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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OFFICE OF PREVENTION,
PESTICIDES AND TOXIC SUBSTANCES

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

MEMORANDUM

DATE: **9 September 2009**

SUBJECT: **Tribenuron Methyl. Petition to Establish New (and Amend Several Existing) Permanent Tolerances for Residues Associated with Food/Feed Use of the Herbicide on Genetically Modified Soybeans and Field Corn. Summary of Analytical Chemistry and Residue Data.**

PC Code: 128887
Decision Number: 400410
Petition Numbers: 8F7432 and 8F7441
Risk Assessment Type: NA
TXR Number: NA
MRID Numbers: 47548201, 47548202, 47548203, 47548204, 47548208, 47637801
Chemical Class: Triazinylsulfonylurea Herbicide

DP Barcode: 360846
Registration Number: 352-632
40CFR §180.451
Case Number: NA
CAS Number: 101200-48-0
Regulatory Action: Amended Section 3 Registration
Trade Name: DuPont™ Express®

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Received 9/21/2009

Executive Summary

Tribenuron methyl is a triazinylsulfonylurea herbicide that inhibits acetolactate synthase (ALS). Tribenuron methyl is currently registered to DuPont Crop Protection, as dry flowable (DF), or water-soluble granule (SG) formulations, for use on a variety of grain and seed crops, as well as on cotton and flax.

DuPont has submitted 6 volumes of crop field trial, processing, and metabolism (laying hen) data in support of two petitions, PP#8F7432 and PP#8F7441, to establish tolerances for residues of tribenuron methyl in soybean and field corn commodities. Section F of PP#8E7432 has proposed the establishment of tolerances for residues of the herbicide tribenuron methyl (with CAS Name methyl-2-[[[[[4-methoxy-6-methyl-1,3,5-triazin-2-yl] methylamino] carbonyl] amino] sulfonyl] benzoate, and CAS Number 101200-48-0) in or on soybean commodities, at the levels listed below.

Soybean, hay	0.25 ppm
Soybean, forage	0.06 ppm
Soybean, seed	0.01 ppm
Soybean, hulls	0.04 ppm
Soybean, aspirated grain fractions	3.46 ppm

Section F of PP#8E7441 has proposed the establishment of tolerances for residues of the herbicide tribenuron methyl in or on field corn commodities, at the levels listed below.

Corn, field, grain	0.01 ppm
Corn, field, forage	0.2 ppm
Corn, field, stover	1.1 ppm
Corn, field, aspirated grain fractions	3.55 ppm

The end-use product (EP) relevant to these tolerance actions is DuPont™ Express®, an SG formulation containing 50% of the active ingredient (ai), tribenuron methyl. Express® is proposed for use as one or two foliar spray treatments to genetically modified soybeans or field corn, at a maximum single (and seasonal) use rate of 0.03125 pounds of ai per acre (lb ai/A), which corresponds to the proposed label's stated maximum use rate of 1 ounce of EP per acre per crop season. The label specifies pre-harvest intervals (PHIs) of 7 days for field corn commodities, and 14 days for soybean forage and hay. As the label directions for use on soybeans prohibit applications after the R2 stage, a specific PHI for soybean seeds was not proposed, and is not required. Re-treatment intervals (RTIs) for use on soybeans and field corn were not specified.

Tribenuron methyl tolerances in plant commodities are listed in 40CFR §180.451[a] and [c]; they are currently expressed in terms of the parent compound, tribenuron methyl.

The nature of the residue in plants is adequately understood. HED has determined that, in target crops, tribenuron methyl *per se* is the residue of concern (ROC) for purposes of risk assessment and tolerance expression.

There are significant livestock feedstuffs associated with the proposed use patterns on soybeans and field corn. Based on the data from the goat metabolism study, ARIA/RD and HED conclude that a cattle feeding study is not required for this petition. Based on the data from the poultry metabolism study, residues in liver resulting from the 10X dosing level would be 0.012 ppm. Normally, a poultry feeding study would be required (due to residues being detected above 0.01 ppm at the 10X dosing level), but none were previously requested. Because no significant poultry feed items are associated with the current petitions, a poultry feeding study is not required at this time. However, should the registrant submit any future petition proposing use on a commodity (or commodities) associated with poultry feed items, a poultry feeding study will be required, and that study should be submitted in conjunction with any such petition.

Adequate confined rotational crop data are available to support a minimum 30-day plantback interval (PBI) for all crops without registered uses. As labels for tribenuron methyl currently specify minimum PBIs of no less than 60 days for canola, rape, and sugar beets, and 45 days for all other crops not listed on the label, data requirements for rotational crops are fulfilled, and tolerances are not required in rotational crops.

Several adequate analytical methods are available for enforcing tolerances for tribenuron methyl in plant commodities. Residues in samples from the soybean and field corn field trials associated with these petitions were determined using a liquid chromatography with tandem mass-spectrometric detection (LC/MS/MS) method, DuPont Method 13412 (Revision 1). This method was adequately validated prior to, and in conjunction with, the field trial analyses; the validated limit of quantitation (LOQ) is 0.010 ppm for tribenuron methyl in all corn and soybean commodities.

The available data indicate that residues of tribenuron methyl are not recovered by the FDA multiresidue methods.

The available storage stability data adequately support the sample storage durations and conditions incurred during the corn and soybean field trial and processing studies.

The available corn and soybean field trial data are acceptable, and support the proposed use patterns for tribenuron methyl (50% ai SG) on genetically modified soybeans and field corn. An adequate number of trials were conducted on each crop in the appropriate geographical regions. All samples were analyzed for the ROC using an adequate method, and sample storage conditions and durations are supported by the available storage stability data. The data support tolerances of 0.01 ppm in/on corn grain, 0.15 ppm in/on corn forage, 1.1 ppm in/on corn stover, 0.01 ppm in/on soybean seeds, 0.07 ppm in/on soybean forage, and 0.35 ppm in/on soybean hay.

The available corn and soybean processing data for tribenuron methyl are adequate. As residues were <LOQ in corn grain, and all corn processed fractions following an application at 5X the proposed use rate, separate tolerances are not required in corn grain processed fractions. For soybeans, residues concentrated only in hulls (4.05X). Based on HAFT residues of 0.01 ppm for soybean seeds (14-day PHI), the tolerance in/on soybean hulls should be set at 0.04 ppm.

Tribenuron methyl residues were shown to concentrate in aspirated grain fractions (AGF) from both field corn grain (13X), and soybean seeds (150X). Based on the HAFT residues of field corn grain (0.01 ppm), and soybean seeds (0.01 ppm), the maximum expected residues would be 0.13 ppm in AGF from corn grain, and 1.5 ppm in AGF from soybean seeds. As

residues in soybean AGF are higher than in corn grain AGF, the tolerance in/on AGF should be set at 1.5 ppm.

There are no established nor proposed Codex or Mexican maximum residue limits (MRLs) for residues of tribenuron methyl (Appendix II). Canada has established MRLs for tribenuron methyl in several plant commodities. However, no Canadian MRLs for tribenuron methyl have been proposed nor established in the commodities being considered under these petitions. Therefore, there are no concerns regarding compatibility of the proposed tolerances.

An analytical standard for tribenuron methyl is currently available in the National Pesticide Standards Repository.

Regulatory Recommendations and Residue Chemistry Deficiencies

Pending submission of revised Sections F, there are no residue chemistry issues that would preclude the establishment of permanent tolerances for tribenuron methyl residues in soybean and field corn commodities. Provided that the forthcoming human health risk assessment does not identify any issues of concern, the submitted data support tolerances for residues of tribenuron methyl, including its metabolites and degradates, in or on soybean and field corn commodities, at the levels listed below. Compliance with the tolerance levels specified below is to be determined by measuring tribenuron methyl only.

Soybean, hay	0.35 ppm
Soybean, forage	0.07 ppm
Soybean, seed	0.01 ppm
Soybean, hulls	0.04 ppm
Corn, field, grain	0.01 ppm
Corn, field, forage	0.15 ppm
Corn, field, stover	1.1 ppm
Grain, aspirated fractions	1.5 ppm

860.1480 Meat, Milk, Poultry, and Eggs

Based on the data from the poultry metabolism study, residues in liver resulting from the 10X dosing level would be 0.012 ppm. Normally, a poultry feeding study would be required (due to residues being detected above 0.01 ppm at the 10X dosing level), but none were previously requested. Because no significant poultry feed items are associated with the current petitions, a poultry feeding study is not required at this time. **However, should the registrant submit any future petition proposing use on a commodity (or commodities) associated with poultry feed items, a poultry feeding study will be required, and that study should be submitted in conjunction with any such petition.**

860.1550 Proposed Tolerances

The petitioner should submit revised Sections F to correct the tolerance levels in field corn forage (PP#8F7441), and soybean forage and hay (PP#8F7432), and to correct

the commodity definition for AGF (PP#8F7432 and PP#8F7441), as recommended in Table 9, on page 19.

Other Considerations

DuPont Method 13412 (Revision 1) has been amended to include comments from the ILV, so it can now be forwarded to FDA for use as an enforcement method.

Background

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of ALS. It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola commodities to 0.5 ppm in/on wheat hay (40CFR §180.451[a] and [c]). Tolerances have also been established at 0.05 ppm in/on field corn forage, grain and stover.

DuPont Crop Protection has submitted petitions supporting the use of tribenuron methyl on soybeans and field corn that are genetically tolerant to sulfonylurea herbicides (PP#8F7432 and PP#8F7441, respectively). These petitions have been submitted in conjunction with related petitions for use of rimsulfuron and chlorimuron ethyl on genetically modified soybeans and field corn in support of a future EP containing all three sulfonylurea herbicides. The chemical structure and nomenclature of tribenuron methyl are presented in Table 1 (below). The physicochemical properties of the technical grade of tribenuron methyl are presented in Table 2 (below).

TABLE 1 Tribenuron Methyl Nomenclature.

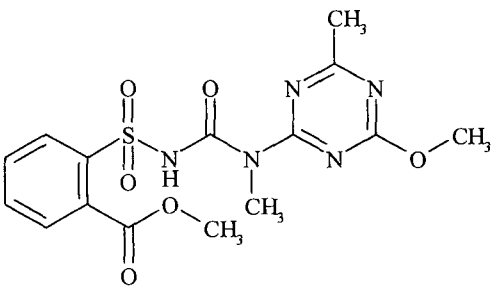
Chemical structure	
Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
Company experimental name	DPX-L5300

TABLE 1 Tribenuron Methyl Nomenclature.	
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)	50% ai SG (DuPont Express herbicide; EPA Registration #352-632)

TABLE 2 Physicochemical Properties of Tribenuron Methyl.			
Parameter	**Value**		**Reference**
Melting point/range	142°C		MRID #47138301
pH (at 20°C)	4.64		
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3		
Water solubility (at 20°C)	pH 5	0.0489 g/L	
	pH 7	2.04	
	pH 9	18.3	
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7 x 10^{-7} mm Hg		
Dissociation constant (pK$_a$)	5.0		
Octanol/water partition coefficient, Log [K$_{OW}$] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

860.1200 Directions for Use

There are currently 10 active EPs containing tribenuron methyl that are registered to DuPont for post-emergence uses on wheat, barley and oats (see Table 3, below). These EPs are formulated as either DFs or SGs. Two of the EPs contain only tribenuron methyl at 50% or 75% ai, and five of the EPs contain combinations of tribenuron methyl (10-37.5% ai), and thifensulfuron methyl (25-50% ai). Two formulations contain combinations of tribenuron methyl (13.6-18.75% ai), thifensulfuron methyl (27.3-37.5% ai), and metsulfuron methyl (10.9-15% ai), and the final formulation is comprised primarily of dicamba (63.6% ai), with no more than 4.7% each of thifensulfuron methyl, tribenuron methyl, and metsulfuron methyl.

TABLE 3 Tribenuron Methyl EPs Registered to DuPont for Post-Emergence Uses.						
EPA Reg. Number	Trade Name	Formulation Type	% Active Ingredients			
			Tribenuron Methyl	Thifensulfuron Methyl	Metsulfuron Methyl	Dicamba (Sodium Salt)
352-509	Express® XP	DF	75%	--	--	--
352-610	Ally® Extra	DF	18.75%	37.5%	15.0%	--
352-611	Harmony® Extra XP	DF	25%	50%	--	--
352-617	HER11	DF	37.5%	37.5%	--	--
352-632	Express® SG	SG	50%	--	--	--
352-641	Affinity™	SG	10%	40%	--	--
352-661	Affinity™ GBF92	SG	25%	25%	--	--
352-714	Harmony® Extra	SG	16.67%	33.33%	--	--
352-715	Ally® Extra	SG	13.6%	27.3%	10.9	--
352-751	Agility™ SG	SG	2.4%	4.7%	1.9%	63.6%

With the current petitions (PP#8F7432 and PP#8F7441), DuPont provided an amended label for Express®, the SG formulation (EPA Registration #352-632) containing 50% ai, intended for use on Optimum® GAT® herbicide-tolerant soybeans and field corn. The amended use directions for modified soybeans and field corn are summarized in Table 4 (below).

TABLE 4 Summary of Directions for Use of Tribenuron Methyl.						
Application Timing; Type; Equipment	Formulation [EPA Reg. #]	Use Rate (lb ai/A)	Number of Uses per Season	Maximum Seasonal Use Rate (lb ai/A)	PHI[1] (Days)	Use Directions and Limitations[2]
Soybean						
Post-emergence (of crop and weeds); broadcast foliar; ground, air, or chemigation equipment.	50% ai SG [352-632]	0.008-0.03	2	0.03	14	Add a non-ionic surfactant (NIS) at 0.25% v/v, or a crop oil concentrate (COC) at 1.0% v/v.
Field Corn						
Post-emergence (of crop and weeds); broadcast foliar; ground, air, or chemigation equipment.	50% ai SG [352-632]	0.008-0.03	2	0.03	7	Add an NIS at 0.25% v/v, or a COC at 1.0% v/v.

1. PHI = Pre-Harvest Interval.
2. For applications up to 0.008 lb ai/A, sugar beet, winter rape, and canola may be planted 60 days after application; other crops may be planted 45 days after application. For applications above 0.008 lb ai/A, non-labeled crops may be planted 4 months after application.

Conclusions: The label directions are adequate to allow evaluation of the residue data relative to the labeled uses. The available soybean and field corn data support the proposed 7-day PHI for field corn, and the proposed 14-day PHI for soybean.

860.1300 Nature of the Residue - Plants

D304059; R. Griffin; 24 June 2004
PP#0F6135; D266130; C. Swartz; 25 July 2006

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

860.1300 Nature of the Residue - Livestock

D304059; R. Griffin; 24 June 2004
DER for MRID #47637801 (NR in Laying Hens)

The nature of the residue in ruminants is adequately understood, based on an acceptable goat metabolism study. The nature of the residue in poultry is adequately understood, based on an acceptable laying-hen metabolism study. The ROC in ruminants and poultry is tribenuron methyl *per se*.

860.1340 Residue Analytical Methods

D311607; S. Ary; 4 January 2005
D304059; R. Griffin; 24 June 2004
D266130; C. Swartz; 25 July 2006
D330633; S. Hummel; 8 August 2006

Enforcement methods: A high-performance liquid chromatography with photo-conductivity detection (HPLC/PC) method, Method AMR 337-85 (Revision A), is available for enforcement of tolerances for residues of tribenuron methyl in grain, forage and straw commodities. For this method, residues are extracted with acetonitrile (ACN), cleaned up using silica-gel chromatography, and analyzed by HPLC/PC. The method was validated by BEAD's Analytical Chemistry Branch (ACB) 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 0.010-0.020 ppm in wheat and barley grains, at 0.020-0.040 ppm in wheat and barley straws, and at 0.010-0.10 ppm in wheat forage.

A liquid chromatography with mass-spectrometric detection (LC/MS) method, DuPont Method 1381, is also available for enforcement of tolerances for residues of tribenuron methyl in canola, cotton and flax commodities. For this method, samples are extracted with an ACN/ammonium carbonate buffer solution, and the concentrated residues are reconstituted in methanol for analysis. If required, a hexane wash step, or cleanup step using a strong anion exchange 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 C_8 column for MS analysis. The validated LOQ was 0.020 ppm. This method may also be used for enforcing tolerances in corn grain, sorghum grain, and soybean seeds.

Field trial samples were analyzed for all of the sulfonylurea residues (chlorimuron ethyl, rimsulfuron, and tribenuron methyl) in soybeans and field corn using a liquid chromatography

with tandem mass-spectrometric detection (LC/MS/MS) method, DuPont Method 13412 (Revision 1), *Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oil Crop Matrices Using SPE Purification and LC/MS/MS Detection.* For this method, samples are hydrated (corn grain and stover, and soybean hay and seeds only) with potassium phosphate buffer, and then extracted twice with acetonitrile (ACN)/K_2HPO_4 (3:1 v:v, pH 7) followed by centrifugation. Residues were then cleaned up by solvent partitioning and elution through a solid-phase extraction (SPE) cartridge. Residues were determined using external standards for quantitation. The LOQ in all corn and soybean commodities is 0.010 ppm, while the limit of detection (LOD) is 0.003 ppm. This method was previously reviewed in conjunction with a petition for thifensulfuron methyl (D330813; S. Hummel; 8 August 2006). One of the comments from that review stated that a new copy of the method was needed, incorporating the comments from the independent laboratory validation (ILV) laboratory. **The submitted copy of the method has been amended to include comments from the ILV, so it can now be forwarded to FDA for use as an enforcement method.** A PMV trial is not required.

An enforcement method for animal commodities is not currently required, as there are no tolerances for tribenuron methyl residues in livestock commodities.

Conclusions: The available residue analytical method data are adequate to satisfy data requirements for crops. The existing tolerance enforcement methods, Method AMR 337-85 (Revision A) and DuPont Method 1381, are adequate to enforce the proposed tolerances for grain, forage and hay. **DuPont Method 13412 (Revision 1) is also adequate for tolerance enforcement purposes.**

860.1360 Multiresidue Methods

D304059; R. Griffin; 24 June 2004

The FDA PESTDATA database, dated June 2005 (*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, despite being sent to Leon Sawyer, a chemist with the Pesticides and Industrial Chemicals Branch of FDA's Division of Contaminants Chemistry, in a memo dated 22 March 1989. The results of the Multiresidue Methods study with tribenuron methyl will be re-sent to the FDA. The available data indicate that residues of tribenuron methyl are not recovered by the FDA multiresidue methods.

860.1380 Storage Stability

D304059; R. Griffin; 24 June 2004
D330633; S. Hummel; 8 August 2006
DER for MRID #47542802 (CFTs with Soybeans)

Adequate data are available indicating that tribenuron methyl is stable under frozen storage conditions for at least 4 months in corn stover and soybean seeds, 6 months in corn

forage, 8.6 months in sunflower seeds, 14 months in cottonseeds and cotton gin byproducts, and 21 months in wheat grain and straw.

To support the storage duration for soybean seeds, a concurrent freezer storage stability study was conducted using control samples of homogenized soybean seeds fortified with tribenuron methyl at 0.10 ppm. The fortified samples were stored under the same conditions (-20°C) as the field trial samples. Samples were analyzed immediately after fortification, and at intervals of 1, 3, 6 and 9.6 months of storage. There was no decline in residue during frozen storage; therefore tribenuron methyl is stable in soybean seeds for intervals of up to 9.6 months.

The storage durations and conditions of samples from the corn and soybean field trial and processing studies submitted to support this petition are presented in Table 5 (below).

TABLE 5 Summary of Storage Conditions and Durations for Samples from the Field Corn and Soybean Field Trial and Processing Studies.

Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)	Interval of Demonstrated Storage Stability (Months)
Field Corn Fodder	-20	12.2	[Wheat grain and straw] 21 [1]
Field Corn Forage		10.9	
Field Corn Stover		10.5	
Field Corn Grain		11.3	
Corn AGF [2]	-20	<1	NA [3]
Corn Starch		<1	
Corn Grits		<1	
Corn Flour		<1	
Corn Refined Oil (Wet)		<1	
Corn Refined Oil (Dry)		<1	
Corn Meal		<1	
Soybean Forage	-20	8.3	[Wheat grain and straw] 21 [1]
Soybean Hay		9.2	
Soybean Seeds		6.9	9.6
Soybean Meal	-20	<1	NA
Soybean Hulls		<1	
Soybean Refined oil		<1	
Soybean AGF		<1	

1. From D304059; R. Griffin; 24 June 2004, and D330633; S. Hummel; 8 August 2006.
2. AGF = Aspirated Grain Fractions.
3. NA = Not Applicable.

Conclusion: The available storage stability data adequately support the sample storage durations and conditions incurred during the corn and soybean field trial and processing studies.

860.1400 Water, Fish, and Irrigated Crops

There are no proposed nor registered uses that are relevant to this guideline topic.

860.1460 Food Handling

There are no proposed nor registered uses that are relevant to this guideline topic.

860.1480 Meat, Milk, Poultry, and Eggs

D304059; R. Griffin; 24 June 2004

HED has previously concluded that tribenuron methyl residues in livestock commodities can be classified under 40CFR §180.6[a][3], as there is no reasonable expectation of detecting finite residues of tribenuron methyl in milk, eggs, meat or poultry. This decision was based on potential dietary exposures of 0.26 ppm for beef and dairy cattle, and 0.04 ppm for poultry and swine.

Based on the recommended tolerances for corn and soybean commodities, and the established tolerances in other livestock feedstuffs, the dietary exposures of livestock were calculated using the most recent guidance from HED (June 2008) concerning revisions to feedstuffs in Table 1 (OPPTS Residue Chemistry Test Guideline 860.1000), and construction of maximum reasonably balanced diets (MRBDs) for livestock. The newly calculated MRBDs are 0.27 ppm for beef cattle, 0.38 for dairy cattle, 0.05 ppm for poultry, and 0.05 ppm for swine (see Table 6, below).

In the available goat metabolism study, residues of tribenuron methyl were not detected (<0.01 ppm) in milk or tissues following 5 days of dosing with [^{14}C]-triazine- or [^{14}C]-phenyl-labeled tribenuron methyl at levels equivalent to 6.7 ppm in the diet (17.6-24.8X the MRBD). Based on the data from the goat metabolism study, ARIA/RD and HED conclude that a cattle feeding study is not required for this petition.

In the submitted poultry metabolism study, maximum residues of tribenuron methyl were 0.281 ppm in liver, 0.074 ppm in egg whites, 0.072 ppm in muscle, 0.052 ppm in fat and 0.003 ppm in egg yolks following 14 days of dosing with [^{14}C]-triazine- or [^{14}C]-phenyl-labeled tribenuron methyl equivalent to 11.5-11.6 ppm in the diet, which is 231X the calculated MRBD. Based on the data from the poultry metabolism study, residues in liver resulting from the 10X dosing level would be 0.012 ppm; therefore, a poultry feeding study would normally be required.

TABLE 6 Maximum Reasonably Balanced Dietary Burdens on Livestock from Tribenuron Methyl Residues.

Feedstuff	Type [1]	% Dry Matter [2]	% Diet [2]	Tolerance (ppm)	Dietary Contribution (ppm) [3]
Beef -Cattle (R 15%, CC 80%, PC 5%)					
Field corn stover	R	83	10	1.1	0.133
Aspirated grain fractions	R	85	5	1.5	0.089
Barley grain	CC	88	50	0.05	0.029
Sorghum grain	CC	88	30	0.05	0.017
Soybean meal	PC	92	5	0.01	0.0006
TOTAL BURDEN			100		**0.27**

TABLE 6 Maximum Reasonably Balanced Dietary Burdens on Livestock from Tribenuron Methyl Residues.

Feedstuff	Type[1]	% Dry Matter[2]	% Diet[2]	Tolerance (ppm)	Dietary Contribution (ppm)[3]
Dairy Cattle (R 45%, CC 45%, PC 10%)					
Field corn stover	R	83	15	1.1	0.20
Field corn forage	R	40	30	0.2	0.15
Barley grain/sorghum grain	CC	88	45	0.05	0.026
Soybean meal	PC	92	10	0.01	0.0011
TOTAL BURDEN			100		**0.38**
Poultry (CC 75%, PC 25%)					
Barley grain	CC	88	75	0.05	0.0375
Sunflower seed meal	PC	92	25	0.05	0.0125
TOTAL BURDEN			100		**0.05**
Swine (CC 85%, PC 15%)					
Barley grain	CC	88	20	0.05	0.01
Sorghum grain	CC	88	65	0.05	0.0325
Sunflower seed meal	PC	92	15	0.05	0.0075
TOTAL BURDEN			100		**0.05**

1. R = Roughage; CC = Carbohydrate Concentrate; PC = Protein Concentrate.
2. OPPTS Residue Chemistry Test Guideline 860.1000, Table 1 Feedstuffs (June 2008).
3. Residue levels for beef and dairy cattle are corrected for moisture content, and dietary burden contributions are determined by formula: Contribution = ([tolerance ÷ %DM] x %diet). Residue levels for poultry and swine are considered "as-is," and dietary burden contributions are determined by formula: Contribution = (tolerance x %diet).

Conclusion: Based on the data from the poultry metabolism study, residues in liver resulting from the 10X dosing level would be 0.012 ppm. Normally, a poultry feeding study would be required (due to residues being detected above 0.01 ppm at the 10X dosing level), but none were previously requested. Because no significant poultry feed items are associated with the current petitions, a poultry feeding study is not required at this time. However, should the registrant submit any future petition proposing use on a commodity (or commodities) associated with poultry feed items, a poultry feeding study will be required, and that study should be submitted in conjunction with any such petition.

860.1500 Crop Field Trials

DER for MRID #47542801 (CFTs with Field Corn)
DER for MRID #47542802 (CFTs with Soybeans)

DuPont submitted field trial data supporting the use of tribenuron methyl (50% ai SG) on genetically modified soybeans and field corn, as a single post-emergence application at 0.03 lb ai/A. The results from these field trials are discussed below, and the residue data are summarized in Table 7 (below).

TABLE 7 Summary of Residue Data from Soybean and Field Corn Trials with Tribenuron Methyl.										
Commodity	Trt #	Total Use Rate (lb ai/A)	PHI (Days)	Residue Levels (ppm) [1]						
				n	Min.	Max.	HAFT [2]	Median	Mean	Std. Dev.
Field Corn										
Forage	1	0.03	6-8	48	<0.01	0.19	0.11	0.02	0.03	0.034
Stover			23-63	48	<0.01	0.07	0.07	0.01	0.02	0.014
Grain			26-63	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Stover	3	0.03	5-22	48	<0.01	1.20	0.98	0.15	0.25	0.272
Grain			5-12	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Forage	6	0.03	23-71	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Stover			50-106	48	<0.01	0.02	0.02	0.01	0.01	0.001
Grain			55-106	46	<0.01	<0.01	<0.01	<0.01	<0.01	0
Soybeans										
Forage [3]	2	0.03	0	36	0.58	3.00	2.95	1.45	1.71	0.69
			14 [4]	36	0.009	0.046	0.045	0.022	0.026	0.011
Hay [3]			0	36	0.61	8.80	8.35	2.75	3.54	2.52
			14 [4]	36	0.013	0.185	0.175	0.058	0.074	0.053
Seeds			68-107	44	<0.01	<0.01	<0.01	<0.01	<0.01	0
Seeds	4	0.03	5-8	44	<0.01	0.07	0.07	0.01	0.01	0.01

1. The LOQ is 0.010 ppm for each commodity. For calculations which included residues >LOQ, the method LOQ (0.010 ppm) was used for residue values <LOQ.
2. HAFT = Highest Average Field Trial.
3. Residue data on soybean forage and hay were not included from Trials #2, 5, 6, 20 and 21 due to anomalies in either the application rate or sampling interval.
4. Residue data for the 14-day PHI were extrapolated from the 0-day data using the decline rate of the longest residue decline curve from the residue decline field trials.

Field Corn: DuPont submitted field trial data supporting the use of tribenuron methyl (50% ai SG) on field corn that is genetically modified to be tolerant to sulfonylurea herbicides. Twenty-four field trials, each including three different treatment regimes, were conducted in Zones 1, 2, 5 and 6 during 2006. At each trial, a 50% ai SG formulation of tribenuron methyl was applied to field corn as a single broadcast foliar application at 0.03 lb ai/A, approximately 7 days prior to normal forage harvest (Trt #1), 7 days prior to grain harvest (Trt #3), or at growth stage R1-R2 (Trt #6). All applications were made using ground equipment, in spray volumes of 5-30 gallons per acre (GPA), and included the use of a non-ionic surfactant (NIS) at 0.25% v/v.

Single control and duplicate treated samples of the appropriate commodities were harvested from each test at the appropriate stage of maturity. For Trt #1, forage was harvested at 6-8 days after treatment (DAT), stover was harvested at 23-63 DAT, and grain was harvested at 26-63 DAT. For Trt #6, forage was harvested at 23-71 DAT, stover was harvested at 50-106 DAT, and grain was harvested at 55-106 DAT. For Trt #3, only samples of stover and grain were harvested at 5-22 and 5-12 DAT, respectively. Duplicate repeated samples of forage and/or stover were also collected from Trts #1, #3 and #6 at five field trials, in order to evaluate residue decline. For Trt #1, forage samples were collected repeatedly from 0-22 DAT, and stover samples were collected repeatedly from 23-84 DAT. For Trt #3, stover samples were collected

repeatedly from 6-28 DAT. For Trt #6, forage samples were collected repeatedly from 0-68 DAT.

Samples were stored frozen for up to 12.2 months prior to analysis. Adequate storage stability data are available indicating that tribenuron methyl is stable at -20°C for intervals of up to 21 months in wheat grain and straw, and up to 6 months in corn forage. These data will support the durations and conditions of samples harvested from the corn field trials.

Residues of tribenuron methyl in corn grain, forage and stover were determined using an adequate LC/MS/MS method (Method 13412, Revision 1). The method LOQ is 0.010 ppm, and the LOD is 0.003 ppm in each corn commodity.

Following a single broadcast foliar application at 0.03 lb ai/A (1X rate), applied approximately 7 days prior to normal forage harvest (Trt #1), tribenuron methyl residues were <0.01-0.19 ppm in 48 samples of forage harvested at 6-8 DAT, <0.01-0.07 ppm in 48 samples of stover harvested at 23-63 DAT, and <LOD in all 48 samples of grain harvested at 26-63 DAT. Average residues were 0.03 ppm for forage, 0.02 ppm for stover, and <0.01 ppm for grain. The highest average field trial (HAFT) residues were 0.11 ppm for forage, 0.07 ppm for stover, and <0.01 ppm for grain.

When the single foliar application was applied at the rate of 0.03 lb ai/A, at growth stage R1-R2 (Trt #6), residues were <0.01 ppm in all forage samples harvested at 23-71 DAT, <0.01-0.02 ppm in 48 samples of stover harvested at 50-106 DAT, and <LOD in all grain samples harvested at 55-106 DAT. Average residues were ≤0.01 ppm for forage, stover and grain, while the HAFT residues were 0.02 ppm for stover, and <0.01 ppm for forage and grain.

When the single foliar application was applied at 0.03 lb ai/A, approximately 7 days prior to normal grain maturity (Trt #3), residues were <LOD in all samples of grain harvested at 5-12 DAT, and <0.01-1.20 ppm in 48 samples of stover harvested at 5-22 DAT. Average residues were <0.01 ppm for grain, and 0.25 ppm for stover, while the HAFT residues were <0.01 ppm for grain, and 0.98 ppm for stover.

In the five residue decline trials, tribenuron methyl residues in forage (Trt #1 and #6) showed a rapid decline within the first 7 DAT, and then declined more slowly until residues were generally <0.05 ppm by 22 DAT. Changes in residue levels in stover (Trt #1 and #3) were more sporadic than for forage, but tribenuron methyl residues in stover generally declined or remained steady at longer post-treatment intervals.

Soybeans: DuPont submitted field trial data supporting the use of tribenuron methyl (50% ai SG) on soybeans that are genetically modified to be tolerant to sulfonylurea herbicides. Twenty-three soybean field trials, each including two different treatment regimes, were conducted in Zones 2, 4 and 5 during 2006. At each trial, tribenuron methyl (50% ai SG) was applied to soybeans as a single broadcast foliar application at 0.03 lb ai/A (1X rate), at growth stage R1-R2 (Trt #2), or approximately 7 days prior to normal seed harvest (Trt #4). In one test (Trial 02), the tribenuron methyl (50% ai SG) was applied under both treatment regimes at 0.06 lb ai/A (2X rate). All applications were made using ground equipment, in spray volumes of 5-27 GPA, and included the use of a non-ionic surfactant at 0.25% v/v.

For Trt #2, single control and duplicate treated samples of forage and hay were harvested on the day of application (0 DAT), while seeds were harvested at normal maturity (68-107 DAT). Repeated samples of forage and hay were also collected from three trials at 0, 1, 3, 7, 14 and 21

DAT, in order to evaluate residue decline. For Trt #4, single control and duplicate treated samples of seeds were harvested at 5-8 DAT. Samples were stored frozen for up to 9.2 months prior to analysis. Adequate storage stability data are available indicating that tribenuron methyl is stable at -20°C for intervals of up to 6 months in corn forage, 21 months in wheat grain and straw, and 9.6 months in soybean seeds. These data support the durations and conditions of samples harvested from the soybean field trials.

