin for poultry

The plant commodities which may be used by poultry as feed items include barley grain, peanut meal, rye grain, and wheat grain and milled byproducts. The maximum theoretical dietary burden, based on ingestion of these pyraclostrobin-treated feed items by poultry, is presented below in Table 71.

Table 71. Estimation (based on U.S. feeding practices as reflected in Table 1 of OPPTS 860.1000) of the maximum theoretical dietary burden of pyraclostrobin to poultry.

Feed Commodity	Proposed Tolerance, ppm	Poultry	
		% of Diet	Burden, ppm
Barley, grain	0.4	75	0.3
Wheat, grain	0.2	25	0.05
TOTAL		100	0.35

Discussion of data

The in-life phase of the study was conducted at Southwest Bio-Labs, Inc. (Las Cruces, NM) and the analytical phase was conducted by BASF APC (Research Triangle Park, NC). Three groups of White Leghorn laying hens (3 subgroups of four hens/low and mid dose groups, 5 subgroups of four hens/high dose group) were dosed orally for 30 consecutive days with pyraclostrobin at a target rate of 0.30, 0.90, and 3.00 ppm once/day; the dose rate was calculated using the average daily feed intake (dry weight basis) from the previous week. An additional group of 3 subgroups of four hens received gelatin capsules with only cellulose for controls. The actual administered doses (average) of 0.28, 0.88, and 3.01 ppm are equivalent to 0.8x, 2.5x, and 8.6x, respectively, the maximum theoretical dietary burden for poultry of 0.35 ppm.

Following an acclimation period of 2 weeks, laying hens (individually caged indoors) were dosed once daily following the morning egg collection with a gelatin capsule containing pyraclostrobin (97.1% a.i.) and cellulose via a balling gun. Hens were fed a commercial laying ration and water *ad libitum* throughout the study. The petitioner submitted adequate information pertaining to body weights, daily food consumption, egg production, and general health of the test birds.

Eggs were collected twice daily; p.m. and subsequent a.m. samples were composited for each subgroup for each sampling day and stored frozen. Hens were sacrificed within 6.5 hours of the final dose; two subgroups from the high-dose level were sacrificed 3 and 7 days after the final dose to determine residue levels post dosing (residue depletion). Samples of fat (composite of mesenteric and peripheral), liver, and muscle (composite) were collected after sacrifice. Tissue samples were pooled by subgroup, homogenized with liquid nitrogen, and frozen (<-15 C). Egg and tissue samples were shipped frozen to BASF for analysis. All egg and tissue samples were stored frozen (<-10 C) at BASF prior to analysis. The maximum storage intervals from collection until analysis were 149 days (~5 months) for eggs, 126 days (~4 months) for fat, 92 days (~3 months) for liver, 174 days (~6 months) for muscle.

Egg and tissue samples were analyzed for residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-9 using common moiety method LC/MS/MS method D9902. For these methods, the reported LOQs were 0.05 ppm in eggs and tissues for pyraclostrobin compounds hydrolyzable to BF 500-5 and 0.05 ppm in eggs and tissues for pyraclostrobin compounds hydrolyzable to BF 500-9.

Apparent residues of pyraclostrobin its metabolites hydrolyzable to BF 500-5 and BF 500-9 were each below the LOQ (0.05 ppm) in all untreated egg (n=13), fat (n=1), liver (n=1), and muscle (n=1) samples. Residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-9 in egg and tissue samples from the high dosing levels are presented in Table 72. Because residues at the high-dose level (8.6x) were below the method LOQ in all samples except one egg sample (which upon reanalysis was determined to be below the LOQ), samples from the low- and mid-level dose groups, and samples from the depletion study at the high-dose level were not analyzed.

Table 72. Residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 and BF 500-9 in egg and tissues from hens dosed once daily with pyraclostrobin at levels equivalent to 3 ppm for 30 consecutive days.

Dosing or Sampling Day	High Dose (3 ppm)		
	Residues hydrolyzable to BF 500-5, ppm pyraclostrobin equivalents ^a	Residues hydrolyzable to BF 500-9, ppm pyraclostrobin equivalents ^b	Total Residues, ppm pyraclostrobin equivalents ^c
Eggs			
1	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
2	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
4	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
7	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
10	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
14	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
17	<0.05, <0.05, 0.064 ^d	<0.05, <0.05, <0.05	<0.10, <0.10, <0.11
21	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
24	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
28	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
30	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
Fat			
30	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
Liver			
30	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10
Muscle			
30	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	<0.10, <0.10, <0.10

^a Pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were determined.

^b Metabolites hydrolyzable to BF 500-9 were determined.

^c Total BF 500-5 and BF 500-9 residues, expressed as pyraclostrobin equivalents.

^d The highest value of replicate analyses is reported; duplicate reanalysis indicated residues below the LOQ (<0.05 ppm).

Study summary:

The submitted poultry feeding data are adequate for the purpose of determining the potential for secondary transfer of pyraclostrobin residues of concern to poultry eggs and tissues. Laying hens were orally dosed once daily for 30 consecutive days with pyraclostrobin at dose levels equivalent to 0.28 ppm, 0.88 ppm, and 3.01 ppm. The maximum theoretical dietary burden of pyraclostrobin for poultry is estimated to be 0.35 ppm. At the feeding level of 3.01 ppm (8.6x

the maximum theoretical dietary burden for poultry), residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were less than the method LOQ (0.05 ppm) in all egg and tissue samples, except for one egg sample (Day 17) where residues of pyraclostrobin were detected at 0.064 ppm and <0.05 ppm upon re-analysis. Residue analysis of BF 500-8 was not conducted (the metabolism data show all metabolites hydrolyzable to BF 500-8 would be less than 10% TRR), but instead an isomeric compound (BF 500-9) was measured. Levels of BF 500-9 also were all <0.05 ppm. Samples from the low and mid dose groups, and depletion samples from the high dose group were not analyzed.

The poultry metabolism studies were conducted at doses equivalent to 35-36x the MTDB. When extrapolated to the 1x burden, the TRRs in eggs, fat and liver would be at least 3 times below 0.05 ppm, which is the LOQ for BF 500-5 or BF 500-8. In combination with the poultry feeding data discussed above, RAB3 concludes that tolerances in poultry and eggs are not needed. A revised Section F in which tolerances for the poultry commodities are deleted needs to be submitted.

OPPTS GLN 860.1850: Confined Accumulation in Rotational Crops

BASF submitted data from a study (citation listed below) investigating the metabolism of [¹⁴C]pyraclostrobin in rotational crops (radish, lettuce, and wheat). The field and analytical phases of the study were conducted at BASF Agricultural Center, Limburgerhof, Germany.

45118622 Veit, P. (2000) Confined Rotational crop Study with ¹⁴C-BAS-500 F. Laboratory Project Identification No. 35510, 1999/11829. Unpublished study submitted by BASF Corporation. 277 p.

The radioactive test substances, uniformly ring-labeled [chlorophenyl-¹⁴C]pyraclostrobin (specific activity 4.34 Mbq/mg, radiochemical purity >99%) and [tolyl-¹⁴C]pyraclostrobin (specific activity 4.5 Mbq/mg, radiochemical purity >99%), were dissolved in acetone and separately applied to sandy soil (89% sand, 6% silt, and 5% clay, 0.8% organic matter, pH 6.4, cation exchange capacity 5.3 mVal/100 g) to create soil premixes at total application rates for each label of 0.8 lb ai/A (900 g ai/ha) or 1.3 lb ai/A (1500 g ai/ha). The soil premixes were spread in 1-cm layers on top of untreated soil in polyethylene containers, and the soil was lightly watered. At 30, 120, and 365 days following application, ploughing was simulated by removing the top 20 cm of soil from each container and mixing in a concrete mixer. After the soil was returned to the containers, radish, head lettuce, and wheat were planted to the pots at each of the plantback intervals. Plants were maintained in growth chambers or greenhouses for the duration of the study. The lower application rate is ~1x the proposed seasonal rate for onions, strawberries, and sugar beets, ~2x the maximum proposed rate for barley, rye, wheat, and grasses (for seed), and ~3x the maximum proposed rate for peas; the higher application rate is ~1x the maximum proposed rate for cucurbits, peanuts, peppers, potatoes, and tomatoes.

Samples of immature radish plants from the 30-day plantback interval were harvested 33-34 days after planting (DAP), immature lettuce plants from all intervals were harvested 33-48 DAP, and wheat forage was harvested 75-85 DAP. Samples of mature radish were harvested 47-65 DAP, lettuce heads were harvested 60-76 DAP, and wheat was harvested 152-167 DAP. Radishes were pulled from the soil and separated into roots and tops, and mature wheat was harvested by cutting plants just above the soil line and separating them into straw, grain, and chaff. Samples were stored at \sim -18 C prior to and throughout the analytical phase of the study.

Total radioactive residues (TRR)

Samples of rotational crop matrices were homogenized along with dry ice using a blender or a mill, and were subjected to combustion/LSC for TRR determination. As in the plant metabolism studies, TRR were also calculated for rotational crop commodities by summing extractable and nonextractable residues following initial extractions. Because combustion values were used for all further TRR calculations, the calculated values are not presented. The TRR in rotational crop commodities are presented in Table 73. The petitioner reported LOQs (all < 1 ppb) for LSC determinations of 0.00093 and 0.00096 ppm for wheat forage and 0.00059 and 0.00061 ppm for wheat straw.

Table 73. Total radioactive residues in samples of rotational crop commodities grown in soil treated with [¹⁴C]pyraclostrobin at 0.8 or 1.3 lb ai/A.

Commodity	TRR, ppm [¹⁴ C]pyraclostrobin equivalents ^a					
	Chlorophenyl label			Tolyl label		
	30 DAT ^b	120 DAT	365 DAT	30 DAT	120 DAT	365 DAT
Application rate 0.8 lb ai/A						
Immature radish tops	0.013	--	--	0.015	--	--
Immature radish roots	0.027	--	--	0.019	--	--
Radish tops ^c	0.028	0.006, 0.011	<i>0.006</i>	0.025	<i>0.007, 0.009</i>	0.010
Radish roots ^c	0.040	0.007, 0.006	<i>0.004</i>	0.025	<i>0.008, 0.008</i>	0.014
Immature lettuce	0.012	0.006	<i>0.005</i>	0.014	<i>0.007</i>	0.013
Head lettuce	0.011	0.009	0.007	0.013	0.011	0.017
Wheat forage	0.019	0.022	0.014	0.019	0.022	0.016
Wheat straw	0.112	0.079	0.069	0.114	0.081	0.067
Wheat grain	0.078	0.079	0.010	0.082	0.089	0.013
Wheat chaff	0.112	0.092	0.038	0.098	0.102	0.032
Application rate 1.3 lb ai/A						
Immature radish tops	0.016	--	--	0.024	--	--
Immature radish roots	0.026	--	--	0.046	--	--
Radish tops ^c	0.021	0.006, 0.009	0.008	0.046, 0.045	0.025, 0.016	0.014
Radish roots ^c	0.025	0.008, 0.007	0.007	0.056	0.015, <i>0.009</i>	0.019
Immature lettuce	0.012	0.006	<i>0.005</i>	0.017	<i>0.009</i>	0.014
Head lettuce	0.014	0.011	0.007	0.017	0.023	0.023
Wheat forage	0.019	0.021	0.018	0.026	0.027	0.018
Wheat straw	0.144	0.075	0.068	0.125	0.088	0.073
Wheat grain	0.080	0.078	0.010	0.085	0.091	0.017
Wheat chaff	0.116	0.096	0.042	0.104	0.109	0.043

^a *Italicized* samples were not subjected to any further extraction/analysis.

^b DAT = number of days after soil treatment that samples were planted.

^c Where two values are listed, the first value represents samples harvested 47-48 days after planting (DAP); the second value represents samples harvested 64-65 DAP, except for 30-DAT tolyl radish tops, for which the values represent two separate work-ups of the same sample.

The petitioner noted that for most matrices, TRR levels did not differ significantly between labels or application levels, and stated that the overall low residue levels in crops indicated that only a small portion of the available radioactive residues in soil were translocated through the roots into the plants.

Extraction and hydrolysis of residues

Samples of homogenized rotational crop commodities were subjected to extraction procedures for residue characterization and identification. During the fractionation procedures, aliquots of extracts and nonextractable residues were analyzed for radioactivity by LSC or combustion/LSC. The general extraction procedures are summarized below.

Homogenized samples of rotational crop commodities were variously extracted with methanol; methanol and water; or methanol, water, and ammonia (selected tolyl-label samples). Following extractions, the respective methanol, water, and/or ammonia extracts were collected by centrifugation or filtration and combined. Methanol extracts or combined methanol and water extracts for most matrices were reserved for HPLC analysis. Aliquots of selected methanol extracts were concentrated to aqueous and subjected to partitioning with cyclohexane (3x) and ethyl acetate or with ethyl acetate alone. Depending on the total radioactivity, certain organic phases were reserved for HPLC analysis.

In general, nonextractable residues with TRR >0.010 ppm following methanol or methanol and water extractions were extracted with aqueous ammonia at 40 C and centrifuged. The remaining nonextractable residues were reserved for further characterization procedures.

The distribution of ¹⁴C-activity in the extracts of rotational crop commodities is presented in Tables 74a (chlorophenyl label, 0.8 lb ai/A), 74b (chlorophenyl label, 1.3 lb ai/A), 74c (tolyl label, 0.8 lb ai/A) and 74d (tolyl label, 1.3 lb ai/A).

Characterization/identification of residues

Extracts and/or hydrolysates of rotational crop commodities were analyzed by HPLC using an Inertsil phenyl column. Separate systems were used for analysis of chlorophenyl- and tolyl-label extracts. Both systems were equipped with UV detectors (270 nm for chlorophenyl-label samples; 230 nm for tolyl-label samples), radioactivity detectors, and fraction collectors; gradient mobile phases of water and acetonitrile, each containing formic acid at 0.5%, were used. Pyraclostrobin and metabolite 500M07 (elsewhere named BF 500-3) were identified by co-chromatography using reference standards. Because overall radioactive residue levels were low, the petitioner did not attempt further identification by co-chromatography; instead, radioactivity was defined by region based on retention times and polarity, with each region containing one or more peaks. Five different regions were defined: a polar region, medium polar regions a, b, and c, and a nonpolar region. The petitioner stated that nonpolar metabolites identified in the soil degradation studies were not observed in any of the rotational crop commodities.

Certain extracts of chlorophenyl-label samples were also subjected to normal-phase TLC analysis on 60F254 plates. Plates were developed in an automated multiple development (AMD) chamber using the following solvent systems: methanol:ACN:formic acid (40:40:1, v:v:v); ACN; ACN:dichloromethane (DCM; 40:40, v:v); DCM; di-isopropylether; and di-isopropylether:n-heptane (40:40, v:v). In general, TLC results confirmed HPLC findings, and

better separation was achieved between pyraclostrobin and 500M07 (BF 500-3) with TLC than with HPLC analysis.

Following partitioning of the methanol extracts of various matrices with cyclohexane and/or ethyl acetate, the petitioner observed that in 30-DAT radish root and wheat straw samples, residue levels were higher in the organic phases than in the aqueous phase; for 30- and 120-DAT lettuce and 30-DAT wheat grain, the concentration in the aqueous phase was equal to or higher than concentration in the organic phases; for 120-DAT wheat straw and grain, a ratio of 1.3:1 was observed for partitioning of residues into the organic vs aqueous phases; and for 365-DAT wheat straw the ratio was 2.3:1 for the 0.8 lb ai/A application and 1.6:1 for the 1.3 lb ai/A application. HPLC analysis of selected organic and aqueous phases confirmed that other more polar metabolites occurred in addition to pyraclostrobin. Pyraclostrobin and 500M07 (BF 500-3) tended to remain in the cyclohexane phase or partition into ethyl acetate; the more polar metabolites tended to partition into the aqueous phase.

