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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

Date: August 8, 2006

Subject: Tribenuron methyl. Addition of Preplant Burndown Uses on Field Corn, Rice, Sorghum, and Soybeans (PRIA R19; PP#4F6890) and Postemergence Uses on Sunflower (IR-4 Request; PP#4E6855). Summary of Analytical Chemistry and Residue Data.

DP Barcodes:	D330633 & D330814	Decision Numbers:	352136, 352139, & 353013
PC Code:	128887	MRID Nos.:	46352002, 46352003, 46358501, 46421901, 46435901
40 CFR 180.	451		
Chemical Class:	Sulfonylurea herbicide (Group 2)		

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This document was originally prepared under contract by Dynamac Corporation (2275 Research Blvd, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The document has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

AUG 18 2006

Executive Summary

Tribenuron methyl [methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate] is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, canola, cotton, flax, oats, and wheat, as well as grass grown for seed. E. I. du Pont de Nemours is requesting that preplant burndown uses of tribenuron methyl on field corn, rice, sorghum, and soybeans be added to the labels for the 75% dry flowable (DF) formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509) and the 25% DF formulation (DuPont™ Harmony7 Extra XP Herbicide; EPA Reg. No. 352-611). The 25% DF formulation is a multiple active ingredient (MAI) formulation which also contains thifensulfuron methyl at 50%. In conjunction with the requested new uses, DuPont has submitted a petition, PP#4F6890, proposing the establishment of tolerances for residues of tribenuron methyl in/on the following commodities:

Corn, field, grain	0.05 ppm
Corn, field, forage	0.05 ppm
Corn, field, stover	0.05 ppm
Grain sorghum, forage	0.05 ppm
Grain sorghum, stover	0.05 ppm
Grain sorghum, grain	0.05 ppm
Rice, grain	0.05 ppm
Rice, straw	0.05 ppm
Soybean	0.05 ppm

In support of this petition, DuPont has submitted residue analytical method, storage stability, and crop field trial data for field corn, rice, sorghum, and soybean. Each of these submissions also contains data for thifensulfuron methyl; refer to the review of PP#4F6889 (D330813, D330702, 8/8/06, S. Hummel) for the thifensulfuron methyl residue results.

The Interregional Research Project No. 4 (IR-4), on behalf of the Agricultural Experiment Station of ND, is proposing to amend the use pattern for the 75% DF formulation (EPA Reg. No. 352-509) to add use on tribenuron-methyl tolerant sunflower seed. In conjunction with the requested use, IR-4 has submitted a petition, PP#4E6855, for the establishment of a tolerance for residues of tribenuron methyl (methyl-2-[[[[*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate) in/on the following raw agricultural commodity:

Sunflower Seed	0.05 ppm

IR-4 has submitted storage stability and crop field trial data for sunflower in support of this petition.

Tolerances have been established for residues of tribenuron methyl under 40 CFR 180.451. Tolerances are currently established for residues of tribenuron methyl in/on barley, canola, cotton, flax, oat, and wheat commodities, at 0.02-0.10 ppm [40 CFR 180.451(a)]. Tolerances with regional registration have been established for residues of tribenuron methyl in/on the grass forage, fodder, and hay group (except Bermudagrass) at 0.10 ppm [40 CFR 180.451(c)].

The nature of the residue in plants is adequately understood based on acceptable metabolism studies with wheat, canola, and cotton. The residue of concern in plants is tribenuron methyl. The tolerance expression specified in Section F of the subject petitions is appropriate.

Acceptable confined rotational crop studies are also available. Based on the results of the confined rotational crop studies, HED has determined that field rotational crop studies (860.1850) are not required to support the registered uses; these studies are also not required to support the proposed uses of tribenuron methyl on field corn, rice, sorghum, soybean, and sunflower. The available rotational crop data indicate that a 30-day plantback interval is appropriate for all crops without registered uses. The current plantback intervals for tribenuron methyl end-use products are adequate.

The nature of the residue in livestock is adequately understood based on an adequate goat metabolism study. A poultry metabolism study is not required to support the proposed uses on field corn, rice, sorghum, soybean, and sunflower based on the fact that residues in/on the seeds of these crops were below the limit of quantitation (LOQ), even at exaggerated application rates. Residues in ruminant and poultry commodities may be classified under 40 CFR §180.6(a)(3); i.e., there is no expectation of finite residues. Therefore, no livestock enforcement methods, storage stability data, or feeding studies are required to support this petition.

The proposed use patterns are adequate to allow evaluation of the residue data submitted in support of this petition. A label amendment to specify that aerial applications be made in a minimum of 2 gal/A is required.

An adequate enforcement method (Method AMR 337-85, Revision A) has been accepted by the Agency for the determination of residues of tribenuron methyl *per se* in/on barley and wheat commodities. Using this method, samples are extracted with acetonitrile, and the extract is cleaned up using silica gel chromatography for analysis by HPLC using a photo-conductivity detector. The method was validated by the Analytical Chemistry Laboratory (ACL; Biological and Economic Analysis Division) in wheat grain at 0.057 and 0.113 ppm and in wheat straw at 0.113 and 0.226 ppm. The petitioner validated the method at 0.01-0.02 ppm in wheat and barley grain, at 0.02-0.04 ppm in wheat and barley straw, and at 0.01-0.1 ppm in wheat forage. This method may be used for the enforcement of tolerances for tribenuron methyl residues in/on corn forage and stover, rice grain and straw, and sorghum forage and stover.

An LC/MS method (DuPont Method 1381) is available for the enforcement of tolerances on canola, cotton, and flax commodities. Using this method, samples are extracted with an acetonitrile/ammonium carbonate buffer solution. The concentrated residues are reconstituted in methanol for LC/MS analysis with column switching. If required, a hexane wash step or cleanup step using a strong anion exchange solid-phase extraction (SPE) column may be incorporated. This method may be used for the enforcement of tolerances for residues of tribenuron methyl in/on corn grain, sorghum grain, soybean seed, and sunflower seed.

Adequate storage stability data were submitted to support the storage conditions and intervals of samples of corn forage, corn stover, sorghum forage, sorghum stover, and soybean seed from the submitted field trials. The available storage stability data for cottonseed and wheat straw and grain may be translated to support the storage conditions and intervals of samples of corn grain,

rice grain, rice straw, sorghum grain, and sunflower seed from the field trials.

Acceptable crop field studies were conducted to support the proposed uses of tribenuron methyl on field corn, rice, sorghum, soybean, and sunflower. The corn, rice, sorghum, and soybean field trials were conducted at 5x, and the sunflower field trials were conducted at 1x. The number and geographic location of field corn, rice, sorghum, and soybean field trials are adequate; HED had previously concluded that three crop field trials would be needed to support preplant burndown use of tribenuron methyl provided that residues were nonquantifiable following treatment at 5x (ChemSAC meeting of 2/13/03). The number and geographic representation of sunflower field trials are in accordance with OPPTS 860.1500. Residues of tribenuron methyl in/on all treated samples were below the method LOQ (<0.05 ppm). These data are adequate to support tolerances at 0.05 ppm for field corn grain, forage, and stover; rice grain and straw; sorghum grain, forage, and stover; soybean seed; and sunflower seed.

Based on the fact that residues were below the LOQ in/on samples of corn grain, rice grain, sorghum grain, soybean seed, and sunflower seed following treatment at 5x, no processing studies are required to support the proposed uses. Tolerances for the processed commodities of these commodities are not required.

There are no established or proposed Codex MRLs for residues of tribenuron methyl. Canadian MRLs have been established for residues of tribenuron methyl; however, no MRLs have been established for the requested crops. No Mexican MRLs have been established for tribenuron methyl.

Regulatory Recommendations and Residue Chemistry Deficiencies

HED has examined the residue chemistry database for tribenuron methyl. Pending submission of a revised Section B (see requirements under Directions for Use), there are no residue chemistry issues that would preclude granting a registration for this herbicide on field corn, rice, sorghum, soybean, and sunflower, or establishment of tolerances for residues of tribenuron methyl as follows:

Corn, field, grain	0.05 ppm
Corn, field, forage	0.05 ppm
Corn, field, stover	0.05 ppm
Rice, grain	0.05 ppm
Rice, straw	0.05 ppm
Sorghum, forage	0.05 ppm
Sorghum, stover	0.05 ppm
Sorghum, grain	0.05 ppm
Soybean, seed	0.05 ppm
Sunflower, seed	0.05 ppm

A human health risk assessment is forthcoming.

860.1200 Directions for Use

- The product label for the 75% DF formulation must be modified to specify that aerial applications be made in a minimum of 2 gallons/acre (GPA).

- The petitioner must modify the proposed label for the 25% DF formulation to specify that only one preplant or preemergence application may be made per season to field corn, rice, sorghum, and soybean.

860.1340 Residue Analytical Methods

The petitioner used DuPont Methods 5367 and 13412 for data collection in the submitted crop field trials and storage stability study, and submitted Independent Laboratory Validation data for both methods. If the petitioner wishes to use DuPont Method 5367 and/or DuPont Method 13412 for enforcement purposes, then the data specified below must be submitted.

- If the petitioner wishes DuPont Method 5367 to be used for enforcement, a revised version of the method, incorporating the method modifications made by the ILV laboratory, must be submitted. In addition, the petitioner must provide confirmation that the ILV study was conducted by analysts unfamiliar with the method, to assure HED that the ILV study was truly independent.

- If the petitioner wishes DuPont Method 13412 to be used for enforcement, the final version of the method must be submitted; the version should include the modifications made by the ILV laboratory in the course of validation.

Background

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, canola, cotton, flax, oats, and wheat, as well as grass grown for seed. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin). The chemical structure and nomenclature of tribenuron methyl are presented in Table 1. The physicochemical properties of the technical grade of tribenuron methyl are presented in Table 2.

Table 1. Tribenuron Methyl Nomenclature.

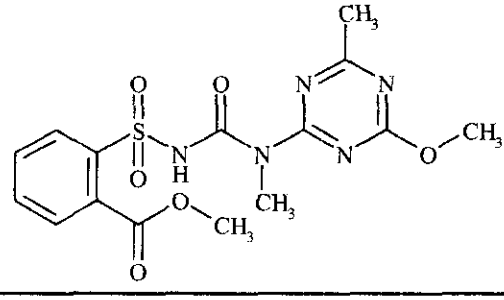
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate

Table 1. Tribenuron Methyl Nomenclature.	
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509); 25% DF formulation (DuPont™ Harmony® Extra; EPA Reg. No. 352-611)

Table 2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, Log(K_{OW})	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

860.1200 *Directions for Use*

DuPont submitted copies of proposed supplemental labels for the 75% DF formulation (EPA Reg. No. 352-509) and the 25% DF formulation (EPA Reg. No. 352-611). The supplemental labels include instructions for preplant burndown use on cotton, field corn, grain sorghum, rice, an soybeans. Use on cotton has been approved previously (PP#0F6135; D266130, x/xx/06, C. Swartz)

IR-4 submitted the proposed use directions for use of the 75% DF formulation (EPA Reg. No. 352-509) on sunflower.

The 25% DF formulation (EPA Reg. No. 352-611) is currently registered for preplant/preemergence application to field corn, rice, sorghum, and soybean at 0.008-0.009 lb

ai/A/application (0.125-0.15 oz ai/A/application; supplemental label approved 10/6/03). Application is to be made at least 45 days prior to planting corn, rice, sorghum, and soybean. The total preplant application rate is 0.016 lb ai/A (0.25 oz ai/A). Application is limited to corn, rice, sorghum, and soybean grown in AL, AR, DE, GA, IA, IN, IL, KY, LA, MD, MO, MS, NC, OH, PA, SC, TN, TX, and VA.

The proposed use patterns on field corn, rice, sorghum, soybeans, and sunflower are presented below in Table 3.

Table 3. Summary of Directions for Use of Tribenuron Methyl on Field Corn, Rice, Grain Sorghum, Soybeans, and Sunflower.

Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Field corn						
Preemergence Broadcast Ground or aerial	75% DF [352-509]	0.008-0.015	Not specified (NS)	NS	NS	Application is to be made prior to crop emergence, in combination with other suitable registered preplant herbicides. Use of a nonionic surfactant (NIS), crop oil concentrate (petroleum based), or vegetable-seed oil-based product is recommended.
	25% DF [352-611]	0.005-0.009				
Grain sorghum						
Preemergence Broadcast Ground or aerial	75% DF [352-509]	0.008-0.015	NS	NS	NS	Application is to be made prior to crop emergence, in combination with other suitable registered preplant herbicides. Use of a NIS, crop oil concentrate (petroleum based), or vegetable-seed oil-based product is recommended.
	25% DF [352-611]	0.005-0.009				
Rice						
Preemergence Broadcast Ground or aerial	75% DF [352-509]	0.008-0.015	NS	NS	NS	Application is to be made prior to crop emergence, in combination with other suitable registered preplant herbicides. Use of a NIS, crop oil concentrate (petroleum based), or vegetable-seed oil-based product is recommended.
	25% DF [352-611]	0.005-0.009				
Soybean						
Preemergence Broadcast	75% DF [352-509]	0.008-0.015	NS	NS	NS	Application is to be made prior to crop emergence,

Table 3. Summary of Directions for Use of Tribenuron Methyl on Field Corn, Rice, Grain Sorghum, Soybeans, and Sunflower.

Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A)	PHI (days)	Use Directions and Limitations
Ground or aerial	25% DF [352-611]	0.005-0.009				in combination with other suitable registered preplant herbicides. The grazing or feeding of forage, hay, or straw from treated fields to livestock is prohibited. Use of a NIS, crop oil concentrate (petroleum based), or vegetable-seed oil-based product is recommended.
Sunflower						
Postemergence Broadcast Ground or aerial	75% DF [352-509]	0.016	3	0.048	70	Application is to be made to tribenuron methyl tolerant sunflower seed lines. The first application is to be made at approximately the 1-leaf stage, with subsequent applications made with a minimum 14-day retreatment interval, at any time prior to flower bud formation (no later than 70 days prior to harvest). A surfactant or wetting agent may be added to the spray solution.

The proposed use directions for sunflower specify that applications be made in 5-20 GPA. Spray volumes for applications to field corn, grain sorghum, rice, and soybeans were not specified on the supplemental labels. The current product labels for the 75% and 25% DF formulations specify that ground applications be made in a minimum of 5 GPA and that aerial applications be made in 1-5 GPA for the 75% DF formulation or 2-5 GPA for the 25% DF formulation (a minimum of 3 GPA in ID, OR, and UT with either formulation); application through any irrigation system is prohibited.

No rotational crop restrictions were specified on the supplemental labels. The current product labels for the 75% and 25% DF formulations specify the following rotational crop restrictions: a 0-day plantback interval for barley, oat, soybean, and wheat; a 60-day plantback interval for canola, winter rape, and sugarbeet; and a 45-day plantback interval for all other crops.

Conclusions. The proposed use directions are adequate to allow for evaluation of the available residue data relative to the proposed use. The available field corn, rice, sorghum, and soybean field trial data, which reflect treatment at 5x, and the available sunflower field trial data, which reflect treatment at 1x, will support the proposed use directions. Although the use pattern used in

the sunflower crop field trials was slightly different than the proposed use (first application made preemergence instead of postemergence), HED does not believe that application according to the proposed use will result in quantifiable residues in sunflower seed, because residues were nonquantifiable in/on sunflower seed following treatment at 5x the proposed maximum seasonal rate.

The product label for the 75% DF formulation must be modified to specify that aerial applications be made in a minimum of 2 GPA.

Supplemental labeling for the 25% DF formulation indicates that preplant applications of tribenuron methyl to field corn, rice, sorghum, and soybean with regional restrictions are currently registered. The petitioner must modify the proposed label to specify that only one preplant or preemergence application may be made per season to field corn, rice, sorghum, and soybean.

860.1300 Nature of the Residue - Plants

D304059, 6/24/04, R. Griffin
PP#0F6135; D266130, x/xx/06, C. Swartz)

The nature of the residue in plants is adequately understood based on metabolism studies with wheat, canola, and cotton. The residue of concern in plant commodities is tribenuron methyl *per se*.

In a wheat metabolism study, [phenyl-U-^{14}C]tribenuron methyl or [triazine-2-^{14}C]tribenuron methyl was foliarly applied to wheat plants at 1 oz ai/A (4x the maximum seasonal rate) when wheat plants were at the tiller stage. Samples were collected 0, 4, 8, 14, 21, and 28 days after treatment (DAT), and at maturity (63 DAT). Total radioactive residues (TRR) were highest in wheat forage collected on the day of treatment (4.23 and 5.49 ppm) and decreased with increasing sampling intervals, to 0.51 and 0.75 ppm at 28 days posttreatment. TRR were 0.37 and 0.55 ppm in straw and 0.01 and 0.05 ppm in grain harvested at maturity. In wheat forage and straw, the major residues were glucose-conjugated saccharin, glucose-conjugated metsulfuron methyl, hydroxylated triazine amine, O-demethyl triazine amine, and hydroxylated saccharin. In wheat grain, sulfonamide urea was the major residue (45% TRR; only phenyl-label samples were analyzed); saccharin, hydroxylated saccharin, sulfonamide, and glucose-conjugated saccharin were also identified.

In a canola metabolism study, [phenyl-U-^{14}C]tribenuron methyl or [triazine-2-^{14}C]tribenuron methyl was foliarly applied to ALS-tolerant canola plants at ~0.35 oz ai/A (5.5x the maximum seasonal rate) when canola plants were at the 2 true leaf or bolting stage. Samples were collected 0, 2, and 35 DAT, and at maturity (78 DAT). TRR declined in canola foliage from 0.24-0.31 ppm at 0 DAT to 0.04 ppm at 35 DAT. TRR in immature canola seed pods were 0.04 ppm at 35 DAT. TRR in mature canola seed samples, the raw agricultural commodity of interest, were 0.02 ppm at 78 DAT. In immature canola forage collected 0 and 2 DAT, tribenuron methyl was the major residue, at 88-99% TRR; tribenuron methyl declined to 11-25% TRR in 35-DAT immature foliage. All other residues identified in canola seed and foliage were found to be present at $\leq$0.02 ppm. The major metabolic processes in canola include hydrolytic cleavage and N-demethylation

of tribenuron methyl with subsequent hydroxylation; formation of the conjugates of the hydroxylated metabolites may also occur.

