

Metaflumizone

Summary of Analytical Chemistry and Residue Data

DP#: 345540



**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**  
WASHINGTON, D.C. 20460

OFFICE OF  
PREVENTION, PESTICIDES  
AND TOXIC SUBSTANCES

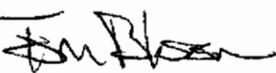
**MEMORANDUM**

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

**Date:** 26-January-2010

**Subject:** **Metaflumizone.** Section 3 Registration for Application of Metaflumizone to Citrus Fruits, Grapes, and Tree Nuts. Summary of Analytical Chemistry and Residue Data. PP#7F7260.

<b>PC Code:</b> 281250 (E Isomer); 281251 (Z isomer)	<b>DP Barcode:</b> D345540
<b>Decision No.:</b> 384160	<b>Registration No.:</b> 7969-###
<b>Petition No.:</b> 7F7260	<b>Regulatory Action:</b> Section 3
<b>Risk Assessment Type:</b> not available	<b>Case No.:</b> none
<b>TXR No.:</b> not available	<b>CAS No.:</b> 139968-49-3
<b>MRID Nos:</b> 47235701, 47235702, and 47235703	<b>40 CFR:</b> 180.###

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This document was originally prepared under contract by Dynamac Corporation (2275 Research Blvd, Suite 300; Rockville, MD 20850; submitted 02/25/2008). The document has been reviewed by the HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

*Received in RDC  
2/25/2010  
EJC*

## Executive Summary

**Background:** Metaflumizone (2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide; E and Z isomers) is a semicarbazone insecticide which blocks the sodium channel and inhibits nerve impulses leading to inhibited feeding and paralysis in susceptible insects (Lepidoptera and Coleoptera). The E and Z isomers are typically present at an E:Z ratio of >9:1.

BASF is proposing application of metaflumizone to citrus fruits, grapes, and tree nuts and proposed the establishment of the following permanent tolerances for the combined residues of metaflumizone (E and Z isomers): Citrus Fruits, Group 10 - 0.01 ppm; Tree Nuts, Group 14 - 0.01 ppm; Grapes, table - 0.01 ppm; and Grapes, wine - 0.01 ppm.

**Proposed Use:** The petitioner is proposing application of Altrevin™ Fire Ant Bait Insecticide (EPA File Symbol No. 7969-###) to citrus fruits, grapes, and tree nuts for the control of fire ants. Altrevin™ is a granular (G) formulation containing 0.063% active ingredient and is proposed for spot or broadcast soil applications of ant mounds with a preharvest interval (PHI) of 5 days (see Table 3; 4 x 0.001 lb ai/acre; retreatment interval (RTI) = 4 weeks). The label also includes directions for use in orchards and nurseries containing field- or container-grown nonbearing stone and pome fruit trees (4 x 0.001 lb ai/acre; application up to one year before the first harvest). **HED requests that the petitioner list the crops for each crop group as defined in 40 CFR 180.41 and eliminate the "including but not limited to" phrase. A revised Section B is requested.**

**Nature of the Residue - Plants and Livestock:** The nature of the residue in plants and livestock is adequately understood based on acceptable metabolism studies with cabbage, cotton, tomato, goat, and hen (see HED risk assessment document D304496 (R. Mitkus *et al.*, 24-Jan-2006)). HED concluded that the residue of concern in plants, for tolerance enforcement and risk assessment, are metaflumizone (E and Z isomers) and the metabolite M320I04; this decision is to be reevaluated upon submission of the additional information concerning the cabbage and cotton metabolism studies (see attachment 2 for structures). The residues of concern for tolerance expression and risk assessment for all livestock commodities, excluding ruminant liver, are metaflumizone (E and Z isomers). For ruminant liver, the residues of concern for tolerance expression are metaflumizone (E and Z isomers), and the residues of concern for risk assessment are metaflumizone (E and Z isomers) and M320I28. These decisions are to be reevaluated if the livestock dietary burden increases significantly.

**Nature/Magnitude of the Residue - Rotational Crops:** Citrus fruits, grapes, and tree nuts are typically not rotated; therefore, data pertaining to rotational crops are not required to support the proposed uses.

**Magnitude of the Residue - Plants:** The submitted citrus fruit, grape, and tree nut magnitude of the residue studies are adequate pending submission of supporting storage stability data. The field trials were conducted according to the proposed use patterns and there was adequate geographic representation. Residues of metaflumizone (E and Z isomers) and M320I04 were <LOQ (limit of quantitation) in/on all samples of citrus fruit, grape, tree nutmeat, and almond hulls harvested 5 days following a single soil application of the test formulation at 0.004 lb

ai/acre (4x/1x the maximum proposed single/seasonal application rate). The submitted data will support tolerances for the combined residues of metaflumizone (E and Z isomers) and the metabolite M320I04 (expressed as parent) in/on citrus fruit, grape, tree nuts, and almond hulls at the combined LOQ of 0.04 ppm. **A revised Section F is requested.**

The submitted grape and orange processing studies are adequate pending submission of supporting storage stability data. Residues of metaflumizone (E and Z isomers) and M320I04 were <LOQ in/on the orange and grape raw agricultural commodity (RAC) and orange oil following application at 5x the proposed rate. Processing data for the grape processed commodities and the remaining orange processed commodities were not provided and are unnecessary since residues were <LOQ in/on the RAC following treatment at 5x. The data indicate that no tolerances are needed for the processed commodities of grape or citrus fruit.

There are no Canadian, Mexican, or Codex Maximum Residue Limits (MRLs) established for residues of metaflumizone. Therefore, harmonization is not an issue for this petition. Based on the submitted residue data and low application rate, HED concludes that application to non-bearing stone and pome fruit trees (application within 1 year of harvest is prohibited) may be considered on non-food use

**Magnitude of the Residue - Livestock:** Considering the proposed/registered uses, the only feedstuffs are almond hulls and dried citrus pulp which may be fed to cattle (no poultry or hog feed commodities). Based on the revised Table 1, the maximum reasonably balanced diet (MRBD) for beef and dairy cattle is 0.004 ppm; based on these dietary burdens and the previously reviewed cattle feeding study (D308394, T. Bloem, 30-Nov-2005), HED concludes that livestock tolerances are unnecessary.

**Analytical Methods:** HED previously determined that the BASF liquid chromatograph/mass spectrometer/mass spectrometer (LC/MS/MS) Method 531/0 is adequate for tolerance enforcement and forwarded this method to the Food and Drug Administration (FDA; D308394, T. Bloem, 30-Nov-2005; D328915, T. Bloem, 17-May-2006). Citrus, grape, and tree nut samples from the field trial and processing studies were analyzed for residues of metaflumizone (E and Z isomers; LOQ = 0.01 ppm) and M320I04 (LOQ = 0.018 ppm) using BASF method 531/0. Based on the adequate validation data submitted with the field trial and processing studies, HED concludes that the current enforcement method is suitable for enforcement of the tolerances associated with the current petition.

**Multiresidue Methods:** Acceptable multiresidue methods testing data have previously been submitted; the multiresidue methods are not appropriate for quantifying metaflumizone residues. These data were forwarded to the Food and Drug Administration (FDA; D323538, T. Bloem, 16-Nov-2005).

**Recommendations:** Pending submission of revised Sections B and F and submission of analytical reference standards to the EPA National Pesticide Standards Repository, there are no residue chemistry issues that would preclude granting conditional registration for the requested uses of metaflumizone. In conjunction with this registration, the residue chemistry database supports the establishment of the tolerances listed below with the tolerance expression, commodity definitions, and numerical tolerances described as follows (a human-health risk assessment will be prepared as a separate document):

Tolerances are established for residues of the insecticide metaflumizone, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only the sum of metaflumizone (E and Z isomers; 2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide) and its metabolite 4-{2-oxo-2-[3-(trifluoromethyl)phenyl]ethyl}-benzoxazole, calculated as the stoichiometric equivalent of metaflumizone, in or on the following commodities: Fruit, citrus, group 10 - 0.04 ppm; Nut, tree, group 14 - 0.04 ppm; Almond, hulls - 0.04 ppm; and Grape - 0.04 ppm.