Residues of tribenuron methyl in soybean forage, hay and seeds were determined using an adequate LC/MS/MS method (Method 13412, Revision 1). The method LOQ is 0.010 ppm, and the LOD is 0.003 ppm in each soybean commodity.

Following a single broadcast foliar application at 0.03 lb ai/A (1X rate), at growth stage R1-R2 (Trt #2), tribenuron methyl residues were 0.58-3.0 ppm in 36 samples of forage, 0.61-8.80 ppm in 36 samples of hay harvested at 0 DAT, and <0.01 ppm in all 44 samples of seeds harvested at 68-107 DAT. Average residues were 1.71 ppm for forage, 3.54 ppm for hay, and <0.01 ppm for seeds. The HAFT residues were 2.95 ppm for forage, 8.35 ppm for hay, and <0.01 ppm for seeds. **NOTE:** Although residue data were submitted from 23 trials (46 samples), residue data for forage and hay from 5 tests were excluded from the dataset because of anomalies in either the application rate or the sampling intervals.

When the single foliar application was applied at 0.03 lb ai/A, approximately 7 days before normal crop maturity (Trt #4), residues were <0.01-0.07 ppm in 44 samples of seeds harvested at 5-8 DAT. The average residue in seeds was 0.01 ppm, while the HAFT residue was 0.07 ppm.

For both forage and hay, tribenuron methyl residues declined rapidly within the first week after application, and then declined more slowly thereafter. For all three decline tests, average residues in forage were 1.72 ppm at 0 DAT, 0.04 ppm by 7 DAT, and <0.01 ppm by 21 DAT. Average residues in hay were 3.83 ppm at 0 DAT, 0.05 ppm by 7 DAT, and <0.01 ppm by 21 DAT.

The use pattern being supported on soybeans by DuPont is Trt#2; however, the petitioner is requesting a 14-day PHI for forage and hay, rather than a 0-day PHI, which is supported by the available residue data. Based on the data from the residue decline studies, DuPont used the rate constant from the decline curve with the longest rate of decline to extrapolate possible residue values for soybean forage and hay at the proposed 14-day PHI. The formula shown below was used to calculate 14-day residue values for forage and hay.

$$\ln(\text{residues at 14 days}) = m(14) + \ln(\text{residues at 0 DAT})$$

The rate of decline (m) was calculated to be -0.298 for soybean forage, and -0.276 for soybean hay. The extrapolated 14-day residue values for forage and hay are presented in Appendix I, and are summarized in Table 7, above.

Conclusions: The available corn and soybean field trial data are acceptable, and support the proposed use patterns for tribenuron methyl (50% ai SG) on genetically modified soybeans and field corn. An adequate number of trials were conducted on each crop in the appropriate

geographical regions. All samples were analyzed for the ROC using an adequate method, and sample storage conditions and durations are supported by the available storage stability data.

The field trial data support the proposed 7-day PHI for all corn commodities, and the proposed 14-day PHI for soybean forage and hay. As the label directions for use on soybeans prohibit applications after the R2 stage, a specific PHI for soybean seeds is not required. The data support tolerances of 0.01 ppm in/on corn grain, 0.15 ppm in/on corn forage, 1.1 ppm in/on corn stover, 0.01 ppm in/on soybean seeds, 0.07 ppm in/on soybean forage, and 0.35 ppm in/on soybean hay.

860.1520 Processed Food and Feed

DER for MRID #47548203 (PFF from Field Corn)
DER for MRID #47548204 (PFF from Soybeans)

Field Corn: DuPont has submitted data from 3 field trials conducted in IA and NE during 2006 used to generate field corn grain for use in processing (2 tests) or for generating AGF (1 test). In the test used to generate AGF samples, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 7 days prior to normal grain maturity, at the rate of 0.031 lb ai/A (1X rate). In the two tests used to generate grain for processing, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application 7 days prior to normal harvest at a rate of 0.15 lb ai/A (5X rate). All applications were made using ground equipment, in spray volumes of 16-20 GPA, and included the use of a non-ionic surfactant at 0.25% v/v.

Single bulk control and treated sample of corn grain, the raw agricultural commodity (RAC), were harvested from each test at 7 DAT. AGF samples were generated using corn grain from the 1X rate test, via procedures designed to simulate the movement of grain through terminal elevators. Corn grain samples from the 5X rate tests were processed, using simulated commercial milling procedures, into starch, grits, meal, flour and refined oil (wet- and dry-milled). Samples of corn grain were stored frozen for up to 6.5 months prior to analysis, while corn AGF and processed commodities were stored frozen for ≤30 days prior to analysis. These sample storage conditions and durations are supported by the available storage stability data.

Residues of tribenuron methyl in corn grain, AGF and processed fractions were determined using an adequate LC/MS/MS method (Method 13412, Revision No. 1). The method LOQ is 0.010 ppm, and the LOD is 0.003 ppm in each corn commodity.

In the test used to generate AGF, tribenuron methyl residues were <LOD in the grain harvested at 7 DAT following an application at the 1X rate. Residues in AGF averaged 0.039 ppm, indicating that tribenuron methyl residues can concentrate by up to 13X in corn AGF. Following an application at the 5X rate, residues of tribenuron methyl were <LOQ in corn grain and all processed fractions from both processing studies (see Table 8, below).

Soybeans: Three soybean field trials were conducted in IL, MN and NE during 2006, in order to generate soybean seed samples for processing (2 tests), and for generating AGF (1 test). In the test used to generate AGF samples, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 5 days prior to normal seed maturity, at the rate of 0.03 lb ai/A (1X rate). In the two tests used to generate seeds for processing, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 7 days prior to normal harvest, at the rate of 0.16

lb ai/A (5X rate). All applications were made using ground equipment, in spray volumes of 15-25 GPA, and included the use of a non-ionic surfactant at 0.25% v/v.

Single bulk control and treated samples of soybean seeds (RAC) were harvested from each test at 5 or 7 DAT. AGF samples were generated using seeds from the 1X rate test, via procedures designed to simulate the movement of grain through terminal elevators. Soybean seeds from the 5X rate tests were processed using simulated commercial procedures into hulls, meal and refined oil. Samples of soybean seeds were stored at ≤-12° C for up to 2 months prior to analysis, while soybean AGF and processed commodities were stored frozen for ≤30 days prior to analysis. These sample storage conditions and durations are supported by the available storage stability data.

Residues of tribenuron methyl in soybean seeds, AGF and processed fractions were determined using an adequate LC/MS/MS method (Method 13412, Revision No. 1). The method LOQ is 0.010 ppm, and the LOD is 0.003 ppm in each soybean commodity.

In the test used to generate AGF, tribenuron methyl residues were <LOD in the seeds harvested at 5 DAT following an application at a 1X rate. Residues in AGF averaged 0.45 ppm, indicating that tribenuron methyl residues can concentrate by up to 150X in soybean AGF.

For the 5X tests, tribenuron methyl residues in whole seeds were <LOD in one test and 0.042 ppm in the other test. For the test with quantifiable residues in seeds, residues averaged 0.17 ppm in hulls, and <LOD in meal and refined oil. Tribenuron methyl residues concentrated by 4.05X in hulls, and were reduced by <0.07X in meal and refined oil.

TABLE 8 Summary of Processing Factors for Tribenuron Methyl.

RAC	Processed Commodity	Processing Factor
Corn Grain	AGF	13X
	Processed fractions	Not calculated.*
Soybean Seeds	AGF	150X
	Hulls	4.05X
	Meal	<0.07X
	Refined oil	<0.07X

*Processing factors for field corn were not calculated, as residues were <LOQ in grain and all processed fractions.

Conclusions: The available corn and soybean processing data for tribenuron methyl are adequate. As residues were <LOQ in corn grain, and all corn processed fractions following an application at 5X the proposed use rate, separate tolerances are not required in corn grain processed fractions. For soybeans, residues concentrated only in hulls (4.05X). Based on HAFT residues of 0.01 ppm for soybean seeds (14-day PHI), the tolerance in/on soybean hulls should be set at 0.04 ppm.

Tribenuron methyl residues were shown to concentrate in AGF from both field corn grain (13X), and soybean seeds (150X). Based on the HAFT residues of field corn grain (0.01 ppm), and soybean seeds (0.01 ppm), the maximum expected residues would be 0.13 ppm in AGF from corn grain, and 1.5 ppm in AGF from soybean seeds. As residues in soybean AGF are higher than in corn grain AGF, the tolerance in/on AGF should be set at 1.5 ppm.

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 T. Cole, BEAD/ACB).

860.1850 and 860.1900 Confined and Field Accumulation in Rotational Crops

D304059; R. Griffin; 24 June 2004

Adequate confined rotational crop data are available to support a minimum 30-day PBI for all crops without registered uses. As labels for tribenuron methyl currently specify minimum PBIs of no less than 60 days for canola, rape and sugar beets, and 45 days for all other crops not listed on the label, data requirements for rotational crops are fulfilled, and tolerances are not required in rotational crops.

860.1550 Proposed Tolerances

Permanent tolerances for residues of tribenuron methyl have been established in/on barley, canola, field corn, cotton, flax, grass, oat, rice, sorghum, soybean, sunflower and wheat commodities, at levels ranging from 0.02 to 0.5 ppm (40CFR §180.451[a] and [c]). No tolerances have been established for residues in either animal commodities or rotational crops. The proposed and recommended tolerances are presented in Table 9, below.

As residues were <LOQ in all samples of soybean seeds, and field corn grain collected at the appropriate PHIs, the recommended tolerances in these commodities are equal to the method LOQ (0.010 ppm). For field corn forage and stover, and soybean forage and hay, tolerances were calculated using the tolerance harmonization spreadsheet (Appendix I). The residue data supporting the 7-day PHI were used to calculate tolerances in field corn forage and stover. For soybean forage and hay, the 0-day residue data were extrapolated to a 14-day PHI, based on the observed residue decline data. The calculated 14-day residues were then used to determine the appropriate soybean tolerances.

As residues were <LOQ in corn grain, and all corn processed fractions following an application at 5X the proposed use rate, separate tolerances are not required in corn grain processed fractions. For soybeans, residues concentrated only in hulls (4.05X). Based on HAFT residues of 0.01 ppm for soybean seeds (14-day PHI), the appropriate tolerance in soybean hulls is 0.04 ppm.

Tribenuron methyl residues were shown to concentrate in AGF from both corn grain (13X), and soybean seeds (150X). Based on the HAFT residues for field corn grain (0.01 ppm), and soybean seeds (0.01 ppm), the maximum expected residues would be 0.13 ppm in AGF from corn grain, and 1.5 ppm in AGF from soybean seeds. As residues in soybean AGF are higher than in corn grain AGF, the recommended tolerance in AGF is 1.5 ppm.

Based on the MRDBs on livestock, and the available metabolism studies, finite residues of tribenuron methyl are not expected to occur in cattle, goat, horse, sheep nor hog commodities (40CFR §180.6[a][3]). Finite residues are also not expected to occur in eggs, poultry meat, nor poultry fat. Based on the available metabolism data, detectable residues could possibly occur in

poultry meat byproducts. However, because no significant poultry feed items are associated with the current petitions, a poultry feeding study is not required at this time.

There are no established nor proposed Codex or Mexican MRLs for residues of tribenuron methyl (Appendix II). Canada has established MRLs for tribenuron methyl in several plant commodities. However, no Canadian MRLs for tribenuron methyl have been proposed nor established in the commodities being considered under these petitions. Therefore, there are no concerns regarding compatibility of the proposed tolerances.

There are no residue chemistry considerations that would preclude establishing permanent tolerances for residues of tribenuron methyl, including its metabolites and degradates, in or on the commodities specified in Table 9, below. Compliance with the tolerance levels specified below is to be determined by measuring tribenuron methyl only.

TABLE 9 Tolerance Summary for Tribenuron Methyl.

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments; *Correct Commodity Definition*
Corn, field, grain	0.01	0.01	Adequate residue data are available. Residues were <0.01 ppm in all grain samples.
Corn, field, forage	0.2	0.15	Adequate residue data on forage are available supporting the 7-day PHI. The tolerance was calculated using the tolerance spreadsheet.
Corn, field, stover	1.1	1.1	Adequate residue data on stover are available supporting the 7-day PHI. The tolerance was calculated using the tolerance spreadsheet.
Corn, aspirated grain fractions	3.45	None	Adequate residue data are available indicating that residues concentrate in corn grain AGF by 13X. Based on a HAFT of 0.01 ppm for corn grain, the maximum expected residues in corn grain AGF would be 0.13 ppm.
Soybean, hay	0.25	0.35	Adequate residue data are available on soybean forage and hay harvested at 0 DAT. These data were extrapolated to calculate residues at 14 DAT, which is the proposed PHI for forage and hay. Tolerances were calculated using the tolerance spreadsheet.
Soybean, forage	0.06	0.07	
Soybean, seed	0.01	0.01	Adequate residue data are available supporting application at the R2 Stage. Residues were <0.01 ppm in all seed samples.
Soybean, hulls	0.04	0.04	Adequate residue data are available. Based on a processing factor of 4.0X for hulls, and a HAFT of 0.01 ppm for soybean seeds, the maximum expected residues in hulls would be 0.04 ppm.
Soybean, aspirated grain fractions	3.55	None	Adequate residue data are available, indicating that residues concentrate in soybean AGF by 150X. Based on a HAFT of 0.01 ppm for soybean seeds, the maximum expected residues in soybean AGF would be 1.5 ppm.

TABLE 9 Tolerance Summary for Tribenuron Methyl.			
Commodity	**Proposed Tolerance (ppm)**	**Recommended Tolerance (ppm)**	**Comments; *Correct Commodity Definition***
Grain, aspirated fractions	None	1.5	A single tolerance should be established in *Grain, aspirated fractions,* based on the soybean AGF data.

References

Tribenuron methyl. Residue Chemistry Considerations.; D304059; R. Griffin; 24 June 2004.

Thifensulfuron methyl. Addition of Uses on Rice and Sorghum (PRIA R19 – 352-611; PP#4F6889). Summary of Analytical Chemistry and Residue Data.; D330813; S. Hummel; 8 August 2006

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.; D330633; S. Hummel; 8 August 2006

Attachments:
Appendix I - Tolerance Assessment Calculations
Appendix II - International Residue Limit Status sheet

Appendix I - Tolerance Assessment Calculations

For each of the crops listed below, the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, along with the tolerance spreadsheet, was used for calculating recommended tolerances. As specified in the SOP, the minimum of the 95% upper confidence limit (UCL) on the 95th percentile, and the point estimate of the 99th percentile, was selected as the tolerance value in cases where the dataset was large (greater than 15 samples) and reasonably lognormal. For datasets that were small (≤15 samples) and reasonably lognormal, the upper bound estimate of the 95th percentile (based on the median residue value) was compared to the minimum of the 95% UCL on the 95th percentile, and the point estimate of the 99th percentile, and the minimum value was selected as the tolerance value. For datasets that were not lognormal, the upper bound on the 89th percentile was selected as the tolerance value (distribution-free method). The rounding procedures specified in the SOP were also used.

The Agency's *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* was utilized for determining the appropriate tolerance levels in field corn forage and stover harvested at 6-8 DAT, and soybean forage and hay harvested at 0 DAT (and extrapolated to 14 DAT). However, the tolerance spreadsheet was not used to calculate the tolerance in field corn grain, or soybean seeds, as the datasets for these commodities contained high percentages of (or all) values <LOQ. For corn grain, all samples, regardless of PHI, were <LOQ. For soybeans, samples of seeds harvested following the harvest of hay (68-107 DAT) were all <LOQ. For seed samples harvested 5-8 DAT, 84% of the residues were <LOQ. The datasets for corn forage and stover, and soybean forage and hay, are presented in Tables I-1 and I-2.

Those datasets used to assess a possible tolerance for tribenuron methyl residues in corn forage harvested at 6-8 DAT, corn stover harvested at 5-7 DAT, and soybean forage and hay harvested at 0 DAT (and extrapolated to 14 DAT), consist of field trial data representing applications of the appropriate formulation, at rates approximately 1X the maximum proposed use rates. As specified by the *Guidance for Setting Pesticide Tolerances Based on Field Trial Data* SOP, the field trial application rates were within 25% of the maximum label application rates.

Corn: The datasets for tribenuron methyl residues in corn forage harvested at 6-8 DAT, and corn stover harvested at 5-7 DAT, were entered into the tolerance spreadsheet. Visual inspection of the lognormal probability plots (Figures I-1 and I-3) indicated that the datasets are somewhat or reasonably lognormal. However, the results of the approximate Shapiro-Francia test statistic rejected this assumption for both forage and stover (Figures I-2 and I-4).

The recommended tolerances in corn forage harvested at 6-8 DAT, and in corn stover harvested at 5-7 DAT, are 0.15 and 1.1 ppm, respectively.

Soybean: The datasets for tribenuron methyl residues in soybean forage and hay harvested at 0 DAT (and extrapolated to 14 DAT) were entered into the tolerance spreadsheet. Visual inspection of the lognormal probability plots (Figures I-5, I-7, I-9 and I-11) indicated that the datasets for forage and hay, at both harvest intervals, are lognormal. The results of the approximate Shapiro-Francia test statistic confirm these assumptions (Figures I-6, I-8, I-10 and I-12).

The recommended tolerances in soybean forage and hay, harvested at 0 DAT, are 4.5 and 15 ppm, respectively. When the residue data from 0 DAT are extrapolated out to 14 DAT, the recommended tolerances in soybean forage and hay are 0.07 ppm and 0.35 ppm, respectively.

TABLE H.1. Tribenuron Methyl Residues in Field Corn Forage and Stover.				
Regulator:	EPA		EPA	
Chemical:	Tribenuron methyl		Tribenuron methyl	
Crop:	Corn forage		Corn stover	
PHI's:	6-8 days		5-7 days	
Application Rate:	0.03 lb a.i./A		0.03 lb a.i./A	
Submitter:	DuPont		DuPont	
MRID Citation:	MRID #47548201		MRID #47548201	
	Residues		Residues	
	0.010	0.019	**0.010**	0.19
	0.010	0.019	**0.010**	0.21
	0.010	0.020	**0.010**	0.25
	0.010	0.021	**0.010**	0.26
	0.010	0.021	**0.010**	0.29
	0.010	0.021	**0.010**	0.29
	0.010	0.023	0.024	0.3
	0.010	0.024	0.026	0.3
	0.010	0.026	0.049	0.31
	0.010	0.028	0.058	0.32
	0.010	0.032	0.067	0.32
	0.010	0.034	0.068	0.34
	0.010	0.039	0.07	0.4
	0.011	0.039	0.07	0.41
	0.012	0.041	0.083	0.42
	0.012	0.044	0.087	0.42
	0.012	0.062	0.087	0.43
	0.013	0.063	0.094	0.49
	0.013	0.067	0.10	0.6
	0.013	0.095	0.10	0.69
	0.014	0.100	0.13	0.85
	0.014	0.120	0.15	1.1
	0.016	0.190	0.15	1.2

NOTE: Values at or below the LOQ (0.010 ppm) are entered as the LOQ, and are listed in **bold red**.

Figure I-1. Lognormal Probability Plot for Residues of Tribenuron Methyl in Corn Forage Harvested 6-8 DAT

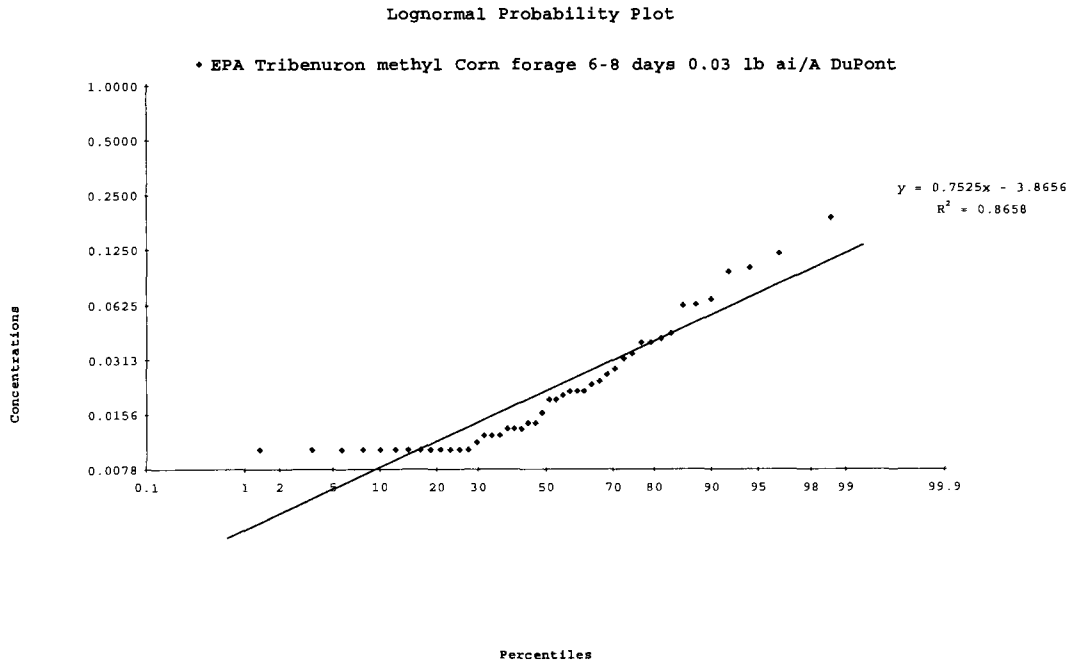


Figure I-2. Data Summary Table for Residues of Tribenuron Methyl in Corn Forage Harvested 6-8 DAT.

	Regulator:	EPA	
	Chemical:	Tribenuron methyl	
	Crop:	Corn forage	
	PHI:	6-8 days	
	App. Rate:	0.03 lb ai/A	
	Submitter:	DuPont	
	n:	46	
	min:	0.01	
	max:	0.19	
	median:	0.02	
	average:	0.03	
	95th Percentile	99th Percentile	99.9th Percentile
EU Method I	0.09	0.15	0.15
Normal	(0.15)	(0.15)	(--)
95/99 Rule	0.08	0.15	0.25
	(0.15)	(0.25)	(--)
EU Method II		0.08	
Distribution-Free			
Mean+3SD		0.15	
UCLMedian95th		0.09	
Approximate Shapiro-Francia Normality Test		0.8658	
	p-value <= 0.01: Reject lognormality assumption		
Would you like the above values rounded? (Y or N)==>			Y

Figure I-3. Lognormal Probability Plot for Residues of Tribenuron Methyl in Corn Stover harvested 5-7 DAT.

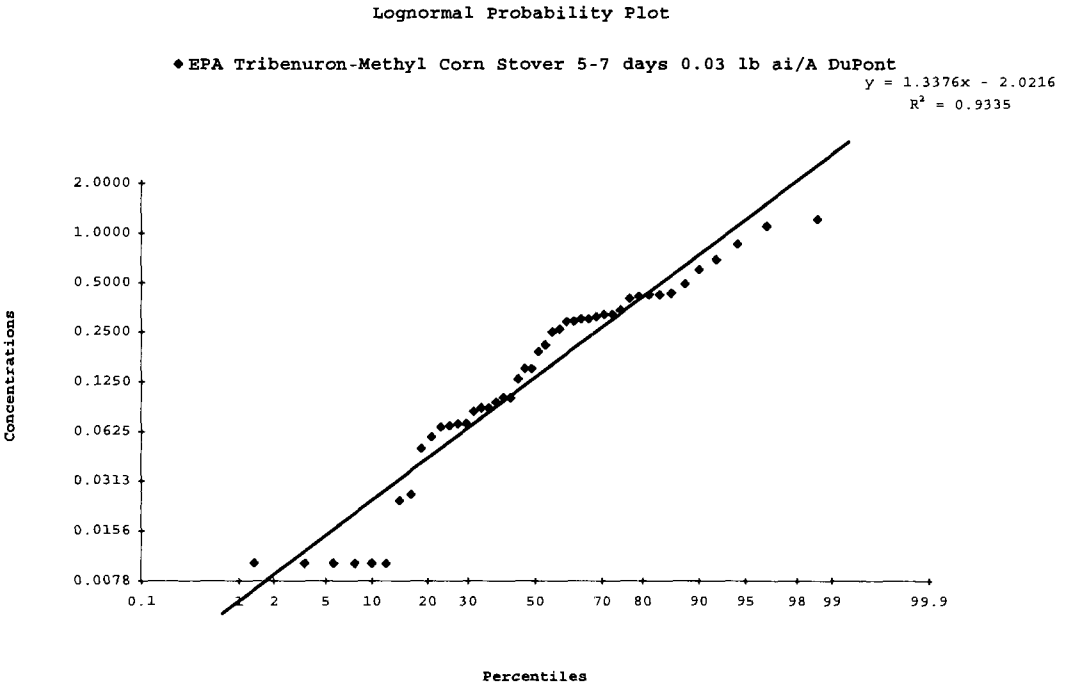


Figure I-4. Data Summary Table for Residues of Tribenuron Methyl in Corn Stover harvested 5-7 DAT.

	Regulator: EPA Chemical: Tribenuron-Methyl Crop: Corn Stover PHI: 5-7 days App. Rate: 0.03 lb ai/A Submitter: DuPont n: 46 min: 0.01 max: 1.20 median: 0.17 average: 0.26		
	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	0.80 (0.90)	0.90 (1.1)	1.2 (--)
95/99 Rule	1.3 (2.5)	3.5 (7.0)	9.0 (--)
EU Method II Distribution-Free	0.80		
Mean+3SD	1.1		
UCLMedian95th	0.90		
Approximate Shapiro-Francia Normality Test	0.9335 0.05 >= p-value > 0.01 : Reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

EXTRACTS: Tribenuron Methyl Residues in Soybean Forage and Hay				
Reg.Nos.	EPA		EPA	
Chemicals	Tribenuron methyl		Tribenuron methyl	
Crop	Soybean Forage		Soybean Hay	
DAT	0 days	14 days (extrapolated)	0 days	14 days (extrapolated)
Application Rate	0.0315 a.i./A		0.0315 a.i./A	
Submitter	DuPont		DuPont	
MRID Citation	MRID #47548202		MRID #47548202	
	Residues	**Residues**	**Residues**	**Residues**
	0.58	**0.010**	0.6	0.013
	0.64	0.010	0.7	0.015
	0.80	0.012	0.8	0.016
	0.95	0.015	0.9	0.018
	1.00	0.015	0.9	0.019
	1.00	0.015	1.0	0.021
	1.00	0.015	1.0	0.021
	1.10	0.017	1.1	0.023
	1.20	0.019	1.4	0.029
	1.20	0.019	1.8	0.038
	1.20	0.019	2.0	0.042
	1.30	0.020	2.3	0.048
	1.30	0.020	2.4	0.050
	1.30	0.020	2.4	0.050
	1.30	0.020	2.5	0.052
	1.40	0.022	2.5	0.052
	1.40	0.022	2.6	0.055
	1.40	0.022	2.6	0.055
	1.50	0.023	2.9	0.061
	1.70	0.026	3.0	0.063
	2.00	0.031	3.0	0.063
	2.00	0.031	3.0	0.063
	2.00	0.031	3.1	0.065
	2.10	0.032	3.5	0.073
	2.20	0.034	3.6	0.076
	2.20	0.034	3.9	0.082
	2.20	0.034	5.4	0.113
	2.30	0.035	5.5	0.115
	2.40	0.037	6.2	0.130
	2.50	0.039	7.0	0.147
	2.50	0.039	7.5	0.157
	2.50	0.039	7.6	0.159

TABLE II-2 Tribenuron Methyl Residues in Soybean Forage and Hay				
Regulator:	EPA		EPA	
Chemical:	Tribenuron methyl		Tribenuron methyl	
Crop:	Soybean forage		Soybean hay	
PHI:	0 days	14 days (extrapolated)	0 days	14 days (extrapolated)
Application Rate:	0.03 lb ai/A		0.03 lb ai/A	
Submitter:	DuPont		DuPont	
MRID Citation:	MRID 47548202		MRID 47548202	
	2.50	0.039	7.9	0.166
	2.90	0.045	7.9	0.166
	2.90	0.045	8.2	0.172
	3.00	0.046	8.8	0.185

NOTES: Values at or below the LOQ (0.010 ppm) are entered as the LOQ, and are listed in **bold red**. The formula shown below was used to calculate the 14-day residue values for forage and hay.

$$\ln(\text{residues at 14 days}) = m(14) + \ln(\text{residues at 0 DAT})$$

Figure I-5. Lognormal Probability Plot for Residues of Tribenuron Methyl in Soybean Forage Harvested at 0 DAT.

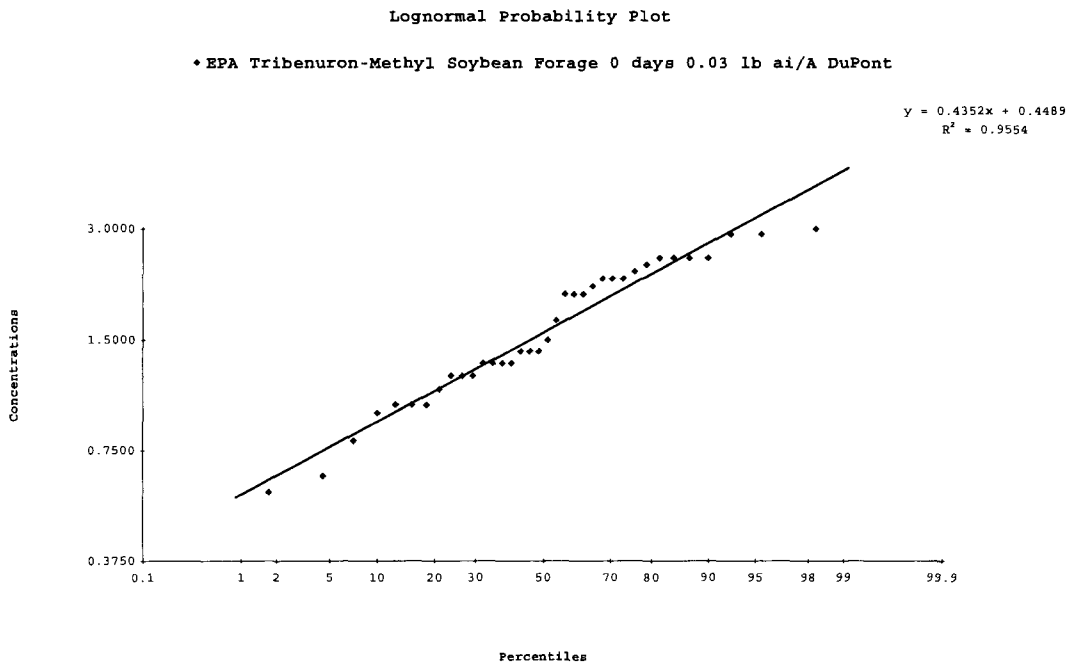


Figure I-6. Data Summary Table for Residues of Tribenuron Methyl in Soybean Forage Harvested at 0 DAT.

	Regulator: EPA **Chemical:** Tribenuron-Methyl **Crop:** Soybean Forage **PHI:** 0 days **App. Rate:** 0.03 lb ai/A **Submitter:** DuPont **n:** 36 **min:** 0.58 **max:** 3.00 **median:** 1.45 **average:** 1.71		
	95th Percentile	**99th Percentile**	**99.9th Percentile**
EU Method I **Normal**	3.0 (3.5)	3.5 (4.0)	4.0 (--)
95/99 Rule	3.5 **(4.5)**	**4.5** (6.0)	7.0 (--)
EU Method II **Distribution-Free**	5.0		
Mean+3SD	**4.0**		
UCLMedian95th	**8.0**		
Approximate **Shapiro-Francia** **Normality Test**	0.9554 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

Figure II-7. Lognormal Probability Plot for Residues of Tribenuron Methyl in Soybean Forage Extrapolated to a 14-day PHI.

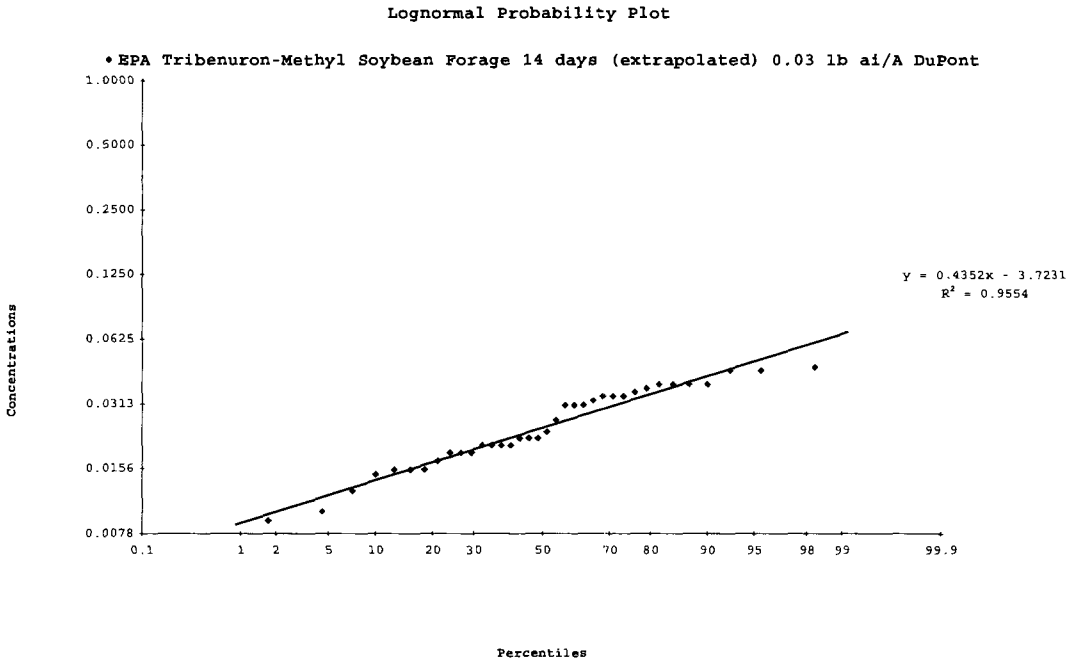


Figure I-8. Data Summary Table for Residues of Tribenuron Methyl in Soybean Forage Extrapolated to a 14-day PHI.