The petitioner utilized three separate procedures to characterize radioactivity associated with lignin and cellulose in rotational crop commodities. To isolate lignin and cellulose, primarily in wheat straw, chaff, and grain, the petitioner subjected the nonextractable residues following ammonia extraction to hydrolysis with 10% NaOH at reflux for 3 hours. Following filtration, the filter cake was washed with 10% NaOH at 80 C followed by water. Lignin was precipitated by acidifying the combined filtrate and wash solutions with concentrated HCl; the petitioner characterized the remaining nonextractable residues as cellulose. To characterize natural products, such as cellulose and hemicelluloses, in radish tops and roots, lettuce, wheat forage, and selected wheat straw and grain samples, the nonextractable residues following ammonia extraction were subjected to enzyme hydrolysis with a mixture of cellulases and Macerozyme, a mixture of cellulase, hemicellulase, and pectinase (in sodium acetate buffer, pH 4.7, at 37 C for 20 hours). Selected hydrolysates were partitioned with ethyl acetate and/or reserved for HPLC analysis using a Resex RNM column. Enzyme hydrolysis with pronase (in tris-buffer, pH 7.3, overnight at 37 C) was also used in some cases for characterization of nonextractable residues in radish tops and roots, lettuce, and wheat forage and straw. The petitioner further noted that the low extractability of residues into aqueous ammonia suggested that residues remaining following methanol and water extractions were most likely not associated with proteins.

To characterize starch in wheat grain, the nonextractable residues following ammonia extraction were extracted with DMSO:water (9:1, v:v; 2x) at room temperature or refrigeration overnight. Following centrifugation, the DMSO:water extracts were combined with ethanol to precipitate starch. To further characterize the starch fraction in tolyl-label samples, the precipitate was redissolved in 0.05 M potassium phosphate buffer containing α - and β -amylases and amyloglucosidases, and was incubated overnight at 40 C.

A summary of the characterized and identified ¹⁴C-residues in selected rotational crop commodities is presented in Tables 75a (chlorophenyl label, 0.8 lb ai/A), 75b (chlorophenyl label, 1.3 lb ai/A), 75c (tolyl label, 0.8 lb ai/A), and 75d (tolyl label, 1.3 lb ai/A). Examples of those mature edible commodities for which significant further characterization/analysis attempts

were made were selected by the study reviewer for inclusion in these tables; for characterization of residues in the remaining matrices, refer to the distribution tables.

Table 74a. Distribution and characterization of radioactive residues in rotational crop commodities grown in soil treated with [chlorophenyl-¹⁴C]pyraclostrobin at 0.8 lb ai/A.

Fraction	% TRR	ppm	Characterization/Identification
30-DAT Immature radish tops (TRR = 0.013 ppm)			
Methanol	39.2	0.005	Not further analyzed (N/A).
Water	8.7	0.001	N/A.
Nonextractable	36.2	0.005	N/A.
30-DAT Immature radish roots (TRR = 0.027 ppm)			
Methanol	47.1	0.013	HPLC analysis resolved: Pyraclostrobin + 500M07 23.5% TRR 0.0065 ppm Polar region 18.6% TRR 0.0052 ppm (2 peaks) Medium polar region a 0.6% TRR 0.0002 ppm Medium polar region b 2.9% TRR 0.0008 ppm Nonpolar region 1.5% TRR 0.0004 ppm Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	18.1	0.005	N/A.
Ethyl acetate	5.9	0.002	N/A.
Aqueous	22.3	0.006	N/A.
Nonextractable	46.7	0.013	Extracted with ammonia.
Ammonia	5.6	0.001	N/A.
Nonextractable	30.1	0.008	N/A.
30-DAT Radish tops (TRR = 0.028 ppm)			
Methanol	38.8	0.011	HPLC analysis resolved: Pyraclostrobin + 500M07 36.4% TRR 0.0103 ppm Polar region 0.3% TRR 0.0001 ppm Medium polar region b 2.2% TRR 0.0006 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	14.8	0.004	N/A.
Ethyl acetate	12.9	0.004	N/A.
Aqueous	15.7	0.004	N/A.
Water	10.4	0.003	N/A.
Nonextractable	26.8	0.007	N/A.

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
30-DAT Radish roots (TRR = 0.040 ppm)			
Methanol	44.3	0.018	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 26.0% TRR 0.0106 ppm Polar region 11.3% TRR 0.0046 ppm Medium polar region b 6.3% TRR 0.0026 ppm (2 peaks) Nonpolar region 0.6% TRR 0.0003 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	17.2	0.007	N/A.
Ethyl acetate	8.0	0.003	N/A.
Aqueous	17.5	0.007	N/A.
Water	4.5	0.002	N/A.
Nonextractable	43.5	0.017	Extracted with ammonia.
Ammonia	3.2	0.001	N/A.
Nonextractable	29.5	0.012	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	8.4	0.003	N/A.
Nonextractable	32.3	0.013	N/A.
30-DAT Immature lettuce (TRR = 0.012 ppm)			
Methanol	45.6	0.005	N/A.
Water	8.4	0.001	N/A.
Nonextractable	23.2	0.003	N/A.
30-DAT Head lettuce (TRR = 0.011 ppm)			
Methanol	42.3	0.005	N/A.
Water	3.5	<0.001	N/A.
Nonextractable	40.6	0.004	N/A.
30-DAT Wheat forage (TRR = 0.019 ppm)			
Methanol	31.9	0.006	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 25.2% TRR 0.0047 ppm Polar region 2.7% TRR 0.0005 ppm (4 peaks) Medium polar region a 1.0% TRR 0.0001 ppm (4 peaks) Medium polar region b 3.0% TRR 0.0006 ppm (4 peaks)
Water	3.0	0.001	N/A.
Nonextractable	41.6	0.008	N/A.

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification		
30-DAT Wheat straw (TRR = 0.112 ppm)					
Methanol	21.4	0.024	HPLC analysis resolved:		
			Pyraclostrobin + 500M07	13.1% TRR	0.0147 ppm
			Polar region (2 peaks)	2.9% TRR	0.0032 ppm
			Medium polar region a	3.3% TRR	0.0037 ppm
			Medium polar region b (2 peaks)	1.1% TRR	0.0012 ppm
			Medium polar region c (3 peaks)	1.1% TRR	0.0012 ppm
			Partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	8.7	0.010	N/A.		
Ethyl acetate	6.3	0.007	N/A.		
Aqueous	7.5	0.008	N/A.		
Water	5.4	0.006	N/A.		
Nonextractable	63.2	0.071	Extracted with ammonia.		
Ammonia	7.6	0.009	N/A.		
Nonextractable	54.5	0.061	Separately subjected to base hydrolysis with NaOH and enzyme hydrolysis with Macerozyme and pronase.		
NaOH hydrolysate (SS1)	31.1	0.035	Acidified with HCl.		
Precipitate	18.8	0.021	Characterized as lignin .		
Supernatant	14.8	0.017			
Nonextractable	17.0	0.019	Characterized as cellulose .		
Macerozyme (SS2)	6.9	0.008	N/A.		
Nonextractable	46.9	0.053	N/A.		
Pronase (SS3)	1.5	0.002	N/A.		
Nonextractable	50.5	0.057	N/A.		
30-DAT Wheat grain (TRR = 0.078 ppm)					
Methanol	4.5	0.003	N/A.		
Water	4.5	0.003	N/A.		
Nonextractable	84.2	0.065	Extracted with ammonia.		
Ammonia	8.4	0.006	N/A.		
Nonextractable	75.8	0.059	Separately subjected to NaOH hydrolysis and extraction with DMSO.		
NaOH hydrolysate (SS1)	7.1	0.006	Acidified with HCl.		
Precipitate	20.5	0.016	Fractions characterized as lignin .		

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Supernatant	20.2	0.016	
Nonextractable	3.2	0.002	Characterized as cellulose .
DMSO (SS2)	3.3	0.003	Extracted with ethanol.
Ethanol	3.2	0.002	N/A.
Precipitate	15.3	0.012	Characterized as starch .
Nonextractable	47.3	0.037	N/A.
30-DAT Wheat chaff (TRR = 0.112 ppm)			
Methanol	13.4	0.015	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 5.9% TRR 0.0066 ppm Polar region 4.4% TRR 0.0049 ppm (3 peaks) Medium polar region a 1.7% TRR 0.0019 ppm Nonpolar region 1.3% TRR 0.0016 ppm (3 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	5.1	0.006	N/A.
Ethyl acetate	2.8	0.003	N/A.
Aqueous	5.4	0.006	N/A.
Water	3.8	0.004	N/A.
Nonextractable	71.4	0.080	Extracted with ammonia.
Ammonia	3.7	0.004	N/A.
Nonextractable	62.0	0.069	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	38.7	0.043	Acidified with HCl.
Precipitate	17.3	0.019	Fractions characterized as lignin .
Supernatant	14.8	0.017	
Nonextractable	17.5	0.020	Characterized as cellulose .
120-DAT Radish tops; 47-DAP (TRR = 0.006 ppm)			
Methanol	41.8	0.003	N/A.
Water	3.6	<0.001	N/A.
Nonextractable	35.4	0.002	N/A.
120-DAT Radish roots; 47-DAP (TRR = 0.007 ppm)			
Methanol	42.6	0.003	N/A.
Water	4.1	<0.001	N/A.
Nonextractable	23.4	0.002	N/A.
120-DAT Radish tops; 64-DAP (TRR = 0.011 ppm)			

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	32.1	0.004	N/A.
Water	5.4	0.001	N/A.
Nonextractable	38.8	0.004	N/A.
120-DAT Radish roots; 64-DAP (TRR = 0.006 ppm)			
Methanol	43.1	0.003	N/A.
Water	4.3	<0.001	N/A.
Nonextractable	36.2	0.002	N/A.
120-DAT Immature lettuce (TRR = 0.006 ppm)			
Methanol	34.1	0.002	N/A.
Water	6.7	<0.001	N/A.
Nonextractable	42.4	0.002	N/A.
120-DAT Head lettuce (TRR = 0.009 ppm)			
Methanol	34.8	0.003	N/A.
Water	8.8	0.001	N/A.
Nonextractable	45.0	0.004	N/A.
120-DAT Wheat forage (TRR = 0.022 ppm)			
Methanol	28.5	0.006	HPLC analysis resolved: Pyraclostrobin + 500M07 4.1% TRR 0.0009 ppm Polar region 21.1% TRR 0.0045 ppm (2 peaks) Medium polar region a 3.2% TRR 0.0006 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	6.6	0.001	N/A.
Ethyl acetate	3.3	0.001	N/A.
Aqueous	17.8	0.004	N/A.
Water	4.9	0.001	N/A.
Nonextractable	54.5	0.012	Extracted with ammonia.
Ammonia	4.7	0.001	N/A.
Nonextractable	42.7	0.010	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	8.6	0.002	N/A.
Nonextractable	39.8	0.009	N/A.
120-DAT Wheat straw (TRR = 0.079 ppm)			

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	15.0	0.012	<u>HPLC analysis resolved:</u>
			Pyraclostrobin + 500M07 1.4% TRR 0.0011 ppm
			Polar region 3.4% TRR 0.0027 ppm
			Medium polar region a (4 peaks) 5.1% TRR 0.0042 ppm
			Medium polar region b 2.0% TRR 0.0016 ppm
Medium polar region c 3.1% TRR 0.0025 ppm			
			Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	0.9	0.001	N/A.
Ethyl acetate	3.6	0.003	N/A.
Aqueous	6.9	0.005	N/A.
Water	3.9	0.003	N/A.
Nonextractable	79.9	0.063	Extracted with ammonia.
Ammonia	8.6	0.007	N/A.
Nonextractable	68.5	0.054	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	40.8	0.032	Acidified with HCl.
Precipitate	22.2	0.017	Fractions characterized as lignin .
Supernatant	17.4	0.014	
Nonextractable	25.6	0.020	Characterized as cellulose .
120-DAT Wheat grain (TRR = 0.079 ppm)			
Methanol	6.6	0.005	<u>HPLC analysis resolved:</u>
			Polar region 6.6% TRR 0.0050 ppm
			Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	2.1	0.002	N/A.
Ethyl acetate	0.4	<0.001	N/A.
Aqueous	2.4	0.002	N/A.
Water	5.1	0.004	N/A.
Nonextractable	72.9	0.058	Extracted with ammonia.
Ammonia	14.3	0.011	N/A.
Nonextractable	51.2	0.040	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	68.0	0.054	Acidified with HCl.
Precipitate	8.4	0.007	Fractions characterized as lignin .
Supernatant	56.9	0.045	
Nonextractable	1.6	0.001	Characterized as cellulose .

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
DMSO (SS2)	1.5	0.001	Extracted with ethanol.
Ethanol	2.7	0.002	N/A.
Precipitate	7.0	0.006	Characterized as starch .
Nonextractable	41.4	0.033	N/A.
120-DAT Wheat chaff (TRR = 0.092 ppm)			
Methanol	11.9	0.011	<u>HPLC analysis resolved:</u>
			Polar region 3.7% TRR 0.0034 ppm
			Medium polar region a 5.8% TRR 0.0054 ppm (2 peaks)
			Medium polar region c 2.4% TRR 0.0023 ppm
Partitioned with cyclohexane and ethyl acetate.			
Cyclohexane	1.8	0.002	N/A.
Ethyl acetate	3.2	0.003	N/A.
Aqueous	4.9	0.005	N/A.
Water	6.6	0.006	N/A.
Nonextractable	74.6	0.069	Extracted with ammonia.
Ammonia	5.6	0.005	N/A.
Nonextractable	66.7	0.061	Subjected to base extraction with NaOH.
NaOH hydrolysate	51.9	0.048	Acidified with HCl.
Precipitate	24.8	0.023	Fractions characterized as lignin .
Supernatant	42.7	0.039	
Nonextractable	23.1	0.021	Characterized as cellulose .
365-DAT Head lettuce (TRR = 0.007 ppm)			
Methanol	39.6	0.003	N/A.
Nonextractable	47.9	0.003	Extracted with ammonia.
Ammonia	9.8	0.001	N/A.
Nonextractable	37.3	0.003	Separately subjected to enzyme hydrolysis with Macerozyme and pronase.
Macero hydrolysate (SS1)	10.6	0.001	N/A.
Nonextractable	12.8	0.001	N/A.
Pronase hydrolysate (SS2)	8.6	0.001	N/A.
Nonextractable	16.8	0.001	N/A.
365-DAT Wheat forage (TRR = 0.014 ppm)			
Methanol	34.5	0.005	N/A.
Nonextractable	59.6	0.008	Extracted with ammonia.

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Ammonia	4.9	0.001	N/A.
Nonextractable	54.0	0.007	N/A.
365-DAT Wheat straw (TRR = 0.069 ppm)			
Methanol	30.8	0.021	<u>HPLC analysis resolved:</u>
			Pyraclostrobin + 500M07 3.3% TRR 0.0023 ppm
			Polar region (3 peaks) 2.7% TRR 0.0019 ppm
			Medium polar region a 2.9% TRR 0.0020 ppm
			Medium polar region c (3 peaks) 21.8% TRR 0.0149 ppm
			Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	13.2	0.009	N/A.
Ethyl acetate	7.3	0.005	N/A.
Aqueous	8.3	0.006	N/A.
Nonextractable	67.0	0.046	Subjected to extraction with ammonia.
Ammonia	9.9	0.007	N/A.
Nonextractable	56.4	0.039	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	31.2	0.022	Acidified with HCl.
Precipitate	12.4	0.009	Fractions characterized as lignin .
Supernatant	16.3	0.011	
Nonextractable	11.6	0.008	Characterized as cellulose .
365-DAT Wheat grain (TRR = 0.010 ppm)			
Methanol	5.5	0.001	N/A.
Nonextractable	94.7	0.009	Extracted with ammonia.
Ammonia	24.9	0.002	N/A.
Nonextractable	56.0	0.005	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	32.7	0.003	Acidified with HCl.
Precipitate	21.4	0.002	Fractions characterized as lignin .
Supernatant	37.9	0.004	
Nonextractable	13.0	0.001	Characterized as cellulose .
DMSO (SS2)	17.0	0.002	Extracted with ethanol.
Precipitate	9.0	0.001	Characterized as starch .
Supernatant	1.9	<0.001	N/A.
Nonextractable	29.8	0.003	N/A.