The conditional registration may be made unconditional pending adequate resolution of the following issues:

- Cabbage metabolism study (46264326.der.wpd) - Information pertaining to sample extraction and analysis dates is required; if the interval from harvest to analysis is greater than the currently validated interval, then additional storage stability data will also be necessary.
- Cotton metabolism study (46264324.der.wpd) - Individual concentrations of the unknowns should be reported; if any unknown comprises >10% of the total radioactive residue (TRR), then further characterization/ identification procedures may be required (based on these data additional residues may be included for risk assessment).
- Storage stability data - To support the subject field trial and processing studies, the following storage stability data are required which demonstrate the stability of metaflumizone (E and Z isomers) and M320I04: grapes - 4.8 months; citrus fruit - 5.6 months; almond hulls - 6.5 months; and almond nutmeat - 5.8 months.

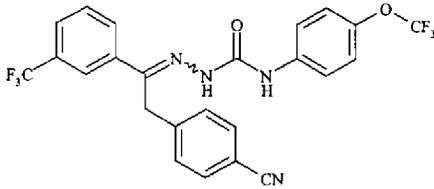
Metaflumizone

Summary of Analytical Chemistry and Residue Data

DP#: 345540

## Background

The chemical structure and nomenclature of metaflumizone and the physicochemical properties of the technical grade of metaflumizone are presented in Tables 1 and 2.

Chemical structure	
Common name	Metaflumizone
Company experimental name	BAS 320 I
IUPAC name	(E)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-4-(trifluoromethoxy)carbanilohydrazide
CAS name	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide
CAS registry number	139968-49-3
End-use product (EP)	Altrevin Fire Ant Bait Insecticide (0.063% G formulation; EPA Reg. No. 7969-###)

Melting point	Two melting points observed at approximately 127 °C and 186 °C.	MRID 46264204	
pH	6.48 at 25 °C (1% aqueous suspension)	MRID 46264524	
Density (20 °C)	1.461 g/cm <sup>3</sup>	MRID 46264204	
Water solubility (20 °C)	D.I. water pH 5 pH 7 pH 9	1.79 µg/L 1.35 µg/L 1.81 µg/L 1.73 µg/L	MRID 46264208
Solvent solubility (20 °C)	Acetone Acetonitrile DCM EtOAc Heptane Methanol Toluene	142.7 mg/L 60.3 mg/L 92.7 mg/L 159.7 mg/L 0.0084 mg/L 13.95 mg/L 3.96 mg/L	MRID 46264212
Vapor pressure	$1.24 \times 10^{-8}$ Pa at 20 °C	MRID 46264206	
Dissociation constant, pK <sub>a</sub>	None in pH range 2-12	MRID 46264217	
Octanol/water partition coefficient, Log(K <sub>OW</sub> )	Log P <sub>OW</sub> = 5.1 (Z isomer) Log P <sub>OW</sub> = 4.4 (E isomer)	MRID 46264213	
UV/visible absorption spectrum	Molar absorptivity: $3.81 \times 10^4$ L/Mcm at 234 nm; $1.93 \times 10^4$ L/Mcm at 280 nm.	MRID 46264207	

**860.1200 Directions for Use**

The petitioner is proposing application of Altrevin™ Fire Ant Bait Insecticide (EPA File Symbol No. 7969-###) to citrus fruits, grapes, and tree nuts for the control of fire ants. Altrevin™ is a granular (G) formulation containing 0.063% active ingredient and is proposed for spot or broadcast soil applications of ant mounds with a PHI of 5 days (see Table 3). The label also includes directions for use in orchards and nurseries containing field- or container-grown nonbearing stone and pome fruit trees. **On page 3 of the label, HED requests that the petitioner list the crops for each crop group as defined in 40 CFR 180.41 and eliminate the "including but not limited to" phrase. A revised Section B is requested.**

Table 3: Summary of Proposed Directions for Metaflumizone.						
Applic. Timing; Type; and Equip.	Formulation [EPA Reg. No.]	App. Rate	Max. No. App. per Season	Max. Seasonal App. Rate	PHI (days)	Use Directions and Limitations
<b>Citrus trees (citrus and <i>Fortunella</i> spp.):</b> including but not limited to orange (sweet, sour), lemon, lime, grapefruit, citrus hybrids (chironja, tangelo, tangor), kumquat, Mandarin (tangerine), pummelo, and Satsuma mandarin; <b>Nut trees:</b> including, but not limited to almond, beech nut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert, hickory nut, macadamia nut, pecan, and walnut; <b>and Grape vineyards; and orchards and nurseries containing field- or container-grown nonbearing stone and pome fruit trees</b>						
Postemergence; Broadcast; Ground	0.063% G [7969-###]	0.0006-0.001 lb ai/acre	4	0.004 lb ai/acre	5 <sup>1</sup>	Broadcast applications are to be made in areas having a mound density of at least 1 mound per 2,000 square feet. Otherwise, individual mound spot treatments are to be made (see below). A minimum RTI of 4 weeks is proposed.
Postemergence; Spot; Ground	0.063% G [7969-###]	0.00004-0.00008 lb ai/mound; not to exceed 0.001 lb ai/acre	not indicated	0.004 lb ai/acre	5 <sup>1</sup>	Spot applications are to be made in areas having a mound density of less than 1 mound per 2,000 square feet. Otherwise, broadcast applications are to be made (see above). A minimum RTI of 4 weeks is proposed.

<sup>1</sup> Application to non-bearing pome and stone fruit trees is permitted up to 1-year before first harvest.

### 860.1300 Nature of the Residue - Plants

No plant metabolism studies were submitted with this petition. Cabbage (4 x 0.25 lb ai/acre), cotton (6 x 0.3 lb ai/acre), and tomato (6 x ~0.3 lb ai/acre) metabolism have been previously submitted and reviewed. These studies were conducted with uniformly ring-labeled [benzotrile-<sup>14</sup>C]metaflumizone (B-label) and [trifluoromethoxyphenyl-<sup>14</sup>C]metaflumizone (T-label). Identified residues accounted for 73-101% TRR in all commodities, excluding cottonseed, where total identified residues accounted for 56-64% TRR. The major identified residue in all commodities was metaflumizone (E and Z isomers; 34-98% TRR; E:Z ratio of ~1:1 to 12:1). M320I04 was a significant residue in all crops accounting for 12-17% TRR. Residues of M320I06, M320I07, and M320I23 were also identified (≤8% TRR). Individual unknowns were <10% of the TRR in/on tomato and cabbage. For cotton, the studies presented only the following total unknown concentrations: cotton gin byproducts (13-16% TRR) and cottonseed (20-28% TRR). Based on these data, it appears that metaflumizone is metabolized in plants via isomerization of the metaflumizone E isomer to the Z isomer, ring closure to form metabolite M320I23, cleavage of the parent molecule to form M320I04, cleavage of M320I23 to form M320I05, and cleavage of M320I23 and/or M320I04 to form M320I06.

Based on these data HED concluded that the residues of concern in plants for tolerance enforcement and risk assessment are metaflumizone (E and Z isomers) and M320I04 (HED risk assessment document D304496, R. Mitkus *et al.*, 24-Jan-2006). **This decision will be re-evaluated upon submission of the additional information concerning the cabbage and cotton metabolism studies (see recommendation section of this document for further information).**

HED notes that identification of M320I04 (12-17% TRR) indicates that the trifluoromethoxyphenyl ring (T-ring) separates from the remainder of the molecule (T-ring is thought to be driving the toxicity). Standards containing only the T-ring were not included in the cabbage study; the tomato and cotton studies included p-trifluoromethoxyaniline (M320I05) as a standard and this compound was identified in cottonseed at 1.5% TRR (0.002 ppm; not identified in tomato). HED concludes that the petitioner has adequately determined that fate of the T-ring for the following reasons (no additional data are requested): (1) the petitioner identified the majority of the TRR in the T-labeled studies (73-100% TRR in all commodities except for cottonseed where 56% TRR was identified); (2) individual unknowns were <10% TRR in tomato and cabbage (only total unknown concentrations were provided for cottonseed and cotton gin byproducts, ≤28% TRR); and (3) by including M320I04 as a residue of concern and converting these residues to metaflumizone equivalents, HED will be accounting for a significant portion of potential free trifluoromethoxyphenyl ring compounds. **This conclusion will be re-evaluated upon submission of information pertaining to the unknowns in cottonseed and cotton gin byproducts.**