	Regulator: EPA **Chemical:** Tribenuron-Methyl **Crop:** Soybean Forage **PHI:** 14 days (extrapolated) **App. Rate:** 0.03 lb ai/A **Submitter:** DuPont **n:** 36 **min:** 0.01 **max:** 0.05 **median:** 0.02 **average:** 0.03		
	95th Percentile	**99th Percentile**	**99.9th Percentile**
EU Method I **Normal**	0.05 (0.05)	0.06 (0.06)	0.06 (--)
95/99 Rule	0.05 **(0.07)**	**0.07** (0.09)	0.10 (--)
EU Method II **Distribution-Free**	0.08		
Mean+3SD	**0.06**		
UCLMedian95th	**0.15**		
Approximate **Shapiro-Francia** **Normality Test**	0.9554 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

Figure I-9. Lognormal Probability Plot for Residues of Tribenuron Methyl in Soybean Hay Harvested at 0 DAT.

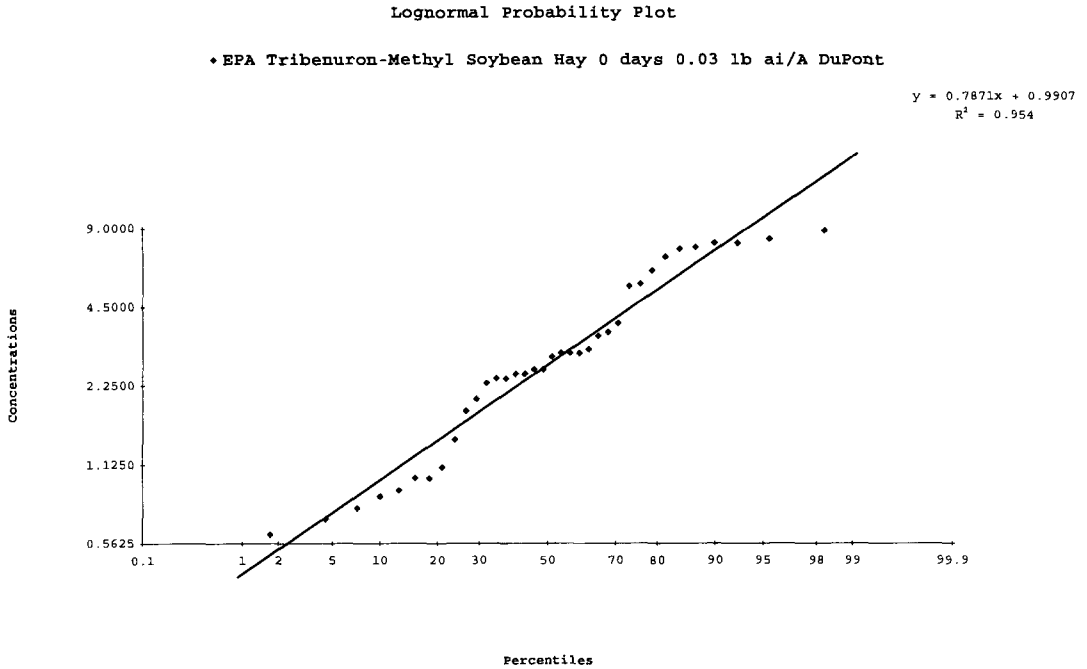


Figure I-10. Data Summary Table for Residues of Tribenuron Methyl in Soybean Hay Harvested at 0 DAT.

	Regulator: EPA Chemical: Tribenuron-Methyl Crop: Soybean Hay PHI: 0 days App. Rate: 0.03 lb ai/A Submitter: DuPont n: 36 min: 0.61 max: 8.80 median: 2.75 average: 3.54		
	95th Percentile	99th Percentile	99.9th Percentile
EU Method I Normal	8.0 (9.0)	10 (12)	12 (--)
95/99 Rule	10 (15)	17 (30)	35 (--)
EU Method II Distribution-Free	11		
Mean+3SD	12		
UCLMedian95th	14		
Approximate Shapiro-Francia Normality Test	0.9540 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

Figure I-11. Lognormal Probability Plot for Residues of Tribenuron Methyl in Soybean Hay Extrapolated to a 14-day PHI.

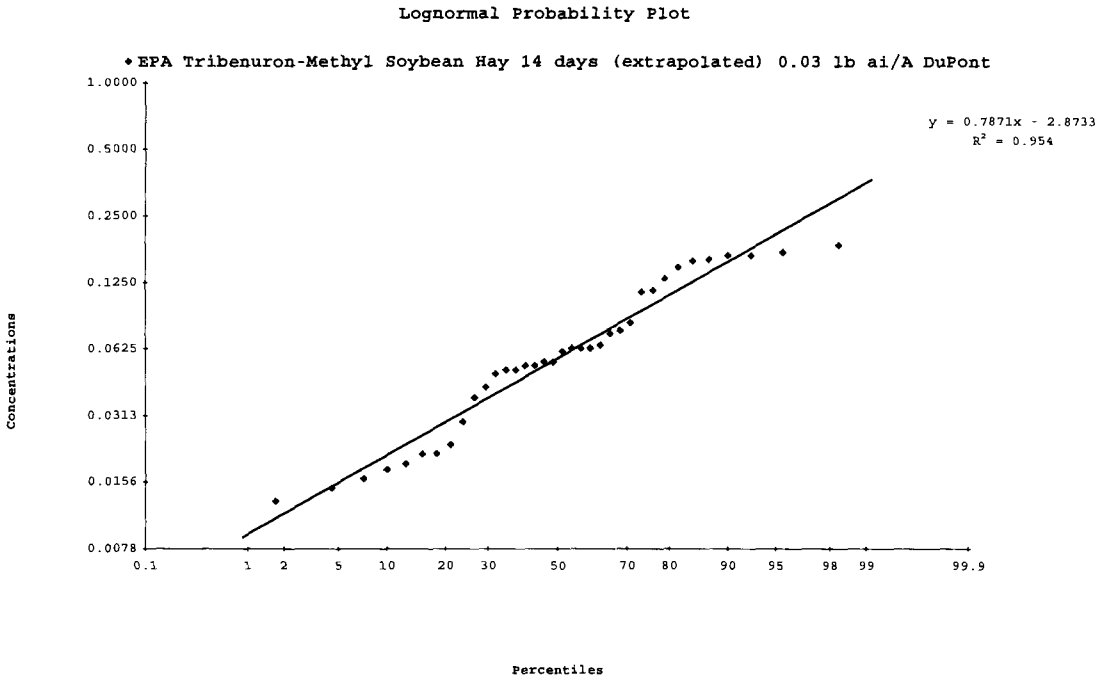


Figure I-12. Data Summary Table for Residues of Tribenuron Methyl in Soybean Hay Extrapolated to a 14-day PHI.

	Regulator: EPA **Chemical:** Tribenuron-Methyl **Crop:** Soybean Hay **PHI:** 14 days (extrapolated) **App. Rate:** 0.03 lb ai/A **Submitter:** DuPont **n:** 36 **min:** 0.01 **max:** 0.18 **median:** 0.06 **average:** 0.07		
	95th Percentile	**99th Percentile**	**99.9th Percentile**
EU Method I **Normal**	0.20 (0.20)	0.20 (0.25)	0.25 (--)
95/99 Rule	0.25 **(0.35)**	**0.40** (0.60)	0.70 (--)
EU Method II **Distribution-Free**	0.25		
Mean+3SD	**0.25**		
UCLMedian95th	**0.30**		
Approximate **Shapiro-Francia** **Normality Test**	0.9540 p-value > 0.05 : Do not reject lognormality assumption		

Would you like the above values rounded? (Y or N)==> Y

Appendix II - International Residue Limit Status Sheet

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 Recommended tolerances** ☐ Reevaluated tolerance ☐ Other	**Date:** 8 July 2009

Codex Status (Maximum Residue Limits)		**US Tolerances**	
X No Codex proposal step 6 or above ☐ No Codex proposal step 6 or above for the crops requested		Petition Numbers: 8F7432, 8F7441 DP Number: 360846 Other Identifier: PC code 128887	
Residue definition (step 8/CXL): NA		Reviewer, Division/Branch/Team: William T. Drew, RD/RIMUERB/ARIA Residue definition: Tribenuron methyl	
Crop	MRL (mg/kg)	Crops	Tolerance (ppm)
		Corn, field, grain	0.01
		Corn, field, forage	0.15
		Corn, field, stover	1.1
		Soybean, hay	0.35
		Soybean, forage	0.07
		Soybean, seed	0.01
		Soybean, hulls	0.04
		Grain, aspirated fractions	1.5

Limits for Canada		**Limits for Mexico**	
☐ No Limits X No Limits for the crops requested		X No Limits ☐ No Limits for the crops requested	
Residue definition: Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoate		Residue definition: NA	
Crop	MRL (mg/kg)	Crop	MRL (mg/kg)

Notes/Special Instructions: NA = Not Applicable. Per Steve Funk, 20 July 2009.

Tribenuron Methyl/352-632/PC Code 128887/E.I. du Pont de Nemours and Company/352
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial/Residue Decline - Field Corn (Forage, Stover, Grain)

Primary Evaluator — Date: 16 June 2009
William T. Drew,
Chemist, RD/RIMUERB/ARIA

Approved by — Date: 9 September 2009
John Redden,
Team Leader, RD/RIMUERB/ARIA

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). The DER has been reviewed by the Registration Division (RD) and the Health Effects Division (HED), and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

MRID #47548201. Andrew Thiel (2008) *Magnitude and Decline of Sulfonylurea Residues in/on Green Plant, Forage, Stover and Seed of a Field Corn Line Containing Event DP-098140-6 Following a Variety of Tank Mix Applications of Two Glyphosate and Rimsulfuron, Tribenuron Methyl, Chlorimuron Ethyl, and Metsulfuron Methyl Containing Herbicides at Maximum Label Rates - United States and Canadian Locations, Season 2006.* Laboratory Project Number: DuPont-20616. Unpublished study prepared by DuPont. 347 pages.

EXECUTIVE SUMMARY

DuPont Crop Protection has submitted field trial data supporting the use of tribenuron methyl on field corn that is tolerant to sulfonylurea herbicides. Twenty-four field trials, each including three different treatment regimes, were conducted in Zones 1, 2, 5 and 6 during 2006. At each trial, a water-soluble granule (SG) formulation of tribenuron methyl, containing 50% active ingredient (ai), was applied to field corn as a single broadcast foliar application at the rate of 0.03 pound ai per acre (lb ai/A), approximately 7 days prior to normal forage harvest (Trt #1), 7 days prior to grain harvest (Trt #3), or at growth stage R1-R2 (Trt #6). All applications were made using ground equipment, in spray volumes of 5-30 gallons per acre (GPA), and included the use of a non-ionic surfactant (NIS) at 0.25% v/v.

Single control, and duplicate treated samples of the appropriate commodities were harvested from each test at the appropriate stage of maturity. For Trt #1, forage was harvested at 6-8 days after treatment (DAT), stover was harvested at 23-63 DAT, and grain was harvested at 26-63 DAT. For Trt #6, forage was harvested at 23-71 DAT, stover was harvested at 50-106 DAT, and grain was harvested at 55-106 DAT. For Trt #3, only samples of stover and grain were harvested at 5-22 and 5-12 DAT, respectively. Duplicate repeated samples of forage and/or stover were also collected from Trts #1, #3 and #6 from five field trials. For Trt #1, forage samples were collected repeatedly from 0-22 DAT, and stover samples were collected repeatedly from 23-84 DAT. For Trt #3, stover samples were collected repeatedly from 6-28 DAT. For Trt #6, forage samples were collected repeatedly from 0-68 DAT.

Samples were stored frozen for up to 12.2 months prior to analysis, and adequate storage stability data are available, indicating that tribenuron methyl is stable at -20°C for intervals of up to 21 months in wheat grain and straw, and up to 6 months in corn forage. These data will support the storage durations and conditions of samples from the corn field trials.

The liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) method used for determining residues of tribenuron methyl was adequately validated in conjunction with the analysis of the field trial samples. For this method, samples are hydrated (grain and stover only) with potassium phosphate buffer, and then extracted twice with acetonitrile (ACN)/K_2HPO_4 (3:1 v/v, pH 7) followed by centrifugation. Residues were then cleaned up by solvent partitioning, and elution through a solid-phase extraction (SPE) cartridge. Residues were determined by LC/MS/MS using external standards for quantitation. The method's limit of quantitation (LOQ) is 0.010 ppm, and the limit of detection (LOD) is 0.003 ppm in each corn commodity.

Following a single broadcast foliar application at 0.03 lb ai/A, applied approximately 7 days prior to normal forage harvest (Trt #1), tribenuron methuyl residues were <0.01-0.19 ppm in 48 samples of forage harvested at 6-8 DAT, <0.01-0.07 ppm in 48 samples of stover harvested at 23-63 DAT, and <LOD in all 48 samples of grain harvested at 26-63 DAT. Average residues were 0.03 ppm for forage, 0.02 ppm for stover, and <0.01 ppm for grain. The highest average field trial (HAFT) residues were 0.11 ppm for forage, 0.07 ppm for stover, and <0.01 ppm for grain.

When the single foliar application (0.03 lb ai/A) was applied at growth stage R1-R2 (Trt #6), residues were <0.01 ppm in all forage samples harvested at 23-71 DAT, <0.01-0.02 ppm in 48 samples of stover harvested at 50-106 DAT, and <LOD in all grain samples harvested at 55-106 DAT. Average residues were ≤0.01 ppm for forage, stover, and grain, while the HAFT residues were 0.02 ppm for stover, and <0.01 ppm for forage and grain.

When the single foliar application (0.03 lb ai/A) was applied approximately 7 days prior to normal grain maturity (Trt #3), residues were <LOD in all samples of grain harvested at 5-12 DAT, and <0.01-1.20 ppm in 48 samples of stover harvested at 5-22 DAT. Average residues were <0.01 ppm for grain, and 0.25 ppm for stover, while the HAFT residues were <0.01 ppm for grain, and 0.98 ppm for stover.

In the five residue decline trials, tribenuron methyl residues in forage (Trt #1 and #6) showed a rapid decline within the first 7 DAT, and then declined more slowly until residues were generally <0.05 ppm by 22 DAT. Changes in residue levels in stover (Trt #1 and #3) were more sporadic than in forage, but tribenuron methyl residues in stover generally declined or remained steady at longer post-treatment intervals.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the corn field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the US EPA Residue Chemistry Summary Document, D360846.

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 adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of acetolactate synthase (ALS). It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola commodities to 0.5 ppm in/on wheat hay (40CFR §180.451[a]). Tolerances have also been established at 0.05 ppm in/on field corn forage, grain and stover.

DuPont Crop Protection has submitted a petition supporting the use of tribenuron methyl on field corn that is genetically tolerant to sulfonylurea herbicides (PP#8F7441). This petition has been submitted in conjunction with related petitions for use of chlorimuron ethyl and rimsulfuron on genetically modified field corn in support of an end-use product (EP) containing all three sulfonylurea herbicides. The nomenclature and physicochemical properties of tribenuron methyl are presented in Tables A.1 and A.2 (below).

TABLE A.1. Tribenuron Methyl Nomenclature.

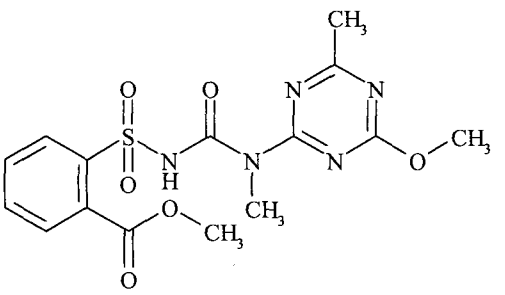
Chemical structure	

TABLE A.1. Tribenuron Methyl Nomenclature.

Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
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)	50% ai SG (Dupont Express herbicide; EPA Registration #352-632)

TABLE A.2. Physicochemical Properties of Tribenuron Methyl.

Parameter	Value		Reference
Melting point/range	142°C		MRID #47138301
pH (at 20°C)	4.64		
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3		
Water solubility (at 20°C)	pH 5	0.0489 g/L	
	pH 7	2.04	
	pH 9	18.3	
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7 x 10^{-7} mm Hg		
Dissociation constant (pK_a)	5.0		
Octanol/water partition coefficient, Log [K_{OW}] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Twenty-four field trials were conducted in the United States and Canada, in Zones 1, 2, 5 and 6 during 2006, using field corn that was genetically modified to be resistant to damage from glyphosate and sulfonylurea herbicides (see Tables B.1.1 and B.1.3, below). Each field trial

consisted of separate plots for up to six different treatments, combining two or more of the herbicides rimsulfuron, tribenuron methyl, chlorimuron ethyl, metsulfuron methyl, and glyphosate. For purposes of this report, only the information and data pertaining to tribenuron methyl are presented (see Table B.1.2, below).

Three of the six treatments included an application of tribenuron methyl (50% ai SG) in each trial. Tribenuron methyl was applied to three separate plots as a single broadcast foliar application at a rate of 0.03 lb ai/A, at either approximately 7 days prior to normal forage harvest (Trt#1), approximately 7 days prior to normal grain harvest (Trt#3), or at growth stage R1-R2 (Trt# 6). All applications were made using ground equipment, in spray volumes of 5-30 GPA, and included the use of an NIS at 0.25% v/v.

Detailed climatic data were provided. There were no reported weather phenomena which would negatively affect the validity of the field trials. The tests were conducted according to commercial agricultural practices, and information was provided on maintenance pesticides and fertilizers used at each site.

TABLE B.1.1 Trial Site Conditions.

Trial Identification (City, State, Year)	Soil Characteristics			
	Type	%OM	pH	CEC (meq/g)
Bumpass, VA; 2006 Trial 01	Sandy Clay Loam	1.8	5.5	3.9
Germansville, PA; 2006 Trial 02	Clay Loam	2.7	6.9	10.2
Quitman, GA; 2006 Trial 03	Loamy Sand	0.5	5.0	NR*
Sycamore, GA; 2006 Trial 04	Loamy Sand	0.88	6.1	NR
Richland, IA; 2006 Trial 05	Silty Clay Loam	3.5	6.8	NR
Richland, IA; 2006 Trial 06	Silty Clay Loam	4.7	6.6	14.4
Richland, IA; 2006 Trial 07	Silt Loam	4.3	6.9	NR
Kirksville, MO; 2006 Trial 08	Silty Clay Loam	3.26	5.6	31.9
Carlyle, IL; 2006 Trial 09	Silt Loam	1.4	6.7	NR
Edgewood, IL; 2006 Trial 10	Silt Loam	2.5	5.7	NR
Wyoming, IL; 2006 Trial 11	Silty Loam	3.4	6.7	NR
Brunswick, NE; 2006 Trial 12	Sandy Loam	2.1	6.6	NR
Polk, NE; 2006 Trial 13	Loam	2.1	6.7	NR

TABLE B.1.1 Trial Site Conditions.

Trial Identification (City, State, Year)	Soil Characteristics			
	Type	%OM	pH	CEC (meq/g)
York, NE; 2006 Trial 14	Silt Loam	2.9	6.3	NR
Paynesville, MN; 2006 Trial 15	Loam	4.3	6.7	24.53
Paynesville, MN; 2006 Trial 16	Loam	5.3	5.3	18.7
Paynesville, MN; 2006 Trial 17	Loam	4.3	6.7	24.53
Geneva, MN; 2006 Trial 18	Clay Loam	4.0	6.8	NR
Geneva, MN; 2006 Trial 19	Clay Loam	4.5	6.6	NR
Gardner, ND; 2006 Trial 20	Clay Loam	3.6	7.8	30.5
Branchton, ON, CAN; 2006 Trial 21	Silt Loam	1.27	6.8	19.4
Thorndale, ON, CAN; 2006 Trial 22	Sandy Loam	4.2	7.2	14.2
Weatherford, OK; 2006 Trial 23	Sandy Loam	0.83	7.6	NR
Hinton, OK; 2006 Trial 24	Sandy Loam	0.9	5.9	7.7

* NR = Not Reported.

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TABLE B.1.2 Study Use Pattern

Location (City, State; Year) Trial ID	EP	Application Information						Adjuvants
		Int.#	Method, Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI (Days)	Total Rate (lb ai/A)	
Bumpass, VA; 2006 Trial 01	50% ai SG	1	Broadcast foliar; 7 days prior to forage harvest	15	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; 7 days prior to grain harvest	15	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	15	0.03	--	0.03	
Germansville, PA; 2006 Trial 02	50% ai SG	1	Broadcast foliar; soft dough	30	0.03	--	0.03	X-77 0.25%
		3	Broadcast foliar; mature grain	30	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	30	0.03	--	0.03	
Quitman, GA; 2006 Trial 03	50% ai SG	1	Broadcast foliar; BBCH 85	15	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; BBCH 89	18	0.03	--	0.03	
		6	Broadcast foliar; BBCH 71	12	0.03	--	0.03	
Sycamore, GA; 2006 Trial 04	50% ai SG	1	Broadcast foliar; BBCH 83-85	15	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; BBCH 89	18	0.03	--	0.03	
		6	Broadcast foliar; BBCH 71	12	0.03	--	0.03	
Richland, IA; 2006 Trial 05	50% ai SG	1	Broadcast foliar; R4-R5	21	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	5	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	
Richland, IA; 2006 Trial 06	50% ai SG	1	Broadcast foliar; R4-R5	21	0.03	--	0.03	Dyne-Amic 0.25%
		3	Broadcast foliar; R6	19	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	
Richland, IA; 2006 Trial 07	50% ai SG	1	Broadcast foliar; R4-R5	21	0.03	--	0.03	Dyne-Amic 0.25%
		3	Broadcast foliar; R6	18	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	
Kirksville, MO; 2006 Trial 08	50% ai SG	1	Broadcast foliar; R4	16	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	16	0.03	--	0.03	
		6	Broadcast foliar; R1	17	0.03	--	0.03	

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TABLE B1.2 Study Use Pattern

Location (City, State; Year) Trial ID	EP	Application Information						Adjuvants
		Trt.[1]	Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI[2] (Days)	Total Rate (lb ai/A)	
Carlyle, IL; 2006 Trial 09	50% ai SG	1	Broadcast foliar; R1-R2	18	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	20	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	17	0.03	--	0.03	
Edgewood, IL; 2006 Trial 10	50% ai SG	1	Broadcast foliar; R4	15	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	17	0.03	--	0.03	
		6	Broadcast foliar; R1	17	0.03	--	0.03	
Wyoming, IL; 2006 Trial 11	50% ai SG	1	Broadcast foliar; R5	12	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	12	0.03	--	0.03	
		6	Broadcast foliar; R2	11	0.03	--	0.03	
Brunswick, NE; 2006 Trial 12	50% ai SG	1	Broadcast foliar; BBCH 87	20	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; BBCH 89	20	0.03	--	0.03	
		6	Broadcast foliar; BBCH 65	20	0.03	--	0.03	
Polk, NE; 2006 Trial 13	50% ai SG	1	Broadcast foliar; BBCH 87	20	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; BBCH 89	20	0.03	--	0.03	
		6	Broadcast foliar; BBCH 65	19	0.03	--	0.03	
York, NE; 2006 Trial 14	50% ai SG	1	Broadcast foliar; BBCH 87	20	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; BBCH 89	20	0.03	--	0.03	
		6	Broadcast foliar; BBCH 65	20	0.03	--	0.03	
Paynesville, MN; 2006 Trial 15	50% ai SG	1	Broadcast foliar; 7 days before black layer	16	0.03	--	0.03	Preference 0.25%
		3	Broadcast foliar; mature grain	16	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	
Paynesville, MN; 2006 Trial 16	50% ai SG	1	Broadcast foliar; 7 days before black layer	16	0.03	--	0.03	Preference 0.25%
		3	Broadcast foliar; mature grain	16	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	

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TABLE B.1.2. Study Use Pattern.

Location (City, State, Year) Trial ID	EP[1]	Application Information						Adjuvants[3]
		Trt #	Method; Timing	Volume (GPA)	Single Rate (lb ai/A)	RTI[2] (Days)	Total Rate (lb ai/A)	
Paynesville, MN; 2006 Trial 17	50% ai SG	1	Broadcast foliar; 7 days before black layer	16	0.03	--	0.03	Preference 0.25%
		3	Broadcast foliar; mature grain	16	0.03	--	0.03	
		6	Broadcast foliar; R1	16	0.03	--	0.03	
Geneva, MN; 2006 Trial 18	50% ai SG	1	Broadcast foliar; R5	17	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	17	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	17	0.03	--	0.03	
Geneva, MN; 2006 Trial 19	50% ai SG	1	Broadcast foliar; R5	17	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	17	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	17	0.03	--	0.03	
Gardner, ND; 2006 Trial 20	50% ai SG	1	Broadcast foliar; R3	20	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	20	0.03	--	0.03	
		6	Broadcast foliar; R1	15	0.03	--	0.03	
Branchton, ON, CAN; 2006 Trial 21	50% ai SG	1	Broadcast foliar; R5-R6	21	0.03	--	0.03	Agral 0.25%
		3	Broadcast foliar; R6	22	0.03	--	0.03	
		6	Broadcast foliar; R2	22	0.03	--	0.03	
Thorndale, ON, CAN; 2006 Trial 22	50% ai SG	1	Broadcast foliar; 7 days prior to forage harvest	15	0.03	--	0.03	Agral 0.25%
		3	Broadcast foliar; R6	15	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	15	0.03	--	0.03	
Weatherford, OK; 2006 Trial 23	50% ai SG	1	Broadcast foliar; milk/soft dough	15	0.03	--	0.03	Baron 0.25%
		3	Broadcast foliar; R6	22	0.03	--	0.03	
		6	Broadcast foliar; R1	20	0.03	--	0.03	
Hinton, OK; 2006 Trial 24	50% ai SG	1	Broadcast foliar; prior to MT	22	0.03	--	0.03	NIS 0.25%
		3	Broadcast foliar; R6	13	0.03	--	0.03	
		6	Broadcast foliar; R1-R2	15	0.03	--	0.03	

1. EP = End-use Product.
2. RTI = Re-Treatment Interval. Not pertinent to these studies, as only one application of tribenuron methyl was made to treated field corn plots.
3. Each application included an NIS at 0.25% v/v.

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TABLE B.1.3 Trial Numbers and Geographical Locations.

NAFTA Growing Zones*	Field Corn		
	Submitted	Requested	
		Canada	US
1	2	--	1
2	2	--	1
3	--	--	--
4	--	--	--
5	16	8	16
5B	2	4	--
6	2	--	2
7	--	--	--
8	--	--	--
9	--	--	--
10	--	--	--
11	--	--	--
12	--	--	--
13	--	--	--
Total	24	12	20

* The proposed use is only for the US.

B.2. Sample Handling and Preparation

Single control and duplicate treated samples of the appropriate commodities were harvested from each test at the appropriate stage of maturity. For Trt #1, forage was harvested at 6-8 DAT, stover was harvested at 23-63 DAT, and grain was harvested at 26-63 DAT. For Trt #6, forage was harvested at 23-71 DAT, stover was harvested at 50-106 DAT, and grain was harvested at 55-106 DAT. For Trt #3, only samples of stover and grain were harvested at 5-22 and 5-12 DAT, respectively.

Duplicate repeated samples of forage and/or stover were also collected from Trts #1, #3 and #6 in five of the field trials (Trials 2, 4, 14, 21 and 24). For Trt #1, forage samples were collected repeatedly from 0-22 DAT, and stover samples were collected repeatedly from 23-84 DAT. For Trt #3, stover samples were collected repeatedly from 6-28 DAT. For Trt #6, forage samples were collected repeatedly from 0-68 DAT.

Samples were frozen (temperature not reported) within 6.5 hours of harvest, and shipped frozen (via ACDS freezer truck) to the analytical laboratory, ABC Laboratories, in Columbia, MO. Upon arrival, samples were stored frozen (at -20°C) until preparation for analysis. The samples were homogenized with dry ice, and returned to frozen storage until extraction for analysis.

B.3. Analytical Methodology

Field corn samples were analyzed for tribenuron methyl using an LC/MS/MS method, DuPont-13412, Revision #1, *Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oil Crop Matrices Using SPE Purification and LC/MS/MS Detection.* This method has been proposed as a new tolerance enforcement method for residues of sulfonylureas, and an independent laboratory validation (ILV) trial for this method has been previously reviewed (D330813; S. Hummel; 8 August 2006).

For this method, grain and stover samples were initially hydrated with 20 mM potassium phosphate buffer. Residues were then extracted from each matrix twice with ACN/K_2HPO_4 (3:1 v/v, pH 7) followed by centrifugation. The combined extracts were partitioned against hexane, the remaining aqueous phase was concentrated, and then diluted with 0.01% acetic acid. Residues were then cleaned up using an ENV SPE cartridge eluted with 25 mM NaOH in methanol. The residues were concentrated, then diluted with 50 mM ammonium acetate/ACN (9:1 v/v), and analyzed via LC/MS/MS using external standards. Tribenuron methyl was detected and quantified using two ion transitions, m/z 396→155 and m/z 396→181. The LOQ in each corn commodity is 0.010 ppm, and the LOD is 0.003 ppm.

The above method was validated in conjunction with the analysis of the field trial samples, using control samples fortified with tribenuron methyl at 0.010-2.0 ppm in forage and fodder (whole plants), 0.010-3.0 ppm in stover, and 0.010-0.10 ppm in grain.

C. RESULTS AND DISCUSSION

The LC/MS/MS method used for determining residues of tribenuron methyl was adequately validated in conjunction with the analysis of the field trial samples. The average concurrent recoveries (±SD) were 77 ± 6% from immature forage, 85 ± 12% from forage, 79 ± 11% from stover, and 90 ± 10% from grain (Table C.1, below). In each matrix, the LOQ is 0.010 ppm, and the LOD is 0.003 ppm. Apparent residues of tribenuron methyl were non-detectable in all control samples. Adequate sample calculations, and example chromatograms were provided, and the fortification levels used for the method recoveries bracketed the measured residue levels.

Samples were stored frozen for up to 12.2 months prior to analysis (Table C.2, below). Adequate data are available indicating that tribenuron methyl is stable under frozen storage conditions for intervals of up to 6 months in corn forage, and up to 21 months in wheat grain and straw (D304059; R. Griffin; 24 June 2004, and D330633; S. Hummel; 8 August 2006). These data will support the storage conditions and durations of samples from the current corn field trials.

Following a single broadcast foliar application at 0.03 lb ai/A, applied approximately 7 days prior to normal forage harvest (Trt #1), tribenuron methuyl residues were <0.01-0.19 ppm

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in 48 samples of forage harvested at 6-8 DAT, <0.01-0.07 ppm in 48 samples of stover harvested at 23-63 DAT, and <LOD in all 48 samples of grain harvested at 26-63 DAT (Table C.3, below). Average residues were 0.03 ppm for forage, 0.02 ppm for stover, and <0.01 ppm for grain (Table C.4, below). The HAFT residues were 0.11 ppm for forage, 0.07 ppm for stover, and <0.01 ppm for grain.

When the single foliar application was applied at 0.03 lb ai/A, at growth stage R1-R2 (Trt #6), residues were <0.01 ppm in all forage samples harvested at 23-71 DAT, <0.01-0.02 ppm in 48 samples of stover harvested at 50-106 DAT, and <LOD in all grain samples harvested at 55-106 DAT. Average residues were ≤0.01 ppm for forage, stover, and grain, while the HAFT residues were 0.02 ppm for stover, and <0.01 ppm for forage and grain.

When the single foliar application was applied at 0.03 lb ai/A, approximately 7 days prior to normal grain maturity (Trt #3), residues were <LOD in all samples of grain harvested at 5-12 DAT, and <0.01-1.20 ppm in 48 samples of stover harvested at 5-22 DAT. Average residues were <0.01 ppm for grain, and 0.25 ppm for stover, while the HAFT residues were <0.01 ppm for grain, and 0.98 ppm for stover.

In the five residue decline trials, tribenuron methyl residues in forage from both Trts #1 and #6 showed a rapid decline in residues within the first 7 DAT. Thereafter, residues in forage declined more slowly, and were ≤0.05 ppm within 22 days of treatment (Figures C.1 and C.4, below). Changes in residues levels in stover from Trts #1 and #3 were more sporadic than for forage, but residues in stover generally declined or remained steady at longer post-treatment intervals (Figures C.2 and C.3, below).