In a cotton metabolism study, [phenyl-U-^{14}C]tribenuron methyl or [triazine-2-^{14}C]tribenuron methyl was applied to cotton plants as a soil treatment at ~0.3 oz ai/A (2x the maximum seasonal rate) or 1.5 oz ai/A (9x). Application was made immediately after planting. Immature samples were collected 89 DAT (minimal boll formation) and 119 DAT (appearance of mature boll), and mature samples were collected 174 DAT. TRR were <0.01 ppm in samples of mature undelinted cotton seed (174 DAT) treated with either label at ~0.3 oz ai/A. TRR in cotton seed treated at the 1.5 oz ai/A rate were not reported. TRR in mature cotton gin trash (174 DAT) treated with [phenyl-U-^{14}C]tribenuron methyl were 0.028 ppm from the 0.3 oz ai/A rate and were 0.047 ppm from the 1.5 oz ai/A rate. TRR in mature cotton gin trash treated with [triazine-2-^{14}C]tribenuron methyl were <0.01 ppm from the lower rate; TRR in samples from the higher rate were not reported.

Chromatographic analysis of the aqueous-soluble residues in gin trash (~53% TRR, 0.0149 ppm) did not detect tribenuron methyl or its known metabolites. The major polar peak in the aqueous extract was characterized as a glucose conjugate based on enzyme hydrolysis. Enzyme hydrolysis of the aqueous extract of mature phenyl-labeled gin trash from the exaggerated rate study indicated that the polar peak was readily converted to a less polar unknown metabolite following treatment with β-glucosidase. The results of the cotton metabolism study suggest that tribenuron methyl is not readily translocated into the cotton plant when applied as a soil treatment immediately after planting. The metabolic pathway of tribenuron methyl in soil involves cleavage of the sulfonylurea bridge of the parent compound, forming metabolites containing either the phenyl or triazine ring. In cotton, the 2-(aminosulfonyl)benzoate and saccharin soil residues from the phenyl ring degradation yielded a phenyl ring polar glucose conjugate.

860.1300 Nature of the Residue - Livestock

D304059, 6/24/04, R. Griffin

The nature of the residue in livestock is adequately understood based on an acceptable goat metabolism study. RRB2 has previously determined that a poultry metabolism study would not be required to support the existing uses on wheat and barley based on the fact that residues in/on wheat and barley grain were nondetectable, even at exaggerated application rates.

The proposed uses on field corn, rice, sorghum, soybean, and sunflower include feedstuffs (field corn grain and milled byproducts; rice grain, bran, and hulls; sorghum grain; soybean seed and hulls; and sunflower meal) which may be fed to poultry. This situation would typically trigger the need for a poultry metabolism study. However, a poultry metabolism study will not be required, for the purpose of this petition only, because the crop field trial data demonstrate that no quantifiable residues of tribenuron methyl are observed in/on corn, rice, sorghum, soybean, and sunflower commodities following treatment at 5x.

860.1340 Residue Analytical Methods

D304059, 6/24/04, R. Griffin
45098401.der1.wpd, 8/10/04, S. Ary (DuPont Method 1381)

46352002.de2.doc (Cereal commodities)
46352003.de2.doc (Oily crop matrices)

Enforcement method: For enforcement of tolerances for residues of tribenuron methyl *per se* in grain, forage, and straw commodities, Method AMR 337-85, Revision A has been accepted. Briefly, samples are extracted with acetonitrile, and the extract is cleaned up using silica gel chromatography for analysis by HPLC using a photo-conductivity detector. The method was validated by ACL in wheat grain at 0.057 and 0.113 ppm and in wheat straw at 0.113 and 0.226 ppm. The petitioner validated the method at 0.01-0.02 ppm in wheat and barley grain, at 0.02-0.04 ppm in wheat and barley straw, and at 0.01-0.1 ppm in wheat forage.

For enforcement of tolerances for residues of tribenuron methyl in canola, cotton, and flax commodities, an LC/MS method, DuPont Method 1381, is available. Briefly, samples are extracted with an acetonitrile/ammonium carbonate buffer solution. The concentrated residues are reconstituted in methanol for analysis. If required, a hexane wash step or cleanup step using a strong anion exchange solid-phase extraction (SPE) column may be incorporated. Analysis is performed by column-switching liquid chromatography. Extracts in methanol are applied to a size exclusion chromatography column, and the eluate is diverted onto a reversed phase XDB-C8 column for MS analysis. The validated LOQ was 0.020 ppm. The method was reviewed in conjunction with PP#0F6135 (D266130, 7/25/06, C. Swartz) and determined to be adequate for enforcement purposes provided confirmation was provided that the independent laboratory validation study was conducted by an analyst unfamiliar with the method. DuPont has provided this confirmation (PP#0F6152; D311607, 1/4/05, S. Ary).

The acceptability of Method 1381 for enforcement purposes for canola, cotton, and flax tolerances was addressed in the thifensulfuron methyl petition (PP#0F6152; D311607, 1/4/05, S. Ary). The method is also adequate for enforcement of tribenuron methyl tolerances. In the first review of the thifensulfuron methyl petition (D301488, 8/12/04, S. Ary) it was concluded that no petition method validation would be required if it was determined that the ILV was conducted by an independent laboratory.

No tolerances or analytical methods are needed for livestock commodities.

Data collection method - cereal commodities: DuPont has submitted an independent laboratory validation (ILV) study for an LC/MS method, DuPont Method 5367, for the determination of residues of tribenuron methyl in/on cereal matrices. This method was also used for data collection in samples of corn forage and stover, rice grain and straw, and sorghum forage and stover from the crop field trial study submitted in conjunction with this petition.

The method is entitled "Analytical Enforcement Method for the Determination of Thifensulfuron Methyl, Metsulfuron Methyl, Chlorsulfuron, Tribenuron Methyl, and Flupyrsulfuron Methyl in Cereals (Wheat Grain, Forage and Straw)." The ILV submission did not include a copy of the

method. A full writeup of the method, dated 4/30/01, was included as an appendix to the analytical laboratory report in the crop field trial submission.

Using DuPont Method 5367, samples of non-oily cereal commodities (corn forage and stover, rice grain and straw, and sorghum forage and stover) are extracted with a potassium phosphate buffer solution, and an aliquot of the extract is cleaned up through an ENVI-Carb SPE column. Residues are eluted from the column with an acidic methanol/methylene chloride solution, and the eluate is evaporated to dryness and redissolved in an acetonitrile/0.01 M acetic acid solution for analysis by LC/MS. The validated LOQ reported in the method was 0.01 ppm for wheat grain and 0.05 ppm for wheat forage and straw; an LOQ of 0.05 ppm was used for commodities from the crop field trials submitted in conjunction with this petition.

Method validation data for DuPont Method 5367 demonstrated adequate method recoveries of tribenuron methyl from corn forage, corn stover, rice grain, wheat grain, wheat forage, and wheat straw. Following fortification of wheat grain samples at 0.010 and 0.100 ppm, recoveries of tribenuron methyl averaged 81 ± 5.3%. Recoveries of tribenuron methyl averaged 98 ± 6.3% and 91 ± 7.7% from wheat forage and straw, respectively, fortified at 0.050 and 0.500 ppm, and 95 ± 2.5%, 80 ± 2.4%, and 88 ± 1.5% from corn forage, corn stover, and rice grain, respectively, fortified at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for rice straw or sorghum forage and stover. Concurrent method recovery data were included with the crop field trial study; adequate recoveries of tribenuron methyl were obtained from rice straw fortified at 0.05 and 0.10 ppm and from sorghum forage and stover fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in this petition.

Analyte identification is to be confirmed by analyzing sample extracts using LC/MS/MS and comparing the ion ratio for the two MS/MS ion transitions acquired during analysis with the average ion ratio obtained for the calibration standards.

Adequate independent laboratory validation data have been submitted for this method, using barley grain, wheat grain, and tomato. The ILV of the method failed for corn grain; however, the petitioner has submitted a separate method for the determination of residues tribenuron methyl in/on oily crop matrices (see below). The ILV laboratory modified one of the solvents used for final extracts and for LC mobile phase, from 0.01 M acetic acid to 50 mM ammonium acetate (buffered to pH 6.2), because the acidic solvent was found to cause degradation of tribenuron methyl.

No radiovalidation data were submitted for the method. The petitioner stated that extraction efficiency data could not be generated because no residues of tribenuron methyl were observed in the wheat metabolism study. The petitioner noted that extraction efficiency data for the method have been generated for chlorsulfuron in wheat and oats, and that tribenuron methyl has similar polarity and solubility to chlorsulfuron which would indicate that extraction efficiency should be similar. No additional radiovalidation data are required for this method at this time.

Data collection method - oily crop matrices: DuPont has submitted an ILV study for an LC/MS/MS method, DuPont Method 13412, for the determination of residues of tribenuron methyl in/on oily crop matrices. This method was also used for data collection in samples of corn grain, sorghum grain, and soybean seed from the crop field trial study submitted in conjunction with this petition.

The ILV submission did not include a copy of the method. The only version of the method, entitled "Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oily Crop Matrices Using SPE Purification and LC/MS/MS Detection," available to the study reviewer for review was a draft version, dated 12/2/03, that was included with the crop field trial submission. Based on the references included in the method, the version of the method that was subjected to ILV was dated 1/28/04.

Using DuPont Method 13412, residues in/on homogenized samples of corn grain, sorghum grain, and soybean seed are extracted with an acetonitrile/potassium phosphate buffer solution. An aliquot of the extract is partitioned with hexane, and the aqueous phase is concentrated for cleanup through an ENV SPE column. Residues are eluted from the column with an ammonium hydroxide/methanol solution, and the eluate is concentrated and mixed with acetonitrile and ammonium acetate solution. Samples are analyzed by LC/MS/MS using electrospray ionization in the positive ion mode. The validated LOQ reported in the method was 0.01 ppm; an LOQ of 0.05 ppm was used for corn grain, sorghum grain, and soybean seed samples from the crop field trials submitted in conjunction with this petition.

Method validation data for DuPont Method 13412 demonstrated adequate method recoveries of tribenuron methyl from corn grain, olive, and soybean seed. Following fortification of samples with each analyte at 0.010 and 0.10 ppm, recoveries of tribenuron methyl averaged 81 ± 2.3%, 86 ± 4.4%, and 78 ± 2.5% from corn grain, olive, and soybean seed, respectively. Recoveries of tribenuron methyl averaged 98 ± 2.6% and 96 ± 3.1% from corn grain and soybean seed, respectively, fortified with tribenuron methyl at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for sorghum grain. Concurrent method recovery data were included with the sorghum crop field trial study; adequate recoveries of tribenuron methyl were obtained from sorghum grain fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in this petition.

Analyte identification is to be confirmed by comparing the ion ratio for the two MS/MS ion transitions acquired during analysis with the average ion ratio obtained for the calibration standards.

A successful ILV trial was conducted using samples of olive and soybean seed fortified with tribenuron methyl at 0.01 and 0.10 ppm.

No radiovalidation data were submitted for the method. In metabolism studies conducted using oil seeds, total radioactive residues were too low in canola seed and cotton seed to allow residue

characterization (0.02 ppm in canola seed and <0.01 ppm in cotton seed). Therefore, it is unlikely that residues of tribenuron methyl would be present in these commodities at levels that would permit adequate determination of extraction efficiency. No radiovalidation data are required for this method at this time.

Data collection - sunflower seed: Samples of sunflower seed from the submitted storage stability and crop field trial studies were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. Briefly, samples of homogenized sunflower seed were extracted with cold phosphate buffer (pH 6), centrifuged under refrigeration, and the aqueous portion cleaned up through an ENVI-Carb SPE column. Residues were eluted with methanol:dichloromethane (10:90, v:v), and the eluate was evaporated to dryness. The residues were redissolved in acetonitrile and phosphate buffer, and analyzed by HPLC/UV using a refrigerated injector and column switching. **The LOQ was 0.05 ppm, and the calculated LOD was 0.008 ppm for sunflower seed.** This method is adequate for data collection based on acceptable concurrent method recovery data submitted with the crop field trial study.

Conclusions. The submitted residue analytical method data are adequate to satisfy data requirements. The existing tolerance enforcement methods, Method AMR 337-85 (Revision A) and DuPont Method 1381, are adequate to enforce the proposed tolerances for non-oily cereal commodities (corn forage and stover, rice grain and straw, and sorghum forage and stover) and oily crop matrices (corn grain, sorghum grain, soybean seed, and sunflower seed), respectively.

The submitted LC/MS and LC/MS/MS methods, DuPont Methods 5367 and 13412, are adequate for data collection purposes. If the petitioner wishes DuPont Method 5367 to be used for enforcement, a revised version of the method, incorporating the method modifications made by the ILV laboratory, must be submitted. In addition, the petitioner must provide confirmation that the ILV study was conducted by analysts unfamiliar with the method, to assure HED that the ILV study was truly independent. If the petitioner wishes DuPont Method 13412 to be used for enforcement, the final version of the method must be submitted; the version should include the modifications made by the ILV laboratory in the course of validation.

The HPLC/UV method, DuPont-3595, is adequate for data collection purposes for sunflower seed.

860.1360 Multiresidue Methods

D304059, 6/24/04, R. Griffin

The FDA PESTDATA database dated 06/05 (PAM Volume I, Appendix I) does not contain any information regarding the recovery of tribenuron methyl using multiresidue methods. Data investigating the behavior of tribenuron methyl using the FDA Multiresidue Methods have been submitted by the registrant (MRID 40927202); these data were apparently not received by FDA for evaluation. The available data indicate that residues of tribenuron methyl are not recovered by the FDA multiresidue methods.

860.1380 Storage Stability

D304059, 6/24/04, R. Griffin
45098405.de11.wpd, 8/10/04, S. Ary

46358501.de2.doc (Sunflower)
46421901.de21.doc (Corn forage and stover and soybean seed; also includes review of 46435901)

Sunflower: IR-4 has submitted storage stability data for tribenuron methyl residues in sunflower seed in conjunction with sunflower field trials. Untreated samples of sunflower seed were fortified with tribenuron methyl at 0.1 ppm and stored frozen (ca. -20 °C) for up to 8.6 months.

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. The LOQ was 0.05 ppm. The results of the concurrent method recovery analyses indicate that the method was not performing adequately during the data collection period; recoveries were low and variable. The petitioner stated that during the analysis month, severe weather conditions caused frequent power outages and instrument instability. Low recoveries were also obtained for stored fortified samples.

The results of the study are considered unreliable, and no conclusions may be made concerning the stability of tribenuron methyl residues in/on sunflower seed, because poor recoveries were obtained for both the fresh and stored fortified sunflower samples.

Corn forage, corn stover, and soybean seed: DuPont has submitted storage stability data for tribenuron methyl residues in corn forage and stover, and soybean seed. The study was initiated in conjunction with corn, rice, sorghum, and soybean field trials (MRID 46421901) and continued to include a longer storage interval for corn forage and soybean seed (MRID 46435901). Untreated samples of corn stover and soybean seed were fortified with a mixture of thifensulfuron methyl and tribenuron methyl at 0.50 ppm each and stored frozen (-20 °C) for up to 4 months (corn stover and soybean seed) or 6 months (corn forage). The results indicate that under these conditions, residues of tribenuron methyl are relatively stable in/on corn stover and soybean seed for up to 4 months, and in/on corn forage for up to 6 months.

Samples of corn forage and stover were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 5367. Samples of soybean seed were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 13412. The validated LOQ for both methods was 0.05 ppm for all matrices. These methods are adequate for data collection based on acceptable concurrent method recovery data.

The storage intervals and conditions of samples from the crop field trials submitted to support this petition are presented in Table 4.

Table 4. Summary of Storage Conditions and Intervals of Samples from Crop Field Trial Studies.			
Matrix	Storage Temperature (°C)	Actual Storage Duration	Interval of Demonstrated Storage Stability
Corn, forage	*ca.* -20	70-85 days (2.3-2.8 months)	6 months in fortified corn forage stored frozen
Corn, grain		73-114 days (2.4-3.8 months)	21 months in fortified wheat grain stored frozen
Corn, stover		55-108 days (1.8-3.6 months)	4 months in fortified corn stover stored frozen
Rice, grain		37-43 days (1.2-1.4 months)	21 months in fortified wheat grain stored frozen
Rice, straw		63-69 days (2.1-2.3 months)	21 months in fortified wheat straw stored frozen
Sorghum, forage		74-93 days (2.4-3.1 months)	6 months in fortified corn forage stored frozen
Sorghum, grain		99-107 days (3.3-3.5 months)	21 months in fortified wheat grain stored frozen
Sorghum, stover		80-108 days (2.6-3.6 months)	4 months in fortified corn stover stored frozen
Soybean, seed		69-94 days (2.3-3.1 months)	4 months in fortified soybean seed stored frozen
Sunflower, seed	-20 to -17	196-235 days (6.4-7.7 months)	14 months in/on fortified cottonseed stored frozen

Previously submitted storage stability data: Storage stability data have been submitted previously which indicate that residues of tribenuron methyl are stable under frozen storage conditions for up to 21 months in/on wheat grain and straw, but that residues decline approximately 60% in fortified barley and wheat grain and straw samples stored at ambient temperatures for 5-6 days (D304059, 6/24/04, R. Griffin). In addition, residues of tribenuron methyl are relatively stable in/on cottonseed stored frozen for up to 14 months (45098405.de11.wpd, 8/10/04, S. Ary).

Conclusions. The submitted storage stability data for corn forage, corn stover, and soybean seed are adequate and will support the storage intervals and conditions of samples of corn forage, corn stover, sorghum forage, sorghum stover, and soybean seed from the submitted crop field trials. The available data for wheat grain and straw will support the storage conditions and intervals of samples of corn grain, rice grain, rice straw, and sorghum grain from the submitted crop field trials.

The submitted storage stability data for sunflower seed are inadequate due to poor method performance on the dates of analysis. However, the available data for cottonseed may be translated to support the storage conditions and intervals of samples from the sunflower field trials.

860.1400 Water, Fish, and Irrigated Crops

There are no proposed uses that are relevant to this guideline topic.

860.1460 Food Handling

There are no proposed uses that are relevant to this guideline topic.

860.1480 Meat, Milk, Poultry, and Eggs

D304059, 6/24/04. R. Griffin

No livestock feeding studies with tribenuron methyl were submitted as part of the subject tolerance petition. HED has previously concluded that tribenuron methyl residues in ruminant commodities may be classified under 40 CFR §180.6(a)(3); i.e., there is no expectation of finite residues. Therefore, no ruminant feeding studies are required. It was also concluded that poultry metabolism data are not required for reregistration.