### 860.1300 Nature of the Residue - Livestock

No livestock metabolism studies were submitted with this petition. Metabolism studies with goat (12 ppm; 4.7x/34x the beef/dairy cattle maximum reasonable dietary burden (MRDB)) and hen (13-14 ppm; 134x MRDB) have been previously submitted and reviewed. Identified residues accounted for 56-108% TRR in goat and 68-106% TRR in hen. The major identified residue in all commodities was metaflumizone (E and Z isomers; 31-108% TRR in goat and 57-106% TRR in hen; TRR; E:Z 7:1 to 99:1). M320I25 (20% TRR) and M320I26 (11% TRR) were identified at significant concentrations in the goat liver hydrolysates; these compounds were found at 7% and 4% TRR, respectively, in hen liver. The following residues were also identified (all at  $\leq 9\%$  TRR): M320I04, M320I07, M320I10, M320I13, M320I22, M320I23, M320I24, M320I25, M320I26, and M320I28. Individual unknowns in ruminant and hen commodities were  $\leq 11\%$  TRR. The petitioner subjected ruminant liver subsamples to direct acetonitrile (ACN)/acetic acid microwave extraction which released 82.5% TRR for the T-label sample and 85.3% TRR for the B-label sample. High-performance liquid chromatograph (HPLC) analysis of the microwave extracts resolved one peak, identified as M320I28, for the T-label sample and one peak, identified as M320I04, for the B-label sample.

Based on these data, it appears that metaflumizone is metabolized in livestock via the following reactions: hydroxylation of metaflumizone at the 3-trifluoromethylphenyl ring forming M320I27; hydroxylation of metaflumizone at the trifluoromethoxyaniline ring forming M320I22 followed by conjugation to glucuronic acid to form M320I24; hydroxylation of metaflumizone at the benzyl position to form M320I07 followed by oxidation and ring formation yielding M320I23; cleavage of metaflumizone at the imine bridge, resulting in the formation of M320I04 and a metabolite containing the trifluoromethoxyaniline moiety; cleavage of M320I04 to form M320I06 which is conjugated with glycine to form M320I13; and/or reduction of M320I04 to form M320I25 which is conjugated with glucuronic acid to form M320I10 or conjugated with glutamic acid to form M320I26.

HED concluded that for all livestock commodities excluding ruminant liver, the residues of concern for tolerance expression and risk assessment are metaflumizone (E and Z isomers). For ruminant liver, the residues of concern for tolerance expression are metaflumizone (E and Z isomers), and the residues of concern for risk assessment are metaflumizone (E and Z isomers) and M320I28 (HED risk assessment document D304496, R. Mitkus *et al.*, 24-Jan-2006). M320I28 is a derivatized/cleavage product formed upon microwave ACN/acetic acid extraction of the residues remaining following extraction (common moiety method). HED notes that by including M320I28 and converting these residues to metaflumizone equivalents and based on the data presented following microwave extraction of liver subsamples, residues of M320I25 and M320I26 in liver should be adequately taken into account.

Due to insignificant residue concentrations, free T-ring compounds were not included as residues of concern in poultry. However, for ruminants M320I28 (free T-ring compound) was included as a residue of concern in liver. The ruminant metabolism study indicated that residues in liver following extraction were significant, and that a common moiety microwave ACN/acetic acid extraction method which results in the formation of M320I28 from all compounds which contain the T-ring and expression of M320I28 residues in parent equivalents is able to quantify a significant portion of these residues. In the remaining ruminant commodities, the identified

residues in the T- and B-labeled ruminant studies were 68-80% and 88-108%, respectively. This difference is most likely the result of the presence of compounds containing only the T-ring and the lack of standards containing only the T-ring in the metabolism studies. In addition, the petitioner isolated and identified M320I17 as a major residue in ruminant urine (53% TRR) which indicates that free T-ring compounds are forming in significant concentrations. However, for this petition, HED concludes that the potential exposure to free T-phenyl compounds is insignificant for the following reasons: (1) based on the current dietary burden and the ruminant feeding study, transfer of residues to livestock is likely to be minimal; (2) individual unknowns in the T-labeled ruminant study were  $\leq 11\%$  TRR; and (3) liver is a low consumption commodity. **However, if a major feed commodity is requested in the future, then additional information concerning the fate of the trifluoromethoxyphenyl ring may be requested.**

#### 860.1340 Residue Analytical Methods

HED previously determined that the BASF LC/MS/MS Method 531/0 is adequate for tolerance enforcement and forwarded this method to the FDA (D308394, T. Bloem, 30-Nov-2005; D328915, T. Bloem, 17-May-2006). Citrus, grape, and tree nut samples from the field trial and processing studies were analyzed for residues of metaflumizone (E and Z isomers; LOQ = 0.01 ppm) and M320I04 (LOQ = 0.018 ppm) using BASF method 531/0. Based on the adequate validation data submitted with the field trial and processing studies, HED concludes that the current enforcement method is suitable for enforcement of the tolerances associated with the current petition.

#### 860.1360 Multiresidue Methods

Acceptable multiresidue methods testing data have previously been submitted; the multiresidue methods are not appropriate for quantifying metaflumizone residues. These data were forwarded to FDA (D323538, T. Bloem, 16-Nov-2005).

#### 860.1380 Storage Stability

47235701.der.doc (tree nuts); 47235702.der.doc (grape); 47235703.de1.doc (citrus)

Previously submitted and reviewed (E)- and (Z)-metaflumizone and M320I04 storage stability data indicated that metaflumizone (Z-isomer) and/or M320I04 are unstable in/on some plant commodities (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005). Based on this and since none of the employed crops are translatable to the proposed crops, the following storage stability data are required (data for metaflumizone (E and Z isomers) and M320I04): grapes - 4.8 months; citrus fruit - 5.6 months; almond hulls - 6.5 months; and almond nutmeat - 5.8 months. Table 4 is a summary of the storage conditions and intervals for the samples collected as part of the current petition.

Matrix	Storage Temp. (°C)	Actual Storage Duration	Interval of Demonstrated Storage Stability
Almond hulls	<-8	127-198 days; (4.2-6.5 months)	None
Almond nutmeat	<-8	106-176 days; (3.5-5.8 months)	None
Grape, fruit	<-10	9-147 days; (0.3-4.8 months)	None
Grapefruit, fruit	<-5	17-79 days; (0.6-2.6 months)	None
Lemon, fruit	<-5	50-171 days; (1.6-5.6 months)	None

**Table 4: Summary of Storage Conditions and Durations.**

Matrix	Storage Temp. (°C)	Actual Storage Duration	Interval of Demonstrated Storage Stability
Orange, fruit	<-5	8-171 days; (0.3-5.6 months)	None
Orange, oil	<-5	6-8 days; (0.2-0.3 months)	None
Pecan nutmeat	<-8	73-91 days; (2.4-3.0 months)	None

**860.1400 Water, Fish, and Irrigated Crops**

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

**860.1460 Food Handling**

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

**860.1480 Meat, Milk, Poultry, and Eggs**

Considering the proposed/registered uses, the only feedstuffs are almond hulls and dried citrus pulp which may be fed to cattle (no poultry or hog feed commodities). Based on the revised Table 1, the MRBD for beef and dairy cattle is 0.004 ppm (see Table 5); based on these dietary burdens and the previously reviewed cattle feeding study (D308394, T. Bloem, 30-Nov-2005), HED concludes that livestock tolerances are unnecessary (see Table 6).

**Table 5: Calculation of Metaflumizone Dietary Burdens.**

Feed Commodity	% Dry Matter <sup>1</sup>	% Diet <sup>1</sup>	Recommended Tolerance (ppm)	Dietary Contribution (ppm) <sup>2</sup>
Beef Cattle				
citrus, dried pulp (roughage)	91	10	0.04	0.004
dietary burden				<b>0.004</b>
Dairy Cattle				
citrus, dried pulp (roughage)	91	10	0.04	0.004
almond hulls	90	10	0.04	0.004
dietary burden				<b>0.004<sup>3</sup></b>

<sup>1</sup> Revised OPPTS 860.1000 Table 1.

<sup>2</sup> Dietary contribution = residue ÷ % dry matter × % diet.

<sup>3</sup> Based on the revised OPPTS 860.1000 Table 1, only of these feed items should be included in the dietary burden calculations.