Table 74a (chlorophenyl label, 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification		
365-DAT Wheat chaff (TRR = 0.038 ppm)					
Methanol	24.2	0.009	HPLC analysis resolved:		
			Pyraclostrobin + 500M07	4.5% TRR	0.0017 ppm
			Polar region (2 peaks)	4.9% TRR	0.0019 ppm
			Medium polar region a	1.2% TRR	0.0004 ppm
			Medium polar region c	12.8% TRR	0.0047 ppm
			Nonpolar region	0.9% TRR	0.0003 ppm
Partitioned with cyclohexane and ethyl acetate.					
Cyclohexane	7.1	0.003	N/A.		
Ethyl acetate	7.4	0.003	N/A.		
Aqueous	8.9	0.003	N/A.		
Nonextractable	82.2	0.031	Extracted with ammonia.		
Ammonia	11.5	0.004	N/A.		
Nonextractable	68.0	0.026	Subjected to base extraction with NaOH.		
NaOH hydrolysate	31.9	0.012	Acidified with HCl.		
Precipitate	18.5	0.007	Fractions characterized as lignin .		
Supernatant	15.5	0.006			
Nonextractable	12.0	0.005	Characterized as cellulose .		

Table 74b. Distribution and characterization of radioactive residues in rotational crop commodities grown in soil treated with [chlorophenyl-¹⁴C]pyraclostrobin at 1.3 lb ai/A.

Fraction	% TRR	ppm	Characterization/Identification
30-DAT Immature radish tops (TRR = 0.016 ppm)			
Methanol	47.1	0.008	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 15.8% TRR 0.0027 ppm Polar region 12.2% TRR 0.0021 ppm (3 peaks) Medium polar region a 2.2% TRR 0.0004 ppm Medium polar region b 12.9% TRR 0.0021 ppm (2 peaks) Nonpolar region 4.0% TRR 0.0007 ppm (2 peaks)
Water	8.6	0.001	Not further analyzed (N/A).
Nonextractable	24.6	0.004	N/A.
30-DAT Immature radish roots (TRR = 0.026 ppm)			
Methanol	55.5	0.014	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 22.0% TRR 0.0055 ppm Polar region 20.3% TRR 0.0051 ppm Medium polar region b 9.5% TRR 0.0024 ppm (2 peaks) Nonpolar region 3.8% TRR 0.0009 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	22.8	0.006	N/A.
Ethyl acetate	7.5	0.002	N/A.
Aqueous	20.1	0.005	N/A.
Nonextractable	59.3	0.015	Extracted with ammonia.
Ammonia	7.4	0.002	N/A.
Nonextractable	33.4	0.009	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	9.5	0.002	N/A.
Nonextractable	42.7	0.011	N/A.
30-DAT Radish tops (TRR = 0.021 ppm)			
Methanol	35.3	0.008	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 7.7% TRR 0.0017 ppm Polar region 13.2% TRR 0.0030 ppm Medium polar region a 1.0% TRR 0.0002 ppm Medium polar region b 10.8% TRR 0.0025 ppm (2 peaks) Nonpolar region 2.6% TRR 0.0006 ppm (2 peaks)
Water	9.9	0.002	N/A.

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable	46.8	0.010	Extracted with ammonia.
Ammonia	2.6	0.001	N/A.
Nonextractable	41.5	0.009	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	20.2	0.004	N/A.
Nonextractable	12.0	0.003	N/A.
30-DAT Radish roots (TRR = 0.025 ppm)			
Methanol	40.5	0.010	HPLC analysis resolved: Pyraclostrobin + 500M07 7.5% TRR 0.0019 ppm Polar region 25.7% TRR 0.0063 ppm (2 peaks) Medium polar region b 6.3% TRR 0.0016 ppm Nonpolar region 1.0% TRR 0.0002 ppm Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	12.0	0.003	N/A.
Ethyl acetate	6.5	0.002	N/A.
Aqueous	20.9	0.005	N/A.
Nonextractable	54.9	0.014	Extracted with ammonia.
Ammonia	4.6	0.001	N/A.
Nonextractable	36.7	0.009	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	11.3	0.003	N/A.
Nonextractable	39.5	0.010	N/A.
30-DAT Immature lettuce (TRR = 0.012 ppm)			
Methanol	54.4	0.006	N/A.
Water	7.0	0.001	N/A.
Nonextractable	42.3	0.005	N/A.
30-DAT Head lettuce (TRR = 0.014 ppm)			
Methanol	40.1	0.005	N/A.
Water	5.8	0.001	N/A.
Nonextractable	35.1	0.005	N/A.
30-DAT Wheat forage (TRR = 0.019 ppm)			

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification		
Methanol	38.2	0.007	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin + 500M07	13.1% TRR	0.0024 ppm
			Polar region (2 peaks)	7.2% TRR	0.0013 ppm
			Medium polar region a (2 peaks)	6.9% TRR	0.0012 ppm
			Medium polar region b (3 peaks)	5.1% TRR	0.0010 ppm
			Nonpolar region (2 peaks)	5.8% TRR	0.0011 ppm
			Partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	20.5	0.005	N/A.		
Ethyl acetate	8.4	0.002	N/A.		
Aqueous	10.7	0.003	N/A.		
Water	3.8	0.001	N/A.		
Nonextractable	45.3	0.009	Extracted with ammonia.		
Ammonia	7.4	0.001	N/A.		
Nonextractable	33.5	0.006	N/A.		
30-DAT Wheat straw (TRR = 0.144 ppm)					
Methanol	26.5	0.038	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin + 500M07	12.3% TRR	0.0176 ppm
			Medium polar region a (2 peaks)	9.6% TRR	0.0138 ppm
			Medium polar region b	4.6% TRR	0.0066 ppm
			Partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	9.6	0.014	N/A.		
Ethyl acetate	8.2	0.012	N/A.		
Aqueous	8.3	0.012	N/A.		
Water	6.2	0.009	N/A.		
Nonextractable	72.7	0.105	Extracted with ammonia.		
Ammonia	8.1	0.012	N/A.		
Nonextractable	69.8	0.100	Separately subjected to base hydrolysis with NaOH and enzyme hydrolysis with Macerozyme and pronase.		
NaOH hydrolysate (SS1)	43.9	0.063	Acidified with HCl.		
Precipitate	21.8	0.031	Characterized as lignin .		
Supernatant	24.1	0.035			
Nonextractable	27.3	0.039	Characterized as cellulose .		

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Macerozyme (SS2)	11.2	0.016	N/A.
Nonextractable	57.3	0.083	N/A.
Pronase (SS3)	5.0	0.007	N/A.
Nonextractable	65.2	0.094	N/A.
30-DAT Wheat grain (TRR = 0.080 ppm)			
Methanol	5.2	0.004	Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	2.8	0.002	N/A.
Ethyl acetate	0.3	<0.001	N/A.
Aqueous	2.9	0.002	N/A.
Water	5.8	0.005	N/A.
Nonextractable	82.8	0.067	Extracted with ammonia.
Ammonia	11.2	0.009	N/A.
Nonextractable	66.1	0.053	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	8.9	0.007	Acidified with HCl.
Precipitate	16.4	0.013	Fractions characterized as lignin .
Supernatant	21.5	0.017	
Nonextractable	3.1	0.003	Characterized as cellulose .
DMSO (SS2)	2.9	0.002	Extracted with ethanol.
Ethanol	1.2	0.001	N/A.
Precipitate	26.7	0.022	Characterized as starch .
Nonextractable	26.6	0.021	N/A.
30-DAT Wheat chaff (TRR = 0.116 ppm)			
Methanol	13.6	0.016	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 8.2% TRR 0.0096 ppm Polar region 3.2% TRR 0.0037 ppm Medium polar region a 2.3% TRR 0.0026 ppm Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	4.8	0.006	N/A.
Ethyl acetate	2.5	0.003	N/A.
Aqueous	3.4	0.004	N/A.
Water	5.4	0.006	N/A.
Nonextractable	70.1	0.081	Extracted with ammonia.
Ammonia	4.4	0.005	N/A.

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable	59.1	0.069	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	50.4	0.059	Acidified with HCl.
Precipitate	21.9	0.025	Fractions characterized as lignin .
Supernatant	25.7	0.030	
Nonextractable	24.7	0.029	Characterized as cellulose .
120-DAT Radish tops; 47-DAP (TRR = 0.006 ppm)			
Methanol	33.5	0.002	N/A.
Water	4.2	<0.001	N/A.
Nonextractable	39.6	0.002	N/A.
120-DAT Radish roots; 47-DAP (TRR = 0.008 ppm)			
Methanol	44.3	0.004	N/A.
Water	11.2	0.001	N/A.
Nonextractable	35.0	0.003	N/A.
120-DAT Radish tops; 64-DAP (TRR = 0.009 ppm)			
Methanol	31.5	0.003	N/A.
Water	5.7	0.001	N/A.
Nonextractable	44.5	0.004	N/A.
120-DAT Radish roots; 64-DAP (TRR = 0.007 ppm)			
Methanol	41.4	0.003	N/A.
Water	5.0	<0.001	N/A.
Nonextractable	33.8	0.002	N/A.
120-DAT Immature lettuce (TRR = 0.006 ppm)			
Methanol	34.8	0.002	N/A.
Water	4.3	<0.001	N/A.
Nonextractable	40.6	0.003	N/A.
120-DAT Head lettuce (TRR = 0.011 ppm)			
Methanol	32.7	0.004	N/A.
Water	9.0	0.001	N/A.
Nonextractable	56.4	0.006	N/A.
120-DAT Wheat forage (TRR = 0.021 ppm)			

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	32.0	0.007	HPLC analysis resolved:
			Polar region 24.8% TRR 0.0054 ppm (3 peaks)
			Medium polar region a 7.2% TRR 0.0016 ppm
			Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	9.6	0.002	N/A.
Ethyl acetate	2.6	0.001	N/A.
Aqueous	18.1	0.004	N/A.
Water	5.8	0.001	N/A.
Nonextractable	45.8	0.010	Extracted with ammonia.
Ammonia	3.3	0.001	N/A.
Nonextractable	31.0	0.007	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	6.5	0.001	N/A.
Nonextractable	29.7	0.006	N/A.
120-DAT Wheat straw (TRR = 0.075 ppm)			
Methanol	20.1	0.015	HPLC analysis resolved:
			Pyraclostrobin + 500M07 0.8% TRR 0.0006 ppm
			Polar region 4.8% TRR 0.0036 ppm
			Medium polar region a 10.8% TRR 0.0081 ppm (2 peaks)
			Medium polar region b 1.9% TRR 0.0014 ppm
			Medium polar region c 1.8% TRR 0.0013 ppm
Partitioned with cyclohexane and ethyl acetate.			
Cyclohexane	4.9	0.004	N/A.
Ethyl acetate	6.1	0.005	N/A.
Aqueous	9.6	0.007	N/A.
Water	4.0	0.003	N/A.
Nonextractable	69.9	0.053	Extracted with ammonia.
Ammonia	5.2	0.004	N/A.
Nonextractable	59.2	0.045	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	29.6	0.022	Acidified with HCl.
Precipitate	22.4	0.017	Fractions characterized as lignin .
Supernatant	17.6	0.013	
Nonextractable	17.8	0.013	Characterized as cellulose .
120-DAT Wheat grain (TRR = 0.078 ppm)			

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	5.5	0.004	N/A.
Water	5.7	0.004	N/A.
Nonextractable	78.1	0.061	Extracted with ammonia.
Ammonia	14.5	0.011	N/A.
Nonextractable	53.4	0.042	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	55.3	0.043	Acidified with HCl.
Precipitate	2.6	0.002	Fractions characterized as lignin .
Supernatant	44.5	0.035	
Nonextractable	13.3	0.010	Characterized as cellulose .
DMSO (SS2)	2.0	0.002	Extracted with ethanol.
Ethanol	1.5	0.001	N/A.
Precipitate	13.9	0.011	Characterized as starch .
Nonextractable	23.9	0.019	N/A.
120-DAT Wheat chaff (TRR = 0.096 ppm)			
Methanol	15.1	0.015	HPLC analysis resolved: Pyraclostrobin + 500M07 0.7% TRR 0.0007 ppm Polar region 4.2% TRR 0.0042 ppm Medium polar region a 10.1% TRR 0.0101 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	1.6	0.002	N/A.
Ethyl acetate	5.3	0.005	N/A.
Aqueous	7.6	0.007	N/A.
Water	6.7	0.006	N/A.
Nonextractable	70.4	0.068	Extracted with ammonia.
Ammonia	6.1	0.006	N/A.
Nonextractable	59.2	0.057	Subjected to base extraction with NaOH.
NaOH hydrolysate	54.0	0.052	Acidified with HCl.
Precipitate	23.5	0.023	Fractions characterized as lignin .
Supernatant	43.1	0.041	
Nonextractable	18.8	0.018	Characterized as cellulose .

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
365-DAT Radish tops (TRR = 0.008 ppm)			
Methanol	27.6	0.002	N/A.
Nonextractable	52.5	0.004	Extracted with ammonia.
Ammonia	6.3	0.001	N/A.
Nonextractable	45.4	0.004	Separately subjected to enzyme hydrolysis with Macerozyme and pronase.
Macero hydrolysate (SS1)	12.2	0.001	N/A.
Nonextractable	30.4	0.003	N/A.
Pronase hydrolysate (SS2)	5.9	<0.001	N/A.
Nonextractable	25.8	0.002	N/A.
365-DAT Radish roots (TRR = 0.007 ppm)			
Methanol	33.2	0.002	N/A.
Nonextractable	33.2	0.002	Extracted with ammonia.
Ammonia	5.5	<0.001	N/A.
Nonextractable	35.3	0.002	Separately subjected to enzyme hydrolysis with Macerozyme and pronase.
Macero hydrolysate (SS1)	6.6	<0.001	N/A.
Nonextractable	12.5	0.001	N/A.
Pronase hydrolysate (SS2)	3.2	<0.001	N/A.
Nonextractable	13.4	0.001	N/A.
365-DAT Head lettuce (TRR = 0.007 ppm)			
Methanol	41.3	0.003	N/A.
Nonextractable	47.1	0.003	Extracted with ammonia.
Ammonia	11.8	0.001	N/A.
Nonextractable	40.1	0.003	N/A.
365-DAT Wheat forage (TRR = 0.018 ppm)			
Methanol	27.5	0.005	N/A.
Nonextractable	52.4	0.010	Extracted with ammonia.
Ammonia	4.0	0.001	N/A.
Nonextractable	47.7	0.009	Separately subjected to enzyme hydrolysis with Macerozyme and pronase.
Macero hydrolysate (SS1)	13.3	0.002	N/A.
Nonextractable	40.9	0.008	N/A.
Pronase hydrolysate (SS2)	7.2	0.001	N/A.

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification		
Nonextractable	38.7	0.007	N/A.		
365-DAT Wheat straw (TRR = 0.068 ppm)					
Methanol	25.3	0.017	<u>HPLC analysis resolved:</u>		
			Polar region	2.3% TRR	0.0015 ppm
			Medium polar region a (3 peaks)	13.1% TRR	0.0089 ppm
			Medium polar region b	1.7% TRR	0.0011 ppm
			Medium polar region c (2 peaks)	5.4% TRR	0.0036 ppm
			Nonpolar region	2.7% TRR	0.0018 ppm
			Partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	4.2	0.003	N/A.		
Ethyl acetate	6.9	0.005	N/A.		
Aqueous	7.2	0.005	N/A.		
Nonextractable	75.3	0.052	Extracted with ammonia.		
Ammonia	11.0	0.008	N/A.		
Nonextractable	63.5	0.043	Subjected to base hydrolysis with NaOH.		
NaOH hydrolysate	31.2	0.021	Acidified with HCl.		
Precipitate	13.5	0.009	Fractions characterized as lignin .		
Supernatant	15.7	0.011			
Nonextractable	18.1	0.012	Characterized as cellulose .		
365-DAT Wheat grain (TRR = 0.010 ppm)					
Methanol	7.8	0.001	N/A.		
Nonextractable	94.4	0.009	Extracted with ammonia.		
Ammonia	18.3	0.002	N/A.		
Nonextractable	42.1	0.004	Separately subjected to NaOH hydrolysis and extraction with DMSO.		
NaOH hydrolysate (SS1)	34.1	0.003	Acidified with HCl.		
Precipitate	12.3	0.001	Fractions characterized as lignin .		
Supernatant	31.1	0.003			
Nonextractable	2.0	<0.001	Characterized as cellulose .		
DMSO (SS2)	17.9	0.002	Extracted with ethanol.		
Precipitate	6.7	0.001	Characterized as starch .		
Supernatant	12.7	0.001	N/A.		
Nonextractable	34.8	0.003	N/A.		