Following reassessment of tolerances eligible for reregistration, the maximum theoretical dietary burdens (MTDBs) of tribenuron methyl to livestock were calculated to be 0.26 ppm for beef and dairy cattle, and 0.04 ppm for poultry and swine. The proposed uses of tribenuron methyl on field corn, rice, sorghum, soybean, and sunflower are not expected to change the previously calculated MTDBs because residues in/on the RACs of these crops were below the LOQ, even at exaggerated application rates. Therefore, livestock feeding studies are not required to support the proposed uses.

860.1500 Crop Field Trials

46358501.del.doc (Sunflower)
46421901.del1.doc (Corn, rice, sorghum, soybean)

Table 5. Summary of Residue Data from Crop Field Trials with Tribenuron Methyl.

Crop matrix	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median	Mean	Std. Dev.
FIELD CORN (proposed use = pre-plant application at 0.015 lb ai/A total application rate)									
Corn, forage	0.078-0.080	75-106	6	<0.05	<0.05	<0.05	0.025	0.025	0
Corn, grain	0.078-0.080	112-150	6	<0.05	<0.05	<0.05	0.025	0.025	0
Corn, stover	0.078-0.080	112-150	6	<0.05	<0.05	<0.05	0.025	0.025	0
RICE (proposed use = pre-plant application at 0.015 lb ai/A total application rate)									
Rice, grain	0.078-0.079	106-129	6	<0.05	<0.05	<0.05	0.025	0.025	0
Rice, straw	0.078-0.079	106-129	6	<0.05	<0.05	<0.05	0.025	0.025	0
SORGHUM (proposed use = pre-plant application at 0.015 lb ai/A total application rate)									
Sorghum, forage	0.078-0.079	87-103	6	<0.05	<0.05	<0.05	0.025	0.025	0
Sorghum, grain	0.078-0.079	133-144	6	<0.05	<0.05	<0.05	0.025	0.025	0
Sorghum, stover	0.078-0.079	133-144	6	<0.05	<0.05	<0.05	0.025	0.025	0
SOYBEAN (proposed use = pre-plant application at 0.015 lb ai/A total application rate)									
Soybean, seed	0.078-0.079	135-148	6	<0.05	<0.05	<0.05	0.025	0.025	0

Table 5. Summary of Residue Data from Crop Field Trials with Tribenuron Methyl.									
Crop matrix	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT [1]	Median	Mean	Std. Dev.
SUNFLOWER (proposed use = 0.048 lb ai/A total application rate, 70-day PHI)									
Sunflower seed	0.047-0.049	66-83	14	<0.05	<0.05	<0.05	0.025	0.025	0

[1] HAFT = Highest average field trial result.

Field corn, rice, sorghum, and soybean

DuPont has submitted field trial data for tribenuron methyl on corn, rice, sorghum, and soybeans. Three field trials were conducted in the United States during the 2003 growing season for each crop. Field corn trials were conducted in Zones 1 (PA), 2 (GA), and 5 (NE); rice trials were conducted in Zones 4 (AR), 6 (TX), and 10 (CA); sorghum trials were conducted in Zones 5 (NE), 6 (OK), and 8 (OK); and soybean trials were conducted in Zones 2 (GA), 4 (AR), and 5 (NE).

Each field test consisted of one untreated plot and one treated plot. A single burndown application of a 75% DF formulation of tribenuron methyl was made at ~0.078 lb ai/A (~5x the proposed maximum seasonal rate) on the day of crop planting. It is noted that a 75% DF formulation of thifensulfuron methyl was tank-mixed with the tribenuron methyl formulation for application. The application was made using ground equipment in ~10-29 gal/A, with an adjuvant added to the spray mixture. Samples of corn forage were harvested 75-106 days after planting (DAP), and samples of sorghum forage were harvested 87-103 DAP. Samples of mature corn grain and stover were harvested 112-150 DAP, samples of mature rice grain and straw were harvested 106-129 DAP, samples of mature sorghum grain and stover were harvested 133-144 DAP, and samples of mature soybean seed were harvested 135-148 DAP.

Samples of non-oily crop matrices (corn forage and stover, rice grain and straw, and sorghum forage and stover) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 5367. Samples of oily crop matrices (corn grain, sorghum grain, and soybean seed) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 13412. The validated LOQ for both methods was 0.05 ppm, and the estimated limit of detection (LOD) was 0.02 ppm for all matrices. These methods are adequate for data collection based on acceptable concurrent method recovery data.

The storage intervals of crop samples from harvest to analysis are presented in Table 4. Adequate storage stability data, for corn forage and stover, soybean seed, and wheat grain, and straw are available to support the storage conditions and intervals of samples from the corn, rice, sorghum, and soybean field trials.

The results of the crop field trials are presented in Table 5. Residues of tribenuron methyl were below the method LOQ (<0.05 ppm) in/on all samples of field corn forage, grain and stover, rice grain and straw, sorghum forage, grain, and stover, and soybean seed harvested at the appropriate growth stage following a burndown treatment made on the day of planting. No residue decline studies were conducted because application was made prior to crop emergence.

Sunflower

IR-4 has submitted field trial data for tribenuron methyl on sunflower. Seven trials were conducted in the United States in Zones 5 (ND; 2 trials), 7 (NE and ND; 4 trials), and 8 (CO; 1 trial) during the 2001 growing season.

Each field test consisted of one untreated plot and one treated plot. One preemergence ground application and two broadcast foliar applications of a 75% tribenuron methyl DF formulation were made to sulfonylurea-tolerant sunflower at ~0.016 lb ai/A/application for a total application rate of ~0.048 lb ai/A (1x the proposed maximum seasonal rate). The first foliar application was made 17-32 days following the preemergence application, and the second foliar application was made 10-21 days later. An additional plot at one trial site was treated in the same manner at an exaggerated rate: ~0.08 lb ai/A/application for a total rate of ~0.24 lb ai/A (5x the nominal field trial rate). All applications were made using ground equipment in ~10-23 gal/A, with an adjuvant added to the spray mixture. Samples of mature sunflower seed were harvested 66-83 days after the last application.

The storage intervals of sunflower seed samples from harvest to analysis are reported in Table 4. The available storage stability data for cottonseed may be translated to support the storage conditions and intervals of samples from the sunflower field trials.

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. The LOQ is 0.05 ppm, and the calculated LOD is 0.008 ppm for sunflower seed. This method is adequate for data collection based on acceptable concurrent method recovery data.

The results of the sunflower field trials are presented in Table 5. Residues of tribenuron methyl were less than the LOQ (<0.05 ppm) in/on sunflower seed (sulfonylurea-tolerant hybrid varieties) harvested 66-83 days after treatment at a total rate of 0.047-0.049 lb ai/A. Residues were also nonquantifiable (<0.05 ppm) in/on sunflower seed harvested 83 days after treatment at an exaggerated rate of 0.242 lb ai/A. No residue decline studies were conducted because applications were made early in the season.

Conclusions. The submitted crop field trial data for field corn, rice, sorghum, and soybean are adequate to satisfy data requirements. The crop field trial data for corn, rice, sorghum, and soybeans reflect a total of three trials for each crop conducted at a 5x treatment rate. HED had previously concluded that three crop field trials would be adequate to support preplant burndown use of tribenuron methyl provided that residues were nonquantifiable following treatment at 5x (ChemSAC meeting of 2/13/03). The Zones in which the trials were conducted [Zones 1, 2, and 5 for field corn; Zones 4, 6, and 10 for rice; Zones 5, 6, and 8 for sorghum; and Zones 2, 4, and 5 for soybean] represent the major growing regions for each crop. Applications in the crop field trials were made with an adjuvant added to the spray mixture, which supports the proposed use pattern. No data were submitted for soybean forage and hay, however, a restriction against the feeding of these commodities has been proposed on the label.

No data were submitted for aspirated grain fractions. Because tribenuron methyl is proposed to be applied preemergence to corn, sorghum, and soybean, no data for aspirated grain fractions are required.

The available data would support tolerances for residues of tribenuron methyl at 0.05 ppm (LOQ) in/on field corn forage, field corn grain, field corn stover, rice grain, rice straw, sorghum forage, sorghum grain, sorghum stover, and soybean seed. The ChemSac (2/13/03 minutes; min_201) determined that that limited field trials (3 trials in Regions 2, 4, and 5) would be acceptable to support burndown use of tribenuron methyl for soybean if residues were <LOQ following 5x treatment. Further discussion between DuPont and R. Loranger resulted in the expansion to corn, rice, and sorghum.

The submitted crop field trial data for sunflower are adequate to satisfy data requirements. The number and locations of sunflower field trials are in accordance with OPPTS Guideline 860.1500, in consideration of the fact that residues were below the LOQ in/on all samples. The available data would support a total of three applications of a DF formulation of tribenuron methyl to sulfonyl-urea tolerant sunflower at 0.016 lb ai/A/application with a 70-day PHI; the data also support the use of an adjuvant in the spray mixture. The available data indicate that a tolerance of 0.05 ppm (LOQ) would be appropriate for residues of tribenuron methyl in/on sunflower seed.

860.1520 Processed Food and Feed

No processing studies were submitted with this petition. Because residues of tribenuron methyl were below the LOQ in/on all samples of corn grain, rice grain, sorghum grain, soybean seed, and sunflower seed following treatment at 5x the proposed maximum seasonal rate, no processing data will be required to support the proposed uses.

860.1650 Submittal of Analytical Reference Standards

An analytical standard for tribenuron methyl is currently available in the National Pesticide Standards Repository (personal communication with Dallas Wright, ACB, 5/3/06).

860.1850 Confined Accumulation in Rotational Crops

D304059, 6/24/04, R. Griffin

The reregistration requirements for confined accumulation in rotational crops are satisfied. Two confined rotational crop studies, with triazine- and phenyl-labeled tribenuron methyl, have been submitted by the petitioner and reviewed by EFED. The results of these studies indicate that tribenuron methyl was not detected in any sample of confined rotational crop commodity planted on sandy loam soils which had been treated at 0.028-0.031 lb ai/A (~2x the maximum proposed seasonal rate to corn, rice, sorghum, and soybean; ~0.6x the maximum proposed seasonal rate to sunflower).

In the phenyl-label study, TRR accumulated ≥0.01 ppm in/on wheat forage (0.010-0.020 ppm), wheat straw (0.054 ppm), soybean forage (0.008-0.017 ppm), soybean hay (0.052 ppm), sorghum forage (0.007-0.016 ppm), and sorghum stover (0.082 ppm) planted 30 days posttreatment; TRR

were <0.01 ppm in/on cabbage heads and foliage, beet roots and tops, wheat grain, soybean seed, and sorghum grain from the same plantback interval. At the 120-day plantback interval, TRR were 0.010 ppm in soybean forage, and 0.019 ppm in sorghum stover; TRR were <0.01 ppm in/on cabbage heads and foliage, beet roots and tops, wheat forage, straw, and grain, soybean hay and seed, and sorghum grain from the 120-day plantback interval. Samples of 30-day PBI wheat straw, soybean hay, and sorghum stover as well as 120-day PBI sorghum stover were subjected to extraction/characterization of residues, which identified saccharin as the major degradate (0.007-0.021 ppm). Tribenuron methyl was not detected in any sample.

In the other study, TRR accumulated ≥0.01 ppm in/on beet tops (0.075-0.156 ppm), cabbage foliage (0.018-0.135 ppm), sorghum forage (0.031-0.177 ppm), sorghum straw (0.281 ppm), and sorghum grain (0.016 ppm) planted 30 days posttreatment; TRR were <0.01 ppm in/on beet roots and cabbage heads from the same plantback interval. At the 120-day plantback interval, TRR were 0.013-0.031 ppm in beet tops, 0.010-0.047 ppm in cabbage foliage, 0.013-0.086 ppm in sorghum forage, 0.148 ppm in sorghum straw, and 0.010 ppm in sorghum grain; TRR were <0.01 ppm in/on beet roots and cabbage heads from the 120-day plantback interval. Samples of 30-day beet tops, cabbage foliage, and sorghum straw, and 120-day PBI beet tops, cabbage foliage, and sorghum straw and grain were subjected to extraction/characterization of residues. The following metabolites were detected in 30-day PBI samples: triazine amine (beet tops only), N-demethyl triazine amine (beet tops, cabbage foliage, and sorghum straw), O-demethyl triazine amine (beet tops only), and α-hydroxy triazine amine (beet tops only). Tribenuron methyl was not detected in any sample.

Conclusions. The available confined rotational crop data are adequate to support the proposed uses on field corn, rice, sorghum, and soybean. For the proposed use on sunflower, the application rate used in the confined rotational crop studies is <1x the maximum proposed seasonal rate. In consideration of the fact that no residues of tribenuron methyl were detected in any of the crop commodities from the confined rotational crop studies, and residues were below the LOQ in corn, rice, sorghum, and soybean commodities following at-planting treatment at 5x and in sunflower seed following postemergence treatment at 5x, HED concludes that the available confined rotational crop data are adequate to support the proposed use on sunflower.

860.1900 Field Accumulation in Rotational Crops

D304059, 6/24/04. R. Griffin

HED concluded that the available confined rotational crop data indicate that a 30-day plantback interval is appropriate for all crops without registered uses.

Currently, the following plantback intervals exist on the product labels for EPA Reg. Nos. 352-509 and 352-611: The current product labels for the 75% and 25% DF formulations specify the following rotational crop restrictions: a 0-day plantback interval for barley, oat, soybean, and wheat; a 60-day plantback interval for canola, winter rape, and sugarbeet; and a 45-day plantback interval for all other crops. The current plantback intervals are adequate.

860.1550 Proposed Tolerances

Tolerances for residues of tribenuron methyl are currently expressed in terms of tribenuron methyl *per se*; the existing tolerance definition is adequate.

There are no established or proposed Codex MRLs for residues of tribenuron methyl. Canadian MRLs have been established for residues of tribenuron methyl; however, no MRLs have been established for the requested crops. No Mexican MRLs have been established for tribenuron methyl.

A summary of the recommended tolerances for the current petition is presented in Table 6. Acceptable crop field trial data are available to support the proposed uses on field corn, rice, sorghum, soybean, and sunflower. In the acceptable corn, rice, sorghum, and soybean field trials conducted at 5x the maximum proposed rate, residues of tribenuron methyl were below the LOQ (<0.05 ppm) in/on all samples. In the acceptable sunflower field trials conducted at 1x the maximum proposed rate, residues of tribenuron methyl were below the LOQ (<0.05 ppm) in/on all samples. Therefore, tolerances at the LOQ are appropriate for field corn, rice, sorghum, sorghum, and sunflower commodities. The petitioner has proposed a restriction against feeding treated soybean forage and hay to livestock; therefore, no tolerances for soybean forage and hay are needed.

The proposed tolerances should be revised to reflect the correct commodity definitions as specified in Table 6.

Table 6. Tolerance Summary for Tribenuron Methyl.

Commodity	Established/Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments; *Correct Commodity Definition*
Corn, field, grain	0.05	0.05	
Corn, field, forage	0.05	0.05	
Corn, field stover	0.05	0.05	
Grain sorghum, forage	0.05	0.05	*Sorghum, forage*
Grain sorghum, stover	0.05	0.05	*Sorghum, stover*
Grain sorghum, grain	0.05	0.05	*Sorghum, grain*
Rice, grain	0.05	0.05	
Rice, straw	0.05	0.05	
Soybean	0.05	0.05	*Soybean, seed*
Sunflower seed	0.05	0.05	*Sunflower, seed*

References

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

DP Barcode:	D305958
Subject:	860.1340 DER for MRID 45098401 (Residue analytical method for tribenuron methyl residues in/on Cotton)
Primary Reviewer:	S. Ary
Approved by:	A. Nielsen
Date:	8/10/04
MRID:	45098405

DP Barcode:	D305958
Subject:	860.1380 DER for MRID 45098405 (Tribenuron methyl in/on Cotton)
Primary Reviewer:	S. Ary
Approved by:	A. Nielsen
Date:	8/10/04
MRID:	45098405 and 45098402

DP Barcode:	D311607
Subject:	Thifensulfuron Methyl. HED=s Response to E.I. du Pont de Nemours and Company=s Comments to the ASummary of Residue Chemistry Data Evaluation Records for the Establishment of Tolerances for New Uses of Thifensulfuron Methyl on Canola, Flax, and Cotton.@
From:	S. Ary
To:	J. Tompkins
Date:	1/4/05
MRIDs:	None

DP Barcode:	D266130
Subject:	Tribenuron Methyl. PP#0F6135. Summary of Residue Chemistry Data Evaluation Records for the Establishment of Permanent Tolerances for New Uses of Tribenuron Methyl on Canola, Cotton, and Flax.
From:	C. Swartz
To:	J. Tompkins
Date:	x/xx/06
MRIDs:	45089801-45089804 and 45098405

Attachments:
International Residue Limit Status sheet

Template Version September 2005

INTERNATIONAL RESIDUE LIMIT STATUS

Chemical Name: methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate	Common Name: Tribenuron methyl	X Proposed tolerance 9 Reevaluated tolerance 9 Other	Date: 04/03/06

Codex Status (Maximum Residue Limits)	U. S. Tolerances
X No Codex proposal step 6 or above 9 No Codex proposal step 6 or above for the crops requested	Petition Number: PP#4F6890 and PP#4E6855 DP Barcode: D312493 & D314429 Decision Numbers: 352136 & 353013
Residue definition (step 8/CXL): N/A	*Reviewer/Branch:* S. Hummel, RRB4
	Residue definition: Tribenuron methyl

Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Corn, field, grain	0.05
		Corn, field, forage	0.05
		Corn, field stover	0.05
		Grain sorghum, forage	0.05
		Grain sorghum, stover	0.05
		Grain sorghum, grain	0.05
		Rice, grain	0.05
		Rice, straw	0.05
		Soybean	0.05
		Sunflower seed	0.05

Limits for Canada	Limits for Mexico
9 No Limits X No Limits for the crops requested	X No Limits 9 No Limits for the crops requested
Residue definition: tribenuron methyl [methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate]	*Residue definition:*

Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)

Notes/Special Instructions:
S. Funk, 04/24/2006.