Common cultural practices were used to maintain field corn crops, and the weather conditions, maintenance chemicals, and fertilizers used in the study did not have a notable impact on the residue data.

TABLE C.1 Summary of Concurrent Recoveries of Tribenuron Methyl from Fortified Field Corn Samples.

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Immature Forage	0.010	5	86, 83, 72, 83, 76	80 ± 6
	0.10	7	66, 74, 82, 73, 81, 73, 75	75 ± 5
	2.0	1	72	72
	Total	**13**	**66-86**	**77 ± 6**
Forage	0.010	16	82, 78, 84, 99, 88, 86, 90, 91, 82, 95, 125, 101, 81, 94, 97, 78	91 ± 12
	0.10	21	69, 69, 78, 74, 90, 84, 78, 79, 87, 82, 84, 84, 83, 78, 110, 61, 65, 95, 82, 70, 75	80 ± 11
	2.0	1	98	98
	Total	**38**	**61-125**	**85 ± 12**

TABLE C.1 Summary of Concurrent Recoveries of Tribenuron Methyl from Fortified Field Corn Samples

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Stover	0.010	25	84, 87, 75, 72, 80, 88, 80, 86, 94, 81, 88, 101, 90, 111, 58, 84, 71, 74, 88, 73, 60, 69, 79, 74, 97	82 ± 12
	0.10	30	73, 78, 80, 74, 73, 79, 73, 84, 78, 87, 77, 75, 76, 84, 92, 69, 68, 70, 81, 71, 77, 80, 65, 83, 77, 60, 66, 74, 90, 86	77 ± 7
	3.0	2	73, 109	91
	Total	**57**	**58-111**	**79 ± 11**
Grain	0.010	16	94, 97, 83, 112, 86, 90, 92, 78, 99, 93, 84, 100, 80, 88, 81, 115	92 ± 11
	0.10	18	80, 81, 92, 83, 83, 81, 80, 75, 85, 93, 94, 85, 87, 90, 109, 94, 75, 95	87 ± 8
	Total	**34**	**75-115**	**89 ± 10**

TABLE C.2 Summary of Storage Conditions

Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)[1]	Interval of Demonstrated Storage Stability (Months)[2]
Fodder	-20	12.2	[Wheat grain and straw] 21 [Corn forage] 6
Forage		10.9	
Stover		10.5	
Grain		11.3	

1. Interval from harvest to analysis.
2. From D304059; R. Griffin; 24 June 2004, and D330633; S. Hummel; 8 August 2006.

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

Trial ID (City, State, Year)	Zone	Variety	Trt #	Total Rate (lb ai/A)	Commodity	PHI[2] (Days)	Residues (ppm)[3]	
Bumpass, VA; 2006 Trial 01	1	DP 098140-6	1	0.03	Forage	7	0.028	0.047
					Stover	36	ND[4]	ND
					Grain	21	ND	ND
			3	0.03	Stover	22	*0.003*	ND
					Grain	7	ND	ND
			6	0.03	Forage	35	*0.009*	0.010
					Stover	64	ND	ND
					Grain	49	ND	ND

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

Trial ID (City, State; Year)	Zone	Variety	Trt #	Total Rate (lbai/A)	Commodity	PHI (Days)	Residues (ppm)	
Germansville, PA; 2006 Trial 02	1	DP 098140-6	1	0.03	Forage	-0	ND	ND
						0	0.12	0.12
						1	0.052	0.063
						3	0.041	0.052
						7	0.016	0.024
						14	*0.007*	0.010
						21	*0.005*	*0.006*
					Stover	38	*0.004*	*0.007*
						39	*0.005*	*0.003*
						42	*0.003*	ND
						45	*0.003*	ND
						52	*0.003*	*0.004*
						59	ND	ND
					Grain	38	ND	ND
			3	0.03	Stover	7	0.15	0.25
						8	0.16	0.16
						11	0.10	0.11
						14	0.059	0.080
						21	0.049	0.040
						28	0.053	0.047
					Grain	7	ND	ND
			6	0.03	Forage	-0	ND	ND
						0	0.24	0.23
						1	0.13	0.14
						3	0.018	0.012
						7	*0.007*	0.010
						14	ND	ND
						21	ND	ND
						39	ND	ND
					Stover	70	ND	ND
					Grain	70	ND	ND
Quitman, GA; 2006 Trial 03	2	DP 098140-6	1	0.03	Forage	7	0.023	0.014
					Stover	41	0.018	0.018
					Grain	41	ND	ND
			3	0.03	Stover	7	0.083	0.070
					Grain	7	ND	ND
			6	0.03	Forage	28	ND	ND
					Stover	62	ND	ND
					Grain	62	ND	ND

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TABLE C.3 Residue Data From Corn Field Trials with Tribenuron Methyl

Trial ID (City, State, Year)	Zone	Variety	Trt#	Total Rate (lb ai/A)	Commodity	PHI (Days)	Residues (ppm)	
Sycamore, GA; 2006 Trial 04	2		1	0.03	Forage	-0	ND	ND
						0	0.19	0.24
						1	0.21	0.11
						3	0.060	0.068
						7	0.021	0.039
						14	0.018	0.023
						21	0.016	0.022
					Stover	44	0.048	0.053
						45	0.22	0.33
						47	0.022	0.031
						51	0.026	0.017
						58	0.025	0.024
						65	0.027	0.031
					Grain	44	ND	ND
			3	0.03	Stover	7	0.30	0.30
						8	0.48	0.61
						10	0.12	0.12
						14	0.23	0.21
						21	0.082	0.12
						28	0.092	0.043
					Grain	7	ND	ND
			6	0.03	Forage	-0	ND	ND
						0	0.13	0.12
						1	0.085	0.078
						3	0.074	0.050
						7	0.029	0.023
						14	*0.009*	*0.006*
						21	*0.005*	*0.005*
						27	*0.003*	ND
					Stover	64	*0.004*	*0.003*
					Grain	64	ND	ND
Richland, IA; 2006 Trial 05	5	DP 098140-6	1	0.03	Forage	6	0.013	*0.009*
					Stover	53	ND	ND
					Grain	53	ND	ND
			3	0.03	Stover	7	0.067	0.087
					Grain	7	ND	ND
			6	0.03	Forage	36	ND	ND
					Stover	83	ND	ND
					Grain	83	ND	ND

TABLE C.5 Residue Data from Corn Field Trials with Tribenuron Methyl

Trial ID (City, State, Year)	Zone	Variety	Trt #	Total Rate (lb ai/A)	Commodity	PHI (Days)	Residues (ppm)	
Richland, IA; 2006 Trial 06	5	DP 098140-6	1	0.03	Forage	7	0.011	0.012
					Stover	41	*0.003*	*0.003*
					Grain	41	ND	ND
			3	0.03	Stover	7	0.15	0.13
					Grain	7	ND	ND
			6	0.03	Forage	37	ND	ND
					Stover	71	ND	ND
					Grain	71	ND	ND
Richland, IA;2006 Trial 07	5	DP 098140-6	1	0.03	Forage	6	*0.007*	*0.006*
					Stover	54	ND	ND
					Grain	54	ND	ND
			3	0.03	Stover	6	0.087	0.10
					Grain	6	ND	ND
			6	0.03	Forage	36	ND	ND
					Stover	84	ND	ND
					Grain	84	ND	ND
Kirksville, MO; 2006 Trial 08	5	DP 098140-6	1	0.03	Forage	8	*0.005*	*0.005*
					Stover	44	*0.003*	*0.003*
					Grain	44	ND	ND
			3	0.03	Stover	7	0.29	0.29
					Grain	7	ND	ND
			6	0.03	Forage	31	ND	ND
					Stover	67	ND	ND
					Grain	67	ND	ND
Carlyle, IL; 2006 Trial 09	5	DP 098140-6	1	0.03	Forage	7	0.063	0.067
					Stover	63	ND	ND
					Grain	63	ND	ND
			3	0.03	Stover	5	0.41	0.34
					Grain	5	ND	ND
			6	0.03	Forage	23	*0.005*	ND
					Stover	79	0.015	0.016
					Grain	79	ND	ND
Edgewood, IL; 2006 Trial 10	5	DP 098140-6	1	0.03	Forage	7	0.028	0.026
					Stover	63	ND	ND
					Grain	63	ND	ND
			3	0.03	Stover	7	0.094	0.10
					Grain	7	ND	ND
			6	0.03	Forage	29	ND	ND
					Stover	85	ND	ND
					Grain	85	ND	ND

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TABLE C.3.7 Residue Data from Corn Field Trials with Tribenuron Methyl

Trial ID (City, State; Year)	Zone	Variety	Trt#	Total Rate (lb ai/A)	Commodity	PHI[2] (Days)	Residues (ppm)[3]	
Wyoming, IL; 2006 Trial 11	5	DP 098140-6	1	0.03	Forage	7	0.041	0.044
					Stover	40	0.010	0.010
					Grain	40	ND	ND
			3	0.03	Stover	7	0.31	0.26
					Grain	7	ND	ND
			6	0.03	Forage	59	ND	ND
					Stover	92	*0.006*	ND
					Grain	92	ND	ND
Brunswick, NE; 2006 Trial 12	5	DP 098140-6	1	0.03	Forage	7	0.019	0.013
					Stover	57	*0.006*	*0.004*
					Grain	57	ND	ND
			3	0.03	Stover	7	0.40	0.42
					Grain	7	ND	ND
			6	0.03	Forage	31	ND	ND
					Stover	88	ND	ND
					Grain	88	ND	ND
Polk, NE; 2006 Trial 13	5	DP 098140-6	1	0.03	Forage	7	0.039	0.032
					Stover	54	*0.005*	*0.003*
					Grain	54	ND	ND
			3	0.03	Stover	6	0.85	1.1
					Grain	6	ND	ND
			6	0.03	Forage	28	ND	ND
					Stover	82	*0.004*	*0.004*
					Grain	82	ND	ND

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

Trial ID (City, State, Year)	Zone	Variety	Trt #	Total Rate (lbai/A)	Commodity	PHI (Days)	Residues (ppm)	
York, NE; 2006 Trial 14	5	DP 098140-6	1	0.03	Forage	-0	ND	ND
						0	0.26	0.24
						1	0.13	0.14
						3	0.071	0.068
						7	0.021	0.021
						15	ND	ND
						21	ND	ND
					Stover	63	*0.006*	0.040
						64	*0.007*	*0.005*
						66	*0.006*	*0.004*
						70	0.008	0.068
						77	0.020	0.021
						84	0.014	0.011
					Grain	63	ND	ND
			3	0.03	Stover	7	0.49	1.2
						8	1.1	0.85
						10	1.1	0.92
						14	0.61	0.51
						21	0.89	0.92
						28	0.96	0.68
					Grain	7	ND	ND
			6	0.03	Forage	-0	ND	ND
						0	0.35	0.44
						1	0.011	0.018
						3	0.012	0.011
						7	ND	ND
						14	ND	ND
						21	ND	ND
						28	ND	ND
					Stover	91	ND	ND
					Grain	91	ND	ND
Paynesville, MN; 2006 Trial 15	5	DP 098140-6	1	0.03	Forage	7	*0.005*	*0.003*
					Stover	49	ND	ND
					Grain	49	ND	ND
			3	0.03	Stover	7	*0.005*	*0.006*
					Grain	7	ND	ND
			6	0.03	Forage	45	*0.004*	*0.003*
					Stover	87	ND	ND
					Grain	87	ND	ND

TABLE C.8.2 Residue Data from Corn Field Trials with Tribenuron Methyl

Trial ID (City, State, Year)	Zone	Variety	DAT #	Total Rate (lb ai/A)	Commodity	PHI (Days)	Residues (ppm)	
Paynesville, MN; 2006 Trial 16	5	DP 098140-6	1	0.03	Forage	7	*0.005*	*0.004*
					Stover	49	ND	ND
					Grain	49	ND	ND
			3	0.03	Stover	7	*0.003*	*0.003*
					Grain	7	ND	ND
			6	0.03	Forage	45	*0.005*	*0.006*
					Stover	87	ND	ND
					Grain	87	ND	ND
Paynesville, MN; 2006 Trial 17	5	DP 098140-6	1	0.03	Forage	7	*0.003*	*0.007*
					Stover	49	ND	ND
					Grain	49	ND	ND
			3	0.03	Stover	7	ND	ND
					Grain	7	ND	ND
			6	0.03	Forage	45	*0.004*	*0.008*
					Stover	87	ND	ND
					Grain	87	ND	ND
Geneva, MN; 2006 Trial 18	5	DP 098140-6	1	0.03	Forage	7	0.012	0.012
					Stover	40	*0.009*	*0.005*
					Grain	40	ND	ND
			3	0.03	Stover	6	0.60	0.69
					Grain	6	ND	ND
			6	0.03	Forage	47	ND	ND
					Stover	87	*0.003*	*0.003*
					Grain	87	ND	ND
Geneva, MN; 2006 Trial 19	5	DP 098140-6	1	0.03	Forage	7	ND	*0.006*
					Stover	47	*0.003*	*0.004*
					Grain	47	ND	ND
			3	0.03	Stover	6	0.42	0.43
					Grain	6	ND	ND
			6	0.03	Forage	40	ND	ND
					Stover	87	ND	ND
					Grain	87	ND	ND
Gardner, ND; 2006 Trial 20	5	DP 098140-6	1	0.03	Forage	7	0.013	0.014
					Stover	26	*0.005*	*0.008*
					Grain	26	ND	ND
			3	0.03	Stover	7	0.21	0.19
					Grain	7	ND	ND
			6	0.03	Forage	40	ND	ND
					Stover	59	ND	ND
					Grain	59	ND	ND

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

Trial ID (City, State, Year)	Zone	Variety	Lot #	Total Rate (lbai/A)	Commodity	PHI (Days)	Residues (ppm)	
Branchton, ON, CAN; 2006 Trial 21	5	DP 098140-6	1	0.03	Forage	-0	ND	ND
						0	0.25	0.38
						1	0.30	0.23
						3	0.21	0.18
						7	0.12	0.10
						15	0.084	0.068
						22	0.048	0.043
					Stover	34	0.074	0.061
						35	0.095	0.081
						38	0.12	0.078
						41	0.094	0.083
						49	0.047	0.033
					Grain	34	ND	ND
			3	0.03	Stover	6	0.058	0.11
						7	0.068	0.070
						10	0.064	0.10
						13	0.069	0.076
						21	0.028	0.024
					Grain	6	ND	ND
			6	0.03	Forage	-0	ND	ND
						0	0.31	0.26
						2	0.31	0.24
						3	0.013	0.011
						7	ND	ND
						14	ND	ND
						21	ND	ND
						68	ND	ND
					Stover	95	ND	ND
					Grain	95	ND	ND
Thorndale, ON, CAN; 2006 Trial 22	5	DP 098140-6	1	0.03	Forage	6	0.062	0.034
					Stover	41	0.018	0.015
					Grain	41	ND	ND
			3	0.03	Stover	7	0.32	0.32
					Grain	7	ND	ND
			6	0.03	Forage	71	ND	ND
					Stover	106	ND	ND
					Grain	106	ND	ND

TABLE C.3 Residue Data from Corn Field Trials with Tribenuron Methyl[1]

Trial ID (City, State, Year)	Zone	Variety[1]	Trt #	Total Rate (lb ai/A)	Commodity	PHI[2] (Days)	Residues (ppm)[3]	
Weatherford, OK; 2006 Trial 23	6	DP 098140-6	1	0.03	Forage	7	0.020	0.019
					Stover	43	*0.003*	ND
					Grain	43	ND	ND
			3	0.03	Stover	7	0.058	0.049
					Grain	7	ND	ND
			6	0.03	Forage	34	ND	ND
					Stover	70	ND	ND
Hinton, OK; 2006 Trial 24	6	DP 098140-6	1	0.03	Forage	-0	ND	ND
						0	0.42	0.39
						1	0.33	0.47
						3	0.28	0.22
						7	0.19	0.095
						14	0.092	0.10
					Stover	23	0.021	0.013
						24	0.011	0.012
						26	0.019	0.012
						30	*0.009*	0.010
						37	*0.005*	*0.006*
					Grain	28	ND	ND
			3	0.03	Stover	7	0.026	0.024
						8	0.026	0.017
						10	0.019	0.012
						14	0.016	0.012
						21	0.014	0.017
					Grain	12	ND	ND
			6	0.03	Forage	34	ND	*0.003*
					Stover	50	ND	ND
					Grain	55	ND	ND

1. Each field trial used the same sulfonylurea-tolerant variety of field corn.
2. PHI = Pre-Harvest Interval.
3. The LOQ and LOD were 0.010 and 0.003 ppm, respectively. Residue values <LOQ, but ≥LOD are listed in italics.
4. ND = Not Detected.

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Figure C.1. Residue Decline in Forage Following Trt #1.

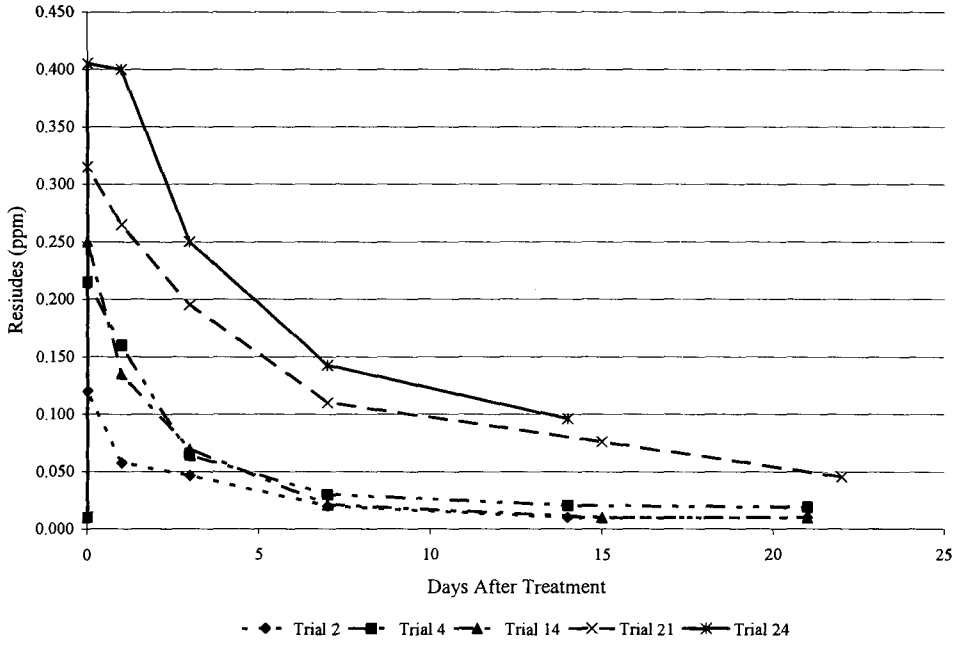

Figure C.2. Residue decline in Stover Following Trt #1.

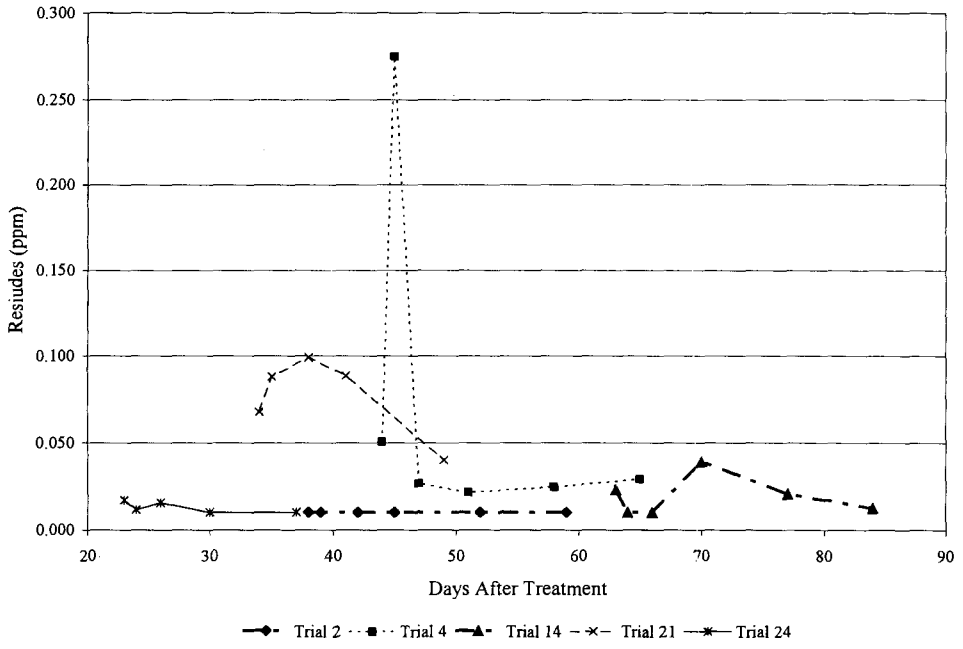

Figure C.3. Residue Decline in Stover Following Trt #3.

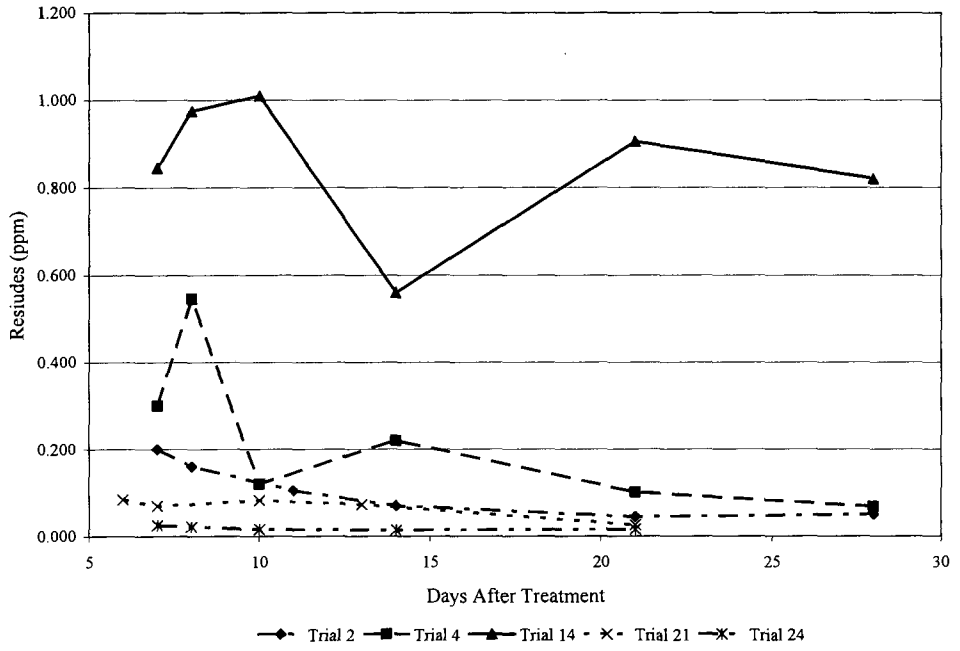

Figure C.4. Residue Decline in Forage Following Trt #6.

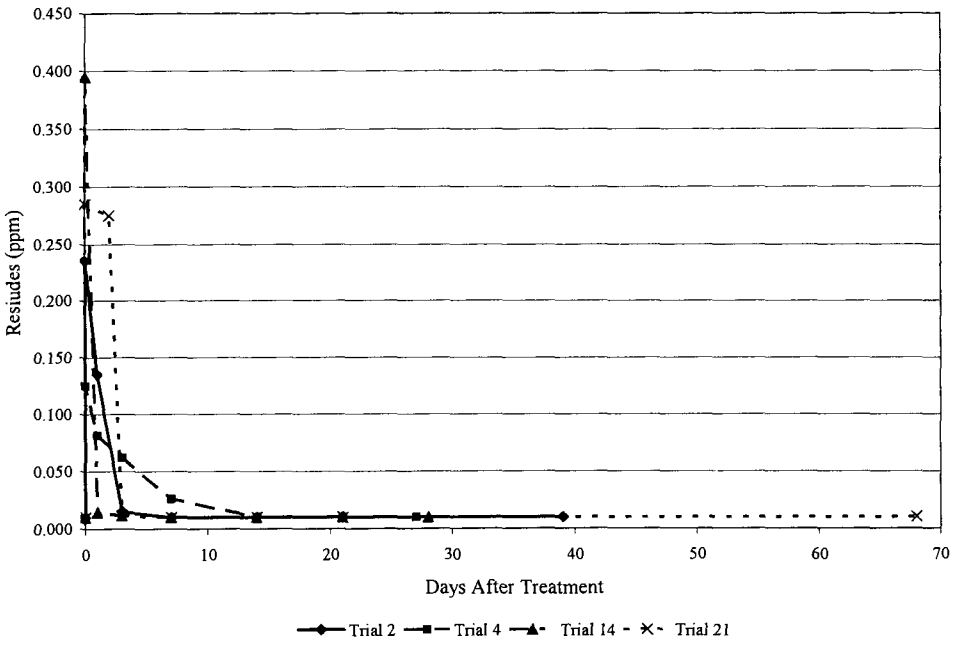

TABLE C.4 Summary of Residue Data from Field Corn Trials with Tribenuron Methyl

Commodity	Trt #	Total Rate (lb ai/A)	PHI (Days)	Residue Levels (ppm)						
				n	Min.	Max.	HAFT [2]	Median	Mean	Std. Dev.
Forage	1	0.03	6-8	48	<0.01	0.19	0.11	0.02	0.03	0.034
Stover			23-63	48	<0.01	0.07	0.07	0.01	0.02	0.014
Grain			26-63	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Stover	3	0.03	5-22	48	<0.01	1.20	0.98	0.15	0.25	0.272
Grain			5-12	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Forage	6	0.03	23-71	48	<0.01	<0.01	<0.01	<0.01	<0.01	0
Stover			50-106	48	<0.01	0.02	0.02	0.01	0.01	0.001
Grain			55-106	46	<0.01	<0.01	<0.01	<0.01	<0.01	0

1. The LOQ is 0.010 ppm for each commodity. For calculations which included residues >LOQ, the method LOQ (0.010 ppm) was used for residue values <LOQ.
2. HAFT = Highest Average Field Trial.

D. CONCLUSION

The field corn field trial data are adequate, and support the use of tribenuron methyl on sulfonylurea-tolerant field corn as single or split broadcast foliar applications, totaling up to 0.03 lb ai/A per season. The available residue data support a minimum PHI of 7 days for forage, grain and stover, along with use of an NIS as an adjuvant, at up to 0.25% of the spray volume.

E. REFERENCES

Tribenuron methyl. Residue Chemistry Considerations.; D304059; R. Griffin; 24 June 2004.

Thifensulfuron methyl. Addition of Uses on Rice and Sorghum (PRIA R19 – 352-611; PP#4F6889). Summary of Analytical Chemistry and Residue Data.; D330813; S. Hummel; 8 August 2006

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.; D330633; S. Hummel; 8 August 2006

F. DOCUMENT TRACKING

RDI: William T. Drew (16 June 2009); John Redden (9 September 2009)
Petition Number: 8F7441
DP Barcode: 360846
PC Code: 128887

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Tribenuron Methyl/352-632/PC Code 128887/E.I. du Pont de Nemours and Company/352
DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial/Residue Decline - Soybean (Forage, Hay, Seed)

Primary Evaluator — Date: 16 July 2009
William T. Drew,
Chemist, RD/RIMUERB/ARIA

Approved by — Date: 9 September 2009
John Redden,
Team Leader, RD/RIMUERB/ARIA

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). The DER has been reviewed by the Registration Division (RD) and the Health Effects Division (HED), and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

MRID #47548202. Emily Shepard (2007) *Magnitude and Decline of Sulfonylurea Residues in/on Forage, Hay and Seed of a Soybean Line Containing Event DP-356043 with the GAT and GM-HRA Genes, Following a Variety of Tank Mix Applications of Two Glyphosate Formulations and Rimsulfuron, Tribenuron Methyl, Chlorimuron Ethyl, and Metsulfuron Methyl Containing Herbicides at Proposed Maximum Label Rates - United States and Canadian Locations, Season 2006.* Laboratory Project Number: DuPont-20617. Unpublished study prepared by DuPont. 337 pages.

EXECUTIVE SUMMARY

DuPont Crop Protection has submitted field trial data supporting the use of tribenuron methyl on soybeans that are tolerant to sulfonylurea herbicides. Twenty-three field trials, each including two different treatment regimes, were conducted in Zones 2, 4 and 5 during 2006. At each trial, a water-soluble granule (SG) formulation of tribenuron methyl, containing 50% active ingredient (ai), was applied to soybeans as a single broadcast foliar application at the rate of 0.03 pound ai per acre (lb ai/A), at growth stage R1-R2 (Trt #2), or approximately 7 days prior to normal seed harvest (Trt #4). In one test (Trial 02), the tribenuron methyl (50% ai SG) was applied to both treatment regimes at 0.06 lb ai/A (2X rate). All applications were made using ground equipment, in spray volumes of 5-27 gallons per acre (GPA), and included the use of a non-ionic surfactant (NIS) at 0.25% v/v.

For Trt #2, single control and duplicate treated samples of forage and hay were harvested on the day of application, and seeds were harvested at normal maturity, 68-107 days after treatment (DAT). Repeated samples of forage and hay were also collected from three trials at 0, 1, 3, 7, 14 and 21 DAT to evaluate residue decline. For Trt #4, single control and duplicate treated samples of seeds were harvested at 5-8 DAT.

Samples were stored frozen for up to 9.2 months prior to analysis, and adequate storage stability data are available indicating that tribenuron methyl is stable at -20°C for intervals of up to 6 months in corn forage, 21 months in wheat grain and straw, and 9.6 months in soybean

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seeds. These data support the storage durations and conditions of samples from the soybean field trials.

The liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) method used for determining residues of tribenuron methyl on soybean commodities was adequately validated in conjunction with the analysis of the field trial samples. For this method, samples are hydrated (hay and seeds only) with potassium phosphate buffer, and then extracted twice with acetonitrile (ACN)/K_2HPO_4 (3:1 v/v, pH 7) followed by centrifugation. Residues were then cleaned up by solvent partitioning, and elution through a solid-phase extraction (SPE) cartridge. Residues were determined by LC/MS/MS using external standards for quantitation. The method limit of quantitation (LOQ) is 0.010 ppm, and the limit of detection (LOD) is 0.003 ppm in each soybean commodity.

Following a single broadcast foliar application at 0.03 lb ai/A, at growth stage R1-R2 (Trt #2), tribenuron methyl residues were 0.58-3.0 ppm in 36 samples of forage, and 0.61-8.80 ppm in 36 samples of hay harvested at 0 DAT, while residues were <0.01 ppm in all 44 samples of seeds harvested at 68-107 DAT. Average residues were 1.71 ppm for forage, 3.54 ppm for hay, and 0.01 ppm for seeds. The highest average field trial (HAFT) residues were 2.95 ppm for forage, 8.35 ppm for hay, and <0.01 ppm for seeds.

When the single foliar application was applied at 0.03 lb ai/A, approximately 7 days before normal crop maturity (Trt #4), residues were <0.01-0.07 ppm in 44 samples of seeds harvested at 5-8 DAT. Average residues in seeds were 0.01 ppm, and the HAFT residues were 0.07 ppm.

In both forage and hay, tribenuron methyl residues declined rapidly within the first week after application, and then declined more slowly thereafter. For all three decline tests, average residues in forage were 1.72 ppm at 0 DAT, 0.04 ppm by 7 DAT, and <0.01 ppm by 21 DAT. Average residues in hay were 3.83 ppm at 0 DAT, 0.05 ppm by 7 DAT, and <0.01 ppm by 21 DAT.

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 US EPA Residue Chemistry Summary Document, D360846.

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 adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of acetolactate synthase (ALS). It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola commodities to 0.5 ppm in/on wheat hay (40 CFR §180.451[a]). Tolerances have also been established at 0.05 ppm in/on soybean seeds, but there are no tolerances in soybean forage or hay.

DuPont has submitted a petition supporting the use of tribenuron methyl on soybeans that are genetically modified to be tolerant to sulfonylurea herbicides (PP#8F7432). This petition has been submitted in conjunction with related petitions for use of chlorimuron ethyl and rimsulfuron on genetically modified soybeans in support of an end-use product (EP) containing all three sulfonylurea herbicides. The nomenclature and physicochemical properties of tribenuron methyl are presented in Tables A.1 and A.2 (below).

TABLE A.1 Tribenuron Methyl Nomenclature

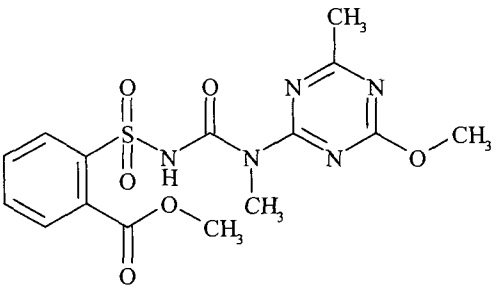
Chemical structure	
Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
Company experimental name	DPX-L5300
IUPAC name	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	50% ai SG (Dupont Express herbicide; EPA Registration #352-632)

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TABLE A.2. Physicochemical Properties of Tribenuron Methyl			
Parameter	Value		Reference
Melting point/range	142°C		MRID #47138301
pH (at 20°C)	4.64		
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3		
Water solubility (at 20°C)	pH 5	0.0489 g/L	
	pH 7	2.04	
	pH 9	18.3	
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7 x 10^{-7} mm Hg		
Dissociation constant (pK$_a$)	5.0		
Octanol/water partition coefficient, Log [K$_{OW}$] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Twenty-three field trials were conducted in the United States and Canada in Zones 2, 4 and 5 during 2006 using a soybean variety (Event DP-356043-5) that is genetically modified to be resistant to damage from glyphosate and sulfonylurea herbicides (Tables B.1.1 and B.1.3, below). Each field trial consisted of separate plots for up to five different treatments combining two or more of the herbicides rimsulfuron, tribenuron methyl, chlorimuron ethyl, metsulfuron methyl, and glyphosate. For purposes of this report, only the information and data pertaining to tribenuron methyl are presented (Table B.1.2, below).