Table 74b (chlorophenyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
365-DAT Wheat chaff (TRR = 0.042 ppm)			
Methanol	16.4	0.007	<u>HPLC analysis resolved:</u>
			Polar region 2.3% TRR 0.0010 ppm
			Medium polar region a 11.8% TRR 0.0050 ppm (3 peaks)
			Medium polar region b 1.6% TRR 0.0007 ppm
			Medium polar region c 0.8% TRR 0.0003 ppm
			Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	3.3	0.001	N/A.
Ethyl acetate	4.9	0.002	N/A.
Aqueous	9.0	0.004	N/A.
Nonextractable	74.6	0.031	Extracted with ammonia.
Ammonia	13.2	0.006	N/A.
Nonextractable	59.6	0.025	Subjected to base extraction with NaOH.
NaOH hydrolysate	36.1	0.015	Acidified with HCl.
Precipitate	13.8	0.006	Fractions characterized as lignin .
Supernatant	19.7	0.008	
Nonextractable	13.5	0.006	Characterized as cellulose .

Table 74c. Distribution and characterization of radioactive residues in rotational crop commodities grown in soil treated with [tolyl-¹⁴C]pyraclostrobin at 0.8 lb ai/A.

Fraction	% TRR	ppm	Characterization/Identification		
30-DAT Immature radish tops (TRR = 0.015 ppm)					
Methanol	61.0	0.009	Partitioned with cyclohexane and ethyl acetate.		
Cyclohexane	19.1	0.003	Not further analyzed (N/A).		
Ethyl acetate	12.1	0.002	N/A.		
Aqueous	22.6	0.003	N/A.		
Nonextractable	57.1	0.008	N/A.		
30-DAT Immature radish roots (TRR = 0.019 ppm)					
Methanol	55.4	0.011	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin	7.0% TRR	0.0014 ppm
			500M07	3.6% TRR	0.0007 ppm
			Polar region	41.9% TRR	0.0083 ppm
			Medium polar region b	2.9% TRR	0.006 ppm
Nonextractable	32.8	0.006	N/A.		
30-DAT Radish tops (TRR = 0.025 ppm)					
Methanol	39.5	0.010	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin + 500M07	4.4% TRR	0.0011 ppm
			Polar region	8.1% TRR	0.0021 ppm
			Medium polar region a (3 peaks)	20.4% TRR	0.0051 ppm
			Medium polar region b (2 peaks)	6.7% TRR	0.0017 ppm
Nonextractable	52.5	0.013	Subjected to enzyme hydrolysis with Macerozyme.		
Macero hydrolysate	24.9	0.006	HPLC analysis resolved two regions, one corresponding to [¹⁴ C]glucose.		
Nonextractable	19.1	0.005	N/A.		
30-DAT Radish roots (TRR = 0.025 ppm)					
Methanol	45.9	0.012	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin	9.0% TRR	0.0024 ppm
			500M07	0.8% TRR	0.0002 ppm
			Polar region	29.9% TRR	0.0078 ppm
			Medium polar region a	1.7% TRR	0.0004 ppm
			Medium polar region b (2 peaks)	4.6% TRR	0.0012 ppm
Nonextractable	44.7	0.011	Sequentially extracted with ammonia and subjected to enzyme hydrolysis with Macerozyme.		
Ammonia	5.0	0.001	N/A.		
Macero hydrolysate	13.6	0.003	N/A.		
Nonextractable	15.2	0.004	N/A.		
30-DAT Immature lettuce (TRR = 0.014 ppm)					
Methanol	47.0	0.006	N/A.		
Nonextractable	64.9	0.009	N/A.		

Table 74c (tolyl label 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
30-DAT Head lettuce (TRR = 0.013 ppm)			
Methanol	42.1	0.005	N/A.
Nonextractable	55.3	0.007	N/A.
30-DAT Wheat forage (TRR = 0.019 ppm)			
Methanol	26.5	0.005	N/A.
Nonextractable	65.0	0.013	Sequentially subjected to enzyme hydrolysis with Macerozyme and pronase, and extracted with ammonia.
Macero hydrolysate	18.9	0.004	HPLC resolved three regions.
Pronase hydrolysate	12.0	0.002	N/A.
Ammonia	3.1	0.001	N/A.
Nonextractable	22.4	0.004	N/A.
30-DAT Wheat straw (TRR = 0.114 ppm)			
Methanol	16.6	0.019	HPLC analysis resolved: Pyraclostrobin + 500M07 10.5% TRR 0.0120 ppm Polar region 6.1% TRR 0.0070 ppm (2 peaks)
Water	6.7	0.008	N/A.
Ammonia	2.7	0.003	N/A.
Nonextractable	63.2	0.072	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	38.9	0.044	Acidified with HCl.
Precipitate	0.3	<0.001	Characterized as lignin .
Supernatant	29.3	0.033	
Nonextractable	17.9	0.020	Characterized as cellulose .
30-DAT Wheat grain (TRR = 0.082 ppm)			
Methanol	6.5	0.005	N/A.
Water	7.0	0.006	N/A.
Ammonia	10.5	0.009	N/A.
Nonextractable	73.7	0.060	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	61.0	0.050	Acidified with HCl.
Precipitate	8.8	0.007	Fractions characterized as lignin .
Supernatant	55.6	0.045	
Nonextractable	3.8	0.003	Characterized as cellulose .
DMSO (SS2)	22.4	0.018	Sequentially extracted with ethanol and subjected to enzyme hydrolysis with amylase/amyloglucosidase.
Ethanol	2.0	0.002	N/A.
Amylase hydrolysate	16.4	0.013	Characterized as starch .
Amylase residue	2.3	0.002	N/A.

Table 74c (tolyl label 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable	47.6	0.039	N/A.
30-DAT Wheat chaff (TRR = 0.098 ppm)			
Methanol	13.2	0.013	HPLC analysis resolved: Pyraclostrobin + 500M07 7.4% TRR 0.0073 ppm Polar region 5.8% TRR 0.0057 ppm (2 peaks)
Water	4.8	0.005	N/A.
Ammonia	2.9	0.003	N/A.
Nonextractable	79.6	0.078	Subjected to base extraction with NaOH.
NaOH hydrolysate	48.9	0.048	Acidified with HCl.
Precipitate	12.0	0.012	Fractions characterized as lignin .
Supernatant	26.2	0.026	
Nonextractable	20.7	0.020	Characterized as cellulose .
120-DAT Radish tops (TRR = 0.011 ppm)			
Methanol	35.2	0.003	N/A.
Nonextractable	67.9	0.006	N/A.
120-DAT Head lettuce (TRR = 0.007 ppm)			
Methanol	37.1	0.004	N/A.
Nonextractable	62.1	0.007	N/A.
120-DAT Wheat forage (TRR = 0.022 ppm)			
Methanol	29.7	0.006	N/A.
Nonextractable	75.4	0.016	Sequentially subjected to enzyme hydrolysis with Macerozyme, extraction with ammonia, and enzyme hydrolysis with pronase.
Macero hydrolysate	16.3	0.004	HPLC analysis resolved two major regions.
Ammonia	11.1	0.002	N/A.
Pronase hydrolysate	2.2	<0.001	N/A.
Nonextractable	36.0	0.008	N/A.
120-DAT Wheat straw (TRR = 0.081 ppm)			
Methanol	11.6	0.009	N/A.
Water	3.9	0.003	N/A.
Ammonia	1.9	0.002	N/A.
Nonextractable	68.2	0.055	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	37.2	0.030	Acidified with HCl.

Table 74c (tolyl label 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Precipitate	1.3	0.001	Fractions characterized as lignin .
Supernatant	25.7	0.021	
Nonextractable	23.0	0.018	Characterized as cellulose .
120-DAT Wheat grain (TRR = 0.089 ppm)			
Methanol	6.3	0.006	N/A.
Water	5.7	0.005	N/A.
Ammonia	10.1	0.009	N/A.
Nonextractable	71.6	0.064	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	58.6	0.052	Acidified with HCl.
Precipitate	0.9	0.001	Fractions characterized as lignin .
Supernatant	60.1	0.054	
Nonextractable	2.5	0.002	Characterized as cellulose .
DMSO (SS2)	43.3	0.039	Sequentially extracted with ethanol and subjected to enzyme hydrolysis with amylase/amyloglucosidase.
Ethanol	4.5	0.004	N/A.
Amylase hydrolysate	40.5	0.036	Characterized as starch . HPLC analysis resolved one major and two smaller regions.
Amylase residue	1.9	0.002	N/A.
Nonextractable	20.4	0.018	N/A.
120-DAT Wheat chaff (TRR = 0.102 ppm)			
Methanol	9.3	0.009	N/A.
Water	6.2	0.006	N/A.
Ammonia	6.8	0.007	N/A.
Nonextractable	64.1	0.065	Subjected to base extraction with NaOH.
NaOH hydrolysate	46.6	0.048	Acidified with HCl.
Precipitate	5.5	0.006	Fractions characterized as lignin .
Supernatant	40.0	0.041	
Nonextractable	12.6	0.013	Characterized as cellulose .
365-DAT Radish tops (TRR = 0.010 ppm)			
Methanol	23.6	0.002	N/A.
Nonextractable	43.4	0.004	N/A.
365-DAT Radish roots (TRR = 0.014 ppm)			
Methanol	40.4	0.006	N/A.
Nonextractable	48.3	0.007	N/A.

Table 74c (tolyl label 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
365-DAT Immature lettuce (TRR = 0.013 ppm)			
Methanol	39.0	0.005	N/A.
Nonextractable	31.5	0.004	Separately subjected to extraction with ammonia and enzyme hydrolysis with Macerozyme.
Ammonia (SS1)	3.6	<0.001	N/A.
Nonextractable	12.3	0.002	N/A.
Macero hydrolysate (SS2)	8.3	0.001	N/A.
Nonextractable	13.5	0.002	N/A.
365-DAT Head lettuce (TRR = 0.017 ppm)			
Methanol	32.3	0.006	N/A.
Nonextractable	40.2	0.007	N/A.
365-DAT Wheat forage (TRR = 0.016 ppm)			
Methanol	48.3	0.008	HPLC analysis resolved: 500M07 2.2% TRR 0.0004 ppm Polar region 35.9% TRR 0.0059 ppm Medium polar region a 10.2% TRR 0.0017 ppm
Nonextractable	68.9	0.011	Separately subjected to enzyme hydrolysis with Macerozyme and extraction with ammonia.
Macero hydrolysate (SS1)	23.5	0.004	N/A.
Nonextractable	43.1	0.007	N/A.
Ammonia (SS2)	9.4	0.002	N/A.
Nonextractable	40.4	0.007	N/A.
365-DAT Wheat straw (TRR = 0.067 ppm)			
Methanol	12.9	0.009	HPLC analysis resolved: Pyraclostrobin + 500M07 1.4% TRR 0.0010 ppm Polar region 3.2% TRR 0.0022 ppm Medium polar region c 8.3% TRR 0.0058 ppm (2 peaks)
Water	4.8	0.003	N/A.
Ammonia	3.5	0.002	N/A.
Nonextractable	68.8	0.046	Extracted with ammonia.
Ammonia	2.9	0.002	N/A.
Nonextractable	69.9	0.047	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	6.9	0.005	Acidified with HCl.
Precipitate	4.4	0.003	Fractions characterized as lignin .
Supernatant	6.0	0.004	
Nonextractable	21.2	0.014	Characterized as cellulose .
365-DAT Wheat grain (TRR = 0.013 ppm)			
Methanol	4.6	0.001	N/A.

Table 74c (toyl label 0.8 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Water	5.6	0.001	N/A.
Ammonia	15.4	0.002	N/A.
Nonextractable	53.7	0.007	Extracted with ammonia.
Ammonia	9.9	0.001	N/A.
Nonextractable	45.3	0.006	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	26.9	0.003	Acidified with HCl.
Precipitate	36.0	0.005	Fractions characterized as lignin .
Supernatant	31.9	0.004	
Nonextractable	2.5	<0.001	Characterized as cellulose .
DMSO (SS2)	28.3	0.004	Extracted with ethanol.
Precipitate	14.1	0.002	Characterized as starch .
Supernatant	11.8	0.002	N/A.
Nonextractable	20.1	0.003	N/A.
365-DAT Wheat chaff (TRR = 0.032 ppm)			
Methanol	12.6	0.004	N/A.
Water	5.4	0.002	N/A.
Ammonia	5.7	0.002	N/A.
Nonextractable	78.8	0.025	Extracted with ammonia.
Ammonia	7.1	0.002	N/A.
Nonextractable	82.4	0.027	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	41.8	0.013	Acidified with HCl.
Precipitate	28.4	0.009	Fractions characterized as lignin .
Supernatant	33.6	0.011	
Nonextractable	29.7	0.010	Characterized as cellulose .

Table 74d. Distribution and characterization of radioactive residues in rotational crop commodities grown in soil treated with [tolyl-¹⁴C]pyraclostrobin at 1.3 lb ai/A.