Primary Evaluator — Susan V. Hummel — Date: 8/8/06

Susan V. Hummel, Sr. Scientist, RRB4

Peer Reviewer — Date: 8/8/06

Thurston G. Morton, Chemist, RRB4

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORTS:

46352002 Bramble, F.Q. and Pentz, A.M. (2004) Independent Laboratory Validation of DuPont-5367 "Analytical Enforcement Method for the Determination of Thifensulfuron Methyl, Metsulfuron Methyl, Chlorsulfuron, Tribenuron Methyl, and Flupysulfuron Methyl in Cereals (Wheat Grain, Forage and Straw)" in Wheat Grain, Barley Grain, Corn Grain, and Tomato: Project Number: DuPont-8054. Unpublished study prepared by E.I. du Pont de Nemours and Company. 48 pages.

46421901 Carringer, S.J. (2004) Magnitude of Residues of Thifensulfuron Methyl and Tribenuron Methyl in Rice, Corn, Sorghum, and Soybeans Following Pre-Plant Burn-Down Applications of DPX-M6316 75 GT XP Herbicide and DPX-L5300 75 XP Herbicide at Maximum Label Rates – U.S.A., 2003: Lab Project Number: ML03-1101-DUP. Study No. TCI-03-080. Unpublished study prepared by The Carringers, Inc. 552 pages.

EXECUTIVE SUMMARY:

E.I. du Pont de Nemours and Company have submitted an independent laboratory validation (ILV) study for an LC/MS method, DuPont Method 5367, for the determination of residues of tribenuron methyl in/on cereal matrices. This method was also used for data collection in samples of corn forage and stover, rice grain and straw, and sorghum forage and stover from the crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901).

The method is entitled "Analytical Enforcement Method for the Determination of Thifensulfuron Methyl, Metsulfuron Methyl, Chlorsulfuron, Tribenuron Methyl, and Flupyrsulfuron Methyl in Cereals (Wheat Grain, Forage and Straw)." The ILV submission did not include a copy of the method. A full writeup of the method, dated 4/30/01, was included as an appendix to the analytical laboratory report in the crop field trial submission.

We note that the submission contains ILV data for thifensulfuron methyl, metsulfuron methyl, chlorsulfuron, and flupyrsulfuron methyl which are not reviewed herein. Data for thifensulfuron methyl were reviewed separately (46352002.del.doc).

Using DuPont Method 5367, samples of non-oily cereal commodities (corn forage and stover, rice grain and straw, and sorghum forage and stover) are extracted with a potassium phosphate buffer solution, and an aliquot of the extract is cleaned up through an ENVI-Carb solid-phase extraction (SPE) column. Residues are eluted from the column with an acidic methanol/methylene chloride solution, and the eluate is evaporated to dryness and redissolved in an acetonitrile/0.01 M acetic acid solution for analysis by LC/MS. The validated limit of quantitation (LOQ) reported in the method was 0.01 ppm for wheat grain and 0.05 ppm for wheat forage and straw; an LOQ of 0.05 ppm was used for commodities from the crop field trials submitted in conjunction with DP Barcode D314429.

Method validation data for DuPont Method 5367 demonstrated adequate method recoveries of tribenuron methyl from corn forage, corn stover, rice grain, wheat grain, wheat forage, and wheat straw. Following fortification of wheat grain samples at 0.010 and 0.100 ppm, recoveries of tribenuron methyl averaged 81 ± 5.3%. Recoveries of tribenuron methyl averaged 98 ± 6.3% and 91 ± 7.7% from wheat forage and straw, respectively, fortified at 0.050 and 0.500 ppm, and 95 ± 2.5%, 80 ± 2.4%, and 88 ± 1.5% from corn forage, corn stover, and rice grain, respectively, fortified at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for rice straw or sorghum forage and stover. Concurrent method recovery data were included with the crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901); adequate recoveries of tribenuron methyl were obtained from rice straw fortified at 0.05 and 0.10 ppm and from sorghum forage and stover fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in the petition associated with DP Barcode D314429.

Analyte identification is to be confirmed by analyzing sample extracts using LC/MS/MS and comparing the ion ratio for the two MS/MS ion transitions acquired during analysis with the average ion ratio obtained for the calibration standards.

Adequate independent laboratory validation data have been submitted for this method, using barley grain, wheat grain, and tomato. The ILV of the method failed for corn grain; however, the petitioner has submitted a separate method for the determination of tribenuron methyl residues in/on oily crop matrices (refer to the tribenuron methyl DER for MRID 46352003). The ILV laboratory modified one of the solvents used for final extracts and for LC mobile phase, from 0.01 M acetic acid to 50 mM ammonium acetate (buffered to pH 6.2), because the acidic solvent was found to cause degradation of tribenuron methyl. No additional radiovalidation data are required for this method at this time.

No radiovalidation data were submitted for the method. The petitioner stated that extraction efficiency data could not be generated because no residues of tribenuron methyl were observed in the wheat metabolism study (see DP Barcode 304059, 6/24/04, R. Griffin). The petitioner noted that extraction efficiency data for the method have been generated for chlorsulfuron in wheat and oats, and that tribenuron methyl has similar polarity and solubility to chlorsulfuron which would indicate that extraction efficiency should be similar.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, analytical method test data are tentatively classified as scientifically acceptable, pending confirmation by the petitioner that the ILV study was conducted by analysts unfamiliar with the method. If the petitioner wishes DuPont Method 5367 to be used for enforcement, a revised version of the method, incorporating the method modifications made by the ILV laboratory, must be submitted.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D330633, D330814, D330702.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, oats, and wheat, and grass grown for seed and for nonfood/feed use on cotton grown in TX only. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

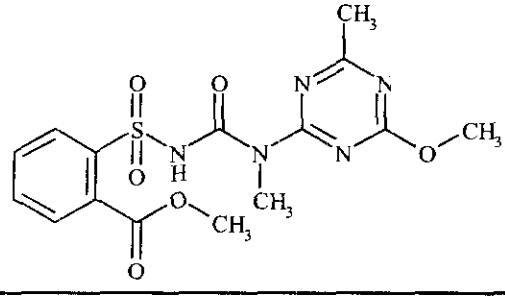
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate

TABLE A.1. Tribenuron Methyl Nomenclature.	
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin
Solvent solubility	At 25 °C: *acetone* - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

Samples of corn forage and stover from the storage stability study and samples of corn forage and stover, rice grain and straw, and sorghum forage and stover from the crop field trial study submitted in conjunction with DP Barcode D314429 were analyzed for residues of tribenuron methyl using LC/MS method DuPont Method 5367 entitled "Analytical Enforcement Method for the Determination of Thifensulfuron Methyl, Metsulfuron Methyl, Chlorsulfuron, Tribenuron Methyl, and Flupyrsulfuron Methyl in Cereals (Wheat Grain, Forage and Straw)."

B.1.1. Principle of the Method:

Samples of non-oily cereal commodities (corn forage and stover, rice grain and straw, and sorghum forage and stover) are extracted with a potassium phosphate buffer solution and an aliquot of the extract is cleaned up through an ENVI-Carb SPE column. Residues are eluted from the column with an acidic methanol/methylene chloride solution and the eluate is evaporated to dryness and redissolved in an acetonitrile/0.01 M acetic acid solution for analysis by LC/MS.

TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of Tribenuron Methyl Residues in Cereal Commodities.	
Method ID	DuPont Method 5367
Analyte	Tribenuron methyl [also thifensulfuron methyl, metsulfuron methyl, chlorsulfuron, and flupyrsulfuron]
Extraction solvent/technique	Samples are extracted with 20 mM potassium phosphate buffer (pH 6.0) under refrigeration for one hour; the mixture is then homogenized and the extract is isolated by centrifugation. The extraction is repeated and the extracts are combined and brought to volume in purified water.
Cleanup strategies	Aliquots of the extract are applied to ENVI-Carb SPE columns. Residues are eluted with methanol:methylene chloride (10:90, v:v) containing 0.1 M formic acid. The eluate is evaporated to dryness and redissolved in acetonitrile:0.01 M acetic acid (10:90, v:v).
Instrument/Detector	HPLC employing mass selective (MS) detection, using a C8 column and a gradient mobile phase of acetonitrile and 0.01 M acetic acid.
Standardization method	External standardization; the response factor (concentration of analyte divided by analyte peak area) is calculated for a series of standards and the average response factor is used to calculate analyte concentration in samples.
Stability of std solutions	Standard stock (1000 µg/ml) in acetonitrile were reported to be stable for 1 month when stored at -20 to 0 °C. Fortification standards (10 and 1.0 µg/ml) were reported to be stable for 2 weeks when stored at -20 to 0 °C. The method specifies that fresh chromatographic standard solutions should be prepared daily (from the fortification standard).
Retention times	Tribenuron methyl: ~34 minutes

B.2. Enforcement Method

The petitioner did not state whether the submitted method is intended for enforcement purposes. An HPLC method with electrochemical detection exists for the enforcement of tolerances for residues of tribenuron methyl in/on barley and wheat commodities.

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Method validation data for wheat forage, grain, and straw were included with method writeup. These data were generated by DuPont during method development; the origin of the samples was not specified. In addition, method validation data for corn forage and stover and rice grain were included with the crop field trial results reported in MRID 46421901; these data were generated by Morse Laboratories, the laboratory that conducted the crop field trial analyses. We note that Morse Laboratories modified Method 5367 to include the modifications made during ILV (see Section C.3) and analyzed samples using LC/MS/MS instead of LC/MS. Method validation data are presented in Table C.1.1; adequate recoveries of tribenuron methyl were obtained. Following fortification of wheat grain samples at 0.010 and 0.100 ppm, recoveries of tribenuron methyl averaged 81 ± 5.3%. Recoveries of tribenuron methyl averaged 98 ± 6.3% and 91 ± 7.7% from wheat forage and straw, respectively, fortified at 0.050 and 0.500 ppm, and 95 ± 2.5%, 80 ± 2.4%, and 88 ± 1.5% from corn forage, corn stover, and rice grain, respectively, fortified at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for rice straw or sorghum forage and stover. Concurrent method recovery data for rice straw and sorghum forage and stover were included with the crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901); adequate recoveries of tribenuron methyl were obtained from rice straw fortified at 0.05 and 0.10 ppm and from sorghum forage and stover fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in the petition associated with DP Barcode D314429.

Confirmatory analysis procedures are included in the method. For analyte confirmation, sample extracts are to be analyzed by LC/MS/MS and the ion ratio for the two MS/MS ion transitions acquired during analysis is to be compared with the average ion ratio obtained for the calibration standards.

No radiovalidation data were submitted for the method. The petitioner stated that extraction efficiency data could not be generated because no residues of tribenuron methyl were observed in the wheat metabolism study (see DP Barcode 304059, 6/24/04, R. Griffin). The petitioner noted that extraction efficiency data for the method have been generated for chlorsulfuron in wheat and oats, and that tribenuron methyl has similar polarity and solubility to chlorsulfuron which would indicate that extraction efficiency should be similar.

The LOQ reported in the method is 0.01 ppm for wheat grain and 0.05 ppm for wheat forage and straw. In the analysis of crop field trial samples, Morse Laboratories reported the LOQ to be 0.05 ppm for all matrices.

TABLE C.1.1. Recovery Results from Method Validation of Cereal Commodities using the Data-Gathering Analytical Method. [1]

Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD [CV] (%)
Method validation conducted by DuPont			
Wheat grain	0.010	72, 81, 81, 90, 91	83 ± 5.3 [6.4]
	0.100	82, 82, 84, 85, 85	
Wheat forage	0.050	84, 96, 96, 102, 104	98 ± 6.3 [6.4]
	0.500	93, 99, 100, 100, 106	
Wheat straw	0.050	80, 82, 84, 98, 98	91 ± 7.7 [8.4]
	0.500	87, 88, 97, 97, 100	
Method validation conducted by Morse Laboratories [2]			
Rice grain	0.05	89, 90	88 ± 1.5 [1.7]
	0.5	87, 87	
Corn forage	0.05	92, 98	95 ± 2.5 [2.6]
	0.5	95, 96	

TABLE C.1.1. Recovery Results from Method Validation of Cereal Commodities using the Data-Gathering Analytical Method. [1]

Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD [CV] (%)
Corn stover	0.05	77, 82	80 ± 2.4 [3.0]
	0.5	79, 82	

[1] Standards were prepared in LC mobile phase (acetonitrile/0.01 M acetic acid for validation conducted by DuPont, and acetonitrile/50 mM ammonium acetate for validation conducted by Morse Laboratories).
[2] Samples were analyzed using tandem mass spectrometry (MS/MS) detection.

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Tribenuron Methyl Residues in Cereal Commodities.

Method ID	DuPont Method 5367
Analyte	Tribenuron methyl [also thifensulfuron methyl, metsulfuron methyl, chlorsulfuron, and flupyrsulfuron]
Equipment ID	HP1100 HPLC with HP model G1946B mass spectrometer system; Zorbax Eclipse® XDB-C8 column (4.6 mm x 150 mm; 5-µm).
Limit of quantitation (LOQ)	0.01 ppm for wheat grain and 0.05 ppm for wheat forage and straw
Limit of detection (LOD)	Not determined in the method.
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision for residues of tribenuron methyl in wheat grain, forage, and straw, rice grain, and corn forage and stover at the LOQ and 10x LOQ. The overall recovery range was 72-106% with an average recovery of 90% (CV = 9%). See Table C.1.1 above.
Reliability of the Method [ILV]	An independent laboratory method validation [ILV], was conducted to verify the reliability of DuPont Method 5367 for the determination of tribenuron methyl residues in wheat grain, barley grain, corn grain, and tomato. The values obtained are indicative that the LC/MS/MS is reliable in barley and wheat grain and tomato, but not reliable for corn grain (51-61% recovery). See Section C.3.
Linearity	The linearity of the method was not addressed in the method writeup. In the analysis of crop field trial samples, Morse Laboratories found the method/deteetor response to be linear (coefficient of determination, r^2= 1.000) within the range of 0.001-0.030 µg/mL.
Specificity	The control chromatograms generally have no peaks above tbe chromatographic background and the spiked sample chromatograms contain only the analyte peak of interest. Peaks were well defined and symmetrical. There appeared to be no carryover to the following chromatograms.

C.2. Enforcement Method

The petitioner did not state whether the submitted method is intended for enforcement purposes.

C.3. Independent Laboratory Validation

An independent laboratory validation (ILV) study was conducted for DuPont Method 5367 using samples of wheat grain, barley grain, corn grain, and tomato. The ILV was conducted at DuPont Crop Protection Stine-Haskell Research Center (Newark, Delaware). DuPont Method 5367 was developed by DuPont Crop Protection at the Stine-Haskell Research Center. The ILV report did not include a discussion of the personnel who conducted the analyses or their familiarity with the method.

Samples of homogenized untreated wheat grain, barley grain, corn grain, and tomato, from crop field trials, were fortified with tribenuron methyl at 0.010 ppm (LOQ) and 0.10 ppm. Fortified and unfortified (control) samples were analyzed using DuPont Method 5367 as described in Table B.1.1. The ILV laboratory stated that barley and wheat grain were chosen for the study to be representative of cereal grains, that corn grain was chosen to be representative of an oily crop, and that tomato was chosen to be representative of a high water/acid crop. We note that the ILV laboratory used LC/MS/MS for analysis of samples.

The first ILV trial failed for wheat and barley grain (actual data were not presented); significant degradation of tribenuron methyl was observed. The laboratory noted that the acidity of the solutions used for chromatographic analysis was contributing to the degradation of tribenuron methyl, and the method was modified to replace 0.01 M acetic acid with 50 mM ammonium acetate (buffered to pH 6.2). The second ILV trial was successful for wheat and barley grain. The first ILV trial for tomato was successful. Low recoveries were observed for corn grain (51-61% recovery) during the first trial. No additional trials for corn grain were conducted.

Recoveries of tribenuron methyl from the ILV study are reported in Table C.3.1. Residues of tribenuron methyl were less than the LOQ (<0.01 ppm) in two unfortified samples each of wheat grain, barley grain, corn grain, and tomato.

The laboratory reported that a set of 6 samples required 6 person-hours to be prepared for HPLC analysis, with automated LC/MS/MS analysis, run unattended overnight, requiring approximately 1 hour per sample or standard injected. Data processing required approximately 30 minutes.

The ILV report noted that method modifications were required to obtain adequate recoveries of tribenuron methyl. A log of communication between the ILV laboratory and the sponsor representative was included. The ILV laboratory did not identify any critical steps.

TABLE C.3.1. Recovery Results Obtained by an Independent Laboratory Validation of DuPont Method 5367 for the Determination of Tribenuron Methyl in Wheat Grain, Barley Grain, Corn Grain, and Tomato.

Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD [CV] (%)
Wheat grain	0.010	65, 75, 81, 81, 87	77 ± 8.1 [11]
	0.10	64, 72, 77, 84, 85	
Barley grain	0.010	73, 73, 80, 81, 86	82 ± 5.7 [6.9]
	0.10	79, 83, 86, 86, 90	
Corn grain	0.010	55, 56, 57, 59, 61	55 ± 3.2 [5.8]
	0.10	51, 51, 53, 54, 56	
Tomato	0.010	67, 67, 68, 69, 77	71 ± 3.3 [4.7]
	0.10	70, 71, 72, 72, 75	

D. CONCLUSION

Adequate concurrent method recovery and method validation data have been submitted for DuPont LC/MS Method 5367 for the determination of residues of tribenuron methyl in cereal commodities. Based on the method validation and concurrent method validation, the LC/MS method is adequate for data collection. No radiovalidation data have been submitted for the method; however, radiovalidation data are not required because no residues of tribenuron methyl were detected in any treated wheat commodities from the wheat metabolism study.