Two of the five treatments in each trial included an application of tribenuron methyl (50% ai SG). Tribenuron methyl was applied to two separate plots as a single broadcast foliar application at a rate of 0.03 lb ai/A, at either flowering (R1-R2 stage; Trt #2), or at approximately 7 days prior to normal seed harvest (Trt #4). However, in Trial 02, the application rate for tribenuron methyl was 0.06 lb ai/A for both treatments. All applications

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were made using ground equipment, in spray volumes of 5-27 GPA, and included the use of an NIS at 0.25% v/v.

The tests were conducted according to commercial agricultural practices, and information was provided on maintenance pesticides and fertilizers used at each site. Detailed climactic data were also provided, and with the exception of one trial (Trial 02), there were no unusual climatic conditions that adversely impacted the field trial data. At Trial 02, a hurricane produced excessive winds and rainfall during the R5 growth stage, resulting in poor seed yield. Therefore, the residue data on seeds from this site were excluded from the dataset.

TABLE B.1.1. Trial Site Conditions.

Trial Identification (City, State, Year)	Soil Characteristics			
	Type	%OM	pH	CEC (meq/g)
Sycamore, GA 2006 Trial 01	Loamy sand	0.88	6.1	2.4
Bumpass, VA 2006 Trial 02	Sandy clay loam	1.8	5.5	3.9
Baptistown, NJ 2006 Trial 03	Loam	2.3	6.7	9.1
Cheneyville, LA 2006 Trial 04	Sandy clay loam	0.8	8.1	14.3
Washington, LA 2006 Trial 05	Silty loam	2.3	5.2	NR*
Washington, LA 2006 Trial 06	Silty loam	2.3	5.2	NR
Newport, AR 2006 Trial 07	Sandy loam	1.5	6.5	4.4
Newport, AR 2006 Trial 08	Silty clay loam	2.8	5.5	14.1
Carlyle, IL 2006 Trial 09	Silt loam	1.5	6.9	NR
Carlyle, IL 2006 Trial 10	Silt loam	1.5	6.9	NR
Richland, IA 2006 Trial 11	Silt loam	3.68	6.2	22.5
Richland, IA 2006 Trial 12	Silt loam	NR	6.6	14.2
Paynesville, MN 2006 Trial 13	Loam	5.3	5.3	18.7
Paynesville, MN 2006 Trial 14	Sandy loam	3.2	6.2	19.6
York, NE 2006 Trial 16	Silt loam	2.9	6.3	NR
Polk, NE 2006 Trial 17	Loam	2.1	6.7	NR
Gardner, ND 2006 Trial 18	Clay loam	3.6	7.8	30.5

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TABLE B5.1 Trial Site Conditions

Trial Identification (City, State, Year)	Soil Characteristics			
	Type	%OM	pH	CEC (meq/g)
Rochelle, IL 2006 Trial 19	Silty clay loam	4.2	7.7	40.4
Ellendale, MN 2006 Trial 20	Clay loam	4.0	6.8	NR
Geneva, MN 2006 Trial 21	Clay loam	4.5	6.6	NR
Branchton, ON, Canada 2006 Trial 22	NR	NR	NR	NR
Springford, ON, Canada 2006 Trial 23	NR	NR	NR	NR
Thorndale, ON, Canada 2006 Trial 24	Silt loam	4.2	7.2	14.2

* NR = Not Reported.

TABLE B.1.2 Study Use Pattern

Location (City, State; Year) Trial ID[1]	EP[2]	Application Information						Adjuvants[4]
		Trt.#	Method; Timing	Volume (GPA)	Rate (lbai/A)	RTI[3] (Days)	Total Rate (lbai/A)	
Sycamore, GA;2006 Trial 01	50% ai SG	2	Broadcast foliar; BBCH 64-65	20	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; BBCH 87-89	24	0.03	--	0.03	
Bumpass, VA;2006 Trial 02	50% ai SG	2	Broadcast foliar; R1-R2	15	0.06[5]	--	0.06	NIS 0.25%
		4	Broadcast foliar; R8	15	0.06[5]	--	0.06	
Baptistown, NJ;2006 Trial 03	50% ai SG	2	Broadcast foliar; late bloom	27	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	27	0.03	--	0.03	
Cheneyville, LA;2006 Trial 04	50% ai SG	2	Broadcast foliar; mid-flower	18	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	18	0.03	--	0.03	
Washington, LA;2006 Trial 05	50% ai SG	2	Broadcast foliar; early flower	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R7	16	0.03	--	0.03	
Washington, LA;2006 Trial 06	50% ai SG	2	Broadcast foliar; early flower	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R7	16	0.03	--	0.03	
Newport, AR;2006 Trial 07	50% ai SG	2	Broadcast foliar; V5 and V9-10	20	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	20	0.03	--	0.03	
Newport, AR;2006 Trial 08	50% ai SG	2	Broadcast foliar at V11-12	20	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	20	0.03	--	0.03	
Carlyle, IL;2006 Trial 09	50% ai SG	2	Broadcast foliar; R1	18	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	25	0.03	--	0.03	
Carlyle, IL;2006 Trial 10	50% ai SG	2	Broadcast foliar; R1	18	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	25	0.03	--	0.03	
Richland, IA;2006 Trial 11	50% ai SG	2	Broadcast foliar; R2	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	19	0.03	--	0.03	
Richland, IA;2006 Trial 12	50% ai SG	2	Broadcast foliar; R1-R2	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	19	0.03	--	0.03	
Paynesville, MN;2006 Trial 13	50% ai SG	2	Broadcast foliar; flowering	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; mature	16	0.03	--	0.03	

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TABLE B.1.2 Study Use Pattern

Location[1] (City, State; Year) Trial ID	EP[2]	Application Information						Adjuvants[4]
		Trt #	Method; Timing	Volume (GPA)	Rate (lb ai/A)	RTI[3] (Days)	Total Rate (lb ai/A)	
Paynesville, MN; 2006 Trial 14	50% ai SG	2	Broadcast foliar; flowering	16	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; mature	16	0.03	--	0.03	
York, NE;2006 Trial 16	50% ai SG	2	Broadcast foliar; BBCH 63-65	15	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; BBCH 89	15	0.03	--	0.03	
Polk, NE; 2006 Trial 17	50% ai SG	2	Broadcast foliar; flowering	15	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; BBCH 89	15	0.03	--	0.03	
Gardner, ND;2006 Trial 18	50% ai SG	2	Broadcast foliar; BBCH 65	15	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; BBCH 87	20	0.03	--	0.03	
Rochelle, IL;2006 Trial 19	50% ai SG	2	Broadcast foliar; BBCH 65	5	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; BBCH 96	15	0.03	--	0.03	
Ellendale, MN; 2006 Trial 20	50% ai SG	2	Broadcast foliar; R1-R2	17	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	18	0.03	--	0.03	
Geneva, MN; 2006 Trial 21	50% ai SG	2	Broadcast foliar; R1-R2	17	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	18	0.03	--	0.03	
Branchton, ON, Canada; 2006 Trial 22	50% ai SG	2	Broadcast foliar; R1-R2	21	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	21	0.03	--	0.03	
Springford, ON, Canada; 2006 Trial 23	50% ai SG	2	Broadcast foliar; R1-R2	21	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; R8	21	0.03	--	0.03	
Thorndale, ON, Canada; 2006 Trial 24	50% ai SG	2	Broadcast foliar; flowering	15	0.03	--	0.03	NIS 0.25%
		4	Broadcast foliar; 7 days before harvest	15	0.03	--	0.03	

1. An additional trial (Trial 15) was conducted in Northwood, ND, but failed due to an application error. The plot was replanted, but failed to produce seeds.
2. EP = End-use Product.
3. RTI = Re-Treatment Interval. Not pertinent to these studies, as only one application of tribenuron methyl was made to treated soybean plots.
4. Each application included an NIS at 0.25% (v/v).
5. Tribenuron methyl was applied at 2X the target rate in both treatments at Trial 02.

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TABLE B.1.3 Trial Numbers and Geographical Locations

NAFTA Growing Zones	Soybean		
	Trials Submitted	Trials Required	
		Canada	US
1	--	--	--
2	3	--	2
3	--	--	--
4	5	--	3
5	12	11	15
5B	3	1	--
6	--	--	--
7	--	--	--
8	--	--	--
9	--	--	--
10	--	--	--
11	--	--	--
12	--	--	--
13	--	--	--
Total	23	12	20

B.2. Sample Handling and Preparation

With a few exceptions, single control and duplicate treated samples of hay and forage were harvested from Trt #2 at 0 DAT, and seed samples were harvested at normal crop maturity (68-107 DAT). In Trials 5 and 6, the forage and hay samples were collected prior to application, and in Trials 20 and 21, the forage and hay samples were collected at 7 DAT. Therefore, the residue data from these samples were not included in the datasets for forage and hay. For Trt #4, single control and duplicate treated samples of seeds were collected at normal crop maturity (5-8 DAT).

To evaluate residue decline, duplicate samples of forage and hay were also collected repeatedly from Trt #2 in three field trials (Trials 4, 9 and 16). From these tests, forage and hay samples were collected at 0, 1, 3, 7, 14 and 21 DAT.

Samples were frozen (temperature not reported) within 5 hours of harvest, and shipped frozen (via ACDS freezer truck) to the analytical laboratory, ABC Laboratories, in Columbia, MO. Upon arrival, samples were stored frozen (at -20°C) until preparation for analysis. The samples were homogenized with dry ice, and returned to frozen storage until extraction for analysis.

B.3. Analytical Methodology

Soybean samples were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont-13412, Revision #1, *Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and*

Chlorimuron Ethyl in Oil Crop Matrices Using SPE Purification and LC/MS/MS Detection. This method has been proposed as a new tolerance enforcement method for residues of sulfonylureas, and an independent laboratory validation (ILV) trial for this method has been previously reviewed (D330813; S. Hummel; 8 August 2006).

For this method, hay and seed samples were initially hydrated for 15 minutes with 20 mM potassium phosphate buffer. Residues were then extracted from each matrix twice with ACN/K_2HPO_4 (3:1 v/v, pH 7) followed by centrifugation. The combined extracts were partitioned against hexane, the remaining aqueous phase was concentrated, and then diluted with water. Residues were then cleaned up using an ENV SPE cartridge eluted with 25 mM NaOH in methanol. The residues were concentrated, then diluted with 50 mM ammonium acetate/ACN (9:1 v/v), and analyzed via LC/MS/MS using external standards. Tribenuron methyl was detected and quantified using the m/z 396→155 ion transition. The LOQ in each soybean commodity is 0.010 ppm, and the LOD is 0.003 ppm.

The above method was validated in conjunction with the analysis of the field trial samples, using control samples fortified with tribenuron methyl at 0.010-20 ppm in forage, 0.010-30 ppm in hay, and 0.010-0.40 ppm in seeds.

C. RESULTS AND DISCUSSION

The LC/MS/MS method used for determining residues of tribenuron methyl was adequately validated in conjunction with the analysis of the field trial samples. The average concurrent recoveries (±SD) were 90 ± 9% from forage, 85 ± 9% from hay, and 88 ± 8% from seeds (Table C.1, below). In each matrix, the LOQ is 0.010 ppm, and the LOD is 0.003 ppm. Apparent residues of tribenuron methyl were <LOQ in all control samples. Adequate sample calculations, and example chromatograms were provided, and the fortification levels used for the method recoveries bracketed the measured residue levels.

Samples were stored frozen for up to 9.2 months prior to analysis (Table C.2.1, below). Adequate data are available indicating that tribenuron methyl is stable under frozen storage conditions for intervals of up to 6 months in corn forage, and 21 months in wheat grain and straw (D304059; R. Griffin; 24 June 2004, and D330633; S. Hummel; 8 August 2006). In addition, a concurrent freezer storage stability study was conducted, using control samples of homogenized soybean seeds fortified with tribenuron methyl at 0.10 ppm. The fortified samples were stored under the same conditions (-20°C) as the field trial samples, and were analyzed immediately after fortification, as well as after 1, 3, 6, and 9.6 months of storage (Table C.2.2, below). There was no decline in residues in seeds during frozen storage, indicating that tribenuron methyl is stable in soybean seeds for intervals of up to 9.6 months. These data will support the storage conditions and durations of samples from the current soybean field trials.

Following a single broadcast foliar application at 0.03 lb ai/A, applied at growth stage R1-R2 (Trt #2), tribenuron methyl residues were 0.58-3.0 ppm in 36 samples of forage, 0.61-8.80 ppm in 36 samples of hay harvested at 0 DAT, and <0.01 ppm in all 44 samples of seeds

harvested at 68-107 DAT (Table C.3, below). Average residues were 1.71 ppm for forage, 3.54 ppm for hay, and <0.01 ppm for seeds (Table C.4, below). The HAFT residues were 2.95 ppm for forage, 8.35 ppm for hay, and <0.01 ppm for seeds.

When the single foliar application was applied at 0.03 lb ai/A, approximately 7 days before normal crop maturity (Trt #4), residues were <0.01-0.07 ppm in 44 samples of seeds harvested at 5-8 DAT. Average residues in seeds were 0.01 ppm, and the HAFT residues were 0.07 ppm.

In both forage and hay, tribenuron methyl residues declined rapidly within the first week after application, and then declined more slowly thereafter (Figures C.1 and C.2, below). For all three decline tests, average residues in forage were 1.72 ppm at 0 DAT, 0.04 ppm by 7 DAT, and <0.01 ppm by 21 DAT. Average residues in hay were 3.83 ppm at 0 DAT, 0.05 ppm by 7 DAT, and <0.01 ppm by 21 DAT.

Common cultural practices were used to maintain the soybean crops, and the maintenance chemicals and fertilizers used in the study did not have a notable impact on the residue data. With the exception of Trial 2, the weather conditions also did not have an adverse effect on the residue data.

TABLE C.1 Summary of Concurrent Recoveries of Tribenuron Methyl from Fortified Soybean Samples

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Forage	0.010	19	83, 92, 106, 95, 83, 84, 84, 95, 91, 98, 113, 107, 81, 89, 97, 83, 92, 91, 96	93 ± 9
	0.10	16	92, 82, 89, 90, 81, 81, 81, 87, 93, 79, 77, 85, 90, 78, 90, 102	86 ± 7
	5.0	2	77, 90	84
	20	1	99	99
	Total	**38**	**77-113**	**90 ± 9**
Hay	0.010	18	93, 90, 95, 80, 98, 96, 91, 106, 92, 101, 70, 87, 83, 102, 88, 82, 96, 72	90 ± 10
	0.10	17	82, 75, 78, 82, 75, 87, 83, 88, 76, 80, 68, 82, 72, 81, 83, 76, 82	79 ± 5
	5.0	1	88	88
	10	3	95, 83, 88	89 ± 6
	30	1	88	88
	Total	**40**	**68-106**	**85 ± 9**
Seeds	0.010	22	95, 87, 87, 95, 79, 111, 91, 85, 93, 81, 92, 87, 91, 94, 99, 86, 81, 88, 80, 88, 91, 84	89 ± 7
	0.10	36	90, 89, 87, 86, 96, 95, 81, 72, 94, 100, 86, 97, 99, 82, 81, 93, 91, 97, 97, 89, 86, 95, 96, 85, 73, 82, 74, 93, 82, 85, 81, 78, 78, 78, 91, 80	87 ± 8
	0.40	1	88	88
	Total	**59**	**72-111**	**88 ± 8**

TABLE C.2.1 Summary of Storage Conditions.

Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)[1]	Interval of Demonstrated Storage Stability (Months)[2]
Forage	-20	8.3	21
Hay		9.2	21
Seed		6.9	9.6

1. Interval from harvest to analysis.
2. From D304059; R. Griffin; 24 June 2004, and D330633; S. Hummel; 8 August 2006, and Table C.2.2 (below).

TABLE C.2.2 Stability of Tribenuron Methyl in Frozen Soybean Seeds.

Analyte	Spike Level (ppm)	Storage Interval (Months)	Freshly Fortified Recovery (%)	Stored Sample Residues (%)	Average Corrected Stored Recovery (%)
Tribenuron methyl	0.10	0	86, 89	--	100
		1	78, 86	77, 84	99
		3	104, 95	104, 96	100
		6	88, 88	90, 86	100
		9.6	84, 84	75, 77	90

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

Trial ID (City, State; Year)	Zone	Variety	Trt #	Total Rate (lb ai/A)	Commodity	PHI[3] (Days)	Residues (ppm)[3]	
Sycamore, GA; 2006 Trial 01	2	DP 356043-5	2	0.03	Forage	0	2.5	2.0
					Hay	0	3.5	3.6
					Seed	84	ND[4]	ND
			4	0.03	Seed	7	ND	*0.004*
Bumpass, VA; 2006[5] Trial 02	2	DP 356043-5	2	0.06[6]	Forage	0	ND	ND
					Hay	0	*0.003*	ND
Baptistown, NJ; 2006 Trial 03	1	DP 356043-5	2	0.03	Forage	0	1.4	1.2
					Hay	0	1.0	0.90
					Seed	84	ND	ND
			4	0.03	Seed	8	ND	ND

TABLE C3 Residue Data from Soybean Field Trials with Tribenuron Methyl

Trial ID (City, State, Year)	Zone	Variety	TRR #	Trial Rate (lb ai/A)	Commodity	PHI[4] (Days)	Residues (ppm)[5]	
Cheneyville, LA; 2006 Trial 04	4	DP 356043-5	2	0.03	Forage	-0	ND	ND
						0	2.0	1.3
						1	0.53	0.58
						3	0.65	0.25
						7	0.020	0.019
						14	*0.004*	*0.004*
						21	ND	ND
					Hay	-0	ND	ND
						0	2.4	2.3
						1	2.1	1.7
						3	1.6	0.34
						7	0.053	0.043
						14	0.030	*0.006*
						21	ND	ND
					Seed	68	ND	ND
			4	0.03	Seed	7	0.073	0.057
Washington, LA; 2006[7] Trial 05	4	DP 356043-5	2	0.03	Seed	69	ND	ND
			4	0.03	Seed	7	*0.005*	*0.005*
Washington, LA; 2006[7] Trial 06	4	DP 356043-5	2	0.03	Seed	69	ND	ND
			4	0.03	Seed	7	*0.004*	ND
Newport, AR; 2006 Trial 07	4	DP 356043-5	2	0.03	Forage	0	2.9	2.4
					Hay	0	8.8	7.9
					Seed	91	ND	ND
			4	0.03	Seed	7	ND	ND
Newport, AR; 2006 Trial 08	4	DP 356043-5	2	0.03	Forage	0	3.0	2.9
					Hay	0	8.2	7.9
					Seed	89	ND	ND
			4	0.03	Seed	7	ND	ND

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

Trial ID (City, State, Year)	Zone	Variety	Trt #	Total Rate (lb ai/A)	Commodity	PHI (Days)	Residues (ppm)	
Carlyle, IL; 2006 Trial 09	5	DP 356043-5	2	0.03	Forage	-0	ND	ND
						0	1.3	1.2
						1	0.89	0.92
						3	0.36	0.38
						7	0.058	0.064
						14	*0.009*	0.012
						21	ND	*0.003*
					Hay	-0	ND	ND
						0	1.8	1.4
						1	1.2	1.4
						3	0.27	0.24
						7	0.073	0.064
						14	0.020	0.022
						21	*0.006*	*0.003*
					Seed	77	ND	ND
			4	0.03	Seed	5	0.018	0.013
Carlyle, IL; 2006 Trial 10	5	DP 356043-5	2	0.03	Forage	0	1.7	2.0
					Hay	0	1.1	0.61
					Seed	77	ND	ND
			4	0.03	Seed	5	*0.003*	*0.004*
Richland, IA; 2006 Trial 11	5	DP 356043-5	2	0.03	Forage	0	1.0	0.95
					Hay	0	3.0	3.0
					Seed	90	ND	ND
			4	0.03	Seed	8	*0.003*	*0.003*
Richland, IA; 2006 Trial 12	5	DP 356043-5	2	0.03	Forage	0	1.4	1.3
					Hay	0	3.9	3.1
					Seed	95	ND	ND
			4	0.03	Seed	5	ND	ND
Paynesville, MN; 2006 Trial 13	5	DP 356043-5	2	0.03	Forage	0	0.58	0.80
					Hay	0	0.85	0.77
					Seed	107	ND	ND
			4	0.03	Seed	7	ND	ND
Paynesville, MN; 2006 Trial 14	5	DP 356043-5	2	0.03	Forage	0	0.64	1.4
					Hay	0	0.70	1.0
					Seed	105	ND	ND
			4	0.03	Seed	7	ND	ND

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

Trial ID (City, State, Year)	Zone	Variety [1]	Trt #	Total Rate (lb ai/A)	Commodity	PHI [2] (Days)	Residues (ppm) [3]	
York, NE; 2006 Trial 16	5	DP 356043-5	2	0.03	Forage	-0	ND	ND
						0	2.3	2.2
						1	0.22	0.21
						3	0.15	0.12
						7	0.034	0.034
						14	*0.003*	ND
						21	ND	ND
					Hay	-0	ND	ND
						0	7.5	7.6
						1	0.45	0.55
						3	0.40	0.40
						7	0.04	0.04
						14	*0.005*	*0.004*
						21	ND	ND
					Seed	85	ND	ND
			4	0.03	Seed	7	ND	ND
Polk, NE; 2006 Trial 17		DP 356043-5	2	0.03	Forage	0	2.2	2.1
					Hay	0	2.4	2.6
					Seed	84	ND	ND
			4	0.03	Seed	7	*0.005*	*0.005*
Gardner, ND; 2006 Trial 18	5	DP 356043-5	2	0.03	Forage	0	2.2	2.5
					Hay	0	2.9	2.6
					Seed	73	ND	ND
			4	0.03	Seed	8	*0.007*	*0.005*
Rochelle, IL; 2006 Trial 19	5	DP 356043-5	2	0.03	Forage	0	1.1	1.2
					Hay	0	3.0	2.5
					Seed	89	ND	ND
			4	0.03	Seed	7	*0.008*	0.01
Ellendale, MN; 2006 [8] Trial 20	5	DP 356043-5	2	0.03	Seed	104	ND	ND
			4	0.03	Seed	7	ND	ND
Geneva, MN; 2006 [8] Trial 21	5	DP 356043-5	2	0.03	Seed	104	ND	ND
			4	0.03	Seed	7	ND	ND
Branchton, ON, Canada; 2006 Trial 22	5	DP 356043-5	2	0.03	Forage	0	2.5	2.5
					Hay	0	5.4	6.2
					Seed	86	ND	ND
			4	0.03	Seed	5	ND	ND
Springford, ON, Canada; 2006 Trial 23	5	DP 356043-5	2	0.03	Forage	0	1.0	1.0
					Hay	0	2.0	2.5
					Seed	85	ND	ND
			4	0.03	Seed	5	*0.002*	*0.003*

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

Trial ID (City, State, Year)	Zone	Variety	Trt.[2]	Total Rate (lb ai/A)	Commodity	PHI[2] (Days)	Residues (ppm)[3]	
Thorndale, ON, Canada; 2006 Trial 24	5	DP 356043-5	2	0.03	Forage	0	1.3	1.5
					Hay	0	7.0	5.5
					Seed	106	ND	ND
			4	0.03	Seed	7	*0.005*	*0.006*

1. Each field trial used the same sulfonylurea-tolerant variety of soybeans.
2. PHI = Pre-Harvest Interval.
3. The LOQ and LOD were 0.010 and 0.003 ppm, respectively. Residue values <LOQ, but ≥LOD are listed in italics.
4. ND = Not Detectable.
5. Residue data for seeds were not reported for Trial 2, as hurricane-force winds, and excessive rain occurred at growth stage R5, reducing the crop yield.
6. The application rate in Trial 02 was 0.06 lb ai/A (2X rate); therefore, the forage and hay residue data were not included in the residue dataset.
7. Residue data for forage and hay samples from Trials 5 and 6 were not presented, as these samples were collected prior to application.
8. Residue data for forage and hay samples from Trials 20 and 21 were not presented, as the samples were collected at 7 DAT, rather than at the targeted 0 DAT.

Figure C.1. Residue Decline in Soybean Forage.

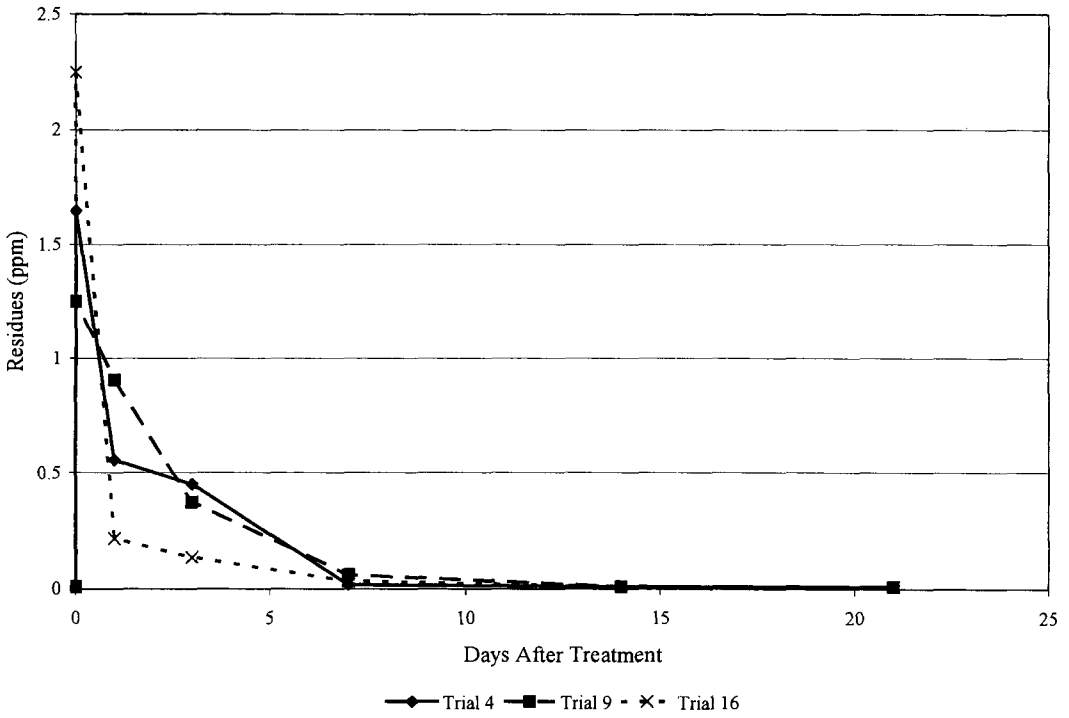

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Figure C.2. Residue Decline in Soybean Hay.

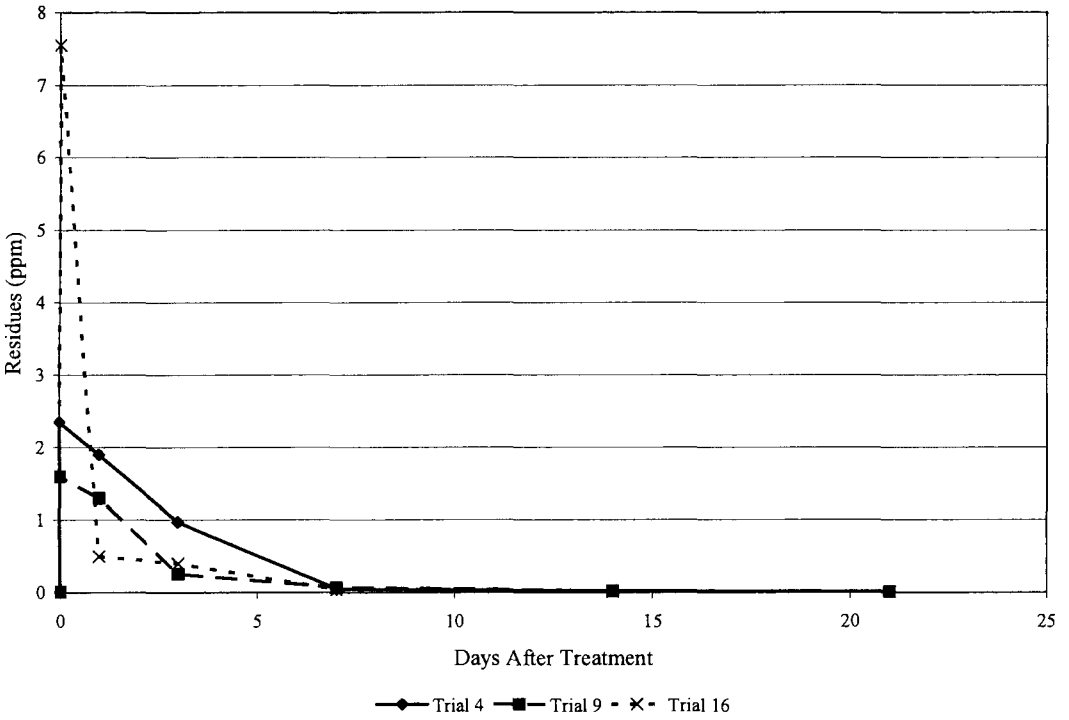

TABLE C.4. Summary Of Residue Data From Soybean Field Trials with Tribenuron Methyl										
Commodity	T.F.[1]	Total Rate (lb ai/A)	PHI (Days)	Residue Levels (ppm)						
				n	Min.	Max.	HAFT[2]	Median	Mean	Std. Dev.
Forage	2	0.03	0	36	0.58	3.00	2.95	1.45	1.71	0.69
Hay			0	36	0.61	8.80	8.35	2.75	3.54	2.52
Seed			68-107	44	<0.01	<0.01	<0.01	<0.01	<0.01	0
Seed	4	0.03	5-8	44	<0.01	0.07	0.07	0.01	0.01	0.01

1. The LOQ is 0.010 ppm for each commodity. For calculations which included residues >LOQ, the method LOQ (0.010 ppm) was used for residue values <LOQ.
2. HAFT = Highest Average Field Trial.

D. CONCLUSION

The soybean field trial data are adequate, and support the use of tribenuron methyl on sulfonylurea-tolerant soybeans as single or split broadcast foliar applications, totaling up to 0.03 lb ai/A per season. The available residue data support a minimum PHI of 0 days for forage and hay, along with the use of an NIS as an adjuvant, at up to 0.25% of the spray volume. As the label directions for use on soybeans prohibit applications after the R2 stage, a specific PHI for soybean seeds is not required.

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F. DOCUMENT TRACKING

RDI: William T. Drew (16 July 2009); John Redden (9 September 2009)
Petition Number: 8F7432
DP Barcode: 360846
PC Code: 128887

Tribenuron Methyl/352-632/PC Code 128887/E.I. du Pont de Nemours and Company/352
DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed - Field Corn (AGF, Starch, Grits, Flour, Refined Oil, Meal)

Primary Evaluator — Date: 11 August 2009

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Approved by — Date: 9 September 2009

John Redden,
Team Leader, RD/RIMUERB/ARIA

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). The DER has been reviewed by the Registration Division (RD) and the Health Effects Division (HED), and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

MRID #47548203. Andrew Thiel (2008) *Magnitude of Sulfonylurea Residues in/on Grain, Aspirated Grain Fractions and Processed Fractions (Starch, Grits, Flour, Refined Oil (Wet Milling), Refined Oil (Dry Milling) and Meal (Dry Milling) of a Field Corn Line Containing Event DP-098140-6 Following a Variety of Tank Mix Applications of Two Glyphosate and Rimsulfuron, Tribenuron Methyl, Chlorimuron Ethyl and Metsulfuron Methyl Containing Herbicides at Maximum Label Rates - United States and Canadian Locations, Season 2006.* Laboratory Project Number: DuPont-20025. Unpublished study prepared by DuPont. 303 pages.

EXECUTIVE SUMMARY

Three field trials were conducted in IA and NE during 2006; 2 trials to generate field corn grain for use in processing studies, and 1 trial to generate aspirated grain fractions (AGF). At the trial used to generate AGF samples, a water-soluble granule (SG) formulation of tribenuron methyl, containing 50% active ingredient (ai), was applied as a single broadcast foliar application, 7 days prior to normal grain maturity at the rate of 0.031 pound ai per acre (lb ai/A), the 1X rate. In the two trials used to generate grain for processing, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 7 days prior to normal harvest at the rate of 0.15 lb ai/A (5X rate). All applications were made using ground equipment, in spray volumes of 16-20 gallons per acre (GPA), and included the use of a non-ionic surfactant (NIS) at 0.25% v/v.