Fraction	% TRR	ppm	Characterization/Identification
30-DAT Immature radish tops (TRR = 0.024 ppm)			
Methanol	54.8	0.013	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 5.4% TRR 0.0013 ppm Polar region 17.4% TRR 0.0041 ppm Medium polar region a 17.0% TRR 0.0040 ppm Medium polar region b 13.5% TRR 0.0032 ppm Nonpolar region 1.4% TRR 0.0003 ppm
Nonextractable	46.0	0.011	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	28.3	0.007	Not further analyzed (N/A).
Nonextractable	12.5	0.003	N/A.
30-DAT Immature radish roots (TRR = 0.046 ppm)			
Methanol	66.9	0.031	<u>HPLC analysis resolved:</u> Pyraclostrobin 24.9% TRR 0.0115 ppm 500M07 2.2% TRR 0.0010 ppm Polar region 24.8% TRR 0.0115 ppm Medium polar region b 15.0% TRR 0.0069 ppm (2 peaks)
Nonextractable	29.2	0.013	N/A.
30-DAT Radish tops (Work-up 1; TRR = 0.046 ppm)			
Methanol	47.0	0.022	<u>HPLC analysis resolved:</u> Pyraclostrobin 13.0% TRR 0.0061 ppm 500M07 0.4% TRR 0.0002 ppm Polar region 5.1% TRR 0.0024 ppm Medium polar region a 20.3% TRR 0.0095 ppm (3 peaks) Medium polar region b 7.9% TRR 0.0037 ppm (2 peaks) Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	10.2	0.005	HPLC analysis resolved pyraclostrobin; quantitative results were not provided.
Ethyl acetate	15.3	0.007	HPLC analysis resolved the peaks in the medium polar region b; quantitative results were not provided.
Aqueous	20.7	0.010	HPLC analysis resolved peaks in the polar and medium polar region a; quantitative results were not provided..
Nonextractable	53.5	0.025	Sequentially subjected to enzyme hydrolysis with Macerozyme and amylase/amyloglucosidase.
Macero hydrolysate	31.2	0.014	HPLC analysis resolved two regions, one corresponding to [¹⁴ C]glucose by co-chromatography.
Amylase hydrolysate	3.0	0.001	N/A.
Nonextractable	15.7	0.007	N/A.
30-DAT Radish tops (Work-up 2; TRR = 0.045 ppm)			

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	47.7	0.021	N/A.
Nonextractable	50.9	0.023	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	31.7	0.014	Acidified with HCl.
Precipitate	1.3	0.001	Fractions characterized as lignin .
Supernatant	22.3	0.010	
Nonextractable	5.5	0.002	Characterized as cellulose .
30-DAT Radish roots (TRR = 0.056 ppm)			
Methanol	46.1	0.026	<u>HPLC analysis resolved:</u> Pyraclostrobin 22.0% TRR 0.0124 ppm 500M07 1.4% TRR 0.0008 ppm Polar region 15.3% TRR 0.0086 ppm Medium polar region a 1.1% TRR 0.0006 ppm Medium polar region b 4.4% TRR 0.0025 ppm (2 peaks) Nonpolar region 1.9% TRR 0.0010 ppm (2 peaks) Partitioned with ethyl acetate
Ethyl acetate	23.6	0.013	HPLC analysis resolved pyraclostrobin; quantitative results were not provided.
Aqueous	16.8	0.009	HPLC one major polar peak.
Nonextractable	45.4	0.025	Sequentially extracted with ammonia, and subjected to enzyme hydrolysis with Macerozyme, amylase/amyloglucosidase, and pronase.
Ammonia	5.6	0.003	N/A.
Macero hydrolysate	8.9	0.005	Partitioned with ethyl acetate
Ethyl acetate	0.2	<0.001	N/A.
Aqueous	9.2	0.005	HPLC analysis resolved one major peak that corresponded to [¹⁴ C]glucose by co-chromatography.
Amylase hydrolysate	2.8	0.002	N/A.
Pronase hydrolysate	1.2	0.001	N/A.
Nonextractable	16.7	0.009	N/A.
30-DAT Immature lettuce (TRR = 0.017 ppm)			
Methanol	45.9	0.008	Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	7.6	0.001	N/A.
Ethyl acetate	4.0	0.001	N/A.
Aqueous	29.9	0.005	N/A.
Nonextractable	57.2	0.010	N/A.
30-DAT Head lettuce (TRR = 0.017 ppm)			
Methanol	36.9	0.006	<u>HPLC analysis resolved:</u> Polar region 36.9% TRR 0.0060 ppm

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Water	7.1	0.001	N/A.
Nonextractable	50.0	0.008	N/A.
30-DAT Wheat forage (TRR = 0.026 ppm)			
Methanol	34.0	0.009	<u>HPLC analysis resolved:</u>
			Polar region 25.6% TRR 0.0068 ppm Medium polar region a 8.4% TRR 0.0022 ppm
			Partitioned with ACN:water and iso-octane.
ACN:water	18.3	0.005	Partitioned with ACN:water and iso-octane.
ACN:water	19.1	0.005	N/A.
iso-Octane	1.0	<0.001	N/A.
Aqueous	2.0	0.001	N/A.
iso-Octane	4.6	0.001	N/A.
Aqueous	9.8	0.003	N/A.
Nonextractable	68.5	0.018	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	25.9	0.007	N/A.
Nonextractable	51.1	0.013	N/A.
30-DAT Wheat straw (Work-up 1; TRR = 0.125 ppm)			
Methanol	19.5	0.024	Separately combined with water extract for HPLC analysis and partitioned with ethyl acetate.
Ethyl acetate	11.6	0.014	HPLC analysis resolved pyraclostrobin and several minor peaks; quantitative results were not provided.
Water	6.9	0.009	N/A.
Water	7.9	0.010	Combined with methanol extract for HPLC analysis (27.4% TRR, 0.034 ppm).
			<u>HPLC analysis resolved:</u>
			Pyraclostrobin 9.2% TRR 0.0113 ppm
			500M07 1.7% TRR 0.0021 ppm
			Polar region 5.6% TRR 0.0069 ppm (3 peaks)
Medium polar region a 6.7% TRR 0.0085 ppm			
Medium polar region b 4.3% TRR 0.0053 ppm			
Ammonia	3.6	0.004	N/A.
Nonextractable	62.3	0.078	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	39.3	0.049	Acidified with HCl.
Precipitate	27.2	0.034	Characterized as lignin .
Supernatant	24.3	0.030	Characterized as lignin . Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	6.7	0.008	N/A.
Nonextractable	6.1	0.008	N/A.

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Nonextractable	22.0	0.027	Characterized as cellulose . Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	3.6	0.004	N/A.
Nonextractable	11.1	0.014	N/A.
30-DAT Wheat straw (Work-up 2; TRR = 0.125 ppm)			
Methanol	19.7	0.025	N/A.
Water	7.3	0.009	N/A.
Ammonia	2.9	0.004	N/A.
Nonextractable	58.7	0.073	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	31.3	0.039	Acidified with HCl.
HCl precipitate	1.6	0.002	Characterized as lignin .
Supernatant	21.9	0.027	
Nonextractable	18.2	0.023	Characterized as cellulose .
30-DAT Wheat grain (Work-up 1; TRR = 0.085 ppm)			
Methanol + Water	11.4	0.010	HPLC analysis resolved: Polar region 11.4% TRR 0.0100 ppm (2 peaks) Partitioned with ethyl acetate.
Ethyl acetate	0.9	0.001	N/A.
Water	7.8	0.007	N/A.
Ammonia	10.6	0.009	N/A.
Nonextractable	74.2	0.063	Separately subjected to base hydrolysis with NaOH and two separate extractions with DMSO.
NaOH hydrolysate (SS1)	60.1	0.051	Acidified with HCl.
Precipitate	23.0	0.020	Fractions characterized as lignin .
Supernatant	47.9	0.041	
Nonextractable	2.2	0.002	Characterized as cellulose .
DMSO (SS2)	36.2	0.031	Extracted with ethanol.
Precipitate	43.3	0.037	Characterized as starch .
Supernatant	6.4	0.005	N/A.
Nonextractable	28.5	0.024	N/A.
DMSO (SS3)	21.8	0.019	Sequentially extracted with ethanol and subjected to enzyme hydrolysis with amylase/amyloglucosidase
Ethanol	2.4	0.002	N/A.
Amylase hydrolysate	23.1	0.020	N/A.
Amylase residue	1.7	0.001	N/A.
Nonextractable	37.4	0.032	N/A.
30-DAT Wheat grain (Work-up 2; TRR = 0.085 ppm)			

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification		
Methanol	4.8	0.004	N/A.		
Water	5.6	0.005	N/A.		
Ammonia	14.2	0.012	N/A.		
Macero hydrolysate	6.0	0.005	N/A.		
Nonextractable	63.3	0.054	Separately subjected to NaOH hydrolysis and extraction with DMSO.		
NaOH hydrolysate (SS1)	55.0	0.047	Acidified with HCl.		
Precipitate	12.7	0.011	Fractions characterized as lignin .		
Supernatant	43.1	0.037			
Nonextractable	2.5	0.002	Characterized as cellulose .		
DMSO (SS2)	16.0	0.014	Sequentially extracted with ethanol and subjected to enzyme hydrolysis with amylase/amyloglucosidase.		
Ethanol	3.6	0.003	N/A.		
Amylase hydrolysate	13.0	0.011	Characterized as starch .		
Amylase residue	0.9	0.001	N/A.		
Nonextractable	43.5	0.037	N/A.		
30-DAT Wheat chaff (TRR = 0.104 ppm)					
Methanol	10.1	0.011	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin	1.6% TRR	0.0018 ppm
			500M07	0.3% TRR	0.0003 ppm
			Polar region	8.2% TRR	0.0090 ppm
Water	5.7	0.006	N/A.		
Ammonia	4.0	0.004	N/A.		
Nonextractable	76.3	0.079	Subjected to acid hydrolysis with HCl.		
HCl hydrolysate	0.7	0.001	N/A.		
Nonextractable	71.5	0.074	Subjected to base hydrolysis with NaOH.		
NaOH hydrolysate	59.3	0.062	Acidified with HCl.		
Precipitate	14.5	0.015	Fractions characterized as lignin .		
Supernatant	27.8	0.029			
Nonextractable	9.2	0.010	Characterized as cellulose .		
120-DAT Radish tops (48 DAP; TRR =0.025 ppm)					
Methanol	58.1	0.015	<u>HPLC analysis resolved:</u>		
			Pyraclostrobin	45.6% TRR	0.0118 ppm
			500M07	7.1% TRR	0.0018 ppm
			Polar region	2.6% TRR	0.0007 ppm
			Medium polar region b (2 peaks)	2.7% TRR	0.0006 ppm
Nonextractable	30.3	0.008	N/A.		
120-DAT Radish roots (48 DAP; TRR =0.015 ppm)					

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	42.1	0.006	Partitioned with ethyl acetate.
Ethyl acetate	21.8	0.003	N/A.
Aqueous	18.6	0.003	N/A.
Nonextractable	45.0	0.007	N/A.
120-DAT Radish tops (64 DAP; TRR = 0.016 ppm)			
Methanol	37.9	0.006	N/A.
Nonextractable	60.0	0.010	N/A.
120-DAT Head lettuce (TRR = 0.023 ppm)			
Methanol	34.7	0.008	Partitioned with cyclohexane and ethyl acetate.
Cyclohexane	9.5	0.002	N/A.
Ethyl acetate	1.9	<0.001	N/A.
Aqueous	21.1	0.005	N/A.
Nonextractable	63.5	0.014	Subjected to enzyme hydrolysis with Macerozyme.
Macero hydrolysate	29.5	0.007	N/A.
Nonextractable	27.3	0.006	N/A.
120-DAT Wheat forage (TRR = 0.027 ppm)			
Methanol	25.4	0.007	N/A.
Nonextractable	66.0	0.018	Sequentially subjected to enzyme hydrolysis with Macerozyme and pronase, and extracted with ammonia.
Macero hydrolysate	16.5	0.004	N/A.
Pronase hydrolysate	8.6	0.002	N/A.
Ammonia	1.8	<0.001	N/A.
Nonextractable	27.7	0.007	N/A.
120-DAT Wheat straw (TRR = 0.088 ppm)			
Methanol	15.5	0.014	HPLC analysis resolved: Pyraclostrobin + 500M07 1.4% TRR 0.0013 ppm Polar region 2.5% TRR 0.0023 ppm (2 peaks) Medium polar region a 4.8% TRR 0.0044 ppm Medium polar region b 4.8% TRR 0.0043 ppm (2 peaks) Medium polar region c 2.0% TRR 0.0018 ppm
Water	4.8	0.004	N/A.
Ammonia	1.8	0.002	N/A.
Nonextractable	65.1	0.058	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	37.9	0.034	Acidified with HCl.
Precipitate	0.8	0.001	Fractions characterized as lignin .
Supernatant	33.0	0.029	
Nonextractable	21.6	0.019	Characterized as cellulose .

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
120-DAT Wheat grain (TRR = 0.091 ppm)			
Methanol	6.9	0.006	N/A.
Water	6.9	0.006	N/A.
Ammonia	11.6	0.011	Partitioned with ethyl acetate.
Ethyl acetate	0.1	<0.001	N/A.
Aqueous	11.9	0.011	N/A.
Nonextractable	64.6	0.059	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	55.8	0.051	Acidified with HCl.
Precipitate	0.2	<0.001	Fractions characterized as lignin .
Supernatant	53.3	0.049	
Nonextractable	2.2	0.002	Characterized as cellulose .
DMSO (SS2)	34.9	0.032	Sequentially extracted with ethanol and subjected to enzyme hydrolysis with amylase/amyloglucosidase.
Ethanol	2.9	0.003	N/A.
Amylase hydrolysate	32.0	0.029	Characterized as starch . HPLC analysis resolved two peak regions.
Amylase residue	1.7	0.002	N/A.
Nonextractable	24.5	0.022	N/A.
120-DAT Wheat chaff (TRR = 0.109 ppm)			
Methanol	12.6	0.014	<u>HPLC analysis resolved:</u> Polar region 12.6% TRR 0.0140 ppm (2 peaks)
Water	7.8	0.008	N/A.
Ammonia	6.5	0.007	N/A.
Nonextractable	61.3	0.067	Subjected to base extraction with NaOH.
NaOH hydrolysate	35.5	0.039	Acidified with HCl.
Precipitate	7.1	0.008	Fractions characterized as lignin .
Supernatant	33.3	0.036	
Nonextractable	13.5	0.015	Characterized as cellulose .
365-DAT Radish tops (TRR = 0.014 ppm)			
Methanol	23.9	0.003	N/A.
Nonextractable	39.9	0.006	N/A.
365-DAT Radish roots (TRR = 0.019 ppm)			
Methanol	42.6	0.008	<u>HPLC analysis resolved:</u> Polar region 41.4% TRR 0.0078 ppm Nonpolar region 1.2% TRR 0.0002 ppm
Nonextractable	24.2	0.005	N/A.
365-DAT Immature lettuce (TRR = 0.014 ppm)			

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Methanol	35.3	0.005	N/A.
Nonextractable	35.0	0.005	N/A.
365-DAT Head lettuce (TRR = 0.023 ppm)			
Methanol	32.6	0.008	<u>HPLC analysis resolved:</u> Polar region 32.6% TRR 0.0080 ppm
Nonextractable	32.4	0.007	N/A.
365-DAT Wheat forage (TRR = 0.018 ppm)			
Methanol	22.5	0.004	N/A.
Nonextractable	36.2	0.006	N/A.
365-DAT Wheat straw (TRR = 0.073 ppm)			
Methanol	18.3	0.013	<u>HPLC analysis resolved:</u> Pyraclostrobin + 500M07 2.5% TRR 0.0018 ppm Polar region 3.5% TRR 0.0025 ppm Medium polar region c 12.2% TRR 0.0087 ppm (2 peaks)
Water	9.3	0.007	N/A.
Ammonia	4.7	0.003	N/A.
Nonextractable	76.0	0.055	Extracted with ammonia.
Ammonia	6.0	0.004	N/A.
Nonextractable	72.6	0.053	Subjected to base hydrolysis with NaOH.
NaOH hydrolysate	13.7	0.010	Acidified with HCl.
Precipitate	9.1	0.007	Fractions characterized as lignin .
Supernatant	7.3	0.005	
Nonextractable	22.6	0.016	Characterized as cellulose .
365-DAT Wheat grain (TRR = 0.017 ppm)			
Methanol	5.7	0.001	N/A.
Water	6.0	0.001	N/A.
Ammonia	12.3	0.002	N/A.
Nonextractable	59.0	0.010	Extracted with ammonia.
Ammonia	4.9	0.001	N/A.
Nonextractable	46.8	0.008	Separately subjected to NaOH hydrolysis and extraction with DMSO.
NaOH hydrolysate (SS1)	37.3	0.006	Acidified with HCl.
Precipitate	58.9	0.010	Fractions characterized as lignin .
Supernatant	31.5	0.005	
Nonextractable	2.1	<0.001	Characterized as cellulose .
DMSO (SS2)	14.6	0.002	Extracted with ethanol.
Precipitate	19.3	0.003	Characterized as starch .

Table 74d (tolyl label, 1.3 lb ai/A; continued).

Fraction	% TRR	ppm	Characterization/Identification
Supernatant	8.0	0.001	N/A.
Nonextractable	27.9	0.005	N/A.
365-DAT Wheat chaff (TRR = 0.043 ppm)			
Methanol	10.7	0.005	N/A.
Water	6.5	0.003	N/A.
Ammonia	6.0	0.003	N/A.
Nonextractable	39.9	0.017	Extracted with ammonia.
Ammonia	5.8	0.003	N/A.
Nonextractable	45.0	0.020	Subjected to base extraction with NaOH.
NaOH hydrolysate	19.9	0.009	Acidified with HCl.
Precipitate	12.9	0.006	Fractions characterized as lignin .
Supernatant	31.4	0.014	
Nonextractable	15.4	0.007	Characterized as cellulose .