The petitioner did not state whether the LC/MS method is to be used for enforcement purposes. Adequate independent laboratory validation data have been submitted for this method, using barley and wheat grain and tomato. The ILV of the method failed for corn grain; however, the petitioner has submitted a separate method for the determination of tribenuron methyl residues in/on oily crop matrices (refer to the tribenuron methyl DER for MRID 46352003). If the petitioner wishes DuPont Method 5367 to be used for enforcement, a revised version of the method, incorporating the method modifications made by the ILV laboratory, must be submitted. In addition, a discussion of the personnel used to conduct the ILV study must be submitted, to assure HED that the ILV study was truly independent.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

F. DOCUMENT TRACKING

RDI: SHummel (7/25/06)
Petition Number: 4F6890
DP Barcode: D314429
PC Code: 128887

Template Version June 2005

Primary Evaluator — Susan V. Hummel — Date: 8/8/06
Susan V. Hummel, Sr. Scientist, RRB4

Peer Reviewer — Date: 8/8/06
Thurston G. Morton, Chemist, RRB4

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORTS:

46352003 Charles, E.; Doran, A.M. (2004) Independent Laboratory Validation of Analytical Method DuPont-13412 for the Determination of Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl and Chlorimuron Ethyl in Olives and Soybean Seed Using SPE Purification and LC/MS/MS Detection: Project Number: DuPont-13398. Study No. 303871 Unpublished study prepared by E.I. du Pont de Nemours and Company. 65 pages.

46421901 Carringer, S.J. (2004) Magnitude of Residues of Thifensulfuron Methyl and Tribenuron Methyl in Rice, Corn, Sorghum, and Soybeans Following Pre-Plant Burn-Down Applications of DPX-M6316 75 GT XP Herbicide and DPX-L5300 75 XP Herbicide at Maximum Label Rates – U.S.A., 2003: Lab Project Number: ML03-1101-DUP. Study No. TCI-03-080. Unpublished study prepared by The Carringers, Inc. 552 pages.

EXECUTIVE SUMMARY:

E.I. du Pont de Nemours and Company have submitted an independent laboratory validation (ILV) study for an LC/MS/MS method, DuPont Method 13412, for the determination of residues of tribenuron methyl in/on oily crop matrices. This method was also used for data collection in samples of corn grain, sorghum grain, and soybean seed from the crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901).

The ILV submission did not include a copy of the method. The only version of the method, entitled "Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oily Crop Matrices Using SPE Purification and LC/MS/MS Detection," available to the study reviewer for review was a draft version, dated 12/2/03, that was included with the crop field trial submission. Based on the references included in the method, the version of the method that was subjected to ILV was dated 1/28/04.

We note that the submission contains ILV data for thifensulfuron methyl, ethametsulfuron methyl, rimsulfuron, and chlorimuron ethyl which are not reviewed herein. Data for thifensulfuron methyl were reviewed separately (46352003.de1.doc).

Using DuPont Method 13412, residues in/on homogenized samples of corn grain, sorghum grain, and soybean seed are extracted with an acetonitrile/potassium phosphate buffer solution. An aliquot of the extract is partitioned with hexane, and the aqueous phase is concentrated for cleanup through an ENV solid-phase extraction (SPE) column. Residues are eluted from the column with an ammonium hydroxide/methanol solution, and the eluate is concentrated and mixed with acetonitrile and ammonium acetate solution. Samples are analyzed by LC/MS/MS using electrospray ionization in the positive ion mode. The validated limit of quantitation (LOQ) reported in the method was 0.01 ppm; an LOQ of 0.05 ppm was used for corn grain, sorghum grain, and soybean seed samples from the crop field trials submitted in conjunction with DP Barcode D314429.

Method validation data for DuPont Method 13412 demonstrated adequate method recoveries of tribenuron methyl from corn grain, olive, and soybean seed. Following fortification of samples with each analyte at 0.010 and 0.10 ppm, recoveries of tribenuron methyl averaged 81 ± 2.3%, 86 ± 4.4%, and 78 ± 2.5% from corn grain, olive, and soybean seed, respectively. Recoveries of tribenuron methyl averaged 98 ± 2.6% and 96 ± 3.1% from corn grain and soybean seed, respectively, fortified with tribenuron methyl at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for sorghum grain. Concurrent method recovery data were included with the sorghum crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901); adequate recoveries of tribenuron methyl were obtained from sorghum grain fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in the petition associated with DP Barcode D314429.

Analyte identification is to be confirmed by comparing the ion ratio for the two MS/MS ion transitions acquired during analysis with the average ion ratio obtained for the calibration standards.

A successful ILV trial was conducted using samples of olive and soybean seed fortified with tribenuron methyl at 0.01 and 0.10 ppm.

No radiovalidation data were submitted for the method. In metabolism studies conducted using oil seeds (canola and cotton; refer to the DERs for MRIDs 45089802 and 45089803, currently under review), total radioactive residues were too low in canola seed and cotton seed to allow residue characterization (0.02 ppm in canola seed and <0.01 ppm in cotton seed). Therefore, it is unlikely that residues of tribenuron methyl would be present in these commodities at levels that would permit adequate determination of extraction efficiency. No radiovalidation data are required for this method at this time.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the analytical method test data are classified as scientifically acceptable. If the petitioner wishes DuPont Method 13412 to be used for enforcement, the final version of the method must be submitted; the version should include the modifications made by the ILV laboratory in the course of validation.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D330633, D330814, D330702.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, oats, and wheat, and grass grown for seed and for nonfood/feed use on cotton grown in TX only. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

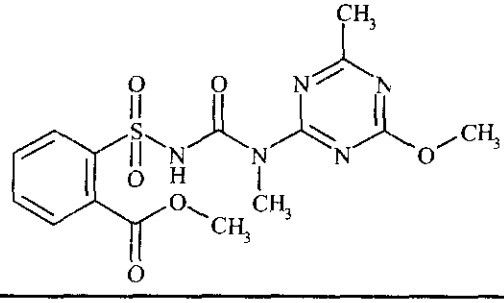
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

Samples of soybean seed from the storage stability study and samples of corn grain, sorghum grain, and soybean seed from the crop field trial study submitted in conjunction with DP Barcode D314429 were analyzed for residues of tribenuron methyl using LC/MS/MS DuPont Method 13412 entitled "Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oily Crop Matrices Using SPE Purification and LC/MS/MS Detection" (draft dated 12/2/03).

B.1.1. Principle of the Method:

Samples of corn grain, sorghum grain, and soybean seed are extracted with an acetonitrile/potassium phosphate buffer solution. An aliquot of the extract is partitioned with hexane and the aqueous phase is concentrated for cleanup through an ENV SPE column. Residues are eluted from the column with an ammonium hydroxide/methanol solution and the eluate is concentrated and mixed with acetonitrile and ammonium acetate solution. Samples are analyzed using LC/MS/MS with electrospray ionization in the positive ion mode.

TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of Tribenuron Methyl Residues in Oily Crop Matrices.	
Method ID	DuPont Method 13412 (draft version, dated 12/2/03)
Analyte	Tribenuron methyl [as well as nicosulfuron, thifensulfuron methyl, ethametsulfuron methyl, rimsulfuron, and chlorimuron ethyl]
Extraction solvent/technique	Homogenized samples are extracted two times with acetonitrile:pH 7 K_2HPO_4 (75:25, v:v); the extracts are isolated by centrifugation, combined, and diluted to volume with acetonitrile.
Cleanup strategies	An aliquot of the extract is partitioned with hexane and the hexane phase is discarded. An aliquot of the remaining aqueous phase is concentrated to near aqueous and then diluted with deionized water. The extract is then quantitatively transferred to a preconditioned ENV SPE column using 10 mM ammonium acetate rinses. Residues are eluted from the SPE column using 25 mM ammonium hydroxide:methanol (1:99, v:v). The eluate is mixed with 5 mM ammonium acetate, concentrated to remove the methanol, mixed with acetonitrile, and then diluted to volume with 50 mM ammonium acetate.
Instrument/Detector	HPLC employing tandem mass spectrometric (MS/MS) detection, using a phenyl-hexyl column and a gradient mobile phase of water and methanol, each containing 0.05% formic acid. The total ion chromatogram from two molecular ion transitions is used for quantitation.
Standardization method	Calibration curve of external standards, with a correlation coefficient of >0.99 using linear regression analysis.
Stability of std solutions	Stock standard solutions (100 µg/ml) in acetonitrile were reported to be stable for 6 months when stored at -10°C. Intermediate and fortification standards (10 and 1.0 µg/ml, and 100 ng/ml) were reported to be stable for 1 month when stored refrigerated. The method specifies that fresh chromatographic standard solutions be prepared from the intermediate standard on the day of analysis; these solution are reportedly stable for 2 days when stored refrigerated.
Retention times	Tribenuron methyl: ~25 minutes

B.2. Enforcement Method

The petitioner did not state whether the submitted method is intended for enforcement purposes. An LC/MS method exists for the enforcement of tolerances for residues of tribenuron methyl in/on canola, cotton, and flax commodities.

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Method validation data for corn grain, olive, and soybean seed were included with the draft method. These data were generated by DuPont during method development using samples of untreated corn grain and soybean seed from crop field trials and samples of commercially purchased olives. In addition, method validation data for corn grain and soybean seed were included with the crop field trial results reported in MRID 46421901; these data were generated by Morse Laboratories, the laboratory that conducted the crop field trial analyses. Method validation data are presented in Table C.1.1; adequate recoveries of tribenuron methyl were obtained. Following fortification of samples at 0.010 and 0.10 ppm, recoveries of tribenuron methyl averaged 81 ± 2.3%, 86 ± 4.4%, and 78 ± 2.5% from corn grain, olive, and soybean seed respectively. Recoveries of tribenuron methyl averaged 98 ± 2.6% and 96 ± 3.1% from corn grain and soybean seed, respectively, fortified at 0.05 and 0.5 ppm.

The fortification levels used in method validation are adequate to bracket expected residue levels; however, no validation data were provided for sorghum grain. Concurrent method recovery data were included with the sorghum crop field trial study submitted in conjunction with DP Barcode D314429 (refer to the 860.1500 DER for MRID 46421901); adequate recoveries of tribenuron methyl were obtained from sorghum grain fortified at 0.05 ppm. The method validation and concurrent method recovery data are sufficiently representative of the expected residue levels for the commodities included in the petition associated with DP Barcode D314429.

Analyte identification is to be confirmed by comparing the ion ratio for the two MS/MS ion transitions acquired during analysis with the average ion ratio obtained for the calibration standards.

No radiovalidation data were submitted for the method. In metabolism studies conducted using oil seeds (canola and cotton; refer to the DERs for MRIDs 45089802 and 45089803, currently under review), total radioactive residues were too low in canola seed and cotton seed to allow residue characterization (0.02 ppm in canola seed and <0.01 ppm in cotton seed). Therefore, it is unlikely that residues of tribenuron methyl would be present in these commodities at levels that would permit adequate determination of extraction efficiency. No radiovalidation data are required for this method at this time.

We note that the draft method contains erroneous instructions for preparing the acetonitrile/phosphate buffer extraction solution. The solution is stated several times in the method description to be a 75/25 solution of acetonitrile and 20 mM potassium phosphate solution. However, the instructions in Section 4.2.2 specify that 250 mL of acetonitrile is to be diluted to 1 L with 20 mM potassium phosphate solution, which would result in a 25/75 solution of acetonitrile and potassium phosphate solution.

Several sections of the draft method state "To be completed" or "To be added;" these sections included Extraction Efficiency (Section 5.1.4), Second Lab Tryout (Sections 5.4.4), and Conclusions (Section 6.0).

The LOQ reported in the method is 0.01 ppm. In the analysis of crop field trial samples, Morse Laboratories reported the LOQ to be 0.05 ppm with a limit of detection of 0.02 ppm (estimated at one-third the LOQ).

TABLE C.1.1. Recovery Results from Method Validation of Corn Grain, Olive. and Soybean Seed using the Data-Gathering Analytical Method. [1]

Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD [CV] (%)
Method validation conducted by DuPont			
Corn grain	0.010	81, 81, 82, 83, 85	86 ± 2.3 [2.8]
	0.10	81, 82, 84, 84, 85	
Olive	0.010	85, 87, 90, 91, 95	86 ± 4.4 [5.1]
	0.10	81, 82, 84, 84, 85	
Soybean seed	0.010	77, 78, 80, 80, 82	78 ± 2.5 [3.1]

TABLE C.1.1. Recovery Results from Method Validation of Corn Grain, Olive, and Soybean Seed using the Data-Gathering Analytical Method. [1]			
Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD [CV] (%)
	0.10	75, 76, 77, 77, 82	
Method validation conducted by Morse Laboratories			
Corn grain	0.05	100, 101	98 ± 2.6 [2.7]
	0.50	95, 98	
Soybean seed	0.05	97, 98	96 ± 3.1 [3.3]
	0.50	91, 96	

[1] Standards were prepared in acetonitrile

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Tribenuron Methyl Residues in Oily Crop Matrices.	
Method ID	DuPont Method 13412 (draft version, dated 12/2/03)
Analyte	Tribenuron methyl [as well as nicosulfuron, thifensulfuron methyl, ethametsulfuron methyl, rimsulfuron, and chlorimuron ethyl]
Equipment ID	HP1100 HPLC with a MicroMass Quattro II triple quadrupole mass spectrometer with an electrospray interface; Phenomenex Luna Phenyl-Hexyl column (4.6 mm x 150 mm; 3 µm particle size diameter).
Limit of quantitation (LOQ)	0.01 ppm (target)
Limit of detection (LOD)	Estimated at 0.001 ppm; the method states that the LOD should be determined by each laboratory using the method.
Accuracy/Precision	Percent recoveries and coefficients of variance (CVs) indicate acceptable accuracy/precision for residues of tribenuron methyl in corn grain, olive, and soybean seed at the LOQ, 5x LOQ, 10x LOQ, and 50x LOQ. The overall recovery range was 75-101% with an average recovery of 85% (CV = 9%). See Table C.1.1 above.
Reliability of the Method [ILV]	An independent laboratory method validation [ILV], was conducted to verify the reliability of DuPont Method 13412 for the determination of tribenuron methyl residues in olives and soybean seed. The values obtained are indicative that the LC/MS/MS method is reliable. See Section C.3.
Linearity	The method/detector response was linear (coefficient of determination, r^2= 0.9991) within the range of 0.2-10.0 ng/mL.
Specificity	The control chromatograms generally have no peaks above the chromatographic background and the spiked sample chromatograms contain only the analyte peak of interest. Peaks were well defined and symmetrical. There appeared to be no carryover to the following chromatograms.

C.2. Enforcement Method

The petitioner did not state whether the submitted method is intended for enforcement purposes.

C.3. Independent Laboratory Validation

An independent laboratory validation (ILV) study was conducted for DuPont Method 13412 using olive and soybean seed samples. The ILV was conducted at Inveresk (Tranent, Scotland). Samples of homogenized untreated olives, from crop field trials, and untreated soybean seeds, purchased commercially, were fortified with tribenuron methyl at ~0.01 ppm (LOQ) and ~0.05 ppm. Fortified and unfortified (control) samples were analyzed using DuPont LC/MS/MS Method 13412 as described in Table B.1.1. The ILV laboratory stated that olives and soybean

seed were chosen for the study because these matrices are representative of the matrices to be analyzed using DuPont Method 13412.

The first trial of the ILV analysis failed for olive (actual data were not presented) and the method was modified slightly (to change the centrifuging procedures). The second trial of the ILV also failed for olives. Following a minor modification to the cleanup step, the third trial was successful for olives.

The modifications in the method made for olives were incorporated into the method before the first trial for soybean seeds. The first attempt for soybean seeds was not successful (59.1-77.0% recovery). The method was again modified by keeping the extracts under constant refrigeration during analysis but the second trial for soybeans failed due to poor recovery (actual data were not presented). Additional modifications were made to the SPE cleanup step and the third trial was successful for soybean seeds.

Recoveries of tribenuron methyl from the ILV study are reported in Table C.3.1. Residues of tribenuron methyl were less than the LOQ (<0.01 ppm) in two unfortified samples each of olive and soybean seed.

The laboratory reported that a set of 12 samples could be prepared for LC/MS/MS analysis by a single person within an 8-hour day. The LC/MS/MS analysis could be run unattended overnight. Data processing was done the following day. Overall, complete analysis of a single set of samples takes <24 hours.

The ILV report noted that several minor modifications were made to extraction/cleanup procedures to improve the recovery of tribenuron methyl. A log of communication between the ILV laboratory and the sponsor representative was included. The ILV laboratory did not identify any critical steps or recommend any modifications to the method.

TABLE C.3.1. Recovery Results Obtained by an Independent Laboratory Validation of the Enforcement Method for the Determination of Tribenuron Methyl in Olive and Soybean Seed.

Matrix	Spiking Level (ppm)	Recoveries Obtained (%)	Mean Recovery ± SD (CV) (%)
Olive	0.01	72.1, 72.9, 74.8, 75.8, 79.6	73.0 ± 3.0 [4.1]
	0.05	69.1, 70.3, 71.3, 71.8, 72.4	
Soybean Seed	0.01	79.8, 83.3, 84.4, 87.4, 91.8	89.4 ± 10.0 [11.2]
	0.05	80.1, 86.6, 92.8, 94.2, 114	

D. CONCLUSION

Adequate concurrent method recovery and method validation data have been submitted for DuPont LC/MS/MS Method 13412 for the determination of residues of tribenuron methyl in oily crop matrices. Based on the method validation and concurrent method validation, the LC/MS/MS method is adequate for data collection. No radiovalidation data have been submitted for the method; however, HED has determined that radiovalidation data are not required.

The petitioner did not state whether the LC/MS method is to be used for enforcement purposes. Adequate independent laboratory validation data have been submitted for this method, using olive and soybean seed. If the petitioner wishes DuPont Method 13412 to be used for enforcement, the final version of the method must be submitted; the version should include the modifications made by the ILV laboratory in the course of validation.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

F. DOCUMENT TRACKING

RDI: SHummel (7/24/06)
Petition Number: 4F6890
DP Barcode: D314429
PC Code: 128887

Template Version June 2005

Primary Evaluator — Date: 8/8/06

Susan V. Hummel, Sr. Scientist, RRB4

Peer Reviewer — Date: 8/8/06

Thurston G. Morton, Chemist, RRB4

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORTS:

46421901 Carringer, S.J. (2004) Magnitude of Residues of Thifensulfuron Methyl and Tribenuron Methyl in Rice, Corn, Sorghum, and Soybeans Following Pre-Plant Burn-Down Applications of DPX-M6316 75 GT XP Herbicide and DPX-L5300 75 XP Herbicide at Maximum Label Rates – U.S.A., 2003: Lab Project Number: ML03-1101-DUP. Study No. TCI-03-080. Unpublished study prepared by The Carringers, Inc. 552 pages.