**Table 6: Dairy Cattle Feeding Study and Estimated Residues in Cattle**

Matrix	Maximum Residues of Metaflumizone (E and Z isomers; ppm)				Maximum Combined Residue of Metaflumizone (E and Z isomers) at 1x Dietary Burden at Each Dose Level (ppm) <sup>1</sup>
	0.2 ppm Dose Level	1.0 ppm Dose Level	5.5 ppm Dose Level	16.5 ppm Dose Level	
Milk	<0.01	<0.01	0.0286	0.0832	<0.001, <0.001, <0.001, <0.001
Skim milk	<0.01	<0.01	<0.01	<0.01	<0.001, <0.001, <0.001, <0.001
Cream	<0.01	0.0519	0.242	0.883	<0.001, <0.001, <0.001, <0.001
Fat	<0.02	0.0429	0.182	0.864	<0.001, <0.001, <0.001, <0.001
Kidney	<0.02	<0.02	<0.02	0.053	<0.001, <0.001, <0.001, <0.001
Liver	<0.02	<0.02	<0.02	0.059	<0.001, <0.001, <0.001, <0.001
Muscle	<0.02	<0.02	<0.02	0.063	<0.001, <0.001, <0.001, <0.001

<sup>1</sup> Residue ÷ (dose level ÷ dietary burden); dietary burden = 0.004 ppm (see Table 5).

**860.1500 Crop Field Trials**

47235701.der.doc (tree nuts); 47235702.der.doc (grape); 47235703.de1.doc (citrus)

The submitted tree nut, grape, and citrus field trial studies reflect the use of a 0.063% G formulation applied as a single soil broadcast application at a rate of 0.004 lb ai/acre (5-day PHI; 4x/1x the proposed maximum single/seasonal application rate). The field trials satisfy the geographical data requirements specified in OPPTS 860.1500. The harvested samples were analyzed for residues of metaflumizone (E and Z isomers), M320I04, and M320I23 using an adequately validated method. The following storage stability data are required (data for metaflumizone (E and Z isomers) and M320I04): grapes - 4.8 months; citrus fruit - 5.6 months; almond hulls - 6.5 months; and almond nutmeat - 5.8 months. Residues of metaflumizone (E and Z isomers), M320I04, and M320I23 were <LOQ in/on the all of the harvested samples (see Table 7). At three of the orange trials, additional orange samples were collected where the fruit was harvested from trees and then dropped on the orchard floor under and around the trees where the test substance had been applied; residues of metaflumizone (E and Z isomers), M320I04, and M320I23 were also <LOQ in/on these samples. Table 5 is a summary of the residue data.

Based on these data and provided the petitioner agrees to submit the requested storage stability data, HED concludes that the following tolerances for the combined residues of metaflumizone (E and Z isomers) and M320I04, expressed as metaflumizone, are appropriate: Fruit, citrus, group 10 - 0.04 ppm; Nut, tree, group 14 - 0.04 ppm; Almond, hulls - 0.04 ppm; and Grape - 0.04 ppm. Based on the submitted residue data and the low application rate, HED concludes that application to non-bearing stone and pome fruit trees (application within 1 year of harvest is prohibited) may be considered on non-food use

HED notes that the proposed label advises individual mound treatment when mound density is <1 mound per 2000 ft<sup>2</sup> (0.00008 lb ai/mound; RTI = 4 weeks; PHI = 5 days; product is distributed 3-4 feet around the mound). The mound treatment would yield an effective rate of 0.123 lb ai/acre for that treated area (0.00008 lb ai/mound; circle with a radius of 3 feet = 28.26 ft<sup>2</sup> = 0.000649 acres; 0.00008 lb ai/mound ÷ 0.000649 acres/treated mound = 0.123 lb ai/acre). HED concludes that the recommended 0.04 ppm tolerances are sufficient to cover the mound treatment application scenario for the following reasons: (1) the confined rotational crop study (1 lb ai/acre) resulted in total radioactive residues of ≤0.095 ppm in wheat forage/grain, lettuce, and radish root/tops (30-day plant-back interval (PBI)) and (2) the field rotational crop study (4 x 0.26 lb ai/acre) resulted in <LOQ residues of parent, M320I04, and M320I23 in lettuce, radish roots/tops, and wheat forage/hay/straw/grain (30-day PBI).

**Table 7: Summary of Residue Data from Crop Field Trials with Metaflumizone.**

Crop matrix	Total App. Rate (lb ai/acre)	PHI (days)	Analyte	Residue Levels (ppm)						
				n	Min.	Max.	HAFT <sup>1</sup>	Median	Mean	Std. Dev.
<b>Citrus (proposed use = 4 x 0.001 lb ai/acre, 5-day PHI)</b>										
Orange	0.004	5	(E)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	24	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	24	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	24	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	24	<0.01	<0.01	<0.01	<0.01	<0.01	--

Metaflumizone

Summary of Analytical Chemistry and Residue Data

DP#: 345540

Crop matrix	Total App. Rate (lb ai/acre)	PHI (days)	Analyte	Residue Levels (ppm)						
				n	Min.	Max.	HAFT <sup>1</sup>	Median	Mean	Std. Dev.
Grapefruit	0.004	5	(E)-Metaflumizone	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	12	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	12	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	12	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
Lemon	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
<b>Grape (proposed use = 4 x 0.001 lb ai/acre, 5-dav PHI)</b>										
Grape, fruit	0.004	5	(E)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	24	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	24	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	24	<0.038	<0.038	<0.038	<0.038	<0.038	--
	0.02	5	(E)-Metaflumizone	2	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	2	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	2	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	2	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	2	<0.038	<0.038	<0.038	<0.038	<0.038	--
M320I23	2	<0.01	<0.01	<0.01	<0.01	<0.01	--			
<b>Tree nut (proposed use = 4 x 0.001 lb ai/acre, 5-dav PHI)</b>										
Almond, hulls	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
Almond, nutmeat	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
Pecan, nutmeat	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>2</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--

<sup>1</sup> HAFT = highest-average field trial result.<sup>2</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320I04.

**860.1520 Processed Food and Feed**

47235703.de2.doc (orange); 47235702.der.doc (grape)

Residues of (E)- and (Z)-metaflumizone, and metabolite M320I04 were <LOQ in grape RAC following treatment at 5x the proposed rate (5-day PHI). Therefore, a grape processing study was not conducted (refer to the 860.1500 for results of the exaggerated-rate grape field trial results). Residues of (E)- and (Z)-metaflumizone, and metabolite M320I04 were also <LOQ in orange RAC following treatment at 5x the proposed rate (5-day PHI) and in citrus oil derived from the 5x treated RACs; processing data were not provided for citrus juice or dried pulp. Since residues were <LOQ in the orange and grape RACs following treatment at 5x and based on the citrus oil residue data from the processing study, HED concludes that tolerances in/on the grape and citrus processed commodities are unnecessary. Storage stability data are required to validate these results (see Table 4).

**860.1650 Submittal of Analytical Reference Standards**

An analytical reference standard for metaflumizone is currently available at the EPA National Pesticide Standards Repository (personal communication with Dallas Wright, ACB, 1/2/08). However, the standard for metaflumizone expired 1-Oct-2006. The petitioner must either recertify the lot in the repository and send in an updated certificate of analysis (COA), or submit new standards (different lot #) if the previous lots will not be recertified. If new COAs are being submitted, they should be faxed to the repository at 410-305-2999. If new standards are being submitted, they should be sent to the Analytical Chemistry Lab, which is located at Fort Meade, to the attention of Theresa Cole at the following address (note that the mail will be returned if the extended zip code is not used):

USEPA  
National Pesticide Standards Repository/Analytical Chemistry Branch/OPP  
701 Mapes Road  
Fort George G. Meade, MD 20755-5350

**860.1850 and 860.1900 Confined and Field Accumulation in Rotational Crops**

Because citrus fruits, grapes, and tree nuts are typically not rotated, data pertaining to rotational crops are not required to support the proposed uses.

**860.1550 Proposed Tolerances**

Table 8 is a summary of the HED-recommended tolerances for the combined residues of metaflumizone (E and Z isomers) and M320I04 (expressed as metaflumizone). **A revised Section F is requested which specifies the correct tolerance expression (see below), commodity definition, and numerical tolerance.** There are no Canadian, Mexican, or Codex Maximum Residue Limits (MRLs) established for residues of metaflumizone; therefore, harmonization is not relevant.