Table 75a. Identification/characterization of radioactive residues in rotational crop commodities grown in soil treated with [chlorophenyl-¹⁴C]pyraclostrobin at 0.8 lb ai/A. ^a

Fraction	Radish root		Radish tops		Head lettuce		Wheat forage		Wheat straw		Wheat grain	
30-DAT Plantback	TRR = 0.040 ppm		TRR = 0.028 ppm		TRR = 0.011 ppm		TRR = 0.019 ppm		TRR = 0.112 ppm		TRR = 0.078 ppm	
Identified ^b												
Pyraclostrobin + 500M07 (BF 500-3)	26.0	0.0106	36.4	0.0103			25.2	0.0047	13.1	0.0147	NA	
Characterized												
Polar region	11.3	0.0046	0.3	0.0001			2.7	0.0005	2.9	0.0032	NA	
Med. polar region a	--	--	--	--			1.0	0.0001	3.3	0.0037	NA	
Med. polar region b	6.3	0.0026	2.2	0.0006			3.0	0.0006	1.1	0.0012	NA	
Med. polar region c	--	--	--	--			--	--	1.1	0.0012	NA	
Nonpolar region	0.6	0.0003	--	--			--	--	--	--	NA	
Lignin, precipitate	NA		NA				NA		18.8	0.021	20.5	0.016
Lignin, supernatant	NA		NA				NA		14.8	0.017	20.2	0.016
Cellulose	NA		NA				NA		17.0	0.019	3.2	0.002
Macero hydrolysate	8.4	0.003	NA				NA		NR		NA	
Starch ^c	NA		NA				NA		NA		NR	
Methanol extract	NR		NR				NR		NR		4.5	0.003
Water extract	4.5	0.002	10.4	0.003			3.0	0.001	5.4	0.006	4.5	0.003
Ammonia extract	3.2	0.001	NA				NA		7.6	0.009	8.4	0.006
Total characterized/ identified	60.3	0.024	49.3	0.014			34.9	0.007	85.1	0.096	61.3	0.046
Nonextractable	32.3	0.013	26.8	0.007			41.6	0.008	--	--	--	--

Table 75a (chlorophenyl label, 0.8 lb ai/A).

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage		Wheat straw		Wheat grain	
120-DAT Plantback	TRR = 0.006 ppm	TRR = 0.011 ppm	TRR = 0.009 ppm	TRR = 0.022 ppm		TRR = 0.079 ppm		TRR = 0.079 ppm	
Identified^b									
Pyraclostrobin + 500M07 (BF 500-3)				4.1	0.0009	1.4	0.0011	--	--
Characterized									
Polar region				21.1	0.0045	3.4	0.0027	6.6	0.0050
Med. polar region a				3.2	0.0006	5.1	0.0042	--	--
Med. polar region b				--	--	2.0	0.0016	--	--
Med. polar region c				--	--	3.1	0.0025	--	--
Nonpolar region				--	--	--	--	--	--
Lignin, precipitate				NA		22.2	0.017	8.4	0.007
Lignin, supernatant				NA		17.4	0.014	56.9	0.045
Cellulose				NA		25.6	0.020	1.6	0.001
Macero hydrolysate				8.6	0.002	NA		NA	
Starch ^c				NA		NA		NR	
Water extract				4.9	0.001	3.9	0.003	5.1	0.004
Ammonia extract				4.7	0.001	8.6	0.007	14.3	0.011
Total characterized/ identified				46.6	0.010	92.7	0.073	92.9	0.073
Nonextractable				39.8	0.009	--	--	--	--

Table 75a (chlorophenyl label, 0.8 lb ai/A).

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage	Wheat straw	Wheat grain	
365-DAT Plantback	TRR = 0.004 ppm	TRR = 0.006 ppm	TRR = 0.007 ppm	TRR = 0.014 ppm	TRR = 0.069 ppm	TRR = 0.010 ppm	
Identified							
Pyraclostrobin + 500M07 (BF 500-3)					3.3	0.0023	NA
Characterized							
Polar region					2.7	0.0019	NA
Med. polar region a					2.9	0.0020	NA
Med. polar region b					--	--	NA
Med. polar region c					21.8	0.0149	NA
Nonpolar region					--	--	NA
Lignin, precipitate					12.4	0.009	21.4 0.002
Lignin, supernatant					16.3	0.011	37.9 0.004
Cellulose					11.6	0.008	13.0 0.001
Macero hydrolysate					NA		NA
Starch ^c					NA		NR
Methanol extract					NR		5.5 0.001
Water extract					NA		NA
Ammonia extract					9.9	0.007	24.9 0.002
Total characterized/identified					80.9	0.056	102.7 0.010
Nonextractable					--	--	-- --

^a NA = Not analyzed for; NR = not reported (if more than one procedure was conducted, only results of the most successful procedure for each fraction are reported); -- = not found. Data for shaded RACs were not included in the table as the petitioner did not conduct HPLC analyses of the extracts of these RACs.

^b Chemical names and structures for identified metabolites are presented in Figure 2 (Attachment II).

^c Analysis of separate subsamples of nonextractable residues for wheat grain characterized starch at 15.3% TRR (0.012 ppm) in 30-DAT grain, 7.0% TRR, 0.006 ppm in 120-DAT grain, and 9.0% TRR, 0.001 ppm in 365-DAT grain.

Table 75b. Identification/characterization of radioactive residues in rotational crop commodities grown in soil treated with [chlorophenyl-¹⁴C]pyraclostrobin at 1.3 lb ai/A. ^a

Fraction	Radish root		Radish tops		Head lettuce		Wheat forage		Wheat straw		Wheat grain	
30-DAT Plantback	TRR = 0.025 ppm		TRR = 0.021 ppm		TRR = 0.014 ppm		TRR = 0.019 ppm		TRR = 0.144 ppm		TRR = 0.080 ppm	
Identified ^b												
Pyraclostrobin + 500M07 (BF 500-3)	7.5	0.0019	7.7	0.0017			13.1	0.0024	12.3	0.0176	NA	
Characterized												
Polar region	25.7	0.0063	13.2	0.0030			7.2	0.0013	--	--	NA	
Med. polar region a	--	--	1.0	0.0002			6.9	0.0012	9.6	0.0138	NA	
Med. polar region b	6.3	0.0016	10.8	0.0025			5.1	0.0010	4.6	0.0066	NA	
Med. polar region c	--	--	--	--			--	--	--	--	NA	
Nonpolar region	1.0	0.0002	2.6	0.0006			5.8	0.011	--	--	NA	
Lignin, precipitate	NA		NA				NA		21.8	0.031	16.4	0.013
Lignin, supernatant	NA		NA				NA		24.1	0.035	21.5	0.017
Cellulose	NA		NA				NA		27.3	0.039	3.1	0.003
Macero hydrolysate	11.3	0.003	20.2	0.004			NA		NA		NA	
Starch ^c	NA		NA				NA		NA		NR	
Methanol extract	NR		NR				NR		NR		5.2	0.004
Water extract	NA		9.9	0.002			3.8	0.001	6.2	0.009	5.8	0.005
Ammonia extract	4.6	0.001	2.6	0.001			7.4	0.001	8.1	0.012	11.2	0.009
Total characterized/identified	56.4	0.014	68.0	0.015			49.3	0.019	114	0.164	63.2	0.051
Nonextractable	39.5	0.010	12.0	0.003			33.5	0.006	--	--	--	--

Table 75b (*chlorophenyl label, 1.3 lb ai/A*).

Fraction	Radish root TRR = 0.007 ppm	Radish tops TRR = 0.009 ppm	Head lettuce TRR = 0.011 ppm	Wheat forage TRR = 0.021 ppm	Wheat straw TRR = 0.075 ppm	Wheat grain TRR = 0.078 ppm
120-DAT Plantback Identified^b						
Pyraclostrobin + 500M07 (BF_500-3)				--	0.8	0.0006
Characterized						
Polar region				24.8	4.8	0.0036
Med. polar region a				7.2	10.8	0.0081
Med. polar region b				--	1.9	0.0014
Med. polar region c				--	1.8	0.0013
Nonpolar region				--	--	NA
Lignin, precipitate				NA	22.4	0.017
Lignin, supematant				NA	17.6	0.013
Cellulose				NA	17.8	0.013
Macero hydrolysate				6.5	NA	NA
Starch ^c				NA	NA	NR
Methanol extract				NR	NR	5.5
Water extract				5.8	4.0	0.003
Ammonia extract				3.3	5.2	0.004
Total characterized/identified				47.6	87.1	0.065
Nonextractable				29.7	--	--
				0.006	--	--
				0.001	0.004	0.004
				0.001	0.004	0.011
				0.01	0.065	0.066

Table 75b (chlorophenyl label, 1.3 lb ai/A).

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage	Wheat straw	Wheat grain	
365-DAT Plantback	TRR = 0.007 ppm	TRR = 0.008 ppm	TRR = 0.007 ppm	TRR = 0.018 ppm	TRR = 0.068 ppm	TRR = 0.010 ppm	
Identified^b							
Pyraclostrobin + 500M07 (BF 500-3)					--	--	NA
Characterized							
Polar region					2.3	0.0015	NA
Med. polar region a					13.1	0.0089	NA
Med. polar region b					1.7	0.011	NA
Med. polar region c					5.4	0.0036	NA
Nonpolar region					2.7	0.0018	NA
Lignin, precipitate					13.5	0.009	12.3 0.001
Lignin, supernatant					15.7	0.011	31.1 0.003
Cellulose					18.1	0.012	2.0 <0.001
Macero hydrolysate					NA		NA
Starch ^c					NA		NR
Methanol extract					NR		7.8 0.001
Water extract					NA		NA
Ammonia extract					11.0	0.008	18.3 0.002
Total characterized/identified					83.5	0.067	71.5 <0.008
Nonextractable					--	--	-- --

^a NA = Not analyzed for; NR = not reported (if more than one procedure was conducted, only results of the most successful procedure for each fraction are reported); -- = not found. Data for shaded RACs were not included in the table as the petitioner did not conduct HPLC analyses of the extracts of these RACs.

^b Chemical names and structures for identified metabolites are presented in Figure 2 (Attachment II).

^c Analysis of separate subsamples of nonextractable residues for wheat grain characterized starch at 26.7% TRR (0.022 ppm) in 30-DAT grain, 13.9% TRR, 0.011 ppm in 120-DAT grain, and 6.7% TRR, 0.001 ppm in 365-DAT grain.

Table 75c. Identification/characterization of radioactive residues in rotational crop commodities grown in soil treated with [tolyl-¹⁴C]pyraclostrobin at 0.8 lb ai/A. ^a

Fraction	Radish root		Radish tops		Head lettuce	Wheat forage	Wheat straw		Wheat grain	
30-DAT Plantback	TRR = 0.025 ppm		TRR = 0.025 ppm		TRR = 0.013 ppm	TRR = 0.019 ppm	TRR = 0.114 ppm		TRR = 0.082 ppm	
Identified ^b										
Pyraclostrobin	9.0	0.0024	4.4	0.0011			10.5	0.0120	NA	
500M07	0.8	0.0002								
Characterized										
Polar region	29.9	0.0078	8.1	0.0021			6.1	0.0070	NA	
Med. polar region a	--	--	20.4	0.0051			--	--	NA	
Med. polar region b	4.6	0.0012	6.7	0.0017			--	--	NA	
Med. polar region c	--	--	--	--			--	--	NA	
Nonpolar region	--	--	--	--			--	--	NA	
Lignin, precipitate	NA		NA				0.3	<0.001	8.8	0.007
Lignin, supernatant	NA		NA				29.3	0.033	55.6	0.045
Cellulose	NA		NA				17.9	0.020	3.8	0.003
Macero hydrolysate	13.6	0.003	24.9	0.006			NA		NA	
Starch ^c	NA		NA				NA		NR	
Methanol extract	NR		NR				NR		6.5	0.005
Water extract	NA		NA				6.7	0.008	7.0	0.006
Ammonia extract	5.0	0.001	NA				2.7	0.003	10.5	0.009
Total characterized/identified	62.9	0.016	64.5	0.016			73.5	<0.084	92.2	0.075
Nonextractable	15.2	0.004	19.1	0.005			--	--	--	--

Table 75c (tolyl label, 0.8 lb ai/A).

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage		Wheat straw		Wheat grain	
365-DAT Plantback	TRR = 0.014 ppm	TRR = 0.010 ppm	TRR = 0.017 ppm	TRR = 0.016 ppm		TRR = 0.067 ppm		TRR = 0.013 ppm	
Identified^b									
Pyraclostrobin				--	--	1.4	0.0010	NA	
500M07				2.2	0.0004				
Characterized									
Polar region				35.9	0.0059	3.2	0.0022	NA	
Med. polar region a				10.2	0.0017	--	--	NA	
Med. polar region b				--	--	--	--	NA	
Med. polar region c				--	--	8.3	0.0058	NA	
Nonpolar region				--	--	--	--	NA	
Lignin, precipitate				NA		4.4	0.003	36.0	0.005
Lignin, supernatant				NA		6.0	0.004	31.9	0.004
Cellulose				NA		21.2	0.014	2.5	<0.001
Macero hydrolysate				23.5	0.004	NA		NA	
Starch ^c				NA		NA		NR	
Methanol extract				NR		NR		4.6	0.001
Water extract				NA		4.8	0.003	5.6	0.001
Ammonia extract				NR		3.5	0.002	25.3	0.003
Total characterized/ identified				71.8	0.012	52.8	0.035	105.9	0.015
Nonextractable				43.1	0.007	--	--	--	--

^a NA = Not analyzed for; NR = not reported (if more than one procedure was conducted, only results of the most successful procedure for each fraction are reported); -- = not found. Data for shaded RACs, as well as RACs from the 120-DAT plantback interval, were not included in the table as the petitioner did not conduct HPLC analyses of the extracts of these RACs.

^b Chemical names and structures for identified metabolites are presented in Figure 2 (Attachment II).

^c Analysis of separate subsamples of nonextractable residues for wheat grain characterized starch at 16.4% TRR (0.013 ppm) in 30-DAT grain and 14.1% TRR, 0.002 ppm in 365-DAT grain.