46435901 Carringer, S.J. (2004) Freezer Storage Stability of Thifensulfuron Methyl and Tribenuron Methyl in Plants – U.S.A., 2004: Lab Project Number: ML04-1137-DUP. Study No. TCI-04-086. Unpublished study prepared by The Carringers, Inc.. 297 pages.

EXECUTIVE SUMMARY:

E.I. du Pont de Nemours and Company has submitted storage stability data for tribenuron methyl residues in corn forage and stover, and soybean seed. The study was initiated in conjunction with corn, rice, sorghum, and soybean field trials (MRID 46421901) and continued to include a longer storage interval for corn forage and soybean seed (MRID 46435901). Untreated samples of corn stover and soybean seed were fortified with a mixture of thifensulfuron methyl and tribenuron methyl at 0.50 ppm each and stored frozen (-20 °C) for up to 4 months (corn stover and soybean seed) or 6 months (corn forage); refer to 46421901.de2.doc (860.1380) for the results concerning thifensulfuron methyl. The results indicate that under these conditions, residues of tribenuron methyl are relatively stable in/on corn stover and soybean seed for up to 4 months, and in/on corn forage for up to 6 months.

Samples of corn forage and stover were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 5367. Samples of soybean seed were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 13412. The validated limit of quantitation (LOQ) for both methods was 0.05 ppm for all matrices. These methods are adequate for data collection based on acceptable concurrent method recovery data.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the storage stability data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D330633, D330814, D330702.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, canola, cotton, flax, oats, and wheat, as well as grass grown for seed. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

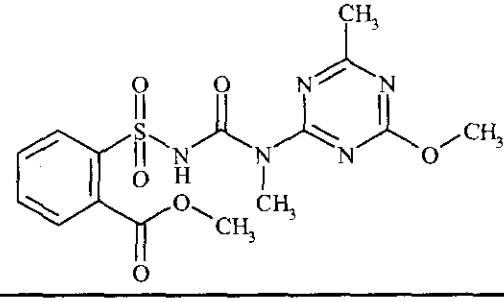
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.

Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Sample Handling and Preparation

Untreated samples of corn forage, corn stover, and soybean seed, obtained from crop field trials, were fortified with a mixture of thifensulfuron methyl and tribenuron methyl at 0.50 ppm each and stored frozen (-20 ± 5 °C); corn stover and soybean seed samples were stored for up to 4 months and corn forage samples were stored for up to 6 months. Refer to 46421901.de2.doc (860.1380) for the results concerning thifensulfuron methyl. The fortification standard was prepared in acetonitrile. Limited information concerning sample preparation and the storage vessels was included in the submission; raw data were provided. Fresh fortification samples were fortified at 0.50 ppm each analyte at each analysis time point.

B.2. Analytical Methodology

Samples of corn forage and stover were analyzed for residues of tribenuron methyl using DuPont LC/MS/MS Method 5367, and samples of soybean seed were analyzed for residues of tribenuron methyl using DuPont LC/MS/MS Method 13412. The same methods were used for analysis of samples from the associated field trials. Descriptions of the methods were included in the submission. For a complete description of the methods, refer to the DER for MRIDs 46352002 and 46352003, respectively. We note that both methods were modified slightly by the analytical laboratory (Morse Laboratories). The validated LOQ for both methods was 0.05 ppm, and the LOD was estimated to be 0.02 ppm (roughly 1/3 the LOQ).

Using DuPont Method 5367, homogenized samples of rice grain and straw, corn forage and stover, and sorghum forage and stover were extracted with a potassium phosphate buffer solution. The extract is cleaned up through a Bond Elut™ ENV solid-phase extraction (SPE) column. Residues were eluted with an ammonium hydroxide/methanol elution solution and the eluate was evaporated to dryness. The residues were redissolved in methanol and diluted to

volume with ammonium acetate. Residues were quantitated using reverse phase HPLC chromatography with MS/MS detection using electrospray ionization in the positive ion mode.

Using DuPont Method 13412, homogenized samples of corn grain, sorghum grain, and soybean seed were extracted with an acetonitrile/potassium phosphate buffer (pH 7) solution. An aliquot of the extract was partitioned with hexane, the hexane layer was discarded, and the aqueous phase was evaporated to near aqueous. The extract was cleaned up through an ENV SPE column; residues were eluted with an ammonium hydroxide/methanol elution solution and mixed with aqueous ammonium acetate. The mixture was evaporated to dryness and residues redissolved in acetonitrile and ammonium acetate. Residues were quantitated using reverse phase HPLC chromatography with MS/MS detection using electrospray ionization in the positive ion mode.

C. RESULTS AND DISCUSSION

Based on the concurrent method recovery data (see Table C.1), DuPont Method 5367 and DuPont Method 13412 are adequate for the determination of residues of tribenuron methyl in/on corn forage and stover, and soybean seed; recoveries ranged 76-98% in corn forage and stover, and soybean seed fortified with tribenuron methyl at 0.5 ppm. Apparent residues of tribenuron methyl were below the method LOQ (<0.05 ppm) in/on two samples of untreated corn stover and three samples each of untreated corn forage and soybean seed.

The results of the storage stability studies are presented in Table C.2. Residues of tribenuron methyl appear to be stable in/on corn forage stored frozen for up to 6 months, and in/on corn stover and soybean seed stored frozen for up to 4 months. A graph of the residue stability was not generated because only one or two storage intervals other than 0-time were analyzed and residues did not vary more than 10%.

TABLE C.1. Summary of Concurrent Recoveries of Tribenuron Methyl from Corn and Soybean

Matrix	Spike Level (ppm)	Storage Interval (days)	Sample Size (n)	Recoveries (%)	Mean (%)
Corn forage	0.5	95	2	86, 87	87
		186	2	90, 92	91
Corn stover	0.5	120	2	76, 80	78
Soybean seed	0.5	64	2	86, 98	92
		122	2	86, 90	88

TABLE C.2. Stability of Tribenuron Methyl Residues in Corn and Soybean Following Storage at -20 °C.

Commodity	Spike Level (ppm)	Storage Interval (days)	Recovered Residues (ppm)	Mean Recovered Residues (ppm)	Mean Recovery (%)	Corrected % recovery [1]
Corn forage	0.5	0	0.48, 0.48	0.48	96	---
		95	0.37, 0.41	0.39	78	90
		186	0.39, 0.41	0.40	80	88
Corn stover	0.5	0	0.40, 0.41	0.41	82	---
		120	0.32, 0.33	0.33	66	85
Soybean seed	0.5	0	0.46, 0.48	0.47	94	---

TABLE C.2. Stability of Tribenuron Methyl Residues in Corn and Soybean Following Storage at -20 °C.						
Commodity	Spike Level (ppm)	Storage Interval (days)	Recovered Residues (ppm)	Mean Recovered Residues (ppm)	Mean Recovery (%)	Corrected % recovery [1]
		64	0.41, 0.42	0.42	84	91
		122	0.44, 0.45	0.45	90	102

[1] Corrected for mean concurrent recovery (see TABLE C.1.); 0-day recoveries represent fresh fortification samples.

D. CONCLUSION

The submitted storage stability results adequately demonstrate the stability of residues of tribenuron methyl in/on corn forage stored frozen for up to 6 months, and corn stover and soybean seed stored frozen for up to 4 months. Acceptable methods were used for quantitation of residues in/on corn forage, corn stover, and soybean seed.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

F. DOCUMENT TRACKING

RDI: SHummel (7/25/06); TMorton (7/25/06)
Petition Number: 4F6890
DP Barcode: D314429
PC Code: 128887

Template Version June 2005

Primary Evaluator — Date: 8/8/06

Susan V. Hummel, Sr. Scientist, RRB4

Peer Reviewer — Date: 8/8/06

Thurston G. Morton, Chemist, RRB4

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

46358501 Corley, J. (2004) Tribenuron Methyl: Magnitude of the Residue on Sunflower: Lab Project Number: 08138.01-ECR01. Study No. IR-4 PR No. 08138. Unpublished study prepared by Interregional Research Project No. 4, Rutgers, The State University of New Jersey. 216 pages.

EXECUTIVE SUMMARY:

The Interregional Research Project No. 4 (IR-4) has submitted storage stability data for tribenuron methyl residues in sunflower seed in conjunction with sunflower field trials (refer to the 860.1500 DER for MRID 46358501). Untreated samples of sunflower seed were fortified with tribenuron methyl at 0.1 ppm and stored frozen (ca. -20 °C) for up to 8.6 months.

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. The limit of quantitation (LOQ) was 0.05 ppm. The results of the concurrent method recovery analyses indicate that the method was not performing adequately during the data collection period; recoveries were low and variable. The petitioner stated that during the analysis month, severe weather conditions caused frequent power outages and instrument instability. Low recoveries were also obtained for stored fortified samples.

The results of the study are considered unreliable and no conclusions may be made concerning the stability of tribenuron methyl residues in/on sunflower seed, because poor recoveries were obtained for both the fresh and stored fortified sunflower samples.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the storage stability data are classified as scientifically unacceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D330633, D330814, D330702.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, oats, and wheat, and grass grown for seed and for nonfood/feed use on cotton grown in TX only. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

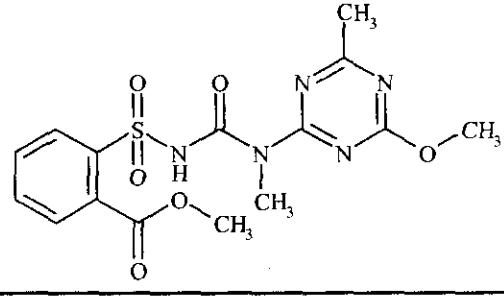
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.

Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

B.1. Sample Handling and Preparation

Untreated samples of sunflower seed, obtained from the associated crop field trials, were fortified with tribenuron methyl at 0.10 ppm and stored frozen (ca. -20 °C) for up to 260 days (8.6 months). The fortification standard was prepared in acetonitrile. Fresh fortification samples were fortified at 0.10 ppm and analyzed with the stored samples; 0-time fortified samples were not analyzed.

B.2. Analytical Methodology

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC method DuPont-3595. The same method was used for analysis of samples from the associated field trials; a description of the method was included in the submission. The validated LOQ was 0.05 ppm for sunflower seed.

Briefly, samples of homogenized sunflower seed were extracted with cold phosphate buffer (pH 6), centrifuged under refrigeration, and the aqueous portion cleaned up through an ENVI-Carb solid phase extraction column. Residues were eluted with methanol:dichloromethane (10:90, v:v) and the eluate was evaporated to dryness. The residues were redissolved in acetonitrile and phosphate buffer, and analyzed by HPLC/UV using a refrigerated injector and column switching (phenol to ODS columns).

C. RESULTS AND DISCUSSION

Concurrent method recovery data are presented in Table C.1. Recoveries of tribenuron methyl ranged 32-72% in sunflower seed fortified with tribenuron methyl at 0.1 ppm. The petitioner stated that during the analysis period for the storage stability study, severe weather conditions

caused frequent power outages and instrument instability. We note that adequate concurrent method recoveries of tribenuron methyl were obtained from sunflower seed samples during analysis of samples from the crop field trials (refer to the 860.1500 DER for MRID 46358501).

Apparent residues of tribenuron methyl were reported as nondetectable in/on two samples of untreated sunflower seed.

The results of the storage stability studies are presented in Table C.2. The results of the study are considered unreliable and no conclusions may be made concerning the stability of tribenuron methyl in/on sunflower seed, because poor recoveries were obtained for both the fresh and stored fortified sunflower samples. Although corrected residues in/on the stored samples demonstrate residue stability, the study results are unacceptable because of the problems with method recoveries.

TABLE C.1. Summary of Concurrent Recoveries of Tribenuron Methyl from Sunflower Seed.

Matrix	Spike Level (ppm)	Storage Interval (days)	Sample Size (n)	Recoveries (%)	Mean ± SD (%)
Sunflower seed	0.1	245	2	53, 72	63
		260	2	32, 52	42

TABLE C.2. Stability of Tribenuron Methyl Residues in Sunflower Seed Following Storage at -20 °C.

Commodity	Spike Level (ppm)	Storage Interval (days)	Recovered Residues (ppm)	Mean Recovered Residues (ppm)	Mean Recovery (%)	Corrected % recovery [1]
Sunflower seed	0.1	245	0.0494, 0.0495, 0.0523	0.0504	50	80
		260	0.0510, 0.0530, 0.0668	0.0569	57	136

[1] Corrected for mean concurrent recovery (see TABLE C.1.).

D. CONCLUSION

The submitted storage stability results may not be used to evaluate tribenuron methyl stability in sunflower seed. The study results are unacceptable because of problems with the method recoveries from sunflower seed.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

F. DOCUMENT TRACKING

RDI: SHummel (7/24/06); TMorton (7/25/06)
Petition Number: 4E6855
DP Barcode: D312493
PC Code: 128887

Template Version June 2005

Primary Evaluator — Susan V. Hummel — Date: 8/8/06
Susan V. Hummel, Sr. Scientist, RRB4

Peer Reviewer — Thurston G. Morton — Date: 8/8/06
Thurston G. Morton, Chemist, RRB4

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

46421901 Carringer, S.J. (2004) Magnitude of Residues of Thifensulfuron Methyl and Tribenuron Methyl in Rice, Corn, Sorghum, and Soybeans Following Pre-Plant Burn-Down Applications of DPX-M6316 75 GT XP Herbicide and DPX-L5300 75 XP Herbicide at Maximum Label Rates – U.S.A., 2003: Lab Project Number: ML03-1101-DUP. Study No. TCI-03-080. Unpublished study prepared by The Carringers, Inc. 552 pages.

EXECUTIVE SUMMARY:

E.I. du Pont de Nemours and Company has submitted field trial data for tribenuron methyl on corn, rice, sorghum, and soybeans. Three field trials were conducted in the United States during the 2003 growing season for each crop. Field corn trials were conducted in Zones 1 (PA), 2 (GA), and 5 (NE); rice trials were conducted in Zones 4 (AR), 6 (TX), and 10 (CA); sorghum trials were conducted in Zones 5 (NE), 6 (OK), and 8 (OK); and soybean trials were conducted in Zones 2 (GA), 4 (AR), and 5 (NE).

Each field test consisted of one untreated plot and one treated plot. A single burndown application of a 75% dry flowable (DF) formulation of tribenuron methyl was made at ~0.078 lb ai/A on the day of crop planting (~8x the maximum application rate). It is noted that a 75% DF formulation of thifensulfuron methyl was tank-mixed with the tribenuron methyl formulation for application; refer to 46421901.de1.doc (860.1500) for the thifensulfuron methyl residue results. The application was made using ground equipment in ~10-29 gal/A, with an adjuvant added to the spray mixture. Samples of corn forage were harvested 75-106 days after planting (DAP), and samples of sorghum forage were harvested 87-103 DAP. Samples of mature corn grain and stover were harvested 112-150 DAP, samples of mature rice grain and straw were harvested 106-129 DAP, samples of mature sorghum grain and stover were harvested 133-144 DAP, and samples of mature soybean seed were harvested 135-148 DAP.

Samples of non-oily crop matrices (corn forage and stover, rice grain and straw, and sorghum forage and stover) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 5367. Samples of oily crop matrices (corn grain, sorghum grain, and soybean

seed) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 13412. The validated limit of quantitation (LOQ) for both methods was 0.05 ppm, and the estimated limit of detection (LOD) was 0.02 ppm for all matrices. These methods are adequate for data collection based on acceptable concurrent method recovery data.

The maximum storage intervals of crop samples from harvest to analysis were 85 days (2.8 months) for corn forage, 108 days (3.6 months) for corn stover, 114 days (3.8 months) for corn grain, 43 days (1.4 months) for rice grain, 69 days (2.3 months) for rice straw, 93 days (3.1 months) for sorghum forage, 108 days (3.6 months) for sorghum stover, 107 days (3.5 months) for sorghum grain, and 94 days (3.1 months) for soybean seed. In conjunction with the field trials, the registrant has submitted storage stability data which demonstrate that residues of tribenuron methyl are relatively stable in/on corn stover and soybean seed for up to ~4 months of frozen storage, and in/on corn forage for up to 6 months of frozen storage (refer to the 860.1380 DER for MRIDs 46421901 and 46435901). In addition, previously submitted storage stability data demonstrate that residues of tribenuron methyl are stable in wheat grain and straw stored frozen for up to 21 months (DP Barcode D304059, 6/24/04, R. Griffin); the corn and wheat storage stability data may be translated to other cereal grain matrices. The available data support the storage conditions and intervals of samples from the corn, rice, sorghum, and soybean field trials.

Residues of tribenuron methyl were below the method LOQ (<0.05 ppm) in/on all samples of field corn forage, grain and stover, rice grain and straw, sorghum forage, grain, and stover, and soybean seed harvested at the appropriate growth stage following a burndown treatment made on the day of planting. No residue decline studies were conducted because application was made prior to crop emergence.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D330633, D330814, D330702.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, oats, and wheat, and grass grown for seed and for nonfood/feed use on cotton grown in TX only. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

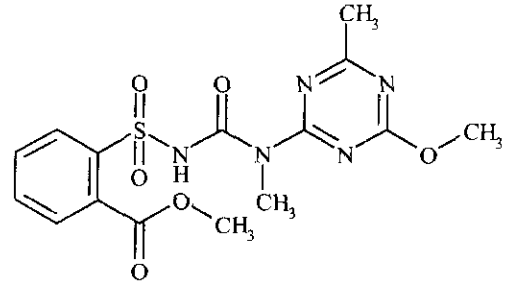
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.

Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barçode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

Three field trials were conducted in the United States during the 2003 growing season for corn, rice, sorghum, and soybean in key producing areas. Field corn trials were conducted in Zones 1 (PA), 2 (GA), and 5 (NE); rice trials were conducted in Zones 4 (AR), 6 (TX), and 10 (CA); sorghum trials were conducted in Zones 5 (NE), 6 (OK), and 8 (OK); and soybean trials were conducted in Zones 2 (GA), 4 (AR), and 5 (NE). The GA trial included both corn and soybean, and the NE trial included corn, sorghum and soybean.

Each field test consisted of one untreated plot and one treated plot; the treated plots were 600 to 4800 ft^2. A single burndown application of a 75% DF formulation of tribenuron methyl was made at a target rate of 0.078 lb ai/A on the day of crop planting. It is noted that a 75% DF formulation of thifensulfuron methyl was tank-mixed with the tribenuron methyl formulation for application; refer to 46421901.de1.doc (860.1500) for the thifensulfuron methyl residue results. The application was made using ground equipment in ~10-29 gal/A, with a non-ionic surfactant added to the spray mixture at 0.20-0.25% ai v/v. Application specifics for each trial site are presented in Table B.1.2.