The tolerance expression should be written as follows: Tolerances are established for residues of the insecticide metaflumizone, including its metabolites and degradates, in or on the commodities in the table below. Compliance with the tolerance levels specified below is to be determined by measuring only the sum of metaflumizone (E and Z isomers; 2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide) and its metabolite 4-{2-oxo-2-[3-(trifluoromethyl)phenyl]ethyl}-benzimidazole, calculated as the stoichiometric equivalent of metaflumizone, in or on the following commodities:

Commodity	Proposed Tolerance (ppm)	HED-Recommended Tolerance (ppm)	Comments; <i>Correct Commodity Definition</i>
Citrus Fruits, Group 10	0.01	0.04	<i>Fruit, citrus, group 10</i>
Tree Nuts, Group 14	0.01	0.04	<i>Nut, tree, group 14</i>
Grapes, table	0.01	0.04	<i>Grape</i>
Grapes, wine	0.01	Remove	A separate tolerance for wine grapes is not required.
Almond, hulls	None proposed	0.04	<i>Almond, hulls</i>

RDI: RAB1 Chemists (1-Apr-2009)

T. Bloem:S10945:Potomac Yard 1:703-605-0217:7509P:RAB1

Attachment 1: International Residue Limit Status Sheet.

Attachment 2: Chemical Names and Structures.

Template Version September 2005

**Attachment 1: International Residue Limit Status Sheet.**

<b>INTERNATIONAL RESIDUE LIMIT STATUS</b>			
Chemical Name: 2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide; E and Z isomers	Common Name: Metaflumizone	<input checked="" type="checkbox"/> Proposed tolerance <input type="checkbox"/> Reevaluated tolerance <input type="checkbox"/> Other	Date: 12/27/07
Codex Status (Maximum Residue Limits)		U. S. Tolerances	
<input checked="" type="checkbox"/> No Codex proposal step 6 or above <input type="checkbox"/> No Codex proposal step 6 or above for the crops requested		Petition Number: PP#7F7260 DP#: 345540 Other Identifier: Decision Number 384160	
Residue definition (step 8/CXL): N/A		Reviewer/Branch: T. Bloem/RAB1 Residue definition: Metaflumizone (E and Z isomers)	
Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
		Citrus Fruits, Group 10	0.01
		Tree Nuts, Group 14	0.01
		Grapes, table	0.01
		Grapes, wine	0.01
Limits for Canada		Limits for Mexico	
<input checked="" type="checkbox"/> No Limits <input type="checkbox"/> No Limits for the crops requested		<input checked="" type="checkbox"/> No Limits <input type="checkbox"/> No Limits for the crops requested	
Residue definition: N/A		Residue definition: N/A	
Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)
Notes/Special Instructions: S.Funk, 01/02/2008.			

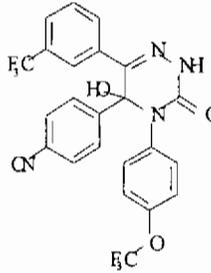
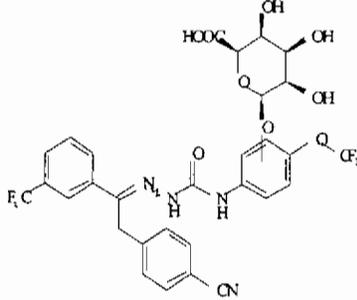
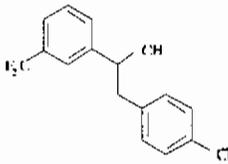
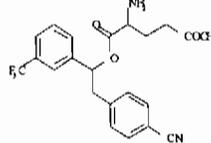
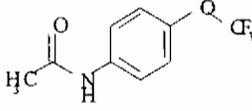
## Attachment 2: Chemical Names and Structures.

Common name/code	Chemical name	Chemical structure
Metaflumizone E isomer	4-((2E)-2-([4-(trifluoromethoxy)anilino]carbonyl)hydrazono)-2-[3-(trifluoromethyl)phenyl]ethyl)-benzonitrile  2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-hydrazinecarboxamide (E)]	
Metaflumizone Z isomer	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-hydrazinecarboxamide (Z)]	
M320I04	4-{2-oxo-2-[3-(trifluoromethyl)phenyl]ethyl}-benzonitrile	
M320I05 (CL 65504)	p-trifluoromethoxyaniline	
M320I06 (found in tomato and cattle urine)	4-cyanobenzoic acid	
M320I07	2-[2-(4-cyanophenyl)-2-hydroxy-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-hydrazinecarboxamide	
M320I10	--	
M320I13	{[(4_cyanophenyl)acetyl]amino}acetic acid	
M320I17 (isolated and identified in goat urine)	oxo{[4_(trifluoromethoxy)phenyl]amino}acetic acid	
M320I22 (E and Z isomers)		

Metaflumizone

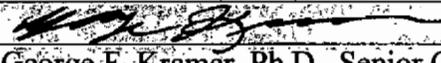
Summary of Analytical Chemistry and Residue Data

DP#: 345540

Common name/code	Chemical name	Chemical structure
M320I23	4-{5-hydroxy-3-oxo-4-[4-(trifluoromethoxy)phenyl]-6-3-(trifluoromethyl)phenyl]-2,3,4,5-tetrahydro-1,2,4-triazin-5-yl} benzonitrile	
M320I24 (E and Z isomers)	--	
M320I25	4-{2-hydroxy-2-[3-(trifluoromethyl)phenyl]ethyl}-benzonitrile	
M320I26	4-amino-5-{2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethoxy}-5-oxopentanoic acid	
M320I28 (hydrolysis product of Metaflumizone)	N-[4-(trifluoromethoxy)phenyl]-acetamide	



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
 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 - Tree Nut, Group 14

Primary Evaluator	 Tom Bloem, Chemist Risk Assessment Branch 1 (RAB1) Health Effects Division (HED; 7509P)	26-January-2010
Approved by	 George F. Kramer, Ph.D., Senior Chemist RAB1/HED (7509P)	26-January-2010

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 04/18/2008). The DER has been reviewed by the HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

### **STUDY REPORT:**

47235701 Carringer, S. (2007) Magnitude of the Residue of Metaflumizone and its Metabolites in or on Tree Nuts Raw Agricultural Commodities Following One Application of BAS 320 04 I: Final Report. Project Number: 7001660, TCI/06/152, 254473. Unpublished study prepared by BASF Agro Research, Southeast Ag Research, Inc. and Pest Management Enterprises. 186 p.

### **EXECUTIVE SUMMARY:**

BASF Corporation submitted field trial data for metaflumizone on almonds and pecans, the representative commodities of the tree nut group 14. Five almond field trials were conducted in the United States in Zone 10 (CA), and five pecan field trials were conducted in Zones 2 (GA; n=2), 4 (LA; n=1), 6 (TX; n=1), and 8 (OK; n=1) during the 2006 growing season. The number and locations of field trials are in accordance with OPPTS Guideline 860.1500 for tree nuts.

Each tree nut field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% granular (G) formulation of metaflumizone at 0.004 lb ai/A. The application was made when almonds were at the BBCH 87-89 growth stage or when pecans were at shuck split to leaf drop or BBCH 89-99. Applications were made using ground equipment; no adjuvant was used with the granular formulation. Samples of mature almonds (hulls and nutmeat) and pecans were harvested 5 days after application.

Samples of almond hull, and almond and pecan nutmeat were analyzed for residues of (E)- and (Z)-metaflumizone, and metabolites M320I04 and M320I23 using the liquid chromatograph/mass spectrometer/mass spectrometer (LC/MS/MS) BASF analytical method 531/0, the enforcement method for plant commodities. The validated limit of quantitation (LOQ) was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively. The method was adequate based on acceptable concurrent recoveries.



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
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 – Tree Nut, Group 14

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Samples were stored frozen from harvest to analysis for up to 198 days (6.5 months) for almond hulls, 176 days (5.8 months) for almond nutmeat, and 91 days (3.0 months) for pecan nutmeat. Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to tree nuts, storage stability data specific to nutmeat and almond hulls are required.

Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of almond hulls, and almond and pecan nutmeat; total metaflumizone residues (sum of E and Z isomers) were <0.02 ppm. Residues of M320I04 and of M320I23 were each below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on the respective samples. Total residues [metaflumizone (E+Z isomers) and M320I04] were <0.038 ppm in/on all samples of almond hulls, and almond and pecan nutmeat harvested 5 days following soil treatment with the 0.063% G at 0.004 lb ai/A. M230I23 is not a residue of concern and, therefore, not included in the totals. No residue decline data have been submitted.

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the field trial residue data are tentatively classified as scientifically acceptable pending submission of storage stability data demonstrating the stability of metaflumizone (E and Z isomers) and M320I04 in/on almond hulls and a tree nutmeat stored frozen for up to 6.5 and 6 months, respectively. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 345540.

#### **COMPLIANCE:**

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



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
 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 – Tree Nut, Group 14

## A. BACKGROUND INFORMATION

Metaflumizone is a voltage-dependent, sodium-channel-blocker insecticide (Group 22B) which leads to inhibited feeding and paralysis in susceptible insects (Lepidoptera and Coleoptera). Metaflumizone is a mixture of the E and Z stereoisomers which are present at a ratio of  $\geq 9:1$  (E:Z). The chemical structure and nomenclature of metaflumizone and its analyzed metabolites, and the physicochemical properties of the technical grade of metaflumizone are presented in Tables A.1 and A.2.

Table A.1. Metaflumizone Nomenclature.	
Chemical structure	
Common name	Metaflumizone
Company experimental name	BAS 320 I
IUPAC name	(EZ)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-4-(trifluoromethoxy)carbanilohydrazide
CAS name	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide
CAS registry number	139968-49-3
End-use product (EP)	Altrevin Fire Ant Bait Insecticide (0.063% G formulation; EPA Reg. No. 7969-###)
Metabolite M320I04	<p>4-[2-oxo-2-[3-(trifluoromethoxy)phenyl]ethyl]-benzonitrile</p>
Metabolite M320I23	<p>4-[5-hydroxy-3-oxo-4-[4-(trifluoromethoxy)phenyl]-6-[3-(trifluoromethyl)phenyl]-2,3,4,5-tetrahydro-1,2,4-triazin-5-yl]benzonitrile</p>



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
 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 – Tree Nut, Group 14

Table A.2. Physicochemical Properties of Metaflumizone.			
Melting point	Two melting points observed at approximately 127 °C and 186 °C.		MRID 46264204
pH	6.48 at 25 °C (1% aqueous suspension)		MRID 46264524
Density (20 °C)	1.461 g/cm <sup>3</sup>		MRID 46264204
Water solubility (20 °C)	D.I. water	1.79 µg/L	MRID 46264208
	pH 5	1.35 µg/L	
	pH 7	1.81 µg/L	
	pH 9	1.73 µg/L	
Solvent solubility (20 °C)	Acetone	142.7 mg/L	MRID 46264212
	Acetonitrile	60.3 mg/L	
	DCM	92.7 mg/L	
	EtOAc	159.7 mg/L	
	Heptane	0.0084 mg/L	
	Methanol	13.95 mg/L	
	Toluene	3.96 mg/L	
Vapor pressure	1.24 x 10 <sup>-8</sup> Pa at 20 °C		MRID 46264206
Dissociation constant, pK <sub>a</sub>	None in pH range 2-12		MRID 46264217
Octanol/water partition coefficient, Log(K <sub>ow</sub> )	Log P <sub>ow</sub> = 5.1 (Z isomer)		MRID 46264213
	Log P <sub>ow</sub> = 4.4 (E isomer)		
UV/visible absorption spectrum	Molar absorptivity: 3.81×10 <sup>4</sup> L/Mcm at 234 nm; 1.93×10 <sup>4</sup> L/Mcm at 280 nm.		MRID 46264207

## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Five almond field trials were conducted in the United States in Zone 10 (CA), and five pecan field trials were conducted in the United States in Zones 2 (GA; n=2), 4 (LA; n=1), 6 (TX; n=1), and 8 (OK; n=1), during the 2006 growing season.

Each tree nut field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% granular (G) formulation of metaflumizone at 0.004 lb ai/A (4.48 g ai/ha). The application was made when almonds were at the BBCH 87-89 growth stage or when pecans were at shuck split to leaf drop or BBCH 89-99. Applications were made using commercial or simulated commercial ground-based granular application equipment; no adjuvant was used with the granular formulation. The study use pattern is presented in Table B.1.2.

The test crops were grown and maintained according to typical agricultural practices for each region; maintenance pesticides and fertilizers were used. Trial site conditions are presented in Table B.1.1, and the crop varieties grown are identified in Table C.3. Rainfall amounts during the trial period, mean monthly temperature minimums and maximums, and ten-year historical averages of rainfall and temperatures were provided. Overall the trials experienced normal weather and no unusual weather events were reported. There was no irrigation between the application and harvest.



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 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 – Tree Nut, Group 14

**TABLE B.1.1. Trial Site Conditions.**

Trial Identification: City, State; Year (Trial ID #)	Soil characteristics			
	Type	%OM <sup>2</sup>	pH	CEC <sup>2</sup> (meq/100 g)
<b>Almond Trials</b>				
Wasco, CA; 2006 (TCI-06-152-06)	Clay loam	NR <sup>1</sup>	NR	NR
Wasco, CA; 2006 (TCI-06-152-07)	Clay loam	NR	NR	NR
Terra Bella, CA; 2006 (TCI-06-152-08)	Loam	1.4	7.5	16.8
Terra Bella, CA; 2006 (TCI-06-152-09)	Loam	1.4	7.5	16.8
Hickman, CA; 2006 (TCI-06-152-10)	Sandy loam	0.451	6.1	8.9
<b>Pecan Trials</b>				
Ray City, GA; 2006 (TCI-06-152-01)	Loamy sand	NR	NR	NR
Chula, GA; 2006 (TCI-06-152-02)	Loamy sand	2.4	6.2	7.8
Port Barre, LA; 2006 (TCI-06-152-03)	Silty clay loam	NR	NR	NR
Madill, OK; 2006 (TCI-06-152-04)	Clay loam	4.5	7.2	32.0
Anton, TX; 2006 (TCI-06-152-05)	Fine sandy loam	0.8	7.2	14.6

NR = not reported.

<sup>2</sup> %OM = percent organic matter; CEC = cation exchange capacity.

**TABLE B.1.2. Study Use Pattern.**

Trial Identification: City, State; Year (Trial ID#)	EP <sup>1</sup>	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume	Rate (lb ai/A)	RTI <sup>2</sup> (days)	Total Rate (lb ai/A)	
<b>Almond Trials</b>							
Wasco, CA; 2006 (TCI-06-152-06)	0.063% G	1. Soil broadcast; BBCH 89	NA <sup>3</sup>	0.004	NA	0.004	NA
Wasco, CA; 2006 (TCI-06-152-07)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Terra Bella, CA; 2006 (TCI-06-152-08)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Terra Bella, CA; 2006 (TCI-06-152-09)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Hickman, CA; 2006 (TCI-06-152-10)	0.063% G	1. Soil broadcast; BBCH 87	NA	0.004	NA	0.004	NA
<b>Pecan Trials</b>							
Ray City, GA; 2006 (TCI-06-152-01)	0.063% G	1. Soil broadcast; 40% shuck split	NA	0.004	NA	0.004	NA
Chula, GA; 2006 (TCI-06-152-02)	0.063% G	1. Soil broadcast; 60% shuck split	NA	0.004	NA	0.004	NA
Port Barre, LA; 2006 (TCI-06-152-03)	0.063% G	1. Soil broadcast; BBCH 99	NA	0.004	NA	0.004	NA
Madill, OK; 2006 (TCI-06-152-04)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Anton, TX; 2006 (TCI-06-152-05)	0.063% G	1. Soil broadcast; shuck split/ leaf drop	NA	0.004	NA	0.004	NA

<sup>1</sup> EP = end-use product; BAS 320 04 I.

<sup>2</sup> RTI = retreatment interval.

<sup>3</sup> NA = not applicable for the granular formulation.