Table 75d. Identification/characterization of radioactive residues in rotational crop commodities grown in soil treated with [tolyl-¹⁴C]pyraclostrobin at 1.3 lb ai/A. ^a

Fraction	Radish root		Radish tops		Head lettuce		Wheat forage		Wheat straw		Wheat grain	
30-DAT Plantback	TRR = 0.056 ppm		TRR = 0.046 ppm		TRR = 0.017 ppm		TRR = 0.026 ppm		TRR 0.125 ppm		TRR = 0.085 ppm	
Identified ^b												
Pyraclostrobin	22.0	0.0124	13.0	0.0061	--	--	--	--	9.2	0.0113	--	--
500M07	1.4	0.0008	0.4	0.0002	--	--	--	--	1.7	0.0021	--	--
Characterized												
Polar region	15.3	0.0086	5.1	0.0024	36.9	0.0060	25.6	0.0068	5.6	0.0069	11.4	0.0100
Med. polar region a	1.1	0.0006	20.3	0.0095	--	--	8.4	0.0022	6.7	0.0085	--	--
Med. polar region b	4.4	0.0025	7.9	0.0037	--	--	--	--	4.3	0.0053	--	--
Med. polar region c	--	--	--	--	--	--	--	--	--	--	--	--
Nonpolar region	1.9	0.0010	--	--	--	--	--	--	--	--	--	--
Lignin, precipitate	NA		NR		NA		NA		27.2	0.034	23.0	0.020
Lignin, supernatant	NA		NR		NA		NA		24.3	0.030	47.9	0.041
Cellulose	NA		NR		NA		NA		22.0	0.027	2.2	0.002
Enzyme hydrolysate ^c	12.9 ^d	0.008	34.2 ^d	0.0015	NA		25.9	0.007	NR		NR	
Starch ^e	NA		NA		NA		NA		NA		NR	
Water extract	NA		NA		7.1	0.001	NA		NR		NR	
Ammonia extract	5.6	0.003	NA		NA		NA		3.6	0.004	10.6	0.009
Total characterized/identified	64.6	0.037	80.9	0.023	44.0	0.007	59.9	0.016	104.6	0.129	95.1	0.082
Nonextractable	16.7	0.009	15.7	0.007	50.0	0.008	51.1	0.013	--	--	--	--

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage	Wheat straw	Wheat grain		
120-DAT Plantback	TRR = 0.015 ppm	TRR = 0.016 ppm	TRR = 0.023 ppm	TRR = 0.027 ppm	TRR = 0.088 ppm	TRR = 0.091 ppm		
Identified^b								
Pyraclostrobin					1.4	0.0013	NA	
500M07							NA	
Characterized								
Polar region					2.5	0.0023	NA	
Med. polar region a					4.8	0.0044	NA	
Med. polar region b					4.8	0.0043	NA	
Med. polar region c					2.0	0.0018	NA	
Nonpolar region					--	--	NA	
Lignin, precipitate					0.8	0.001	0.2	<0.001
Lignin, supernatant					33.0	0.029	53.3	0.049
Cellulose					21.6	0.019	2.2	0.002
Enzyme hydrolysate ^c					NA		NR	
Starch ^c					NA		NR	
Methanol extract					NR		6.9	0.006
Water extract					4.8	0.004	6.9	0.006
Ammonia extract					1.8	0.002	11.6	0.011
Total characterized/ identified					77.5	0.069	81.1	0.075
Nonextractable					--	--	--	--

Fraction	Radish root	Radish tops	Head lettuce	Wheat forage	Wheat straw	Wheat grain		
365-DAT Plantback	TRR = 0.019 ppm	TRR = 0.014 ppm	TRR = 0.023 ppm	TRR = 0.018 ppm	TRR = 0.073 ppm	TRR = 0.017 ppm		
Identified^b								
Pyraclostrobin + 500M07 (BF500-3)					2.5	0.0018	NA	
Characterized								
Polar region					3.5	0.0025	NA	
Med. polar region a					--	--	NA	
Med. polar region b					--	--	NA	
Med. polar region c					12.2	0.0087	NA	
Nonpolar region					--	--	NA	
Lignin, precipitate					9.1	0.007	58.9	0.010
Lignin, supernatant					7.3	0.005	31.5	0.005
Cellulose					22.6	0.016	2.1	<0.001
Enzyme hydrolysate ^c					NA		NA	
Starch ^e					NA		NR	
Methanol extract					NR		5.7	0.001
Water extract					9.3	0.007	6.0	0.001
Ammonia extract					10.7	0.007	17.2	0.003
Total characterized/ identified					77.2	0.055	121.4	0.021
Nonextractable					--	--	--	--

^a NA = Not analyzed for; NR = not reported (if more than one procedure was conducted, only results of the most successful procedure for each fraction are reported); -- = not found. Data for shaded RACs were not included in the table as the petitioner did not conduct HPLC analyses of the extracts of these RACs.

^b Chemical names and structures for identified metabolites are presented in Figure 2 (Attachment II).

^c Represents Macerozyme hydrolysate unless otherwise noted.

^d Includes Macero, amylase, and/or pronase hydrolysates.

^e Analysis of separate subsamples of nonextractable residues for wheat grain characterized starch at 43.3% TRR, 0.037 ppm in 30-DAT grain, 32.0% TRR, 0.029 ppm in 120-DAT grain, and 19.3% TRR, 0.003 ppm in 365-DAT grain.

Storage stability

Samples of rotational crop commodities were stored at ~-18 C prior to and throughout the analytical phase of the study. Although sample collection dates were provided, dates were not provided for completion of analyses or the conclusion of the experimental portion of the study.

To demonstrate the stability of the test materials under frozen storage conditions, the petitioner compared HPLC results for methanol extracts of 30-DAT radish roots (chlorophenyl label, 0.8 lb ai/A) and head lettuce (tolyl label, 1.3 lb ai/A) analyzed at the beginning of the study (<3 months after sampling) and following storage of subsamples and extracts at ~-18 C for ~22 months. Based on the results of HPLC analysis, the metabolite profiles did not change significantly for 22 months. For radish roots, the metabolite profiles for the stored methanol extract and the methanol extract generated following extraction of stored radish root were identical to the metabolite profile generated at the beginning of the study. For head lettuce, although pyraclostrobin was undetected in the first analysis of the methanol extract and was detected on reanalysis following storage, the petitioner noted that its detection was probably the result of the use of a newer column and different column batches; for both head lettuce analyses, the majority of the radioactivity was found in the very polar region.

Provided the petitioner submits additional information confirming that rotational crop samples were analyzed within the interval represented by the storage stability study, no additional storage stability data are required to support the confined rotational crop study.

Study summary

In the RACs of radishes, lettuce, and wheat planted 30, 120, and 365 days following soil treatment with [chlorophenyl-¹⁴C]pyraclostrobin or [tolyl-¹⁴C]pyraclostrobin at total application rates for each label of 0.8 lb ai/A or 1.3 lb ai/A (~0.7x and 1x, respectively, the maximum proposed seasonal rate for annual crops), total radioactive residues (TRR), expressed as pyraclostrobin equivalents, accumulated at levels >0.01 ppm in samples of radish roots and tops, head lettuce, and wheat forage, straw and grain planted 30 days after treatment (DAT); 120-DAT radish tops, head lettuce, and wheat forage, straw, and grain; and 365-DAT radish roots and tops, head lettuce, and wheat forage, straw, and grain.

The petitioner successfully characterized/identified ~35%-121% TRR in rotational crop commodities. Pyraclostrobin and its metabolite 500M07 (elsewhere named BF 500-3) were identified at 7.5%-36.4% TRR (0.0017-0.0176 ppm) in 30-DAT rotational crop commodities except head lettuce and wheat grain, at 0.8%-4.1% (0.0006-0.0013 ppm) TRR in 120-DAT wheat forage and straw, and at 1.4-3.3% TRR (0.0004-0.0023 ppm) in 365-DAT wheat forage and straw. Because TRR levels were low, additional extractable residues were characterized as polar, medium polar, or nonpolar fractions; of these fractions, the polar region was the most significant, accounting for up to 36.9% TRR, and the nonpolar region was the least significant. The

petitioner also successfully demonstrated incorporation of ¹⁴C-residues into cellulose and lignin in all rotational crop commodities and incorporation into starch in wheat grain.

The study indicates that metabolism of pyraclostrobin in rotated crops is similar but more extensive than in primary crops, with pyraclostrobin undergoing demethoxylation to yield 500M07 (BF 500-3), followed by further degradation to medium polar and polar metabolites, and subsequent conjugation reactions and incorporation into natural products.

The HED MARC concluded that the residues of concern in rotational crops consist of pyraclostrobin and its desmethoxy metabolite (D278044, L. Cheng, October 9, 2001).

OPPTS GLN 860.1900: Field Accumulation in Rotational Crops

BASF Corporation submitted data (citation shown below) depicting residues of pyraclostrobin in/on representative rotational crops from limited field studies.

45118623 Wofford, J.; Abdel-Baky, S.; Riley, M. (1999) Limited Rotational Crop Study for the Use of BAS 500 F in Cucurbits: Lab Project Number: 98067: 1999/5126. Unpublished study prepared by BASF Corporation. 78 p.

Six rotational field trials were conducted between 1998 and 1999 in CA(3 trials) and GA(3). Each trial site consisted of one untreated control plot (Plot 1) and one treatment plot (Plot 2). Treatment plots received six sequential foliar applications of the 2 lb/gal EC formulation to the primary crop (cucumbers) at 0.19-0.20 lb ai/A/application (~1x the maximum proposed seasonal rate; cucumbers are representative of crops with higher proposed application rates), made at 6- to 8-day retreatment intervals. Applications were made using ground equipment in 9.7-30.5 gal/A with a spreader sticker added to the spray volume. Cucumbers from the control and treated plots were harvested at maturity (PHI not specified).

Rotational crops were planted following harvest of the primary crop; one rotational crop was planted at each of the CA and GA trials. Representative crops of leafy vegetable (cabbage), root crop (radish), and cereal grains (winter wheat) were planted back 14, 30, and 45 days after the final application of pyraclostrobin to cucumbers. Crop information pertaining to the growing conditions, irrigation, and maintenance pesticides was not provided.

Duplicate untreated and treated samples of the various RACs for each rotational crop were harvested from each plot. Radish samples were harvested at maturity 36-49 days after planting (DAP) for the GA plots and 112-118 DAP for the CA plots, and were separated into roots and tops. Cabbage samples (with and without wrapper leaves) were collected 90-104 DAP for the GA plots and 143-207 DAP for the CA plots. Wheat forage was collected when wheat was 6-8 inches tall (50-85 DAP for GA plots and 115-127 DAP for CA plots); wheat hay was sampled between the early flower (boot) and soft dough stage (141-150 DAP for GA plots and 168-199

DAP for CA plots), and field dried for 5-7 days in GA and 21-24 days in CA. Wheat grain and straw were collected at maturity (174-205 DAP for GA plots and 204-235 DAP for CA plots).

Rotational crop samples were transferred to freezers as soon as possible after collection (time unspecified) and were shipped frozen to BASF APC for analysis. Samples were analyzed for residues of pyraclostrobin and its metabolite BF 500-3 using BASF Analytical Method Number D9808. The LOQs for pyraclostrobin and its metabolite BF 500-3 were each 0.02 ppm. Apparent residues of pyraclostrobin and its metabolite BF 500-3 were each less than the LOQ in/on two samples each of untreated radish roots and tops, cabbage (with and without wrapper leaves), and wheat forage, hay, grain, and straw.

Residues of pyraclostrobin and its metabolite BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on rotational crop matrices (radish, roots and tops; cabbage, with and without wrapper leaves; wheat forage, hay, and grain) from the 14-day PBI plots. Residues of pyraclostrobin in/on one sample of wheat straw from the CA test site were detected at the LOQ (0.02 ppm), but residues of pyraclostrobin in/on a replicate sample from the same plot were found to be <LOQ (actual residues of 0.012 ppm); the petitioner concluded that the average residues were <0.02 ppm. Residues of metabolite BF 500-3 were below LOQ (<0.02 ppm) in/on all samples of wheat straw. Because combined residues of pyraclostrobin and its metabolite BF 500-3 were below the LOQ (<0.04 ppm) in/on all rotational crop samples from the 14-day PBI, samples from the 30- and 45-day PBI were not analyzed.

Study summary:

Residues of pyraclostrobin and its metabolite BF 500-3 were each less than the method LOQ (<0.02 ppm) in/on rotational crop matrices (radish, roots and tops; cabbage, with and without wrapper leaves; and wheat forage, hay, and grain) planted 14 days following the last of six sequential foliar applications to the primary crop, cucumbers, of the 2 lb/gal EC formulation at 0.19-0.20 lb ai/A/application (~1x the maximum proposed seasonal rate for annual crops). Residues of pyraclostrobin in/on one sample of wheat straw from the CA test site were at the LOQ (0.02 ppm), but residues of pyraclostrobin in/on a replicate sample from the same plot were below the LOQ (0.012 ppm) for an average residue of <0.02 ppm. Residues of metabolite BF 500-3 were nondetectable (<0.02 ppm) in/on all samples of wheat straw.

The limited field rotational crop study is acceptable. The submitted data indicate that a 14-day PBI restriction for all crops that are not registered is required.

International Harmonization Issues

No Codex or Mexican MRLs have been proposed or are established for residues of pyraclostrobin. An International Residue Limit Status sheet, which includes pending Canadian MRLs, is attached.

List of Attachments

- I. International Residue Limit Status Sheet
- II. Figure 2: Chemical names and structures of pyraclostrobin and its metabolites identified in plant and livestock metabolism studies.
- III. Figure 3: Chemical names and structures of compounds used in livestock commodity analytical methods.

ATTACHMENT I

International Residue Limit Status Form

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name: carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenyl]methoxy-, methyl ester	Common Name: Pyraclostrobin	<input checked="" type="checkbox"/> Proposed tolerance <input type="checkbox"/> Reevaluated tolerance <input type="checkbox"/> Other	Date: 10/15/01
---	---------------------------------------	--	-----------------------

Codex Status (Maximum Residue Limits)	U. S. Tolerances
<input checked="" type="checkbox"/> No Codex proposal step 6 or above <input type="checkbox"/> No Codex proposal step 6 or above for the crops requested	Petition Number: PP#0F06139 DP Barcodes: D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, and D278429 Other Identifier:
Residue definition (step 8/CXL): N/A	Reviewer/Branch: L. Cheng/RAB3 Residue definition: Pyraclostrobin and its desmethoxy metabolite methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenylcarbamate, expressed as parent, in plant commodities, and pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol and 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol, expressed as parent, in ruminant commodities.

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Almond hulls	1.6
		Aspirated grain fractions	2.5
		Banana	0.04
		Barley, grain	0.4
		Barley, hay	25
		Barley, straw	6
		Bean, dry	0.3
		Beet, sugar	0.2
		Beet, sugar, tops	8
		Beet, sugar, dried pulp	1
		Berry group	1.3
		Citrus, dry pulp	5.5
		Citrus, oil	4
		Fruit, citrus, group	0.7
		Fruit, stone, group	0.9
		Grape	2
		Grape, raisin	7

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Grass, forage	10
		Grass, hay	4.5
		Grass, seed screenings	27
		Grass, straw	14
		Nut, tree, group	0.04
		Peanut, nutmeat	0.05
		Peanut, refined oil	0.1
		Pistachio	0.7
		Radish, tops	16
		Rye, grain	0.04
		Rye, straw	0.5
		Strawberry	0.4
		Vegetable, bulb, group	0.9
		Vegetable, cucurbit, group	0.5
		Vegetable, fruiting, group	1.4
		Vegetable, root, except sugar beet, subgroup	0.4
		Vegetable, tuberous and corm, subgroup	0.04
		Wheat, grain	0.2
		Wheat, hay	6
		Wheat, straw	8.5
		Cattle*, fat	0.1
		Cattle*, liver	1.5
		Cattle*, meat	0.1
		Cattle*, meat byproducts, except liver	0.2
		* also includes goats, hogs, horses, and sheep	
		Milk	0.1

Limits for Canada	Limits for Mexico
<input type="checkbox"/> No Limits	<input checked="" type="checkbox"/> No Limits
<input type="checkbox"/> No Limits for the crops requested	<input type="checkbox"/> No Limits for the crops requested
Residue definition: Pending	Residue definition:

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)
Banana	pending		
Barley, grain	pending		
Fruit, citrus, group	pending		
Citrus, dry pulp	pending		
Citrus, oil	pending		
Peanut, nutmeat	pending		

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
Peanut, refined oil	pending		
Pistachio	pending		
Rye, grain	pending		
Fruit, stone, group	pending		
Vegetable, tuberous and corm, subgroup	pending		
Nut, tree, group	pending		
Wheat, grain	pending		
Milk	pending		
Muscle of cattle, goats, hogs, horses and sheep	pending		
Liver of cattle, goats, hogs, horses and sheep	pending		
Fat of cattle, goats, hogs, horses and sheep	pending		
Eggs	pending		
Poultry, muscle	pending		
Poultry, liver	pending		
Poultry, fat	pending		
Notes/Special Instructions:			

Rev. 1998

ATTACHMENT II

Figure 2: Chemical names and structures of pyraclostrobin and its metabolites identified in plant and animal metabolism studies and confined rotational crop studies.

Figure 2. Chemical names and structures of pyraclostrobin and its metabolites in plant, animal, and rotational crop commodities.