The test crops were grown and maintained according to normal agricultural practices; maintenance pesticides used were documented for each trial. Trial site conditions are presented in Table B.1.1. The crop varieties grown are provided in Table C.3. Average minimum and maximum temperatures and monthly precipitation during the trial period were recorded for each trial; irrigation was applied at all trial sites. Historical information concerning temperature and rainfall was not provided for any of the trial sites; however, the petitioner noted that weather conditions were typical at all trial sites with a few minor exceptions.

Single untreated and duplicate treated samples were collected from each trial. Samples of corn forage were harvested 75-106 DAP and samples of sorghum forage were harvested 87-103 DAP. Samples of mature corn grain and stover were harvested 112-150 DAP, samples of mature rice grain and straw were harvested 106-129 DAP, samples of mature sorghum grain and stover were harvested 133-144 DAP, and samples of mature soybean seed were harvested 135-148 DAP.

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year	Soil characteristics			
	Type	%OM[1]	pH[1]	CEC[1]
Tillar, AR; 2003	Silt loam	N/A		
Brookshire, TX; 2003	Sandy loam	N/A		
Glenn, CA; 2003	Silty clay loam	N/A		
Germansville, PA; 2003	Loam	N/A		
Ashburn, GA; 2003	Sand	N/A		
Tillar, AR; 2003	Silt loam	N/A		
York, NE; 2003	Hastings silt loam	N/A		

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year	Soil characteristics			
	Type	%OM[1]	pH[1]	CEC[1]
Eakly, OK; 2003	Sand	N/A		
Dill City, OK; 2003	Loamy sand	N/A		

[1] N/A = Not applicable. These parameters are not applicable since they do not affect the proposed use pattern for this chemical.

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State; Year	EP[1]	Application					Tank Mix/ Adjuvants[5]
		Method; Timing	Volume[2]	Rate[3] (lb ai/A)	RTI[4] (days)	Total Rate (lb ai/A)	
Tillar, AR; 2003	75% DF	Preplant broadcast; on the day of planting	10.4	0.142	N/A	0.142	Preference
Brookshire, TX; 2003	75% DF	Preplant broadcast; on the day of planting	20	0.142	N/A	0.142	Triton AG98
Glenn, CA; 2003	75% DF	Preplant broadcast; on the day of planting	20.5	0.139	N/A	0.139	Kinetic
Germansville, PA; 2003	75% DF	Preplant broadcast; on the day of planting	28.5	0.144	N/A	0.144	Kinetic
Ashburn, GA; 2003	75% DF	Preplant broadcast; on the day of planting	28.4	0.143	N/A	0.143	DeFac 820
Tillar, AR; 2003	75% DF	Preplant broadcast; on the day of planting	10.8	0.143	N/A	0.143	Preference
York, NE; 2003	75% DF	Preplant broadcast; at planting	20.0	0.141	N/A	0.141	Activator 90
Eakly, OK; 2003	75% DF	Preplant broadcast; on the day of planting	10.6	0.144	N/A	0.144	X-77
Dill City, OK; 2003	75% DF	Preplant broadcast; on the day of planting	10.6	0.140	N/A	0.140	X-77

[1] EP = End-use Product; Express XP, EPA Reg. No. 352-509.
[2] GPA = Gallons per acre
[3] Calculated by the study reviewer from actual rates reported as oz ai/A.
[4] RTI = Retreatment Interval; Not applicable (N/A) because a single application was made.
[5] A non-ionic surfactant was used at all trials at 0.20-0.25% ai v/v.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Corn, field			Rice			Sorghum			Soybean		
	Submitted	Requested [1]		Submitted	Requested [1]		Submitted	Requested [1]		Submitted	Requested [1]	
		Canada	U.S.		Canada	U.S.		Canada	U.S.		Canada	U.S.
1	1		1									
1A												
2	1		1							1		2
3												
4				1		7			1	1		2
5	1		12			1	1		3	1		11
5A												
5B												
6			1	1		2	1		2			
7									1			
7A												
8							1		2			
9												
10				1		2						
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
Total	3		15	3		12	3		9	3		15

[1] Required as per OPPTS 860.1500, Table 5, reflecting a 25% reduction due to non-quantifiable residues.

The petitioner noted that through personal communication between Jake Vukich (DuPont) and R. Loranger (EPA) on 2/19/03 and 4/23/93, three trials per crop were determined to be adequate to support burndown use, if residues were non-quantifiable at a 5x exaggerated use rate.

The ChemSac (2/13/03 minutes; min_201) determined that that limited field trials (3 trials in Regions 2, 4, and 5) would be acceptable to support burndown use of tribenuron methyl for soybean if residues were <LOQ following 5x treatment. Further discussion between DuPont and R. Loranger resulted in the expansion to corn, rice, and sorghum.

B.2. Sample Handling and Preparation

A single untreated and duplicate treated samples were collected from the field trials. Immature corn forage was harvested at the early dough to late dent growth stage (75-106 DAP) and immature sorghum forage were harvested at the soft to hard dough growth stage (87-103 DAP).

Mature corn grain and stover were harvested 112-150 DAP, mature rice grain and straw were harvested 106-129 DAP, mature sorghum grain and stover were harvested 133-144 DAP, and mature soybean seed were harvested 135-148 DAP. Sorghum stover samples from two trials were field dried for 7 or 10 days prior to collection. All samples were frozen within 3 hours of collection and shipped frozen to Morse Laboratories, Inc (Sacramento, CA) for residue analysis. Samples were stored frozen (-20 ± 5 °C) at the analytical laboratory until homogenization, in the presence of dry ice, and analysis.

B.3. Analytical Methodology

Samples of non-oily crop matrices (corn forage and stover, rice grain and straw, and sorghum forage and stover) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 5367. Samples of oily crop matrices (corn grain, sorghum grain, and soybean seed) were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont Method 13412. Descriptions of the methods were included in the submission. For a complete description of the methods, refer to the DER for MRIDs 46352002 and 46352003, respectively. We note that both methods were modified slightly by Morse Laboratories. The validated LOQ for both methods was 0.05 ppm, and the LOD was estimated to be 0.02 ppm (roughly 1/3 the LOQ).

Using DuPont Method 5367, homogenized samples of corn forage and stover, rice grain and straw, and sorghum forage and stover were extracted with a potassium phosphate buffer solution. The extract is cleaned up through a Bond Elut™ ENV solid-phase extraction (SPE) column. Residues were eluted with an ammonium hydroxide/methanol elution solution and the eluate was evaporated to dryness. The residues were redissolved in methanol and diluted to volume with ammonium acetate. Residues were quantitated using reverse phase HPLC chromatography with MS/MS detection using electrospray ionization in the positive ion mode.

Using DuPont Method 13412, homogenized samples of corn grain, sorghum grain, and soybean seed were extracted with an acetonitrile/potassium phosphate buffer (pH 7) solution. An aliquot of the extract was partitioned with hexane, the hexane layer was discarded, and the aqueous phase was evaporated to near aqueous. The extract was cleaned up through an ENV SPE column; residues were eluted with an ammonium hydroxide/methanol elution solution and mixed with aqueous ammonium acetate. The mixture was evaporated to dryness and residues redissolved in acetonitrile and ammonium acetate. Residues were quantitated using reverse phase HPLC chromatography with MS/MS detection using electrospray ionization in the positive ion mode.

Method verification was conducted with corn forage, corn grain, corn stover, rice grain, and soybean seed samples prior to analysis of the treated samples; refer to the 860.1340 DERs for MRIDs 46352002 and 46352003 for the results of method verification.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.2. The maximum storage intervals of crop samples from harvest to analysis were 85 days (2.8 months) for corn forage, 108 days (3.6 months) for corn stover, 114 days (3.8 months) for corn grain, 43 days (1.4 months) for rice grain, 69 days (2.3 months) for rice straw, 93 days (3.1 months) for sorghum forage, 108 days (3.6 months) for sorghum stover, 107 days (3.5 months) for sorghum grain, and 94 days (3.1 months) for soybean seed. In conjunction with the field trials, the registrant has submitted storage stability data which demonstrate that residues of tribenuron methyl are relatively stable in/on corn stover and soybean seed for up to ~4 months of frozen storage, and in/on corn forage for up to 6 months of frozen storage (refer to the 860.1380 DER for MRIDs 46421901 and 46435901). In addition, previously submitted storage stability data demonstrate that residues of tribenuron methyl are stable in wheat grain and straw stored frozen for up to 21 months (DP Barcode D304059, 6/24/04, R. Griffin); the corn and wheat storage stability data may be translated to other cereal grain matrices. The available data support the storage conditions and intervals of samples from the corn, rice, sorghum, and soybean field trials.

Concurrent method recovery data are presented in Table C.1. Samples of non-oily crop matrices (corn forage and stover, rice grain and straw, and sorghum forage and stover) were analyzed for residues of tribenuron methyl using DuPont LC/MS/MS Method 5367, and samples of oily crop matrices (corn grain, sorghum grain, and soybean seed) were analyzed for residues of tribenuron methyl using DuPont LC/MS/MS Method 13412. The validated LOQ for both methods was 0.05 ppm, and the estimated LOD was 0.02 ppm for all matrices. These methods are adequate for data collection based on acceptable concurrent method recovery data. Using method 5367, recoveries were 978-83% for corn forage, 0-100% for rice grain, 89-95% for sorghum forage, and 85-88% for sorghum stover fortified with tribenuron methyl at 0.05 ppm; and 68-84% for corn stover and 89-97% for rice straw fortified at 0.05 and 0.1 ppm. Using method 13412, recoveries were 95-100% for corn grain, 108-110% for sorghum grain, and 92-109% for soybean seed fortified with tribenuron methyl at 0.05 ppm. Apparent residues of tribenuron methyl were reported as nondetectable in/on untreated samples of all matrices.

Residue data from the corn, rice, sorghum, and soybean field trials are reported in Table C.3. A summary of residue data following treatment with the 75% DF is presented in Table C.4. Residues of tribenuron methyl were below the method LOQ (<0.05 ppm) in/on all samples of field corn forage, grain and stover, rice grain and straw, sorghum forage, grain, and stover, and soybean seed harvested at the appropriate growth stage following a burndown treatment made on the day of planting. No residue decline studies were conducted because application was made prior to crop emergence.

The petitioner reported that crop injury was observed in all rice trials, one corn trial and one soybean trial. Approximately 25-80% of the stand was reduced with delayed emergence and/or stunting; however, the crops recovered and yields were normal. In addition, the crop stand in a second corn field trial (NE) was severely damaged by Southern Rust disease, yielding grain samples which were small and of poor quality; the disease did not impact forage and stover

samples. The petitioner concluded that because residues levels in corn grain from this trial were the same (nondetectable) as the other two corn trials, the data are acceptable.

TABLE C.1. Summary of Concurrent Recoveries of Tribenuron Methyl from Corn, Rice, Sorghum, and Soybean Matrices.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean (%)
Corn forage	0.05	2	78, 83	81
Corn stover	0.05	1	84	76
	0.10	1	68	
Corn grain	0.05	2	95, 100	98
Rice grain	0.05	2	90, 100	95
Rice straw	0.05	1	89	93
	0.10	1	97	
Sorghum forage	0.05	2	89, 95	92
Sorghum stover	0.05	2	85, 88	87
Sorghum grain	0.05	2	108, 110	109
Soybean seed	0.05	2	92, 109	101

TABLE C.2. Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability
Corn, forage	ca. -20	70-85 days (2.3-2.8 months)	6 months in fortified corn forage stored frozen [2]
Corn, grain		73-114 days (2.4-3.8 months)	21 months in fortified wheat grain stored frozen [3]
Corn, stover		55-108 days (1.8-3.6 months)	4 months in fortified corn stover stored frozen [2]
Rice, grain		37-43 days (1.2-1.4 months)	21 months in fortified wheat grain stored frozen [3]
Rice, straw		63-69 days (2.1-2.3 months)	21 months in fortified wheat straw stored frozen [3]
Sorghum, forage		74-93 days (2.4-3.1 months)	6 months in fortified corn forage stored frozen [2]
Sorghum, grain		99-107 days (3.3-3.5 months)	21 months in fortified wheat grain stored frozen [3]
Sorghum, stover		80-108 days (2.6-3.6 months)	4 months in fortified corn stover stored frozen [2]
Soybean, seed		69-94 days (2.3-3.1 months)	4 months in fortified soybean seed stored frozen [2]

[1] Actual storage duration from collection to analysis; samples were analyzed within 1-10 days of extraction.
[2] Storage stability study conducted in conjunction with the field trials; refer to the 860.1380 DER for MRIDs 46421901 and 46435901.
[3] Refer to the Residue Chemistry Chapter of the Tribenuron Methyl RED (DP Barcode D304059, 6/24/04).

TABLE C.3. Residue Data from Crop Field Trials with Tribenuron Methyl.

Trial Identification: City, State; Year	Zone	Crop; Variety	Total Rate (lb ai/A)	PHI/DAP [1] (days)	Commodity or Matrix	Tribenuron Methyl (ppm) [2]
Germansville, PA; 2003	1	Corn (field); Doeblers 609XRR	0.080	106	Forage	ND, ND
				150	Grain	ND, ND
				150	Stover	ND, ND
Ashburn, GA; 2003	2	Corn (field); Pioncer Hybrid 31G98-N007	0.079	75	Forage	ND, ND
				112	Grain	ND, ND
				112	Stover	ND, ND
		Soybean; Haskell	0.079	148	Seed	ND, ND
Tillar, AR; 2003	4	Soybean; Pioneer 95B42	0.079	147	Seed	ND, ND

TABLE C.3. Residue Data from Crop Field Trials with Tribenuron Methyl.

Trial Identification: City, State; Year	Zone	Crop; Variety	Total Rate (lb ai/A)	PHI/DAP [1] (days)	Commodity or Matrix	Tribenuron Methyl (ppm) [2]
York, NE; 2003	5	Corn (field); DKC60-19 RR	0.078	95	Forage	ND, ND
				129	Grain	ND, ND
				129	Stover	ND, ND
		Sorghum; NC+6B50	0.078	87	Forage	ND, ND
				144	Grain	ND, ND
				144	Stover	ND, ND
		Soybeans; Midland 9A331	0.078	135	Seed	ND, ND
Tillar, AR; 2003	4	Rice; Francis (long grain)	0.079	129	Grain	ND, ND
					Straw	ND, ND
Brookshire, TX; 2003	6	Rice; Cocodrie	0.079	119	Grain	ND, ND
					Straw	ND, ND
Glenn, CA; 2003	10	Rice; GM104	0.078	106	Grain	ND, ND
					Straw	ND, ND
Eakly, OK; 2003	6	Sorghum; Cherokee	0.079	96	Forage	ND, ND
				133	Grain	ND, ND
				133	Stover	ND, ND
Dill City, OK; 2003	8	Sorghum; Cherokee	0.078	103	Forage	ND, ND
				133	Grain	ND, ND
				133	Stover	ND, ND

[1] PHI = preharvest interval; DAP = days after planting. Because treatment was made on the day of planting, PHI and DAP are equivalent.
[2] Residues were reported as ND (nondetectable); the validated LOQ was 0.05 ppm and the estimated LOD was 0.02 ppm.

TABLE C.4. Summary of Residue Data from Crop Field Trials with Tribenuron Methyl.

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels [1] (ppm)						
			n	Min.	Max.	HAFT[2]	Median (STMdR)	Mean (STMR)	Std. Dev.
Corn, forage	0.078-0.080	75-106	6	<0.05	<0.05	<0.05	0.025	0.025	0
Corn, grain	0.078-0.080	112-150	6	<0.05	<0.05	<0.05	0.025	0.025	0
Corn, stover	0.078-0.080	112-150	6	<0.05	<0.05	<0.05	0.025	0.025	0
Rice, grain	0.078-0.079	106-129	6	<0.05	<0.05	<0.05	0.025	0.025	0
Rice, straw	0.078-0.079	106-129	6	<0.05	<0.05	<0.05	0.025	0.025	0
Sorghum, forage	0.078-0.079	87-103	6	<0.05	<0.05	<0.05	0.025	0.025	0
Sorghum, grain	0.078-0.079	133-144	6	<0.05	<0.05	<0.05	0.025	0.025	0
Sorghum, stover	0.078-0.079	133-144	6	<0.05	<0.05	<0.05	0.025	0.025	0
Soybean, seed	0.078-0.079	135-148	6	<0.05	<0.05	<0.05	0.025	0.025	0

[1] For the determination of the minimum, maximum, and HAFT residues, the LOQ (<0.05 ppm) was used for residues reported as ND in Table C.3.; for calculation of the median, mean, and standard deviation, ½ the LOQ was used for ND residues.
[2] HAFT = Highest Average Field Trial.

D. CONCLUSION

The submitted corn, rice, sorghum, and soybean field trial data reflect the use of the 75% DF formulation of tribenuron methyl at ~0.078 lb ai/A made on the day of planting. Burndown applications were made in 10-29 gal/A with an adjuvant added to the spray mixture. Acceptable

methods were used for quantitation of residues in/on corn, rice, sorghum, and soybean commodities.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

F. DOCUMENT TRACKING

RDI: SHummel (7/25/06)
Petition Number: 4F6890
DP Barcode: D314429
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Primary Evaluator — Date: 8/8/06

Susan V. Hummel, Sr. Scientist

Peer Reviewer — Date: 8/8/06

Thurston G. Morton, Chemist

This DER was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 05/08/2006). The DER has been reviewed by the Health Effects Division (HED) and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT:

46358501 Corley, J. (2004) Tribenuron Methyl: Magnitude of the Residue on Sunflower: Lab Project Number: 08138.01-ECR01. Study No. IR-4 PR No. 08138. Unpublished study prepared by Interregional Research Project No. 4, Rutgers, The State University of New Jersey. 216 pages.

EXECUTIVE SUMMARY:

The Interregional Research Project No. 4 (IR-4) has submitted field trial data for tribenuron methyl on sunflower. Seven trials were conducted in the United States in Zones 5 (ND; 2 trials), 7 (NE and ND; 4 trials), and 8 (CO; 1 trial) during the 2001 growing season.