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 Crop Field Trial/Residue Decline – Tree Nut, Group 14

NAFTA Growing Zones	Almond		Pecan	
	Submitted	Requested <sup>1</sup>	Submitted	Requested <sup>1</sup>
1	--	--	--	--
2	--	--	2	2
3	--	--	--	--
4	--	--	1	1
5	--	--	--	--
6	--	--	1	1
7	--	--	--	--
8	--	--	1	1
9	--	--	--	--
10	5	5	--	--
11	--	--	--	--
12	--	--	--	--
13	--	--	--	--
<b>Total</b>				

As per OPPTS 860.1500, Tables 2 and 5 for almond and pecan as the representative crops of tree nuts group 14.

## **B.2. Sample Handling and Preparation**

Samples of whole almonds and pecans were harvested from trees using mechanical shakers or poles or by hand 5 days after application. Nuts were raked into piles and single untreated and duplicate treated samples were randomly collected. Almond hulls were separated from the almond nuts by hand. Nuts were shelled at the field sites using mechanical crackers/shellers and cleaned by hand or with the use of blowers, prior to freezing. All samples were placed on dry ice or in freezer storage within 4 hours of collection, maintained frozen at the field facilities, and shipped 2-32 days later by ACDS freezer truck to the analytical laboratory, BASF Agro Research (Research Triangle Park, NC). At the laboratory, samples were stored frozen (<-8 °C) until homogenization and analysis. Samples were homogenized in the presence of dry ice, and then milled in the presence of liquid nitrogen to a fine powder. The moisture content for selected control samples was determined.

## **B.3. Analytical Methodology**

Samples of almond hull, and almond and pecan nutmeat were analyzed for residues of (E)- and (Z)-metaflumizone and metabolites M320I04 and M320I23 using the LC/MS/MS BASF analytical method 531/0, the enforcement method for plant commodities. A brief description of the method was included in the submission; for a complete description of the method, refer to D308394 (T. Bloem, 30-Nov-2005).

Briefly, samples of almond and pecan nutmeat were extracted (using a modified version of the method for very oily matrices) with isooctane and acetonitrile (ACN) and centrifuged. The ACN phase was evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC/MS/MS analysis. Samples of almond hull were extracted with methanol:water (70:30, v:v) and centrifuged. The supernatant was diluted with saturated sodium chloride solution and partitioned



against dichloromethane (DCM). The DCM phase was evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC/MS/MS analysis. The validated LOQ was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively, based on molecular weight conversion factors of 1.7507 for M320I04 and 0.97312 for M320I23. The limit of detection (LOD), defined as ~20% of the LOQ, was ~0.002 ppm for each analyte in almond or pecan matrices.

### C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2. Samples were stored frozen from harvest to analysis for 127-198 days (4.2-6.5 months) for almond hulls, 106-176 days (3.5-5.8 months) for almond nutmeat, and 73-91 days (2.4-3.0 months) for pecan nutmeat. Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to tree nuts, storage stability data specific to nutmeat and almond hulls are required.

Concurrent method recovery data are presented in Table C.1. Samples were analyzed for residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 using the LC/MS/MS Method 531/0. The method was adequate for data collection based on acceptable concurrent method recovery data. Concurrent method recoveries were generally within the acceptable range of 70-120% for almond hulls and almond and pecan nutmeat fortified with each analyte at 0.01 ppm. Apparent residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were each below the method LOQ in/on all samples of untreated almond hulls, almond nutmeat, and pecan nutmeat.

Residue data from the almond and pecan field trials are reported in Table C.3. A summary of the residue data is presented in Table C.4. Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of almond hulls, and almond and pecan nutmeat; total metaflumizone residues (sum of E and Z isomers) were <0.02 ppm. Residues of M320I04 and of M320I23 were each below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on the respective samples. Total residues [metaflumizone (E+Z isomers) and M320I04] were <0.038 ppm in/on all samples of almond hulls, and almond and pecan nutmeat harvested 5 days following soil treatment with the 0.063% G at 0.004 lb ai/A. M320I23 is not a residue of concern and, therefore, not included in the totals.



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 Crop Field Trial/Residue Decline – Tree Nut, Group 14

Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean (%)
Almond hulls	(E)-Metaflumizone	0.01	2	62, 65	64
	(Z)-Metaflumizone	0.01	2	66, 71	69
	M320I04	0.01	2	94, 100	97
	M320I23	0.01	2	106, 125	116
Almond nutmeat	(E)-Metaflumizone	0.01	1	92	92
	(Z)-Metaflumizone	0.01	1	90	90
	M320I04	0.01	1	90	90
	M320I23	0.01	1	89	89
Pecan nutmeat	(E)-Metaflumizone	0.01	1	112	112
	(Z)-Metaflumizone	0.01	1	109	109
	M320I04	0.01	1	100	100
	M320I23	0.01	1	127	127

Matrix	Storage Temperature	Actual Storage Duration <sup>1</sup>	Interval of Demonstrated Storage Stability
Almond hulls	<-8 °C	127-198 days (4.2-6.5 months)	Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to tree nuts, storage stability data specific to nutmeat and almond hulls are required.
Almond nutmeat		106-176 days (3.5-5.8 months)	
Pecan nutmeat		73-91 days (2.4-3.0 months)	

<sup>1</sup> Actual storage duration from sampling to analysis; samples were analyzed within 0-2 days of extraction.

 metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
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 Crop Field Trial/Residue Decline - Tree Nut, Group I4

**TABLE C.3. Residue Data from Crop Field Trials with Metaflumizone.**

Trial ID (City, State; Year)	Zone	Variety	Total Rate (lb ai/A)	PHI <sup>1</sup> (days)	Commodity	Residues (ppm, parent equivalents)					
						(E)- Metaflumizone	(Z)- Metaflumizone	Metaflumizone (E+Z) <sup>2</sup>	M320104	M320123	Total <sup>3</sup>
<b>Almond Trials</b>											
Wasco, CA; 2006 (TCL-06-152-06)	10	Price	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
					Hulls	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Wasco, CA; 2006 (TCL-06-152-07)	10	Mission	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
					Hulls	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Terra Bella, CA; 2006 (TCL-06-152-08)	10	Price	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
					Hulls	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Terra Bella, CA; 2006 (TCL-06-152-09)	10	Carmel	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
					Hulls	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Hickman, CA; 2006 (TCL-06-152-10)	10	Carmel	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
					Hulls	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
<b>Pecan Trials</b>											
Ray City, GA; 2006 (TCL-06-152-01)	2	Sumner	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Chula, GA; 2006 (TCL-06-152-02)	2	Sumner	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Port Barre, LA; 2006 (TCL-06-152-03)	4	Melrose	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Madill, OK; 2006 (TCL-06-152-04)	6	Choctaw	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038
Anton, TX; 2006 (TCL-06-152-05)	8	Western Schley	0.004	5	Nutmeat	<0.01, <0.01	<0.01, <0.01	<0.02, <0.02	<0.018, <0.018	<0.01, <0.01	<0.038, <0.038

<sup>1</sup> PHI = pre-harvest interval.

<sup>2</sup> Total of metaflumizone E and Z isomers.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320104; M320123 residues are presented for informational purposes and are not included in the totals.



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 Crop Field Trial/Residue Decline – Tree Nut, Group 14

Commodity	Total App. Rate (lb ai/A)	PHI (days)	Analyte	Residues (ppm)						
				n	Min.	Max.	HAFT <sup>1</sup>	Median	Mean	Std. Dev. <sup>2</sup>
Almond, hulls	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
Almond, nutmeat	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
Pecan, nutmeat	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--

<sup>1</sup> HAFT = highest average field trial.

<sup>2</sup> Standard deviation not applicable as all residues were below the LOQ.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320I04.

#### D. CONCLUSION

The submitted field trial data on tree nuts reflect the use of a 0.063% G formulation applied as a single soil broadcast application at 0.004 lb ai/A, with a 5-day PHI for almonds and pecans. An acceptable method was used for the quantitation of residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23. Supporting storage stability data for metaflumizone residues in almond (nutmeat and hull) and pecan (nutmeat) are required. Residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23 were <LOQ in/on all of the samples.