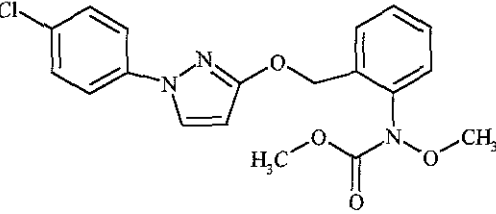
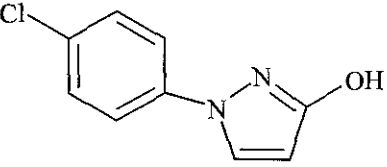
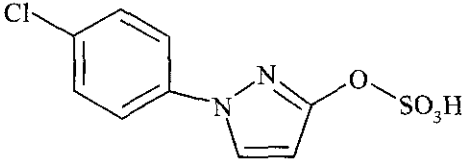
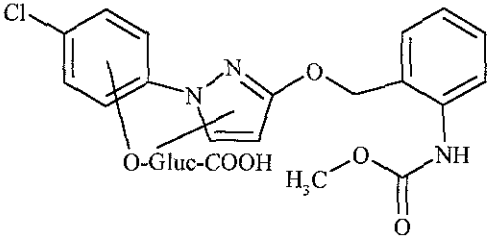
Common name/code Chemical name	Chemical structure	Matrices
<p>Pyraclostrobin; BAS 500 F</p> <p>[Carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl] phenyl]methoxy-, methyl ester]</p>		<p>Grapes Potato foliage and tubers Wheat forage, grain, and straw</p> <p>Rotational Crops: 30-PBI radish roots and tops, and wheat forage and straw; 120-PBI wheat forage and straw; and 365-PBI wheat straw ^a</p> <p>Goat milk, muscle, fat, liver, and kidney ^a</p> <p>Poultry eggs and fat</p>
<p>BF 500-5; 500M04</p> <p>1-(4-Chlorophenyl)-1H-pyrazol-3-ol</p>		<p>Potato foliage and tubers ^b Wheat forage, straw, and grain ^c</p> <p>Poultry eggs, fat, and liver</p> <p>Goat milk, liver, and kidney</p>
<p>500M05</p>		<p>Goat milk, liver, and kidney</p>
<p>500M06</p>		<p>Poultry eggs and liver</p>

Figure 2 (continued).

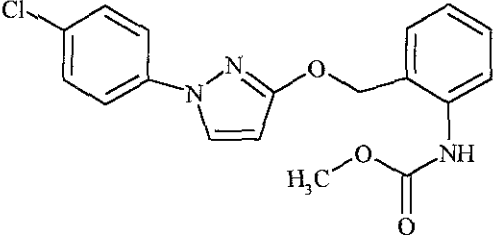
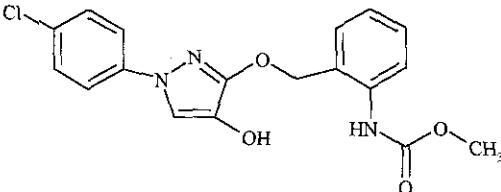
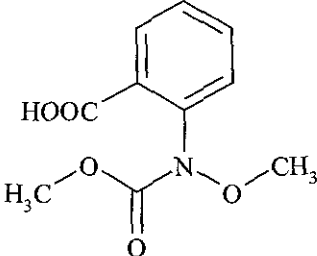
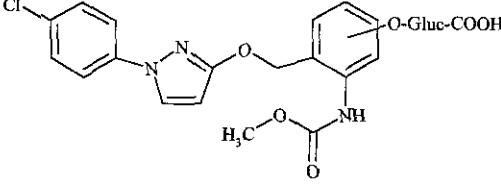
Common name/code Chemical name	Chemical structure	Matrices
<p>BF 500-3; 500M07</p> <p>Methyl-N-[[[1-(4-chlorophenyl)pyrazol-3-yl]oxy]o-tolyl carbamate</p> <p>aka</p> <p>Methyl 2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl]phenylcarbamate</p>		<p>Grapes Potato foliage and tubers Wheat forage, grain, and straw</p> <p>Rotational Crops: 30-PBI radish roots and tops, and wheat forage and straw; 120-PBI wheat forage and straw; and 365-PBI wheat straw ^a</p> <p>Goat milk, muscle, fat, liver, and kidney ^a</p> <p>Poultry eggs and fat</p>
<p>500M08</p>		<p>Goat milk and liver</p>
<p>500M24</p>		<p>Wheat grain</p>
<p>500M32</p>		<p>Poultry liver</p>

Figure 2 (continued).

Common name/code Chemical name	Chemical structure	Matrices
500M34		Wheat forage and straw
500M39		Goat liver Poultry eggs and liver
500M45		Goat milk and liver
500M49		Poultry eggs, fat, and liver

Figure 2 (continued).

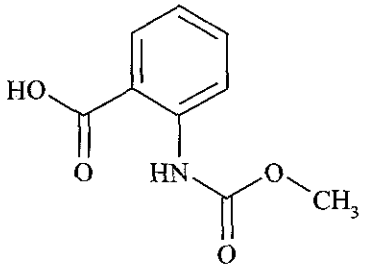
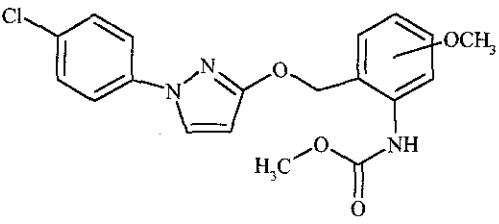
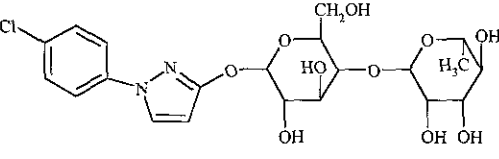
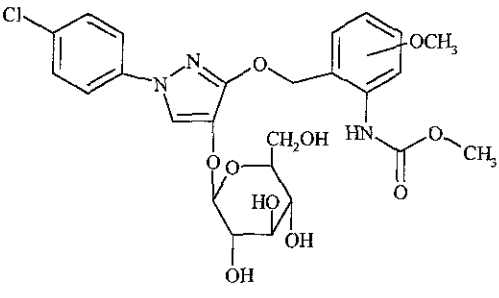
Common name/code Chemical name	Chemical structure	Matrices
500M51		Goat kidney
500M54		Grapes Potato foliage and tubers Wheat forage and straw
M55		Grapes
M56		Grapes

Figure 2 (continued).

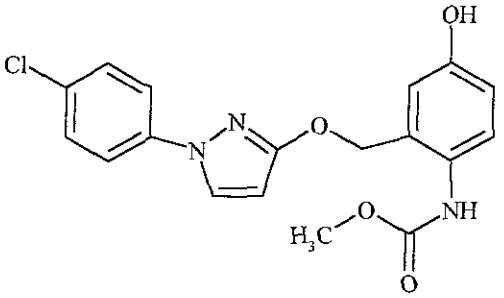
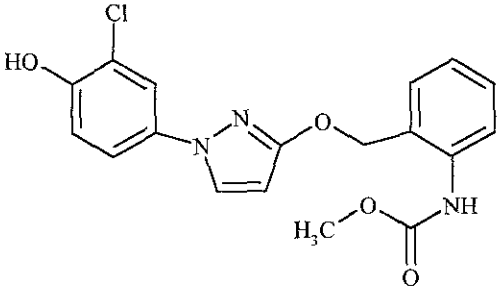
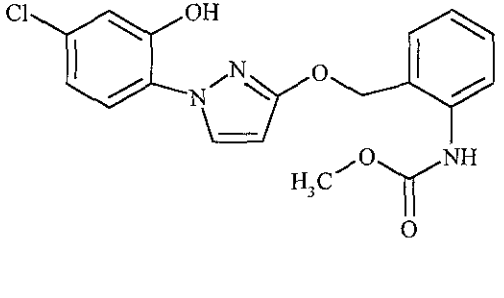
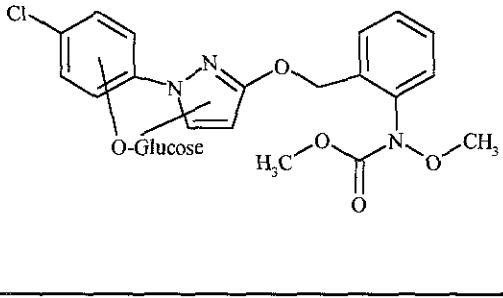
Common name/code Chemical name	Chemical structure	Matrices
500M64		Goat milk and kidney Poultry eggs, fat, and liver
500M66		Goat milk, liver, and kidney Poultry liver
500M67		Goat milk, liver, and kidney
500M68		Potato foliage and tubers ^b Wheat forage, straw, and grain ^{c, d}

Figure 2 (continued).

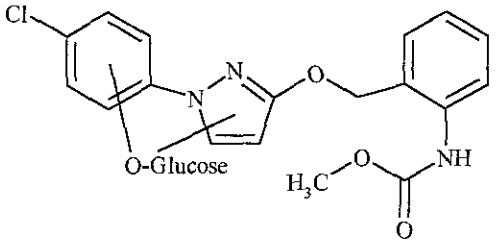
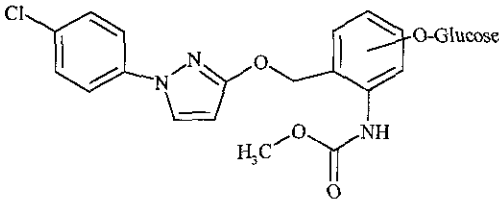
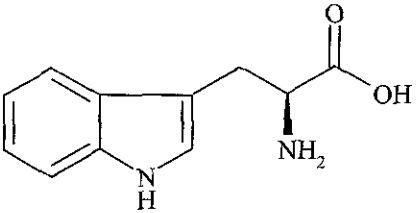
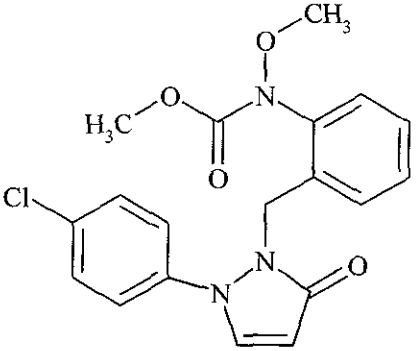
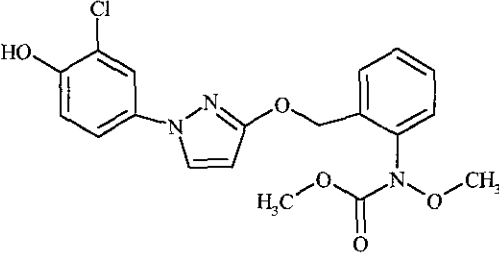
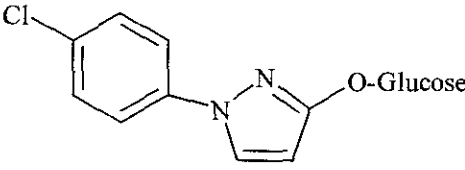
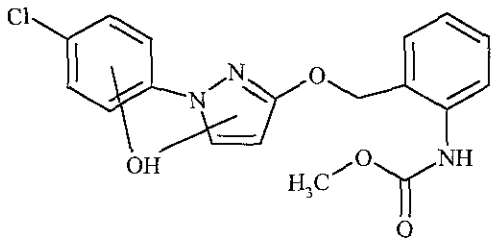
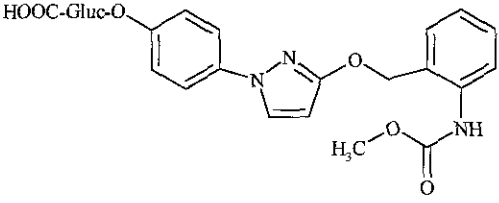
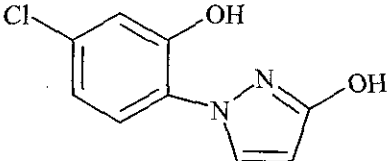
Common name/code Chemical name	Chemical structure	Matrices
500M70		Wheat forage, straw, and grain ^{c, d}
500M71		Wheat forage, straw, and grain ^{c, d}
500M72; L-Tryptophan		Potato tubers Wheat grain
500M76		Wheat forage, straw, and grain ^c

Figure 2 (continued).

Common name/code Chemical name	Chemical structure	Matrices
BF 500-16; 500M77 Methyl N-[2-((1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-yl)oxymethyl)phenyl] N-methoxy carbamate		Poultry eggs, fat, and liver
500M79		Potato foliage and tubers
500M80		Poultry liver
500M83		Poultry liver
BF 500-8; 500M85 1-(4-Chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol		Goat milk, liver, and kidney

^a Pyraclostrobin and metabolite 500M07 co-eluted in goat milk and kidney, and in the rotational crops radish roots and tops, and wheat forage and straw.

^b Metabolites 500M04 and 500M68 co-eluted in potato foliage and tubers.

^c Metabolites 500M04 and 500M76, and glucosides 500M68, 500M70, and 500M71 co-eluted in wheat grain.

^d Glucosides 500M68, 500M70, and 500M71 co-eluted in wheat forage and straw.

ATTACHMENT III

Figure 3: Chemical names and structures of compounds used in animal commodity analytical methods.

Figure 3: Chemical names and structures of compounds used in animal commodity analytical methods.

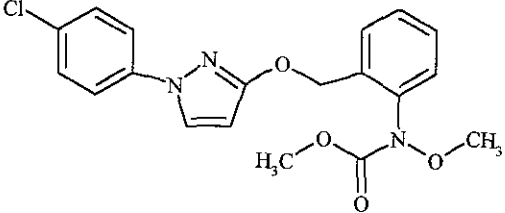
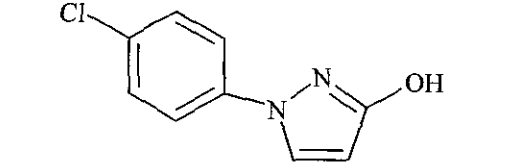
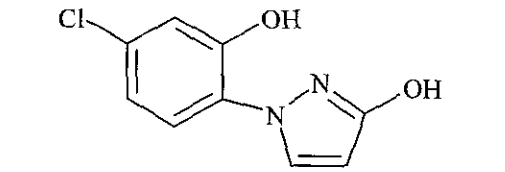
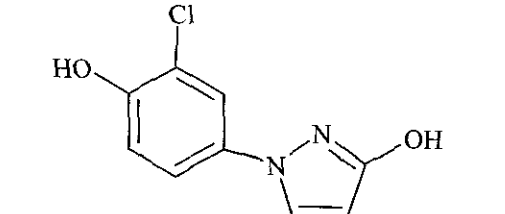
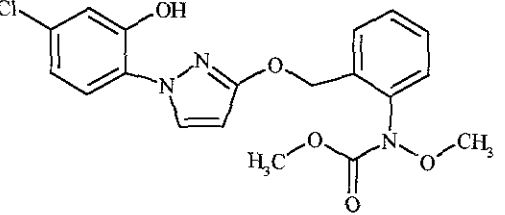
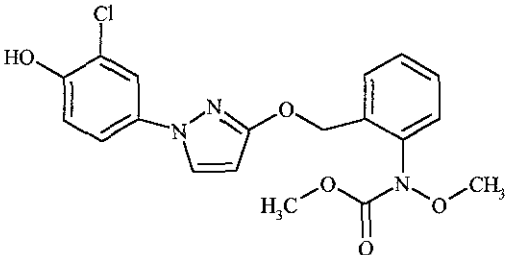
Common name/code Chemical name	Chemical structure	Comment
Pyraclostrobin; BAS 500 F [Carbamic acid, [2-[[[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy]methyl] phenyl]methoxy-, methyl ester]		Parent compound
BF 500-5 1-(4-Chlorophenyl)-1H-pyrazol-3-ol		Hydrolysis product generated and determined in GC/MS method 446/0 and LC/MS/MS methods 446/1 and D9902 ^a
BF 500-8 1-(4-Chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol		Hydrolysis product generated and determined in GC/MS method 446/0 and LC/MS/MS method 446/1 ^a
BF 500-9 1-(3-Chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol		Hydrolysis product generated and determined in LC/MS/MS method D9902
BF 500-10 Methyl N-[2-((1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-yl)oxymethyl)phenyl] N-methoxy carbamate		Compound used in validation studies as representative of metabolites forming BF 500-8

Figure 3 (continued).

Common name/code Chemical name	Chemical structure	Comment
<p>BF 500-16</p> <p>Methyl N-[2-((1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-yl)oxymethyl)phenyl] N-methoxy carbamate</p>		<p>Compound used in validation studies as representative of metabolites forming BF 500-9</p>

^a In GC/MS method 446/0, this compound is determined as the methyl ether.