Each field test consisted of one untreated plot and one treated plot. One preemergence ground application and two broadcast foliar applications of a 75% tribenuron methyl dry flowable (DF) formulation were made to sulfonylurea-tolerant sunflower at ~0.016 lb ai/A/application for a total application rate of ~0.048 lb ai/A. An additional plot at one trial site was treated in the same manner at an exaggerated rate: ~0.08 lb ai/A/application for a total rate of ~0.24 lb ai/A (5x the nominal field trial rate). All applications were made using ground equipment in ~10-23 gal/A, with an adjuvant added to the spray mixture. Samples of mature sunflower seed were harvested 66-83 days after the last application.

The maximum storage interval of sunflower seed samples from harvest to analysis was 235 days (7.7 months). Previously submitted storage stability data for cottonseed (refer to 45098405.dc11.wpd, 8/10/04, S. Ary), which demonstrate that residues of tribenuron methyl are relatively stable in/on cottonseed stored frozen for up to 14 months, may be translated to support the storage conditions and intervals of samples from the sunflower field trials.

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. The limit of quantitation (LOQ) was 0.05 ppm, and the calculated limit of

detection (LOD) was 0.008 ppm for sunflower seed. This method is adequate for data collection based on acceptable concurrent method recovery data.

Residues of tribenuron methyl were less than the LOQ (<0.05 ppm) in/on sunflower seed (sulfonylurea-tolerant hybrid varieties) harvested 66-83 days after treatment at a total rate of 0.047-0.049 lb ai/A. Residues were also nonquantifiable (<0.05 ppm) in/on sunflower seed harvested 83 days after treatment at an exaggerated rate of 0.242 lb ai/A. No residue decline studies were conducted because applications were made early in the season.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP Barcode D312493.

COMPLIANCE:

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 1) registered for food/feed uses on barley, oats, and wheat, and grass grown for seed and for nonfood/feed use on cotton grown in TX only. A summary of the status of residue chemistry data requirements for tribenuron methyl was issued 6/24/04 (DP Barcode D304059, R. Griffin).

TABLE A.1. Tribenuron Methyl Nomenclature.

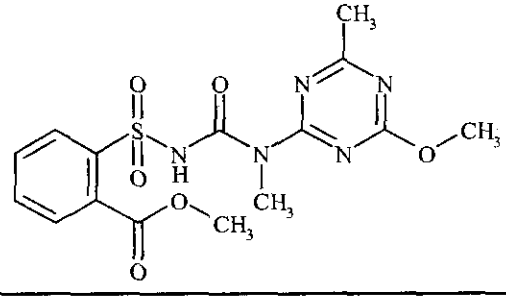
Chemical structure	
Common name	Tribenuron methyl
Company experimental name	DPX-L5300
IUPAC name	methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	75% DF formulation (DuPont™ Express® XP Herbicide; EPA Reg. No. 352-509)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.		
Parameter	Value	Reference
Melting point	141 °C	DP Barcode D304059, 6/24/04, R. Griffin
pH	4.27 (slurry in water)	DP Barcode D304059, 6/24/04, R. Griffin
Density	1.54 g/mL	DP Barcode D304059, 6/24/04, R. Griffin
Water solubility	At 25 °C: pH 4.0 28 mg/L pH 5.0 50 mg/L pH 6.0 280 mg/L	DP Barcode D304059, 6/24/04, R. Griffin
Solvent solubility	At 25 °C: acetone - 43.8 g/L acetonitrile - 54.2 g/L carbon tetrachloride - 3.12 g/L ethyl acetate - 17.5 g/L hexane - 0.028 g/L methanol - 3.39 g/L	DP Barcode D304059, 6/24/04, R. Griffin
Vapor pressure	25 °C (Knudsen) - 3.8×10^{-10} 25 °C (gas saturation) - 2.7×10^{-7} 70 °C (gas saturation) - $<8.3 \times 10^{-7}$	DP Barcode D304059, 6/24/04, R. Griffin
Dissociation constant, pK_a	5.0	DP Barcode D304059, 6/24/04, R. Griffin
Octanol/water partition coefficient, $Log(K_{OW})$	pH 7 - 0.3 pH 5 (calculated) - 15 pH 9 (calculated) - 0.003	DP Barcode D304059, 6/24/04, R. Griffin
UV/visible absorption spectrum	Not available	

B. EXPERIMENTAL DESIGN

Seven field trials were conducted in the United States during the 2001 growing season in Zones 5 (ND; 2 trials), 7 (NE and ND; 4 trials), and 8 (CO; 1 trial). Sulfonylurea-tolerant sunflower hybrid varieties were used for the studies.

Each field test consisted of one untreated plot and one treated plot. One preemergence broadcast ground application and two subsequent broadcast foliar applications of a 75% DF formulation of tribenuron methyl were made at ~0.016 lb ai/A/application, for a total application rate of ~0.048 lb ai/A. Two additional plots at one trial site (ND11) were treated in the same manner at exaggerated rates, ~0.048 lb ai/A/application or ~0.08 lb ai/A/application for a total rate of ~0.144 lb ai/A (3x the nominal field rate) or ~0.24 lb ai/A (5x); because only samples from the 5x treated plot were analyzed, information concerning the 3x plot is not presented herein. All applications were made using ground equipment in ~10-23 gal/A, with a non-ionic surfactant or crop oil concentrate added to the spray mixture. Application specifics for each trial site are presented in Table B.1.2.

The test crops were grown and maintained according to common cultural practices; the maintenance fertilizers and pesticides that were used were documented for each trial. Trial site conditions are presented in Table B.1.1. The crop varieties grown are provided in Table C.3. Temperatures at application and first rainfall after application were recorded for each trial; irrigation was applied at two trials. Actual and historical information concerning temperature and rainfall was not provided for any of the trial sites; however, the petitioner noted that weather

conditions were typical at all trial sites with the exception of two trials in ND. At both trials (ND11 and ND15), it was noted that less than the normal amount of rainfall and late frost during the trial period may have delayed harvest.

Single untreated and duplicate treated samples were collected from each trial. Samples of mature sunflower seed were harvested by hand or using a thresher 66-83 days after the last application.

B.1. Study Site Information

TABLE B.1.1. Trial Site Conditions.

Trial Identification: City, State; Year (Trial ID No.)	Soil characteristics			
	Type	%OM[1]	pH[1]	CEC[1]
Ft. Collins, CO; 2001 (CO15)	Sandy clay loam	N/A		
Minot, ND; 2001 (ND11)	Sandy loam	N/A		
Fargo, ND; 2001 (ND12)	Silty clay	N/A		
Velva, ND; 2001 (ND13)	Loam	N/A		
Fargo, ND; 2001 (ND14)	Silty clay	N/A		
Minot, ND; 2001 (ND15)	Loam	N/A		
Scottsbluff, NE; 2001 (NE05)	Loam sand	N/A		

[1] N/A = Not applicable. These parameters are not applicable since they do not affect the proposed use pattern for this chemical.

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP[1]	Application					Tank Mix/ Adjuvants[4]
		Method; Timing	Volume[2]	Rate (lb ai/A)	RTI[3] (days)	Total Rate (lb ai/A)	
Ft. Collins, CO; 2001 (CO15)	75% DF	1. Broadcast to soil; Pre-emergence	15.10	0.0159	--	0.0481	X-77 NIS
		2. Broadcast foliar; Vegetative	15.14	0.016	22		
		3. Broadcast foliar; Vegetative	15.39	0.0162	10		
Minot, ND; 2001 [5] (ND11)	75% DF	1. Broadcast to soil; Pre-emergence	10.13	0.016	--	0.048	Preference NIS
		2. Broadcast foliar; 8-10 leaf stage	10.15	0.016	32		
		3. Broadcast foliar; Budding	9.95	0.016	10		
	75% DF	1. Broadcast to soil; Pre-emergence	10.12	0.081	--	0.242	Preference NIS
		2. Broadcast foliar; 8-10 leaf stage	10.15	0.081	24		
		3. Broadcast foliar; Budding	10.06	0.080	10		
Fargo, ND; 2001 (ND12)	75% DF	1. Broadcast to soil; Pre-emergence	11.85	0.016	--	0.049	MSO Concentrate
		2. Broadcast foliar; 8 leaf stage	12.40	0.017	23		
		3. Broadcast foliar; Budding	12.25	0.016	13		
Velva, ND; 2001 (ND13)	75% DF	1. Broadcast to soil; Pre-emergence	14.84	0.016	--	0.048	R-11 NIS
		2. Broadcast foliar; 8 leaf stage	15.07	0.016	31		
		3. Broadcast foliar; Budding	14.90	0.016	21		

TABLE B.1.2. Study Use Pattern.

Trial Identification: City, State; Year (Trial ID No.)	EP[1]	Application					Tank Mix/ Adjuvants[4]
		Method; Timing	Volume[2]	Rate (lb ai/A)	RTI[3] (days)	Total Rate (lb ai/A)	
Fargo, ND; 2001 (ND14)	75% DF	1. Broadcast to soil; Pre-emergence	11.81	0.016	--	0.048	MSO Concentrate
		2. Broadcast foliar; 6 leaf stage	11.81	0.016	18		
		3. Broadcast foliar; Budding	12.01	0.016	13		
Minot, ND; 2001 (ND15)	75% DF	1. Broadcast to soil; Pre-emergence	10.18	0.016	--	0.048	Preference NIS
		2. Broadcast foliar; 6-10 leaf stage	10.10	0.016	24		
		3. Broadcast foliar; Budding	10.15	0.016	10		
Scottsbluff, NE; 2001 (NE05)	75% DF	1. Broadcast to soil; Pre-emergence	20.81	0.0154	--	0.0468	Wilfarm Crop Oil Plus
		2. Broadcast foliar; Vegetative	20.53	0.016	17		
		3. Broadcast foliar; Pre-bud formation	22.81	0.0154	18		

[1] EP = End-use Product; Express XP, Reg. No. 352-509
[2] Gallons per acre
[3] RTI = Retreatment Interval
[4] NIS = Non-ionic surfactant
[5] Two additional plots were treated at exaggerated rates (3x and 5x the nominal field trial rate); the 3x samples were not analyzed therefore information is not provided for this treated plot.

TABLE B.1.3. Trial Numbers and Geographical Locations.

NAFTA Growing Zones	Sunflower		
	Submitted	Requested	
		Canada	U.S. [1]
1			
1A			
2			
3			
4			
5	2		2
5A			
5B			
6			
7	4		3
7A			
8	1		1
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
Total	7		6

[1] Required as per OPPTS 860.1500, Table 5, reflecting a 25% reduction due to non-quantifiable residues.

B.2. Sample Handling and Preparation

A single untreated and duplicate treated samples of mature sunflower seed were collected from each field trial. The samples were frozen within 1.5 hours of sampling and shipped frozen to En-Cas Analytical Laboratories (Winston-Salem, NC) for residue analysis. Samples were stored frozen (-20 to -17 °C) at the analytical laboratory until homogenization, in the presence of dry ice, and analysis.

B.3. Analytical Methodology

Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC method DuPont-3595. A description of the method was included in the submission. The validated LOQ was 0.05 ppm for sunflower seed.

Briefly, samples of homogenized sunflower seed were extracted with cold phosphate buffer (pH 6), centrifuged under refrigeration, and the aqueous portion cleaned up through an ENVI-Carb solid phase extraction column. Residues were eluted with methanol:dichloromethane (10:90, v:v), and the eluate was evaporated to dryness. The residues were redissolved in acetonitrile and phosphate buffer, and analyzed by HPLC/UV using a refrigerated injector and column switching (phenol to ODS columns). The submission included calculations for the determination of the LOQ (0.02 ppm) and LOD (0.008 ppm) based on statistical analysis of the recoveries from the lowest fortification level (0.05 ppm). The petitioner used the validated LOQ of 0.05 ppm for reporting residue results.

Method verification was conducted with control sunflower seed samples prior to analysis of the treated samples; recoveries are reported in Table C.1.

C. RESULTS AND DISCUSSION

Sample storage conditions and intervals are summarized in Table C.2. The maximum storage interval of samples from harvest to analysis was 235 days (7.7 months) for sunflower seed. To support sample storage conditions and intervals, the petitioner conducted a storage stability study in conjunction with the field trials; however because of poor recoveries in both the fresh and stored samples, no conclusions could be made from the study results (refer to the 860.1380 DER for MRID 46358501). The petitioner also referenced previously submitted storage stability data for cottonseed (refer to 45098405.de11.wpd, 8/10/04, S. Ary), which demonstrate that residues of tribenuron methyl are relatively stable in/on cottonseed stored frozen for up to 14 months. The cottonseed data may be translated to support the storage conditions and intervals of samples from the sunflower field trials.

Method validation and concurrent recovery data are presented in Table C.1. Samples of sunflower seed were analyzed for residues of tribenuron methyl using HPLC/UV method DuPont-3595. The validated LOQ was 0.05 ppm for sunflower seed. The method is adequate for data collection based on acceptable concurrent method recovery data; recoveries were 73-86% for sunflower seed fortified with tribenuron methyl at 0.05 and 0.5 ppm. Recoveries from the method verification study conducted prior to the analysis of the treated samples ranged 64-75% in sunflower fortified at 0.05 and 0.5 ppm; although several recoveries were low, overall recovery was acceptable. Apparent residues of tribenuron methyl were below the LOQ (<0.05 ppm) in/on seven samples of untreated sunflower seed.

Residue data from the sunflower field trials are reported in Table C.3. A summary of residue data for sunflower seed following treatment with the 75% DF is presented in Table C.4. Residues of tribenuron methyl were less than the method LOQ (<0.05 ppm) in/on sunflower seed (sulfonylurea-tolerant hybrid varieties) harvested 66-83 days after a single preemergence ground application and two subsequent foliar applications for a total rate of 0.047-0.049 lb ai/A. Residues were also nonquantifiable (<0.05 ppm) in/on sunflower seed harvested 83 days after treatment at an exaggerated rate of 0.242 lb ai/A.

The field reports noted that some leaf chlorosis and crop stunting or deformed (capped) heads were observed at 4 out of the 5 ND trial sites. These phytotoxic effects did not adversely affect the crop yields at harvest.

TABLE C.1. Summary of Method Validation and Concurrent Recoveries of Tribenuron Methyl from Sunflower Seed.

Matrix	Spike level (ppm)	Sample size (n)	Recoveries (%)	Mean ± std dev (%)
Method Validation				
Sunflower, seed	0.05	3	64, 72, 75	70 ± 4.0
	0.5	3	68, 69, 73	
Concurrent Recoveries				
Sunflower, seed	0.05	5	73, 74, 75, 78, 80	79 ± 4.1
	0.5	4	80, 80, 81, 86	

TABLE C.2. *Summary of Storage Conditions.*

Matrix	Storage Temperature (°C)	Actual Storage Duration [1]	Interval of Demonstrated Storage Stability
Sunflower, seed	-20 to -17	196-235 days (6.4-7.7 months)	14 months in/on fortified cottonseed stored frozen [2]

[1] Actual storage duration from collection to analysis; samples were analyzed within 1-3 days of extraction.
[2] Storage stability data submitted for sunflower seed are not acceptable; refer to 45098405.de11.wpd, 8/10/04, S. Ary for cottonseed results.

TABLE C.3. Residue Data from Sunflower Crop Field Trials with Tribenuron Methyl.

Trial Identification: City, State; Year (Trial ID No.)	Zone	Crop Variety	Commodity or Matrix	Total Rate (lb ai/A)	PHI (days)	Tribenuron Methyl (ppm) [1]
Ft. Collins, CO; 2001 (CO15)	8	Hybrid 01RL004	Seed	0.0481	69	<0.05, <0.05
Minot, ND; 2001 (ND11)	7	Hybrid 01RL004	Seed	0.048	83	<0.05, <0.05
				0.242	83	<0.05, <0.05
Fargo, ND; 2001 (ND12)	5	SU Resistant Hybrid 01RL004	Seed	0.049	66	<0.05, <0.05
Velva, ND; 2001 (ND13)	7	01RL004	Seed	0.048	70	<0.05, <0.05
Fargo, ND; 2001 (ND14)	5	SU Resistant Hybrid 01RL004	Seed	0.048	67	<0.05, <0.05
Minot, ND; 2001 (ND15)	7	Hybrid 01RL004	Seed	0.048	83	<0.05, <0.05
Scottsbluff, NE; 2001 (NE05)	7	Hybrid 01RL004	Seed	0.0468	71	<0.05, <0.05

[1] The method LOQ was 0.05 ppm for sunflower seed.

TABLE C.4. Summary of Residue Data from Crop Field Trials with Tribenuron Methyl.									
Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Residue Levels [1] (ppm)						
			n	Min.	Max.	HAFT [2]	Median (STMdR)	Mean (STMR)	Std. Dev.
Sunflower seed	0.047-0.049	66-83	14	<0.05	<0.05	<0.05	0.025	0.025	0

[1] For the determination of the minimum, maximum, and HAFT residues, the LOQ (<0.05 ppm) was used; for calculation of the median, mean, and standard deviation, ½ the LOQ was used.
[2] HAFT = Highest Average Field Trial.

D. CONCLUSION

The submitted sunflower field trial data reflect the use of one preemergence ground application and two broadcast foliar applications of a 75% DF formulation of tribenuron methyl at a total rate of ~0.048 lb ai/A with a PHI of 66-83 days for sunflower seed. Data from a single trial conducted at an exaggerated rate reflect use of the 75% DF at a total rate of 0.242 lb ai/A, with an 83-day PHI. Applications were made in 10-23 gal/A with an adjuvant added to the spray mixture. An acceptable method was used for quantitation of residues in/on sunflower seed.

E. REFERENCES

DP Barcode: D304059
Subject: Tribenuron methyl. Residue Chemistry Considerations.
From: R. Griffin
To: K. Rothwell and J. Tompkins
Dated: 6/24/04
MRIDs: None

DP Barcode: D305958
Subject: 860.1380 DER for MRID 45098405 (Tribenuron methyl in/on Cotton)
Primary Reviewer: S. Ary
Approved by: A. Nielsen
Date: 8/10/04
MRID: 45098405

F. DOCUMENT TRACKING

RDI: SHummel (7/24/06); TMorton (7/25/06)
Petition Number: 4E6855
DP Barcode: D312493
PC Code: 128887

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Chemical: Tribenuron

PC Code:
128887

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Memo Date: 8/8/2006
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