Single bulk control and treated samples of corn grain, the raw agricultural commodity (RAC), were harvested from each trial at 7 days after treatment (DAT). AGF samples were generated using corn grain from the 1X-rate trial, via procedures designed to simulate the movement of grain through terminal elevators. Corn grain samples from the 5X-rate trials were processed, using simulated commercial milling procedures, into starch, grits, meal, flour, and refined oil (wet- and dry-milled).

Samples of corn grain were stored frozen for up to 6.5 months prior to analysis, while corn AGF and other processed commodities were stored frozen for no more than 30 days prior to analysis. These sample storage conditions and durations are supported by the available storage stability data.

The liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) method used for determining residues of tribenuron methyl in corn grain, AGF and other processed commodities was adequately validated in conjunction with the analysis of the processing study samples. For this method, residues were extracted twice with acetonitrile (ACN)/K_2HPO_4 (3:1 v:v, pH 7), followed by centrifugation. Residues were then cleaned up by solvent partitioning (grain only), and by elution through a solid-phase extraction (SPE) cartridge. Residues were determined by LC/MS/MS using external standards for quantitation. The method's limit of quantitation (LOQ) is 0.010 ppm, and the limit of detection (LOD) is 0.003 ppm in each corn commodity.

At the trial used to generate AGF, tribenuron methyl residues were <LOD in grain harvested at 7 DAT following application at the 1X rate. Residues in AGF averaged 0.039 ppm, indicating that tribenuron methyl residues can concentrate by up to 13X in corn AGF. Following application at the 5X rate, residues of tribenuron methyl were <LOQ in corn grain, and all processed fractions from both processing studies.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the residue data from the field corn processing study are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming US EPA Residue Chemistry Summary Document, D360846.

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 adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of acetolactate synthase (ALS). It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for

residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola commodities to 0.5 ppm in/on wheat hay (40CFR §180.451[a]). Tolerances have also been established at 0.05 ppm in/on field corn forage, grain and stover.

DuPont Crop Protection has submitted a petition supporting the use of tribenuron methyl on field corn that is genetically tolerant to sulfonylurea herbicides (PP#8F7441). This petition has been submitted in conjunction with related petitions for use of chlorimuron ethyl and rimsulfuron on genetically modified field corn in support of an end-use product (EP) containing all three sulfonylurea herbicides. The nomenclature and physicochemical properties of tribenuron methyl are presented in Tables A.1 and A.2 (below).

TABLE A.1 Tribenuron Methyl Nomenclature

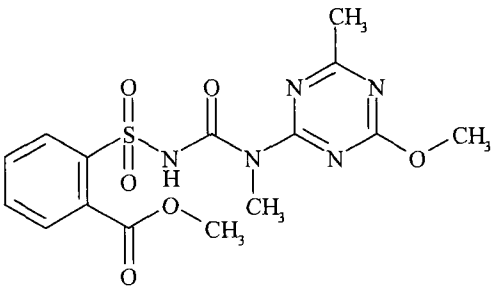
Chemical structure	
Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
Company experimental name	DPX-L5300
IUPAC name	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	50% ai SG (Dupont Express herbicide; EPA Registration #352-632)

TABLE A.2 Physicochemical Properties of Tribenuron Methyl

Parameter	Value		Reference
Melting point/range	142°C		MRID #47138301
pH (at 20°C)	4.64		
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3		
Water solubility (at 20°C)	pH 5	0.0489 g/L	
	pH 7	2.04	
	pH 9	18.3	

TABLE A.2.1. Physicochemical Properties of Tribenuron Methyl			
Parameter	Value		Reference
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7×10^{-7} mm Hg		
Dissociation constant (pK_a)	5.0		
Octanol/water partition coefficient, Log [K_{OW}] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

Three field trials were conducted in IA and NE during 2006 to generate field corn grain for use in processing studies (2 trials), or for generating AGF (1 trial). Tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 7 days prior to normal grain maturity, at the rate of 0.031 lb ai/A in one trial (Trt #3; 1X rate), and at 0.15 lb ai/A in two trials (Trt #7; 5X rate). All applications were made using ground equipment, in spray volumes of 16-20 GPA, and included the use of an NIS at 0.25% v/v. The application information is presented below (see Table B.1.1, below).

TABLE B.1.1. Study Use Pattern							
Location (City, State; Year) Trial ID	EP[1]	Application Information					Adjuvants
		Trt#	Method, Timing	Volume (GPA)	Rate (lb ai/A)	Total Rate (lb ai/A)	
Richland, IA; 2006 Trial 05	50% ai SG	7	Broadcast foliar; R6	16	0.154	0.154	NIS 0.25%
York, NE; 2006 Trial 14	50% ai SG	3	Broadcast foliar; BBCH 89	20	0.031	0.031	NIS 0.25%
		7	Broadcast foliar; BBCH 89	20	0.156	0.156	NIS 0.25%

1. EP = End-use Product.
2. One application of tribenuron methyl was made to treated field corn plots.
3. Each application included an NIS at 0.25% v/v.

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B.2. Sample Handling and Processing Procedures

Single bulk control and treated samples of field corn grain (>500 lb per sample) were harvested at normal maturity, 7 DAT. Samples were shipped by truck, at ambient temperatures, to GLP Technologies (in Texas) for processing. The samples used to generate AGF were stored (at ambient temperatures) at the processing facility, while the samples used for processing were stored at -12°C until processing.

To generate AGF samples, the grain was dried to a moisture content of 10-13% (if necessary). The bulk grain sample was then run, for 120 minutes, through a system of holding bins using bucket and screw conveyors, in a room designed to simulate the movement of grain in terminal elevators. As the grain sample moved through the system, light impurities were removed by aspiration, and sorted into different size classes by sieving (Figure B.1, below). Dust fractions smaller than 2360 μm were then recombined to form the AGF sample.

Bulk samples of corn grain were also processed, using simulated wet- and dry-milling, into starch, grits, meal, flour and refined oil (wet- and dry-milled). An example processing flowchart is shown in Figure B.2, below.

All AGF and processed samples were transferred to frozen storage (<-12°C) immediately after processing. Samples were shipped frozen to the analytical laboratory, ABC Laboratories (in Columbia, MO), where samples were stored at -20°C until analysis.

FIGURE B.1. Flowchart for Generation of Aspirated Grain Fractions from Field Corn.

FORM H.217 Revision 00

MATERIAL BALANCE for GENERATION, CLASSIFICATION, AND ASH CONTENT DETERMINATION OF ASPIRATED GRAIN FRACTIONS

Sample # 2 (Untreated, Trt. No. 999) Code # 22.NE.CN.14.GR.999AGF.MT.A

COMMODITY 1534.3 lbs.

Drying n/a lbs. (No drying)

1534.3 lbs. used for generation (2 batches)

Aspiration 1.7 lbs.

Classification:

- **ASPIRATED GRAIN FRACTION > 2360 micron** 118.2 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 2000 micron** 38.4 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 1180 micron** 68.4 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 850 micron** 33.0 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 425 micron** 93.9 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION < 425 micron** 404.6 g **(Grain Dust)**

All material less than 2360 micron was recombined for aspirated grain fraction.

ASH CONTENT: 3.3 %

DuPont Study Number: DuPont-20025; ABC Study Number: ABC-50165-3
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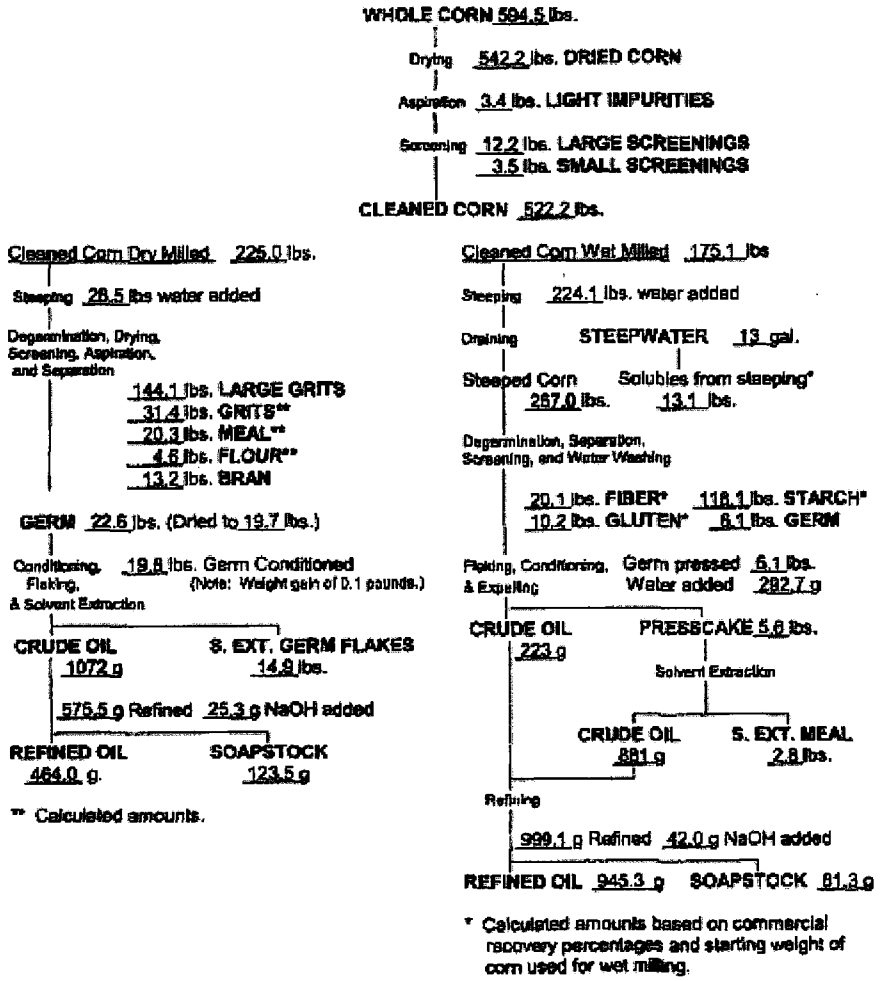
FIGURE B.2. Processing Flowchart for Field Corn Grain.

FORM H.203 Revision 00

CORN PROCESSING MATERIAL BALANCE

Sample # 1 (Control, Trt. No.999) Code # 22.IA.CN.5.GR.999PROC.MT.A(Test No.5)



DuPont Study Number: DuPont-20025; ABC Study Number: ABC-50165-3
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B.3. Analytical Methodology

Grain, AGF and processed fractions were analyzed for tribenuron methyl using an LC/MS/MS method, DuPont-13412, Revision #1, *Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oil Crop Matrices Using SPE Purification and LC/MS/MS Detection.* This method has been proposed as a new tolerance enforcement method for residues of sulfonylureas, and an independent laboratory validation (ILV) trial for the method has been previously reviewed (D330813; S. Hummel; 8 August 2006).

For this method, residues were extracted from each matrix twice with ACN/K_2HPO_4 (3:1 v:v, pH 7), followed by centrifugation. For grain samples only, the combined extracts were partitioned against hexane, the remaining aqueous phase was concentrated, and then diluted with 0.01% acetic acid. Residues from all fractions were then cleaned up, using an ENV SPE cartridge eluted with 25 mM NaOH in methanol. The residues were concentrated, then diluted with 50 mM ammonium acetate/ACN (9:1 v:v), and analyzed by LC/MS/MS using external standards. Tribenuron methyl was detected and quantified using two ion transitions, m/z 396→155, and m/z 396→181. The LOQ in each corn commodity is 0.010 ppm, and the LOD is 0.003 ppm.

The above method was validated in conjunction with the analysis of the processing samples, using control samples fortified with tribenuron methyl at 0.010 and 0.10 ppm in corn grain and each processed fraction, and at 0.010 and 5.0 ppm in corn AGF.

C. RESULTS AND DISCUSSION

The LC/MS/MS method used for determining residues of tribenuron methyl was adequately validated in conjunction with the analysis of the processing study samples. The average concurrent recoveries were 83-109% from all commodities (see Table C.1, below). In each matrix, the LOQ is 0.010 ppm, and the LOD is 0.003 ppm. Apparent residues of tribenuron methyl were <LOQ in all control samples. Adequate sample calculations, and example chromatograms were provided, and the fortification levels used for the method recoveries bracketed the measured residue levels.

Samples of corn grain were stored frozen for up to 6.5 months prior to analysis (see Table C.2, below). Samples of AGF and each processed commodity were analyzed within 30 days of collection.

Adequate data are available indicating that tribenuron methyl is stable at -20°C for intervals of up to 21 months in wheat grain (D304059; R. Griffin; 24 June 2004). These data support the storage durations and conditions of the grain samples (RAC). Because the frozen AGF and processed fractions were analyzed within 30 days of collection, supporting storage stability data are not required for these commodities.

In the trial used to generate AGF, tribenuron methyl residues were <LOD in grain harvested at 7 DAT, following an application at the 1X rate (see Table C.3, below). Residues in AGF averaged 0.039 ppm, indicating that tribenuron methyl residues can concentrate by up to 13X in corn AGF.

In one of the processing studies, tribenuron methyl residues were <LOD in the corn grain, and each processed commodity. In the other study, tribenuron methyl residues were <LOQ in the corn grain (0.004-0.005 ppm), and ≤LOD in all processed fractions. Therefore, reliable processing factors could not be calculated for the corn processed fractions.

TABLE C.1 Summary of Concurrent Recoveries of Tribenuron Methyl from Processed Field Corn Commodities

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Grain (RAC)	0.010	2	87, 88	88
	0.10	2	85, 93	89
	Total	**4**	**85-93**	**88 ± 3**
AGF	0.010	1	87	91
	5.0	1	94	
Starch	0.010	1	89	90
	0.10	1	91	
Grits	0.010	1	101	99
	0.10	1	96	
Flour	0.010	1	80	83
	0.10	1	86	
Refined Oil (Wet)	0.010	1	111	107
	0.10	1	103	
Refined Oil (Dry)	0.010	1	113	109
	0.10	1	104	
Corn Meal	0.010	1	97	96
	0.10	1	94	

TABLE C.2 Summary of Storage Conditions

Matrix	Storage Temperature (°C)	Actual Storage Duration (Days)[1]	Interval of Demonstrated Storage Stability (Months)
Grain (RAC)	≤-12	200	21[2]
AGF		16	NA[3]
Starch		28	
Grits		30	
Flour		28	
Refined Oil (Wet)		28	
Refined Oil (Dry)		27	
Meal		26	

1. Interval from harvest to extraction for analysis. Extracts were stored for up to 6 days prior to analysis.
2. Wheat grain (D304059; R. Griffin; 24 June 2004).
3. NA = Not Applicable (storage stability data are not required for samples stored 30 days or fewer).

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TABLE C-3. Residue Data from Field Corn Processing Study with Tribenuron Methyl[1]

RAC [Trial ID]	Processed Commodity	Total Rate (lb ai/A)	PHI (Days)	Residues (ppm)		Processing Factor[2]
Field Corn Grain [Trial #5]	Grain (RAC)	0.154 [5X]	7	ND[3]	ND	--
	Starch			ND	ND	--
	Grits			ND	ND	--
	Flour			ND	ND	--
	Oil, Wet			ND	ND	--
	Oil, Dry			ND	ND	--
	Meal			ND	ND	--
Field Corn Grain [Trial #14]	Grain (RAC)	0.031 [1X]	7	ND	ND	--
	AGF			0.040	0.038	13X
	Grain (RAC)	0.156 [5X]	7	*0.004*	*0.005*	--
	Starch			ND	ND	--
	Grits			ND	ND	--
	Flour			*0.003*	ND	0.67X
	Oil, Wet			ND	ND	--
	Oil, Dry			ND	ND	--
	Meal			ND	ND	--

1. The LOQ and LOD were 0.010 and 0.003 ppm, respectively. Residue values <LOQ, but ≥LOD, are listed in italics.
2. For calculating processing factors, the LOD is used for values reported as ND.
3. ND = Not Detected.

D. CONCLUSION

The field corn processing studies are adequate, and indicate that residues of tribenuron methyl can concentrate by up to 13X in corn AGF from grain treated at the 1X rate. Following an application at the 5X rate, residues of tribenuron methyl were <LOQ in field corn grain, and all processed fraction from both processing studies.

E. REFERENCES

Tribenuron methyl. Residue Chemistry Considerations.; D304059; R. Griffin; 24 June 2004.

Thifensulfuron methyl. Addition of Uses on Rice and Sorghum (PRIA R19 – 352-611; PP#4F6889). Summary of Analytical Chemistry and Residue Data.; D330813; S. Hummel; 8 August 2006.

F. DOCUMENT TRACKING

RDI: William T. Drew (11 August 2009); John Redden (9 September 2009)
Petition Number: 8F7441
DP Barcode: 360846
PC Code: 128887

Tribenuron Methyl/352-632/PC Code 128887/E.I. du Pont de Nemours and Company/352
DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed - Soybean (Meal, Hulls, Refined Oil, AGF)

Primary Evaluator — Date: 19 August 2009

William T. Drew,
Chemist, RD/RIMUERB/ARIA

Approved by — Date: 9 September 2009

John Redden,
Team Leader, RD/RIMUERB/ARIA

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). The DER has been reviewed by the Registration Division (RD) and the Health Effects Division (HED), and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

MRID #47548204. Emily Shepard (2007) *Magnitude of Residues of Rimsulfuron, Tribenuron Methyl and Chlorimuron Ethyl, in/on Aspirated Grain Fractions and Processed Fractions (Refined oil, Meal and Hulls) of a Soybean Line Containing Event DP 356043 5 Following Applications of Rimsulfuron, Tribenuron Methyl and Chlorimuron Ethyl Containing Herbicides - United States Locations, Season 2006.* Laboratory Project Number: DuPont-20026. Unpublished study prepared by DuPont. 182 pages.

EXECUTIVE SUMMARY

Three soybean field trials were conducted in IL, MN and NE during 2006; 2 trials to generate soybean seed samples for use in processing studies, and 1 trial to generate aspirated grain fractions (AGF). At the trial used to generate AGF samples, a water-soluble granule (SG) formulation of tribenuron methyl, containing 50% active ingredient (ai), was applied as a single broadcast foliar application, 5 days prior to normal seed maturity at the rate of 0.03 pound ai per acre (lb ai/A), the 1X rate. In the two trials used to generate seeds for processing, tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, 7 days prior to normal harvest at the rate of 0.16 lb ai/A (5X rate). All applications were made using ground equipment, in spray volumes of 15-25 gallons per acre (GPA), and included the use of a non-ionic surfactant (NIS) at 0.25% v/v.

Single bulk control and treated samples of soybean seeds, the raw agricultural commodity (RAC), were harvested from each trial at 5 or 7 days after treatment (DAT). AGF samples were generated using seeds from the 1X-rate trial, via procedures designed to simulate the movement of grain through terminal elevators. Soybean seeds from the 5X-rate trials were processed, using simulated commercial procedures, into hulls, meal, and refined oil.

Samples of soybean seeds were stored at ≤-12°C for up to 2 months prior to analysis, while soybean AGF and other processed commodities were stored frozen for no more than 30 days prior to analysis. These sample storage conditions and durations are supported by the available storage stability data.

The liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) method used for determining residues of tribenuron methyl in soybean seeds, AGF and other processed commodities was adequately validated in conjunction with the analysis of the processing study samples. For this method, residues were extracted twice with acetonitrile (ACN)/K_2HPO_4 (3:1 v:v, pH 7), followed by centrifugation. Residues were cleaned up by solvent partitioning (seeds only), and by elution through a solid-phase extraction (SPE) cartridge. Residues were determined by LC/MS/MS using external standards for quantitation. The method's limit of quantitation (LOQ) is 0.010 ppm, and the limit of detection (LOD) is 0.003 ppm in each soybean commodity.

At the trial used to generate AGF, tribenuron methyl residues were <LOD in the seeds harvested at 5 DAT following application at the 1X rate. Residues in AGF averaged 0.45 ppm, indicating that tribenuron methyl residues can concentrate by up to 150X in soybean AGF.

Following application at the 5X rate, tribenuron methyl residues in whole seeds were <LOD at one trial, and 0.042 ppm at the other trial. At the trial with quantifiable residues in seeds, residues averaged 0.17 ppm in hulls, and <0.003 ppm in meal and refined oil. Tribenuron methyl residues concentrated by 4.05X in hulls, and were reduced by <0.07X in meal and refined oil.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the residue data from the soybean processing study are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming US EPA Residue Chemistry Summary Document, D360846.

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 adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of acetolactate synthase (ALS). It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola

commodities to 0.5 ppm in/on wheat hay (40 CFR §180.451[a]). Tolerances have also been established at 0.05 ppm in/on soybean seeds, but there are no tolerances in soybean forage or hay.

DuPont has submitted a petition supporting the use of tribenuron methyl on soybeans that are genetically modified to be tolerant to sulfonylurea herbicides (PP#8F7432). This petition has been submitted in conjunction with related petitions for use of chlorimuron ethyl and rimsulfuron on genetically modified soybeans in support of an end-use product (EP) containing all three sulfonylurea herbicides. The nomenclature and physicochemical properties of tribenuron methyl are presented in Tables A.1 and A.2 (below).

TABLE A.1 Tribenuron Methyl Nomenclature

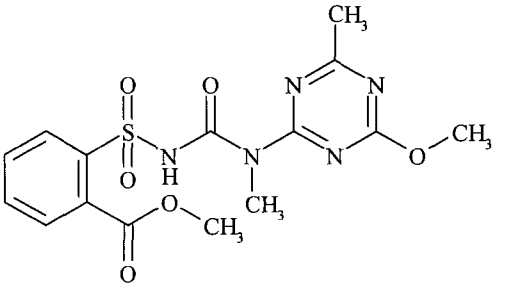
Chemical structure	
Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
Company experimental name	DPX-L5300
IUPAC name	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	50% ai SG (Dupont Express herbicide; EPA Registration #352-632)

TABLE A.2 Physicochemical Properties of Tribenuron Methyl

Parameter	Value	Reference
Melting point/range	142°C	MRID #47138301
pH (at 20°C)	4.64	
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3	
Water solubility (at 20°C)	pH 5 0.0489 g/L pH 7 2.04 pH 9 18.3	

TABLE A.2 Physicochemical Properties of Tribenuron Methyl.

Parameter	Value		Reference
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7×10^{-7} mm Hg		
Dissociation constant (pK_a)	5.0		
Octanol/water partition coefficient, Log [K_{OW}] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

Three soybean field trials were conducted in IL, MN and NE during 2006 to generate soybean seeds for use in processing studies (2 trials), or for generating AGF (1 trial). Tribenuron methyl (50% ai SG) was applied as a single broadcast foliar application, roughly 7 days prior to normal grain maturity, at the rate of 0.03 lb ai/A in one trial (Trt #4; 1X rate), and at 0.16 lb ai/A in two trials (Trt #6; 5X rate). All applications were made using ground equipment, in spray volumes of 15-25 GPA, and included the use of an NIS at 0.25% v/v. The application information is presented (see Table B.1.1, below).

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TABLE B.1.1. Study Use Pattern.

Location (City, State / Year / Trial ID)	EP[1]	Application Information[2]					Adjuvants[3]
		#	Method; Timing	Volume (GPA)	Rate (lb ai/A)	Total Rate (lb ai/A)	
Carlyle, IL; 2006 Trial 10	50% ai SG	4	Broadcast foliar; R-8	25	0.03	0.03	NIS 0.25%
Paynesville MN; 2006 Trial 14	50% ai SG	6	Broadcast foliar; mature seed	16	0.16	0.16	NIS 0.25%
York, NE 2006 Trial 16	50% ai SG	6	Broadcast foliar; BBCH 89	15	0.16	0.16	NIS 0.25%

1. EP = End-use Product.
2. One application of tribenuron methyl was made to treated soybean plots.
3. Each application included an NIS at 0.25% v/v.

B.2. Sample Handling and Processing Procedures

Single bulk control and treated samples of soybean seeds were harvested from each trial, using a combine at normal crop maturity, 5 or 7 DAT. The seed samples (4000 lb/sample) used for generation of AGF were collected from the 1X treatment (IL trial), and the seed samples (80-160 lb/sample) used for processing were collected from the 5X treatments (MN and NE trials). Samples from the IL trial were shipped by truck, under ambient conditions, to the processing facility, GLP Technologies (in Navasota, TX), and were stored under ambient conditions. Samples from the MN and NE trials were frozen, and shipped by freezer truck to GLP Technologies, where the samples were stored at -12°C until processing. The AGF fractions were generated within 14 days of harvest, while the processing of 5X-rate samples was initiated within 7 days of harvest.

To generate AGF samples, the bulk seed samples were run for 120 minutes through a system of holding bins, using bucket and screw conveyors, in a room designed to simulate the movement of grain in terminal elevators. As the seed sample moved through the system, light impurities were removed by aspiration, and sorted into different size classes by sieving (see Figure B.1, below). Dust fractions smaller than 2360 μm were then recombined to form the AGF sample.

For the processing studies, the bulk samples of soybean seeds were processed, using simulated commercial procedures, into hulls, meal and refined oil (see Figure B.2, below).

All AGF and processed samples were transferred to frozen storage (<-12°C) immediately after collection. Samples were shipped frozen to the analytical laboratory, ABC Laboratories (in Columbia, MO), where samples were stored at -16°C until analysis.

FIGURE B.1. Flowchart for Generation of Soybean Aspirated Grain Fractions.

FORM H.217 Revision 00

MATERIAL BALANCE for GENERATION, CLASSIFICATION, AND ASH CONTENT DETERMINATION OF ASPIRATED GRAIN FRACTIONS

Sample # 2 (Treated, Treatment No. 04) Code # 23.IL.SB.10.SD.4.7DAA1.C

COMMODITY 3990.0 lbs.

Drying n/a lbs. (after drying)

3990.0 lbs. used for generation (6 batches @ 665.0 lbs. each)

Aspiration 2.6 lbs.

Classification

- **ASPIRATED GRAIN FRACTION > 2360 micron** 387.7 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 2000 micron** 12.2 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 1180 micron** 28.4 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 850 micron** 16.4 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION > 425 micron** 52.1 g **(Grain Dust)**
- **ASPIRATED GRAIN FRACTION < 425 micron** 678.4 g **(Grain Dust)**

All material less than 2360 micron was recombined for aspirated grain fraction.

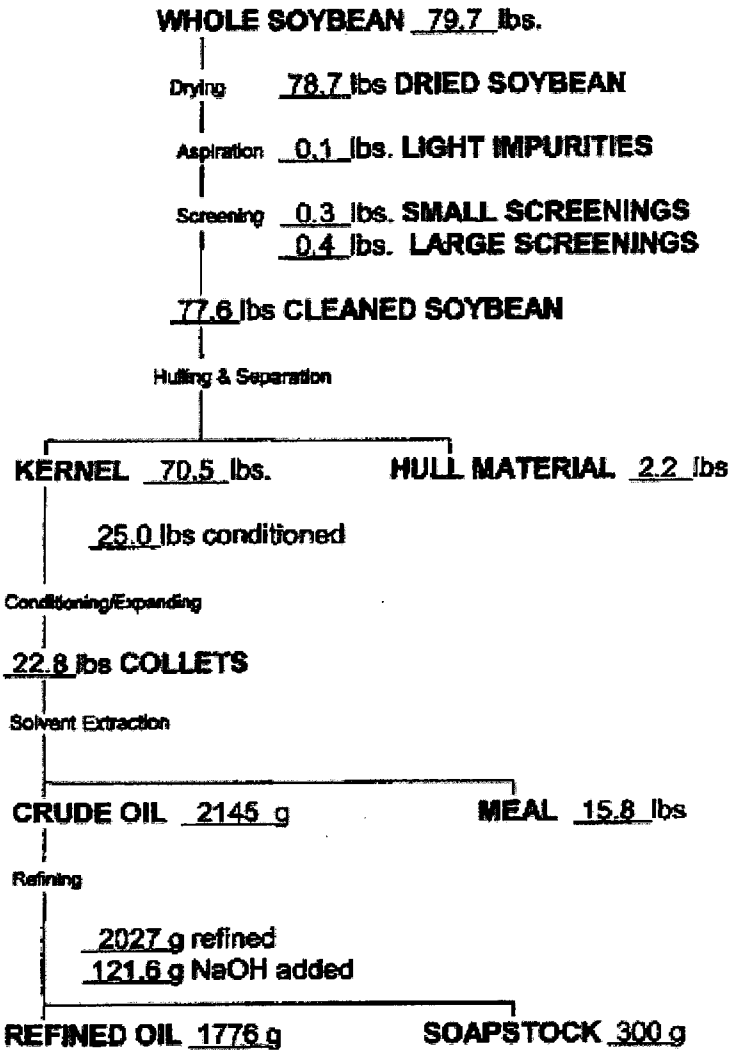
ASH CONTENT: 30.3 %

90

FIGURE B.2. Processing Flowchart for Soybean Seeds.

FORM H.202 Revision 00
SOYBEAN PROCESSING MATERIAL BALANCE

Sample # 1 (Untreated) Code # 23.NE.SB.16.SD.999.14DAA4.C



B.3. Analytical Methodology

Soybean seeds, processed fractions, and AGF were analyzed for residues of tribenuron methyl using an LC/MS/MS method, DuPont-13412, Revision #1, *Analytical Method for the Determination of Nicosulfuron, Thifensulfuron Methyl, Ethametsulfuron Methyl, Rimsulfuron, Tribenuron Methyl, and Chlorimuron Ethyl in Oil Crop Matrices Using SPE Purification and LC/MS/MS Detection.* This method has been proposed as a new tolerance enforcement method for residues of sulfonylureas, and an independent laboratory validation (ILV) trial for this method has been previously reviewed (D330813; S. Hummel; 8 August 2006).

For this method, residues were extracted from each matrix twice with ACN/K_2HPO_4 (3:1 v:v, pH 7), followed by centrifugation. For seed samples only, the combined extracts were partitioned against hexane, the remaining aqueous phase was concentrated, and then diluted with water. Residues from all samples were then cleaned up, using an ENV SPE cartridge eluted with 25 mM NaOH in methanol. The residues were concentrated, then diluted with 50 mM ammonium acetate/ACN (9:1 v:v), and analyzed by LC/MS/MS using external standards. Tribenuron methyl was detected and quantified using two ion transitions, m/z 396→155, and m/z 396→181. The LOQ in each soybean commodity is 0.010 ppm, and the LOD is 0.003 ppm.

The above method was validated in conjunction with the analysis of the processing samples, using control samples fortified with tribenuron methyl at 0.010-0.40 ppm in seeds, 0.010-0.10 ppm in meal and oil, 0.010-2.0 ppm in hulls, and 0.010-5.0 ppm in AGF.

C. RESULTS AND DISCUSSION

The LC/MS/MS method used for determining residues of tribenuron methyl was adequately validated in conjunction with the analysis of the processing study samples. The average concurrent recoveries were 85-101% from each commodity (see Table C.1, below). In each matrix, the LOQ is 0.010 ppm, and the LOD is 0.003 ppm. Apparent residues of tribenuron methyl were <LOQ in all control samples. Adequate sample calculations, and example chromatograms were provided, and the fortification levels used for the method recoveries bracketed the measured residue levels.

Samples of soybean seeds were stored frozen for up to 2 months prior to analysis (see Table C.2, below). Samples of AGF and each processed commodity were analyzed within 30 days of collection.

Adequate data are available indicating that tribenuron methyl is stable at -20°C for intervals of up to 9.6 months in soybean seeds (MRID #47548202). These data support the storage durations and conditions of the soybean seed samples (RAC). Because the frozen AGF and processed fractions were analyzed within 30 days of collection, supporting storage stability data are not required for these commodities.

In the trial used to generate AGF, tribenuron methyl residues were <LOD in the seeds harvested at 5 DAT, following an application at the 1X rate (see Table C.3, below). Residues in

AGF averaged 0.45 ppm, indicating that tribenuron methyl residues can concentrate by up to 150X in soybean AGF.

In the 5X trial from MN, tribenuron methyl residues were <LOD in seeds and hulls. Since residues were <LOD in seeds from this trial, the meal and oil samples were not analyzed. In the 5X trial from NE, residues averaged 0.042 ppm in seeds, 0.17 ppm in hulls, and <0.003 ppm in meal and refined oil. Based on this trial, tribenuron methyl residues concentrated by 4.05X in hulls, and were reduced by <0.07X in meal and refined oil.

TABLE C.1 Summary of Concurrent Recoveries of Tribenuron Methyl from Processed Soybean Commodities

Matrix	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. (%)
Seeds (RAC)	0.010	3	86, 74, 94	85 ± 10
	0.10	1	84	84
	0.30	1	89	89
	0.40	1	101	101
	Total	**6**	**74-101**	**88 ± 9**
Meal	0.010	1	94	92
	0.10	1	90	
Hulls	0.010	2	88, 90	89
	1.2	1	85	85
	2.0	1	92	92
	Total	**4**	**85-92**	**89 ± 3**
Refined Oil	0.010	1	100	100
	0.10	1	99	
AGF	0.010	1	82	85
	5.0	1	87	

TABLE C.2 Summary of Storage Conditions

Matrix	Storage Temperature (°C)	Actual Storage Duration (Days)[1]	Interval of Demonstrated Storage Stability (Months)
Seeds (RAC)	≤-12	61	9.6[2]
Meal		28	NA[3]
Hulls		22	
Refined Oil		27	
AGF		21	

1. Interval from harvest to extraction for analysis.
2. MRID #47548202.
3. NA = Not Applicable (storage stability data are not required for samples stored 30 days or fewer.

TABLE C.3.1 Residue Data from Soybean Processing Study with Tribenuron Methyl.

RAC (Trial ID)	Commodity	Total Rate (lb ai/A)	PHI (Days)	Residues (ppm)		Processing Factor [2]
Soybean Seeds [Trial #10]	Seeds (RAC)	0.03 [1X]	5	ND [3]	ND	--
	AGF			0.44	0.46	150X
Soybean Seeds [Trial #14]	Seeds (RAC)	0.16 [5X]	7	ND	ND	--
	Meal			NA [4]	NA	NC [5]
	Hulls			ND	ND	NC
	Oil			NA	NA	NC
Soybean Seeds [Trial #16]	Seeds (RAC)	0.16 [5X]		0.042	0.042	--
	Meal			ND	ND	<0.07X
	Hulls			0.18	0.16	4.05X
	Oil			ND	ND	<0.07X

1. The LOQ and LOD were 0.010 and 0.003 ppm, respectively.
2. For calculating processing factors, the LOD is used for values reported as ND.
3. ND = Not Detected.
4. NA = Not Analyzed.
5. NC = Not Calculated.

D. CONCLUSION

The soybean processing studies are adequate, and indicate that residues of tribenuron methyl can concentrate by up to 150X in soybean AGF from soybeans treated at the 1X rate. Following an application at the 5X rate, residues of tribenuron methyl concentrated by 4.05X in hulls, but were reduced by <0.07X in both meal and refined oil.

E. REFERENCES

Tribenuron methyl. Residue Chemistry Considerations.; D304059; R. Griffin; 24 June 2004.

Thifensulfuron methyl. Addition of Uses on Rice and Sorghum (PRIA R19 – 352-611; PP#4F6889). Summary of Analytical Chemistry and Residue Data.; D330813; S. Hummel; 8 August 2006.

F. DOCUMENT TRACKING

RDI: William T. Drew (19 August 2009); John Redden (9 September 2009)
Petition Number: 8F7432
DP Barcode: 360846
PC Code: 128887

Tribenuron Methyl/352-632/PC Code 128887/E.I. du Pont de Nemours and Company/352
DACO 6.2/OPPTS 860.1300/OECD II 6.2.2, 6.2.3 & IIIA 8.2, 8.4.1, 8.4.2
Nature of the Residues in Livestock - Laying Hen (Muscle, Fat, Liver, Egg White, Egg Yolk)

Primary Evaluator — Date: 21 August 2009
William T. Drew,
Chemist, RD/RIMUERB/ARIA

Approved by — Date: 9 September 2009
John Redden,
Team Leader, RD/RIMUERB/ARIA

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (1910 Sedwick Road, Building 100, Suite B; Durham, NC 27713). The DER has been reviewed by the Registration Division (RD) and the Health Effects Division (HED), and revised to reflect current Office of Pesticide Programs (OPP) policies.

STUDY REPORT

MRID #47637801. L. Wen (2008) *Metabolism of (Carbon 14) Tribenuron Methyl in Laying Hens*. Laboratory Project Number: DuPont-19649. Unpublished study prepared by ABC Laboratories, and Sinclair Research Center. 186 pages.

EXECUTIVE SUMMARY

In a poultry metabolism study, two groups of Highline W36 hens (5 per group) were dosed orally via capsules, once a day for 14 consecutive days, with [triazine-2-^{14}C] or [phenyl-U-^{14}C] tribenuron methyl, at doses averaging 1.20 and 1.23 mg ai/hen/day, respectively. These dose levels for the two [^{14}C]-labels were equivalent to 0.814 and 0.846 mg ai/kg body weight/day, or 11.6 and 11.5 ppm of tribenuron methyl in the diet. Egg samples were collected twice a day, and separated into yolks and whites, while excreta samples were collected daily. Hens were sacrificed 6-8 hours after the final dose, and samples of composited fat (muscle, visceral, and subcutaneous), composited muscle (thigh and breast), and liver were collected from each hen. All egg, tissue and excreta samples were pooled by dose group.

The recovery of the administered dose averaged at least 95% for both [^{14}C]-labels, with 91.7-94.2% of the dose being recovered in the excreta, and cage washes. Eggs accounted for 0.68-1.85% of the dose, and edible tissues accounted for another 0.53-1.62% of the dose.

For the hens dosed with the [triazine-^{14}C] label, total radioactive residues (TRR) plateaued within 5 days in egg whites (0.588 ppm), and 8 days in yolks (0.523 ppm). For the hens dosed with the [phenyl-^{14}C] label, TRR levels plateaued within 2 days in egg whites (0.187 ppm), and 10 days in yolks (0.236 ppm). After reaching a steady state, TRR levels were similar in egg whites and yolks. TRR levels in edible tissues were 0.956 ppm in liver, 0.545 ppm in muscle, and 0.161 ppm in fat from the [triazine-^{14}C]-dosed hens, and 0.663 ppm in liver, 0.135 ppm in muscle, and 0. 055 ppm in fat from the [phenyl-^{14}C]-dosed hens.

The initial solvent extractions with acetonitrile (ACN)/phosphate buffer released 64.6-99.3% of the TRR from egg whites and tissues, and 32.1-64.0% of the TRR from egg yolks. Subsequent enzymatic treatment released 10.5-36.6% of the TRR from tissues and egg yolks,

and a final mild acid hydrolysis released another 17.0-25.0% of the TRR from egg yolks. Radioactivity remaining in the residual solids accounted for 0.7-14.0% of the TRR, and was <0.05 ppm in all matrices.

Solubilized [^{14}C]-residues were analyzed and quantified by reverse phase high-performance liquid chromatography (HPLC), and metabolite identities were confirmed by co-chromatography with reference standards, and by liquid chromatography with mass spectrometric detection (LC/MS). As [^{14}C]-residues in eggs, tissues and excreta were profiled within roughly 6 months of sampling, storage stability data are not required to support the study.

For the [triazine-^{14}C]-dosed hens, 78.3-98.1% of the TRR was identified in tissues and eggs. Parent was a major [^{14}C]-residue, accounting for 12.7-32.5% of the TRR in tissues and egg whites, but only 0.5% of the TRR in yolks. In eggs and all tissues, the major triazine-derived metabolites were IN-A4098 (39.9-61.9% TRR) and IN-L5296 (9.0-17.4% TRR). An additional eight minor metabolites were also identified, each accounting for 0.3-4.2% of the TRR (0.002-0.033 ppm). One polar unknown (T4) was detected in egg yolks at 10.8% of the TRR (0.051 ppm). Minor amounts of Unknown T4 were also detected in muscle (1.4% TRR) and liver (0.6% TRR). As T4 was recovered only following enzymatic or mild acid hydrolysis, this unknown may be a conjugate.

For the [phenyl-^{14}C]-dosed hens, 32.7-83.5% of the TRR was identified in eggs and tissues. Parent accounted for 28.1-58.5% of the TRR in tissues, but accounted for ≤1.1% of the TRR in egg whites and yolks. The major phenyl-derived metabolites were IN-D5803 in muscle (19.6% TRR), liver (16.6% TRR), egg whites (42.7% TRR) and yolks (11% TRR), and IN-00581 in egg whites (38.6% TRR) and yolks (18.5% TRR). An additional four minor metabolites were identified, with each accounting for 0.6-4.1% of the TRR (0.001-0.027 ppm). Three major polar unknowns (P2, P3 and P6) were detected in liver, each at 8.9-10.5% of the TRR, and Unknowns P2 and P3 were also major components in yolk at 9.0 and 20.4% of the TRR, respectively. Unknown P6 was recovered primarily in the initial solvent extracts; whereas Unknowns P2 and P3 were primarily recovered following enzyme and acid hydrolysis, suggesting that these unknowns may be conjugates. Unknowns P3 and T4 may be the same compound as they were found in the same tissues, had the same retention time in excreta, and were both only released by enzyme and acid hydrolysis.

The major route of metabolism for tribenuron methyl in poultry appears to involve hydrolytic cleavage of the sulfonyl urea bridge, followed by demethylation and/or hydroxylation of the resulting triazine moiety, and hydrolysis or cyclization of the resulting benzyl moiety.

STUDY/WAIVER ACCEPTABILITY/DIFICIENCIES/CLARIFICATIONS

Under the conditions and parameters used in the study, the hen metabolism data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming US EPA Residue Chemistry Summary Document, D360846.

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 adverse impact on the validity of the study.

A. BACKGROUND INFORMATION

Tribenuron methyl is a sulfonylurea herbicide (Group 2) that works via inhibition of acetolactate synthase (ALS). It is currently registered for post-emergence application(s) to barley, canola, cotton, flax, oats, sunflower, wheat, and grasses grown for seed, for the selective control of broadleaf weeds. It is also registered for use as a pre-emergence burndown broadcast application for wheat and barley, and as a preplant or at-planting burndown application for cotton, field corn, rice, grain sorghum, and soybeans. Permanent tolerances are established for residues of tribenuron methyl at levels ranging from 0.02 ppm in/on cotton and canola commodities to 0.5 ppm in/on wheat hay (40CFR §180.451[a]). Tolerances have also been established at 0.05 ppm in/on field corn forage, grain and stover.

DuPont Crop Protection has submitted petitions supporting the use of tribenuron methyl on soybeans and field corn that are genetically tolerant to sulfonylurea herbicides (PP#8F7432 and PP#8F7441, respectively). These petitions have been submitted in conjunction with related petitions for use of chlorimuron ethyl and rimsulfuron on genetically modified soybeans and field corn, in support of an end-use product (EP) containing all three sulfonylurea herbicides. The nomenclature and physicochemical properties of tribenuron methyl are presented in Tables A.1 and A.2 (below).

TABLE A.1 Tribenuron Methyl Nomenclature

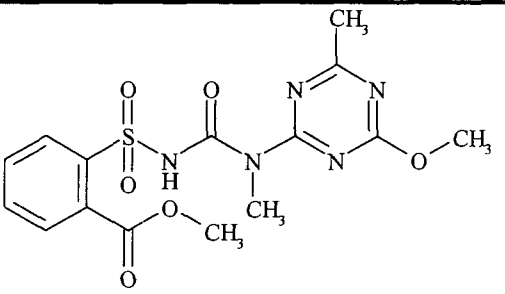
Chemical structure	
Common name	Tribenuron methyl
Molecular formula	$C_{15}H_{17}N_5O_6S$
Molecular weight	395.4
Company experimental name	DPX-L5300
IUPAC name	Methyl-2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)carbamoyl-sulfamoyl]benzoate
CAS name	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoate
CAS registry number	101200-48-0
End-use product (EP)	50% ai SG (Dupont Express herbicide; EPA Registration #352-632)

TABLE A.2 Physicochemical Properties of Tribenuron Methyl

Parameter	Value		Reference
Melting point/range	142°C		MRID #47138301
pH (at 20°C)	4.64		
Density (at 19.6°C)	1.4594 ± 0.001 g/cm^3		
Water solubility (at 20°C)	pH 5	0.0489 g/L	
	pH 7	2.04	
	pH 9	18.3	
Solvent solubility (at 20°C)	Acetone	39.1 g/L	
	Acetonitrile	46.4	
	Dichloromethane	>250	
	Dimethylformamide	98.2	
	Ethyl acetate	16.3	
	n-Heptane	0.02	
	Methanol	2.59	
	n-Octanol	0.383	
	Xylene	13.1	
Vapor pressure (at 25°C)	2.7 x 10^{-7} mm Hg		
Dissociation constant (pK_a)	5.0		
Octanol/water partition coefficient, Log [K_{OW}] (at 20°C)	pH 5	2.60	
	pH 7	0.78	
	pH 9	0.30	
UV/visible absorption (maxima, λ)	pH 1.66	200, 231 nm	
	pH 7	201, 256 nm	
	pH 11.72	208, 256 nm	

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B. EXPERIMENTAL DESIGN

B.1. Livestock

The in-life phase was of the study was conducted by Sinclair Research Center (in Auxvasse, MO) from 18 November 2006 to 20 December 2006 (see Tables B.1.1-B.1.3, below). Following a 19-day acclimation period, two groups (5 hens/group) of laying hens were dosed orally for 14 consecutive days with either [triazine-2-^{14}C]- or [phenyl-U-^{14}C]-tribenuron methyl at doses averaging 1.20 and 1.23 mg ai/hen/day, respectively, which are equivalent to 0.814 and 0.846 mg ai/kg body weight/day. These dose levels are also equivalent to 11.6 and 11.5 ppm of tribenuron methyl in the diet, based on the average feed consumption during the dosing period. The hens were dosed once a day, in the morning. During the dosing period, all test animals were observed daily for general health and appearance. There were no adverse clinical findings during dosing, and macroscopic examination of tissues during necropsy resulted in no unusual findings.

TABLE B.1.1 General Test Animal Information

Species	Breed	Age (Weeks)	Initial Weight of Hens (kg)	Health Status	Description of Housing/Holding Area
Gallus gallus	Highline W 36	30	1.224-1.549	Healthy	Galvanized steel laying hen cages with a 16/8 hour light/dark cycle at 69 ± 1.3 °F, with relative humidity of 34 ± 17%.

TABLE B.1.2 Test Animal Dietary Regime

Diet	Feed Consumption (g/day)	Water	Acclimation Period	Pre-Dosing
PMI Laying Hen Diet 5070	91-110 (acclimation period). 82-111 (treatment period). Averages during dosing period were 104 and 106 for the two treatment groups.	*Ad libitum*	19 days	None

TABLE B.1.3 Test Animal Dosing Regime

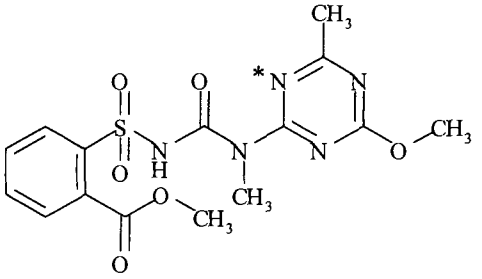
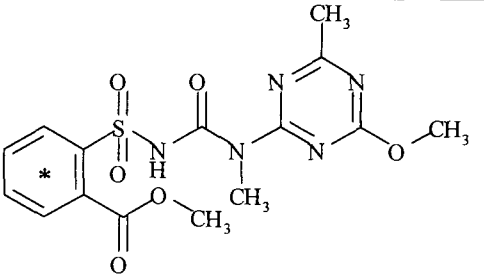
Treatment Type	Treatment Level [^{14}C]-triazine	Treatment Level [^{14}C]-phenyl	Vehicle	Parameters	Timing/Duration
Oral	1.20 mg ai/hen/day = 0.814 mg ai/kg bw/day = 11.6 ppm.	1.23 mg ai/hen/day = 0.846 mg ai/kg bw/day = 11.5 ppm.	Capsule	Test material in vehicle.	Once daily for 14 days.

B.2. Test Materials

To prepare the dosing solutions, the two [^{14}C]-labeled test substances were dissolved in methylene chloride, and isotopically diluted with unlabeled tribenuron methyl to their final specific activities (Table B.2.1, below). Aliquots of each dosing solution were radioassayed, and

analyzed for radiochemical purity by HPLC. The dosing solutions were then loaded into capsules, and the methylene chloride was allowed to evaporate. Five additional capsules were prepared for each [^{14}C]-test substance to conduct storage stability analysis. After preparation, the capsules were stored at -20°C until used. At the end of the dosing period, the extra capsules for each [^{14}C]-label were extracted and analyzed. The results of these analyses indicated that the [^{14}C]-test substances were stable in the capsules during dosing.

TABLE B.2.1. Test Material Characteristics

Chemical structure		
Radiolabel position	Triazine-2-^{14}C	Phenyl-U-^{14}C
Lot number	3562-163	3225-295
Radiochemical purity	>98%	>98%
Final specific activity	32.04 µCi/mg (71,100 dpm/µg)	16.85 µCi/mg (37,400 dpm/µg)

B.3. Sampling Information

Excreta were collected daily from each animal, and cage wash samples (1:1 water/methanol) were obtained at sacrifice (Table B.3.1, below). Eggs were collected twice daily from each hen, and separated into whites and yolks. All samples were pooled by dose group, and study day, and were immediately stored at -20°C at the testing facility.

At 6-8 hours after the final dose, the hens were sacrificed by CO_2 asphyxiation. The entire liver was collected from each hen, and equal portions of fat (composite of visceral, subcutaneous and muscle fat) and muscle (thigh and breast) were collected from each hen. The remaining carcass of each hen was kept frozen until the completion of the study. Tissue samples were pooled by dose group using equal amounts from each hen. All tissue samples were chopped, flash-frozen, and stored at -20°C at the testing facility. At the end of the in-life phase, the frozen samples were shipped on dry ice, by overnight courier, to the analytical laboratory, ABC Laboratories (in Columbia, MO).

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TABLE B.3.1 Sample Collection Information			
Eggs Collected	Excreta and Cage Wash Collected	Interval from Last Dose to Sacrifice	Tissues Harvested and Analyzed
Twice daily; normal production was one egg/hen/day.	Excreta - once daily. Cage wash - prior to initiation, and at sacrifice.	6-8 hours.	Fat, thigh muscle, breast muscle, liver, carcass.

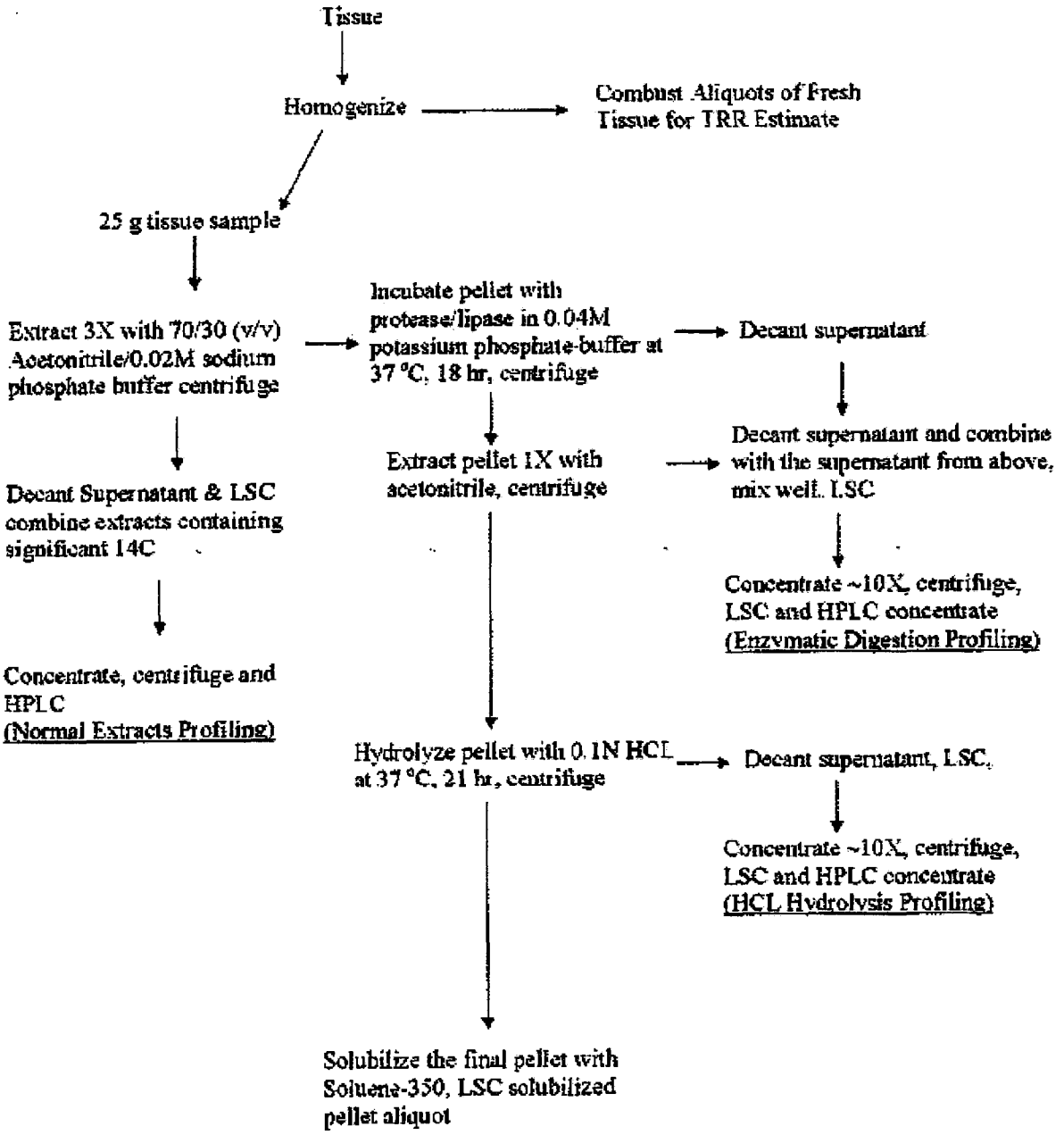
B.4. Identification/Characterization of Residues

B.4.1. Sample Handling, Preparation and Extraction

The pooled samples of each matrix were homogenized in liquid nitrogen. For radioassay, a single subsample of each matrix was then taken, and analyzed by combustion\LSC or solubilized for LSC. Triplicate subsamples of muscle, liver and fat, and composited samples of excreta, and egg whites and yolks were prepared for metabolite analysis. Equal amounts of excreta from Days 1-14 were pooled by dose group, and equal amounts of egg whites and yolks from Days 10-14 were pooled by matrix and dose group.

The general scheme for extraction of [^{14}C]-residues from tissues, and egg whites and yolks is shown in Figure B.4.1 (below). Samples were extracted 3-5 times with ACN/20mM sodium phosphate buffer (pH of roughly 7.5). The resulting extracts were combined by matrix, concentrated, and initially analyzed by LSC and HPLC. For samples of muscle, fat, liver and yolks, the remaining solids were suspended in potassium phosphate buffer, and digested by incubation with protease (muscle, liver and yolks) or lipase (fat) at 37°C for 18 hours. After incubation, the samples were extracted twice with ACN, and the resulting extracts were combined, radioassayed, and analyzed by HPLC. The remaining solids from egg yolks and fat were further extracted by treatment with 0.1N HCl at 37°C for 21 hours. The resulting hydrolysates were centrifuged, and the supernatants were adjusted to a pH of roughly 7, concentrated, and analyzed by HPLC. All extract fractions were stored at -20°C before HPLC analysis. The final PES fractions from each matrix were solubilized, and radioassayed by LSC.

FIGURE B.4.1 Extraction and Analysis Scheme for Tissue and Egg Samples.



B.4.2. Analytical Methodology

Radioactive residues in the various extract fractions from each matrix were initially profiled by HPLC, using a C_{18} column with a mobile phase gradient transitioning from 10 mM ammonium acetate in water to 100% ACN. The HPLC system was equipped with a UV detector, and an in-line radioactivity detector. Radioactive residues were quantified by LSC of the collected HPLC fractions. Residues were initially identified by comparison of their retention times with the retention times for standards. Including parent compound, a total of 22 reference standards were used for comparison with [^{14}C]-residue peaks (see Table C.3.1 and Appendix I).

The initial ACN/phosphate buffer extracts from excreta, liver, and egg white samples were used for further isolation and confirmation of metabolite identities. The extracts were cleaned up and fractionated by elution through C_{18} solid-phase extraction (SPE) columns. The resulting fractions were then concentrated, and analyzed by HPLC/MS, then compared to the reference standards.

C. RESULTS AND DISCUSSION

The methods used to conduct both the in-life and analytical phases of the study were adequate, and no unusual circumstances were noted during the study that would adversely affect the study's results.

Two groups of hens (5/group) were dosed orally via capsules, once a day, for 14 consecutive days with either [triazine-2-^{14}C]- or [phenyl-U-^{14}C]-tribenuron methyl at doses averaging 1.20 and 1.23 mg ai/hen/day, respectively. For the two [^{14}C]-labels, these dose levels were equivalent to 0.814 and 0.846 mg ai/kg body weight/day, or 11.6 and 11.5 ppm of tribenuron methyl in the diet.

The recovery of the administered dose was acceptable, averaging at least 95% of the dose. For both [^{14}C]-labels, 91.7-94.2% of the dose was recovered from the excreta, and cage wash (see Table C.2.1, below). For the [triazine-^{14}C]-label, 1.62% of the dose was recovered in edible tissues, and another 1.85% of the dose was recovered in the eggs. For the [phenyl-^{14}C]-label, 0.53% of the dose was recovered in edible tissues, and another 0.68% of the dose was recovered in the eggs.

For the [triazine-^{14}C]-label, TRR levels plateaued in egg whites within 5 days at 0.588 ppm, and in egg yolks within 8 days at 0.523 ppm (see Figure C.2.1). For the [phenyl-^{14}C]-label, TRR levels plateaued in egg whites within 2 days at 0.187 ppm, and in egg yolks within 10 days at 0.236 ppm. After roughly 10 days of dosing, levels of [^{14}C]-resdiues were similar in whites and yolks for each [^{14}C]-label, but residue levels in whites and yolks from eggs of the [triazine-^{14}C]-dosed hens were 2-3X higher than for the [phenyl-^{14}C]-dosed hens.

TRR levels in edible tissues were 0.956 ppm in liver, 0.545 ppm in muscle, and 0.161 ppm in fat from the [triazine-^{14}C]-dosed hens, and 0.663 ppm in liver, 0.135 ppm in muscle, and 0.055 ppm in fat from the [phenyl-^{14}C]-dosed hens. For the [triazine^{14}C]-dosed hens, TRR levels

were 1.4X higher in liver, and 3-4X higher in muscle and fat than for the [phenyl-^{14}C]-dosed hens.

For the [triazine-^{14}C]-dosed hens, the initial solvent extractions with ACN/phosphate buffer released 86.4-99.3% of the TRR from tissues and egg whites, and 64% of the TRR from egg yolks (see Table C.2.2.1, below). The subsequent enzymatic and mild acid hydrolyses released another 10.5-12.3% of the TRR from tissues, and 33.6% of the TRR from egg yolks. The remaining solids accounted for 0.7-2.5% of the TRR for all matrices. For the [phenyl-^{14}C]-dosed hens, the initial solvent extractions released 64.6-86% of the TRR from egg whites and tissues, and 32.1% of the TRR from egg yolks (see Table C.2.2.2, below). The subsequent enzymatic digestions released another 19.5-36.6% of the TRR from tissues and egg yolks, and the final mild acid hydrolysis released another 25% of the TRR from egg yolks. The remaining solids accounted for 5.4-14.0% of the TRR, with levels of radioactivity being <0.05 ppm in all matrices.

Although example chromatograms were provided from the HPLC analyses of all solvent fractions, the quantitative data associated with each analysis was not provided. Therefore, only the qualitative distribution of the various [^{14}C]-residues among the different extract fractions could be determined. The quantitative recovery of parent and the various metabolites was combined for all the extract fractions.

For the [triazine-^{14}C]-dosed hens, 78.3-98.1% of the TRR was identified in tissues and eggs (see Table C.2.3.1, below). Parent was a major [^{14}C]-residue, accounting for 12.7-32.5% of the TRR in muscle, fat, liver, and egg whites, but only 0.5% of the TRR in yolks. The concentration of parent was 0.074 ppm in egg whites, 0.003 ppm in yolks, 0.072 ppm in muscle, 0.052 ppm in fat, and 0.281 ppm in liver. In eggs and all tissues, the major triazine-derived metabolites were IN-A4098 (39.9-61.9% TRR) and IN-L5296 (9.0-17.4% TRR). An additional eight minor metabolites were identified, with each accounting for 0.3-4.2% of the TRR (0.002-0.033 ppm). One polar unknown (T4) was detected in egg yolks at 10.8% of the TRR (0.051 ppm). Minor amounts of Unknown T4 were also detected in muscle (1.4% TRR) and liver (0.6% TRR). In all three matrices T4 was released following enzymatic or mild acid treatment, suggesting that the unknown may be conjugated in tissues.

For the [phenyl-^{14}C]-dosed hens, 32.7-83.5% of the TRR was identified in eggs and tissues (see Table C.2.3.2, below). Parent was a major [^{14}C]-residue in tissues, accounting for 28.1-58.5% of the TRR; however, parent was not detected in egg whites, and accounted for only 1.1% of the TRR in yolks. The concentration of parent was 0.055 ppm in muscle, 0.032 ppm in fat, and 0.186 ppm in liver. The major phenyl-derived metabolites were IN-D5803 in muscle (19.6% TRR), liver (16.6% TRR), egg whites (42.7% TRR) and yolks (11% TRR), along with IN-00581 in egg whites (38.6% TRR) and yolks (18.5% TRR). An additional four minor metabolites were identified, with each accounting for 0.6-4.1% of the TRR (0.001-0.027 ppm). Three major polar unknowns (P2, P3 and P6) were detected in liver, each at 8.9-10.5% of the TRR, and Unknowns P2 and P3 were also major components in yolks at 9.0 and 20.4% of the TRR, respectively. Minor amounts of P3 and P6 were also detected in muscle (5.8% TRR) and fat (2.1% TRR), respectively. Unknown P6 was recovered primarily in the initial solvent

extracts; whereas Unknowns P2 and P3 were recovered primarily in the enzyme and acid hydrolysates, suggesting that these unknowns may be conjugates. Unknowns P3 and T4 may be the same unknown as they were found in the same tissues, had a similar retention time, and were both only released by enzyme and acid hydrolysis.

In addition to parent compound, a total of 16 metabolites were identified in extracts from excreta (see Table C.2.3.3, below). For the [triazine-^{14}C]-dosed hens, the major metabolites in excreta were IN-QKK48 (16.6% TRR), IN-GK521 (12.6% TRR), IN-R98905 (13.4% TRR) and IN-QHP91/IN-377309 (16.2% TRR). For the [phenyl-^{14}C]-dosed hens, the major metabolites in excreta were IN-QKK48 (16.5% TRR), IN-00581 (21.2% TRR) and IN-D5803 (22.8% TRR). The remaining metabolites each accounted for 1.1-8.4% of the TRR in excreta. Three minor unknowns (T4, P3 and P6) were also detected in excreta, and given the similar retention times for P3 and T4, these unknowns may be the same compound.

C.1. Storage Stability

Immediately following collection, all samples were stored at -20°C for 3.5-4.7 months prior to extraction, and extracts were stored at -20°C for another 1.6-2.6 months prior to initial HPLC analysis (see Table C.1). As [^{14}C]-residues were extracted and profiled within roughly 6 months of collection, storage stability data are not required to support this metabolism study. In addition, reanalysis of excreta extracts, initially analyzed after one month of storage, were reanalyzed after one year of storage. The profile of metabolites in excreta extracts showed no significant changes, indicating metabolites were stable in frozen storage in the sample extracts.

TABLE C.1 Summary of Storage Conditions

Matrix	Storage Temperature (°C)	Actual Storage Duration (Months)	Interval of Demonstrated Storage Stability (Months)
Egg White	-20	4.7	NR
Egg Yolk		4.7	8.1
Liver		4.7	7.5
Muscle		4.6	7.5
Fat		4.6	7.7
Excreta		3.5	NR

* Interval from collection to extraction for analysis. Extracts were stored 1.5-2.6 months prior to HPLC analysis.

C.2. Identification, Characterization, and Distribution of Residues

TABLE C.2.1a Total Radioactive Residues (TRR) in Eggs, Tissue and Excreta

Matrix	Collection Timing (Study Day)	Triazine-2-^{14}C		Phenyl-U-^{14}C	
		% AD[2]	ppm	% AD	ppm
Egg White	1	0.01	0.042	<0.01	0.019
	2	0.07	0.360	0.04	0.187
	3	0.08	0.433	0.03	0.173
	4	0.12	0.538	0.03	0.166
	5	0.13	0.588	0.03	0.179
	6	0.10	0.584	0.05	0.206
	7	0.12	0.570	0.04	0.183
	8	0.11	0.637	0.03	0.174
	9	0.12	0.572	0.04	0.188
	10	0.10	0.548	0.04	0.219
	11	0.12	0.515	0.04	0.205
	12	0.11	0.629	0.04	0.217
	13	0.11	0.537	0.04	0.205
	14	0.10	0.544	0.03	0.193
	Total (1-14 days)	1.39	--	0.49	--
	10-14 Day Composite	--	0.579	--	0.212
Egg Yolk	1	<0.01	0.003	<0.01	<0.001
	2	0.01	0.137	<0.01	0.023
	3	0.02	0.214	<0.01	0.046
	4	0.03	0.308	0.01	0.085
	5	0.03	0.380	0.01	0.120
	6	0.03	0.422	0.02	0.158
	7	0.04	0.445	0.02	0.183
	8	0.04	0.523	0.02	0.207
	9	0.05	0.504	0.02	0.227
	10	0.04	0.521	0.02	0.236
	11	0.05	0.495	0.02	0.246
	12	0.04	0.503	0.02	0.258
	13	0.05	0.488	0.02	0.246
	14	0.04	0.499	0.01	0.239
	Total (1-14 days)	0.46	--	0.19	--
	10-14 Day Composite	--	0.475	--	0.230
Liver	14	0.21	0.956	0.16	0.663
Muscle[3]	14	1.25	0.545	0.32	0.135
Fat[4]	14	0.16	0.161	0.05	0.055

TABLE C.2.1 Total Radioactive Residues (TRR) in Eggs, Tissue and Excreta

Matrix	Collection Timing Day (Study Day)	Triazine-2-^{14}C		Phenyl-UL-^{14}C	
		% AD[2]	ppm	% AD	ppm
Excreta (Cumulative)	1	70.04	--	73.80	--
	2	72.41	--	81.05	--
	3	79.50	--	83.50	--
	4	81.23	--	85.72	--
	5	84.10	--	85.56	--
	6	87.06	--	89.08	--
	7	88.35	--	90.48	--
	8	88.54	--	91.75	--
	9	90.52	--	92.51	--
	10	89.93	--	93.06	--
	11	90.45	--	92.95	--
	12	91.32	--	92.72	--
	13	92.13	--	93.66	--
	14	89.49	--	92.04	--
Cage Wash	14	2.17	--	2.15	--
Broken Eggs/Eggs in Oviduct	14	0.03	--	0.01	--
Total Recovery	--	95.16	--	95.41	--

1. Samples are pooled from the 5 hens in each dose group.
2. %ad = % Adusted Dose.
3. Muscle samples are composites of breast and thigh muscle.
4. Fat samples are composites of subcutaneous, visceral, and muscle fat.

FIGURE C.2.1 TRR in Egg Whites and Yolks from Hens Dosed with [^{14}C-Triazine]- or [^{14}C-Phenyl]-Tribenuron Methyl for 14 Days.

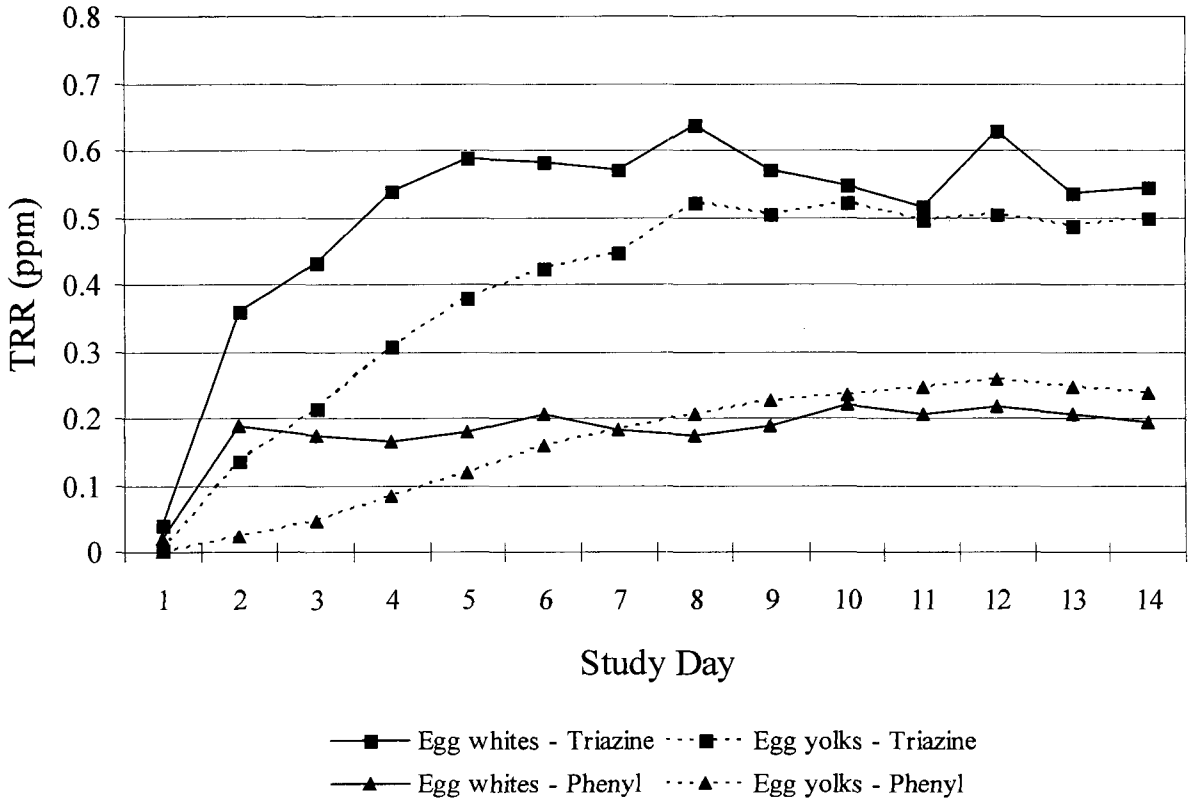


TABLE C.2.2.1 Extraction and Distribution of [^{14}C]-Residues in Eggs and Tissues of Hens Dosed with [Phenyl-2-^{14}C]-Tribenuron Methyl at a Level Equivalent to 10.6 ppm in the Diet[1]

Metabolite Fraction	Muscle		Fat		Liver		Egg Whites (10-14 day)		Egg Yolks (10-14 day)	
	TRR = 0.545 ppm		TRR = 0.161 ppm		TRR = 0.953 ppm		TRR = 0.579 ppm		TRR = 0.475 ppm	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
ACN/Buffer Extracts (HPLC analysis)	87.3	0.476	86.6	0.139	86.4	0.826	99.3	0.575	64.0	0.304
Tribenuron methyl	✓[2]		✓		✓		✓		✓	
IN-L9622	✓		✓		✓		✓		✓	
IN-A4098	✓		✓		✓		✓		✓	
IN-QHP91	✓				✓					
IN-L5296	✓		✓		✓		✓		✓	
IN-QKK48					✓					
IN-GK521					✓					
Protease/lipase treatment (HPLC analysis)	10.5	0.057	6.8	0.011	12.1	0.115			16.6	0.079
IN-A4098	✓		✓		✓				✓	
IN-L5296					✓					
IN-QHP91	✓									
Unknown T4	✓				✓				✓	
0.1N HCl extraction (HPLC analysis)			5.5	0.009					17.0	0.081
IN-L9622									✓	
T-4									✓	
IN-A4098									✓	
IN-QHP91									✓	
Unextractable residues	2.2	0.012	1.2	0.002	1.6	0.015	0.7	0.004	2.5	0.012

1. Shading indicates that the extraction step was not conducted for the matrix in question.
2. The quantitative data for the [^{14}C]-residues in individual extract fractions was not provided. The check mark indicates what compounds were detected in each fraction, based on the chromatographic data.

TABLE C.2.2.2 Extraction and Distribution of [^{14}C]-Residues in Eggs and Tissues of Hens Dosed with Phenyl-U-[^{14}C]-Tribenuron Methyl at a Level Equivalent to 11.5 ppm in the Diet

Metabolite Fraction	Muscle		Fat		Liver		Egg Whites (10-14 days)		Egg Yolks (10-14 days)	
	TRR = 0.155 ppm		TRR = 0.055 ppm		TRR = 0.663 ppm		TRR = 0.212 ppm		TRR = 0.230 ppm	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
ACN/Buffer Extracts (HPLC analysis)	69.1	0.093	71.5	0.040	64.6	0.429	86.0	0.182	32.1	0.074
Tribenuron methyl	✓ [2]		✓		✓		✓		✓	
IN-D5119					✓				✓	
IN-00581	✓		✓		✓		✓		✓	
IN-R9803	✓		✓							
DPX-T6376					✓		✓			
IN-GK521			✓							
IN-D5803	✓		✓		✓				✓	
Unknown P2					✓				✓	
Unknown P6			✓		✓					
Protease/lipase treatment (HPLC analysis)	25.4	0.034	19.5	0.011	30.0	0.199			36.6	0.084
IN-D5119					✓					
IN-00581	✓				✓				✓	
IN-D5803	✓				✓					
Metabolite P2					✓				✓	
Metabolite P3	✓				✓				✓	
Metabolite P6					✓					
0.1N HCl extraction (HPLC analysis)									25.0	0.058
IN-D5119									✓	
IN-00581									✓	
IN-D5803									✓	
Metabolite P3									✓	
Unextractable residues	5.5	0.007	8.9	0.005	5.4	0.036	14.0	0.030	6.2	0.014

1. Shading indicates that the extraction step was not conducted for the matrix in question.
2. The quantitative data for the [^{14}C]-residues in individual extract fractions was not provided. The check mark indicates what compounds were detected in each fraction, based on the chromatographic data.

TABLE C2.3.1 Summary of Characterization and Identification of ^{14}C Residues in Eggs and Tissues from Laying Hens Dosed for 14 Days with Tribenuron-^{14}C-Triazine-2- at Maximum Level Equivalent to 0.16 ppm in the Diet

Components and Fractions	Tissue		Fat		Liver		Egg White (0-24 day)		Egg Yolk (0-14 day)	
	TRR = 0.545 ppm		TRR = 0.161 ppm		TRR = 0.956 ppm		TRR = 0.579 ppm		TRR = 0.476 ppm	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
Tribenuron methyl	13.2	0.072	32.5	0.052	29.4	0.281	12.7	0.074	0.5	0.003
DPX-T6376	ND [1]	--	ND	--	0.5	0.005	ND	--	ND	--
IN-GK521	0.3	0.002	ND	--	3.5	0.033	0.4	0.002	ND	--
IN-QKK48	0.5	0.003	ND	--	1.5	0.014	0.7	0.004	ND	--
IN-B5528	0.4	0.002	ND	--	0.3	0.003	0.3	0.002	0.8	0.004
IN-R9805	0.3	0.002	ND	--	0.5	0.005	0.4	0.002	0.7	0.003
IN-L9622	3.4	0.019	1.2	0.002	2.1	0.020	4.2	0.024	2.9	0.014
IN-A4098	61.9	0.338	39.9	0.064	42.0	0.402	60.5	0.350	61.9	0.294
IN-QHP91/IN-37739	1.3	0.007	ND	--	1.0	0.010	1.5	0.008	1.3	0.006
IN-L5296	9.0	0.049	12.4	0.020	11.6	0.111	17.4	0.101	10.2	0.049
Total identified	**90.3**	**0.494**	**86.0**	**0.138**	**92.4**	**0.884**	**98.1**	**0.567**	**78.3**	**0.373**
Unknown T4 [2]	1.4	0.007	ND	--	0.6	0.006	ND	--	10.8	0.051
Minor HPLC peaks and unresolved radioactivity [3]	4.7	0.026	4.8	0.008	5.0	0.048	0.6	0.004	1.4	0.007
Minor unanalyzed fractions	NA [4]	--	6.2	0.010	0.4	0.004	0.7	0.004	0.3	0.002
Procedural losses [5]	1.3	0.007	1.9	0.003	1.2	0.012	NA	--	6.7	0.032
Total characterized	97.7	0.534	98.9	0.159	99.6	0.954	99.4	0.575	97.5	0.465
Total extractable	97.8	0.533	98.8	0.159	98.4	0.942	99.3	0.575	97.5	0.463
Unextractable (PES) [6]	2.2	0.012	1.2	0.002	1.6	0.015	0.7	0.004	2.5	0.012
Accountability [7]	100		100		100		100		100	

1. ND = Not Detected.
2. Unknown T4 was a polar component with a retention time of 13.9 minutes. As it was released only by hydrolysis, it appears to be a conjugated metabolite.
3. Includes minor HPLC peaks accounting for ≤2.4% of the TRR (≤0.016 ppm), and unresolved radioactivity above background.
4. NA = Not Applicable.
5. Minor losses which occurred during fractionation and concentration procedures.
6. Post-extraction solids (PES), residues remaining after exhaustive extractions.
7. Accountability = (total extractable + total unextractable).

TABLE C.2.3.2 Summary of Characterization and Identification of [^{14}C]-Residues in Eggs and Tissues from Laying Hens Dosed for 14 Days with [Phenyl-U-^{14}C]-Tribenuron Methyl at a Level Equivalent to 11.5 ppm in the Diet

Compounds and Fractions	Muscle		Fat		Liver		Egg White (10-14 day)		Egg Yolk (10-14 day)	
	TRR = 0.135 ppm		TRR = 0.155 ppm		TRR = 0.665 ppm		TRR = 0.212 ppm		TRR = 0.230 ppm	
	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm	%TRR	ppm
Tribenuron methyl	40.4	0.055	58.5	0.032	28.1	0.186	ND [1]	--	1.1	0.003
DPX-T6376	ND	--	ND	--	0.6	0.004	2.2	0.005	ND	--
IN-GK521	ND	--	1.2	0.001	1.3	0.008	ND	--	ND	--
IN-R9803	2.8	0.004	1.3	0.001	ND	--	ND	--	ND	--
IN-D5119	ND	--	ND	--	4.1	0.027	ND	--	2.1	0.005
IN-00581	5.1	0.007	3.7	0.002	4.9	0.032	38.6	0.082	18.5	0.042
IN-D5803	19.6	0.026	2.1	0.001	16.6	0.110	42.7	0.090	11.0	0.025
Total identified	**67.9**	**0.092**	**66.8**	**0.037**	**55.6**	**0.367**	**83.5**	**0.177**	**32.7**	**0.075**
Unknown P2 [2]	ND	--	ND	--	8.9	0.059	ND	--	9.0	0.021
Unknown P3 [2]	5.8	0.008	ND	--	10.3	0.068	ND	--	20.4	0.047
Unknown P6 [2]	ND	--	2.1	0.001	10.5	0.070	ND	--	ND	--
Minor HPLC peaks and unresolved radioactivity [3]	16.5	0.021	0.6	<0.001	6.1	0.041	2.1	0.004	6.1	0.014
Minor unanalyzed fractions	1.1	0.001	15.5	0.009	0.5	0.004	0.5	0.001	1.1	0.002
Procedural losses [4]	3.3	0.004	6.2	0.003	2.7	0.018	NA	--	24.5	0.057
Total characterized	94.6	0.126	91.2	0.05	94.6	0.627	86.1	0.182	93.8	0.216
Total extractable	94.5	0.128	91.1	0.050	94.6	0.627	86.0	0.182	93.8	0.216
Unextractable (PES) [5]	5.5	0.007	8.9	0.005	5.4	0.036	14.0	0.030	6.2	0.014
Accountability [6]	100		100		100		100		100	

1. ND = Not Detected.
2. Unknowns P2, P3 and P6 were polar components with retention times of 12.2, 13.6 and 18.4 minutes, respectively. Unknowns P2 and P3 appear to be conjugated residues, as they were recovered primarily in the enzyme and acid hydrolysates. In addition, P3 may be the same unknown as T4.
3. Includes minor HPLC peaks accounting for ≤1.3% of the TRR (≤0.007 ppm), and unresolved radioactivity above background.
4. Minor losses which occurred during fractionation and concentration procedures.
5. Post-extraction solids (PES), residues remaining after exhaustive extractions.
6. Accountability = (total extractable + total unextractable).

TABLE C.2.3.3 Summary of Characterization and Identification of ^{14}C-Residues in Excreta from Hens Dosed Orally with ^{14}C-Tribenuron Methyl at Levels Equivalent to 11.5 ppm in the Diet

Compound	% TRR	
	^{14}C-Triazine (TRR = 5513 ppm)	^{14}C-Phenyl (TRR = 6619 ppm)
Tribenuron methyl	1.7	1.7
IN-GN815/IN-B5685	1.1	2.0
IN-QKK48	16.6	16.5
IN-GK521	12.6	8.4
DPX-T6376	6.8	6.4
IN-R9803	1.1	3.1
IN-B5528	5.8	ND[2]
IN-R9805	13.4	ND
IN-L9622	1.7	ND
IN-A4098	6.5	ND
IN-QHP91/IN-37739	16.2	ND
IN-L5296	4.6	ND
IN-D5119	ND	7.5
IN-00581	ND	21.2
IN-D5803	ND	22.8
Total identified	**88.1**	**89.6**
Unknown T4 (RT[3] = 14 min)	5.0	ND
Unknown P3 (RT = 14 min)	ND	1.7
Unknown P6 (RT = 17.7 min)	ND	0.8
Total characterized	93.1	92.1
Total extractable	99.2	98.7
Unextractable (PES)[4]	0.8	1.3
Accountability[5]	100	100

1. Excreta samples were pooled from Study Days 1-14.
2. ND = not detected.
3. RT = Retention Time.
4. Post-extraction solids (PES); residues remaining after exhaustive extractions.
5. Accountability = (total extractable + total unextractable).

C.3. Proposed Metabolic Profile

Based on the compounds identified, the metabolism of tribenuron methyl in poultry initially involves *O*-demethylation of the triazine ring to form IN-GK521, *N*-demethylation to form DPX-T6376, or hydroxylation of the triazine methyl moiety to form IN-QKK48 (Figure C.3.1, below). Hydrolysis of the methyl ester of tribenuron methyl, and IN-GK521 occurred to a small extent to form IN-R9803 and IN-GN815, respectively. Sulfonylurea bridge hydrolysis of tribenuron methyl, IN-GK521, IN-QKK48, or DPX-T6376 releases the common metabolites IN-D5803 from the phenyl radiolabel, and IN-L5296, IN-R9805, IN-QHP91 or IN-A4098 from the triazine radiolabel. The IN-D5803 metabolite is hydrolyzed to the carboxylic acid, IN-D5119, or cyclized to IN-00581. IN-D5119 could also be derived from sulfonyl urea bridge cleavage of IN-R9803 and IN-GN815. The triazine-labeled metabolite IN-37739 was the result of either

hydroxylation on the *N*-methyl moiety of parent, followed by bridge hydrolysis, or hydroxylation of IN-L5296 directly. The metabolites IN-L5296 and IN-QHP91 can also be *N*-demethylated to form IN-A4098 and IN-L9622. Metabolites IN-L5296 and IN-A4098 can be *O*- demethylated to IN-R9805 and IN-B5528, respectively. Finally, IN-B5685 was a minor metabolite which probably originated from DPX-T6376.

FIGURE C.3.1 Proposed Metabolic Profile of Tribenuron Methyl in Laying Hens.

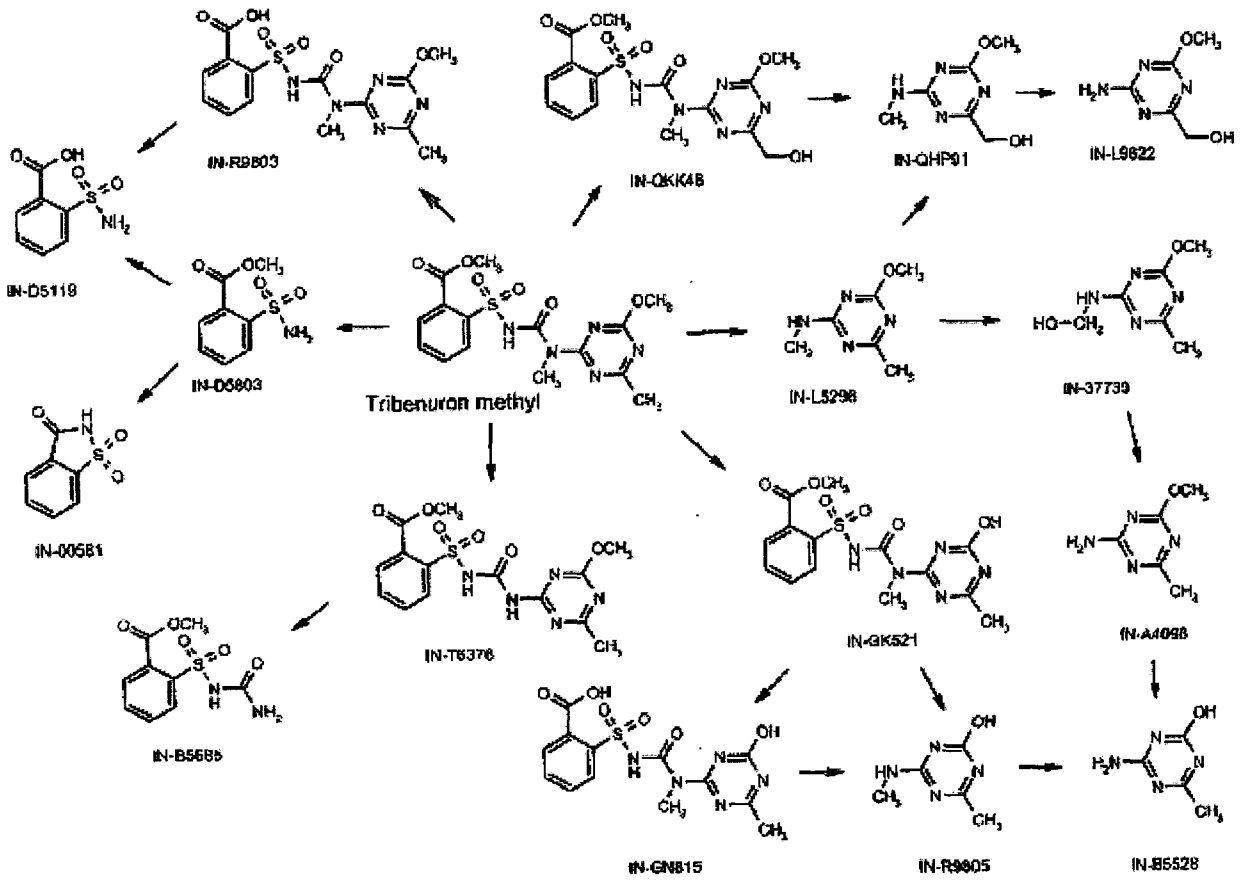


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TABLE C3.1 Identification of Compounds from Poultry Metabolism Study

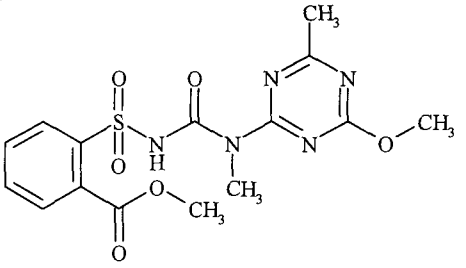
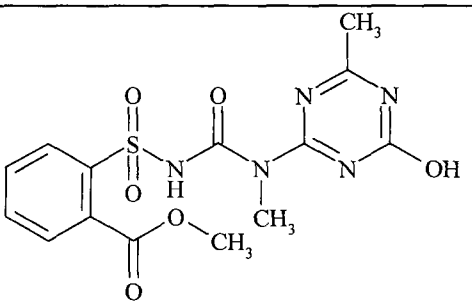
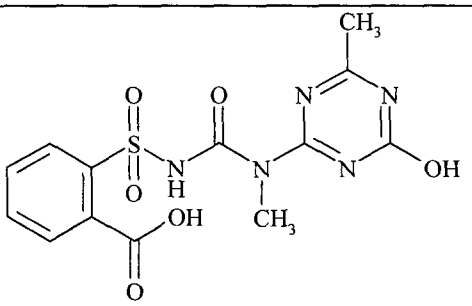
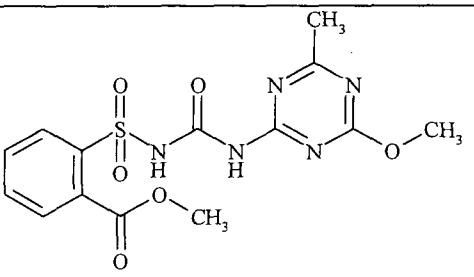
Common Name or Designation [Company Code]	Chemical Name	Chemical Structure	Matrices
Tribenuron methyl [DPX-L5300]	Methyl-2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino] carbonyl]amino]sulfonyl] benzoate		Eggs Muscle Liver Fat Excreta
IN-GK521	Methyl 2-[[[[(4-hydroxy-6-methyl-1,3,5-triazin-2-yl) methylamino] carbonyl] amino]sulfonyl] benzoate		Eggs Muscle Liver Fat Excreta
IN-GN815	Methyl 2-[[[[(4-hydroxy-6-methyl-1,3,5-triazin-2-yl) methylamino] carbonyl] amino] sulfonyl] benzoic acid		Excreta
IN-T6376 [DPX-T6376]	Methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino] sulfonyl] benzoate		Eggs Liver Excreta

TABLE C.3.1 Identification of Compounds from Poultry Metabolism Study

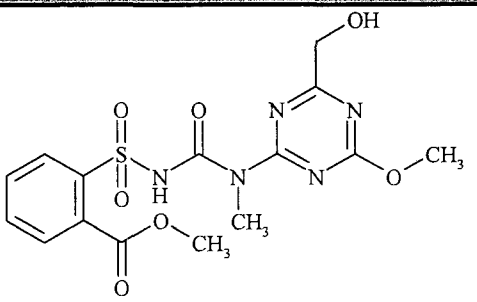
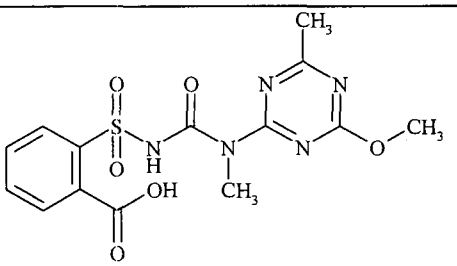
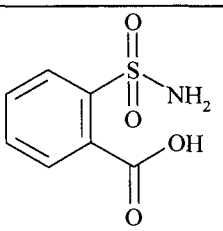
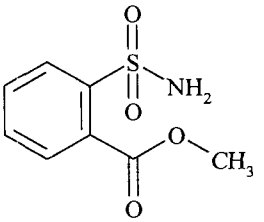
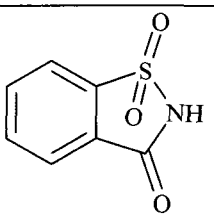
Common Name or Designation [Company Code]	Chemical Name	Chemical Structure	Matrices
IN-QKK48	Methyl 2-[[[[(4-hydroxymethyl-6-methoxy-1,3,5-triazin-2-yl) methylamino] carbonyl] amino] sulfonyl] benzoate		Eggs Muscle Liver Excreta
IN-R9803	2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino] sulfonyl]benzoic acid		Muscle Fat Excreta
IN-D5119	2-(aminosulfonyl) benzoate		Eggs Liver Excreta
IN-D5803	Methyl 2-(amino sulfonyl) benzoate		Eggs Muscle Liver Fat Excreta
IN-00581	1, 2-benzothiazol-3(2H)-one, 1,1-dioxide		Eggs Muscle Liver Fat Excreta

TABLE C.8.1 Identification of Compounds from Poultry Metabolism Study

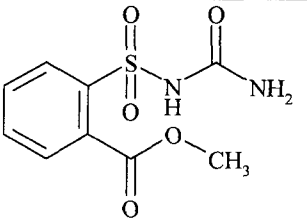
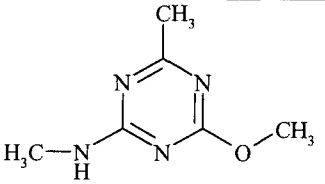
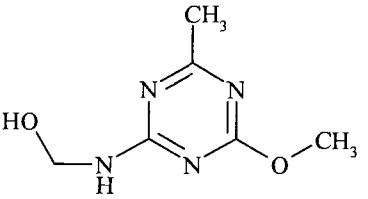
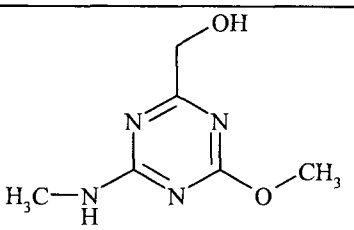
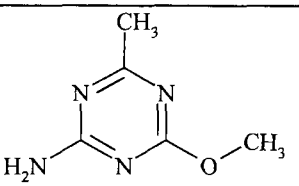
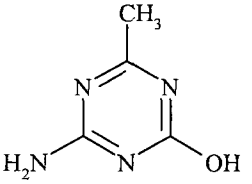
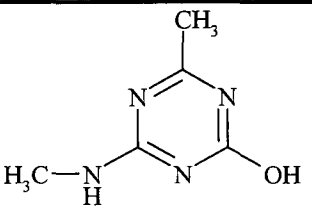
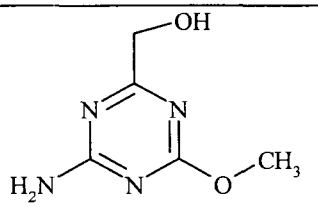
Common Name or Designation (Company Code)	Chemical Name	Chemical Structure	Matrices
IN-B5685 Sulfonamide urea metabolite	Methyl 2-[[(aminocarbonyl)amino] sulfonyl]benzoate		Excreta
IN-L5296 Triazine amine	4-methoxy-N,56-dimethyl-1,3,5-triazin-2-amine		Excreta
IN-37739	[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]methanol		Eggs Muscle Liver Excreta
IN-QHP91	4-methoxy-6-(methylamino)-1,3,5 triazine-2-methanol		Eggs Muscle Liver Excreta
IN-A4098 N-Demethyl triazine amine	4-methoxy-6-methyl-1,3,5-triazin-2-amine		Eggs Muscle Liver Fat Excreta
IN-B5528	4-Amino-6-methyl-1,3,5-triazin-2-ol		Eggs Muscle Liver Excreta

TABLE C.3.1 Identification of Compounds from Poultry Metabolism Study

Common Name or Designation / Company Code	Chemical Name	Chemical Structure	Matrices
IN-R9805 O-Demethyl triazine amine	4-methyl-6-(methylamino)-1,3,5-triazin-2-ol		Eggs Muscle Liver Excreta
IN-L9622	4-amino-6-methoxy-1,3,5-triazine-2-methanol		Eggs Muscle Liver Fat Excreta

D. CONCLUSION

The [^{14}C]-tribenuron methyl poultry metabolism is adequate. In addition to parent compound, 13 metabolites were identified in eggs and tissues, and another 3 metabolites were identified only in excreta. Parent was a major residue for both [^{14}C]-labels, accounting for 13.2-58.5% of the TRR in tissues, and 12.7% of the TRR in egg whites. Besides parent, the major triazine-derived residues in eggs and tissues were IN-A4098 (39.9-61.9% TRR) and IN-L5296 (9.0-17.4% TRR). The major benzyl-derived metabolites were IN-D5803 (2.1-42.7% TRR) in eggs and tissues, and IN-00581 (18.5-38.6% TRR) in egg whites and yolks. The remaining metabolites were each present in eggs and tissues at ≤5.1% of the TRR. Several unknowns (T4, P2, P3 and P6) were detected in liver and egg yolks at ≥10% of the TRR. However, these unknowns are relatively polar compounds, and three of the unknowns (T4, P2, and P3) appear to be conjugated residues, as they were recovered primarily in hydrolysate fractions.

Based upon the metabolite prolife, and the relative abundance of the various metabolites in eggs and tissues, the major route of metabolism for tribenuron methyl in poultry appears to involve hydrolytic cleavage of the sulfonyl urea bridge, followed by demethylation and/or hydroxylation of the resulting triazine moiety, and hydrolysis or cyclization of the resulting benzyl moiety.

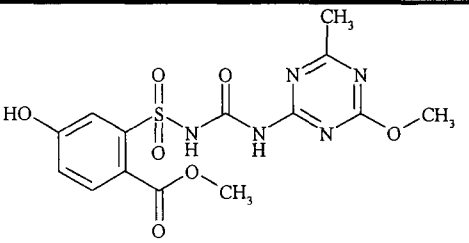
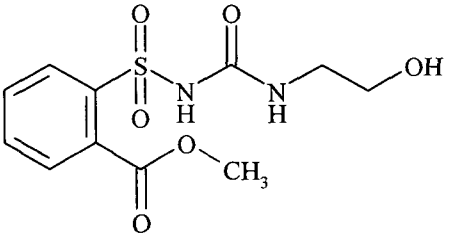
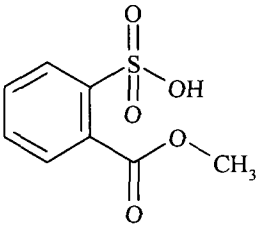
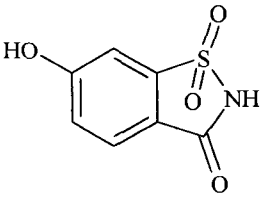
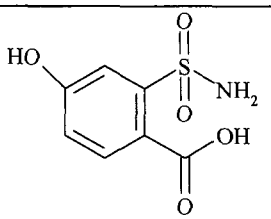
E. REFERENCES

None.

F. DOCUMENT TRACKING

RDI: William T. Drew (21 August 2009); John Redden (9 September 2009)
Petition Numbers: 8F7432 and 8F7441
DP Barcodes: 361306, 361307, 361308
PC Code: 128887

APPENDIX I. Chemical Names and Structures of Additional Reference Standards Used in Poultry Metabolism Study

Designation [Common Name]	Chemical name	Chemical structure
IN-G7460	Methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino] carbonyl] amino] sulfonyl] 4-hydroxybenzoate	
IN-QPR76	Benzoic acid, 2-[[[[(2-hydroxyethyl) amino] carbonyl] amino] sulfonyl]-, methyl ester	
IN-QRC26	Benzoic acid, 2-sulfino-, 1-methyl ester	
IN-F8174 [6-Hydroxy saccharin]	1, 2-benzothiazol-3(2H)-one, 6-hydroxy-, 1,1-dioxide	
IN-G7462	Methyl 2-(aminosulfonyl)-4-hydroxybenzoate	

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R176720

Chemical Name: Tribenuron

PC Code: 128887
HED File Code: 51100 RD Chemistry Reviews
Memo Date: 9/9/2009
File ID: 00000000
Accession #: 000-00-0130

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9/29/2009