#### E. REFERENCES

D308394, T.Bloem, 30-Nov-2008

#### F. DOCUMENT TRACKING

RDI: RAB1 Chemists (18-Mar-2008)

T. Bloem:S10945:Potomac Yard 1:703-605-0217:7509P:RAB1

Template Version June 2005



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
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 Crop Field Trial/Residue Decline - Grape

Primary Evaluator	 Tom Bloem, Chemist Risk Assessment Branch 1 (RAB1) Health Effects Division (HED; 7509P)	26-January-2010
Approved by	 George F. Kramer, Ph.D., Senior Chemist RAB1/HED (7509P)	26-January-2010

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 04/18/2008). The DER has been reviewed by the HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

### **STUDY REPORT:**

47235702 Carringer, S. (2007) Magnitude of the Residue of Metaflumizone and its Metabolites in or on Grape Raw Agricultural and Processed Commodities Following One Application of BAS 320 04 I: Final Report. Project Number: TCI/06/151, 254452, 7001661. Unpublished study prepared by BASF Agro Research and Reality Research and A.C.D.S. Research, Inc. 176 p.

### **EXECUTIVE SUMMARY:**

BASF Corporation has submitted field trial data for metaflumizone on grape. Twelve grape field trials were conducted in the United States and Canada in Zones 1 (NY; n=2), 5 (IL, MI, ON; n=3), 10 (CA; n=6), and 11 (WA; n=1) during the 2006 growing season.

Each grape field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% granular (G) formulation of metaflumizone at 0.004 lb ai/A. At one CA trial site, an additional plot was treated at 0.02 lb ai/A. The application was made when grapes were at the BBCH 85-89 growth stage (maturity). Applications were made using ground equipment; no adjuvant was used with the granular formulation. Samples of mature grapes were harvested 5 days after application.

Samples of grape fruit were analyzed for residues of (E)- and (Z)-metaflumizone and metabolites M320I04 and M320I23 using the liquid chromatograph/mass spectrometer/mass spectrometer (LC/MS/MS) BASF analytical method 531/0, the enforcement method for plant commodities. The validated limit of quantitation (LOQ) was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively. The method was adequate based on acceptable concurrent recoveries.

Grape samples were stored frozen from harvest to analysis for 9-147 days (0.3-4.8 months). Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to grape, storage stability data specific to grape are required.



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
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 - Grape

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Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of grapes; total metaflumizone residues (sum of E and Z isomers) were <0.02 ppm. Residues of M320I04 and of M320I23 were each below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on the respective samples. Total residues [metaflumizone (E+Z isomers) and M320I04] were <0.038 ppm in/on all samples of grapes harvested 5 days following soil treatment with the 0.063% G at 0.004 lb ai/A or 0.02 lb ai/A. M230I23 is not a residue of concern and, therefore, not included in the totals. No residue decline data have been submitted.

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the field trial residue data are tentatively classified as scientifically acceptable pending submission of storage stability data demonstrating the stability of metaflumizone (E and Z isomers) and M320I04 in/on grapes stored frozen for up to 5 months. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 345540.

#### **COMPLIANCE:**

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



Metaflumizone/BAS 320 I/PC Code 281250/BASF Corporation  
 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 - Grape

## A. BACKGROUND INFORMATION

Metaflumizone is a voltage-dependent, sodium-channel-blocker insecticide (Group 22B) which leads to inhibited feeding and paralysis in susceptible insects (Lepidoptera and Coleoptera). Metaflumizone is a mixture of the E and Z stereoisomers which are present at a ratio of  $\geq 9:1$  (E:Z). The chemical structure and nomenclature of metaflumizone, and the physicochemical properties of the technical grade of metaflumizone are presented in Tables A.1 and A.2.

Table A.1. Metaflumizone Nomenclature.	
Chemical structure	
Common name	Metaflumizone
Company experimental name	BAS 320 I
IUPAC name	(E/Z)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-4-(trifluoromethoxy)carbanilohydrazide
CAS name	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide
CAS registry number	139968-49-3
End-use product (EP)	Altrevin Fire Ant Bait Insecticide (0.063% G formulation; EPA Reg. No. 7969-###)
Metabolite M320I04	<p>4-[2-oxo-2-[3-(trifluoromethoxy)phenyl]ethyl]-benzonitrile</p>
Metabolite M320I23	<p>4-[5-hydroxy-3-oxo-4-[4-(trifluoromethoxy)phenyl]-6-[3-(trifluoromethyl)phenyl]-2,3,4,5-tetrahydro-1,2,4-triazin-5-yl]benzonitrile</p>



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Melting point	Two melting points observed at approximately 127 °C and 186 °C.	MRID 46264204
pH	6.48 at 25 °C (1% aqueous suspension)	MRID 46264524
Density (20 °C)	1.461 g/cm <sup>3</sup>	MRID 46264204
Water solubility (20 °C)	D.I. water 1.79 µg/L pH 5 1.35 µg/L pH 7 1.81 µg/L pH 9 1.73 µg/L	MRID 46264208
Solvent solubility (20 °C)	Acetone 142.7 mg/L Acetonitrile 60.3 mg/L DCM 92.7 mg/L EtOAc 159.7 mg/L Heptane 0.0084 mg/L Methanol 13.95 mg/L Toluene 3.96 mg/L	MRID 46264212
Vapor pressure	1.24 x 10 <sup>-8</sup> Pa at 20 °C	MRID 46264206
Dissociation constant, pK <sub>a</sub>	None in pH range 2-12	MRID 46264217
Octanol/water partition coefficient, Log(K <sub>ow</sub> )	Log P <sub>ow</sub> = 5.1 (Z isomer) Log P <sub>ow</sub> = 4.4 (E isomer)	MRID 46264213
UV/visible absorption spectrum	Molar absorptivity: 3.81 × 10 <sup>4</sup> L/Mcm at 234 nm; 1.93 × 10 <sup>4</sup> L/Mcm at 280 nm.	MRID 46264207

## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Twelve grape field trials were conducted in the United States and Canada in Zones 1 (NY; n=2), 5 (IL, MI, ON; n=3), 10 (CA; n=6), and 11 (WA; n=1) during the 2006 growing season. Each grape field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% granular (G) formulation of metaflumizone at 0.004 lb ai/A (4.48 g ai/ha). At one CA trial site, an additional plot was treated at 0.02 lb ai/A (22.4 g ai/ha). The application was made when grapes were at the BBCH 85-89 growth stage (maturity). Applications were made using commercial or simulated commercial ground-based granular application equipment; no adjuvant was used with the granular formulation. The study use pattern is presented in Table B.1.2.

The test crops were grown and maintained according to typical agricultural practices for each region; maintenance pesticides and fertilizers were used. Trial site conditions are presented in Table B.1.1, and the crop varieties grown are identified in Table C.3. Rainfall amounts during the trial period, mean monthly temperature minimums and maximums, and ten-year historical averages of rainfall and temperatures were provided. Overall the trials experienced normal weather and no unusual weather events were reported. There was no irrigation between the application and harvest.



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 Crop Field Trial/Residue Decline - Grape

Trial Identification: City, State; Year (Trial ID#)	Soil characteristics			
	Type	%OM <sup>2</sup>	pH	CEC <sup>2</sup> (meq/100 g)
Williamson, NY; 2006 (TCI-06-151-01)	Gravelly loam	NR <sup>1</sup>	NR	NR
Dundee, NY; 2006 (TCI-05-151-02)	Sandy clay loam	4.1	5.4	10.6
Comstock Park, MI; 2006 (TCI-06-151-03)	Loamy fine sand	NR	NR	NR
Marengo, IL; 2006 (TCI-06-151-04)	Silty clay loam	5-7	5.6-7.8	26-53
St Catherines, ON; 2006 (TCI-06-151-05)	Silty clay loam	2.35	7.2	24.3
Porterville, CA; 2006 (TCI-06-151-06)	Clay	1.3	7.9	NR
Dinuba, CA; 2006 (TCI-06-151-07)	Sandy loam	NR	NR	NR
Lindsay, CA; 2006 (TCI-06-151-08)	Loam	NR	NR	NR
Richgrove, CA; 2006 (TCI-06-151-09)	Sandy loam	NR	NR	NR
Hughson, CA; 2006 (TCI-06-151-10)	Sandy loam	0.8	7.5	7.4
Hickman, CA; 2006 (TCI-06-151-11)	Sandy loam	0.9	5.6	7.2
Ephrata, WA; 2006 (TCI-06-151-12)	Sandy loam	0.9	7.9	13.6

<sup>1</sup> NR = not reported.

<sup>2</sup> %OM = percent organic matter; CEC = cation exchange capacity.

Trial Identification: City, State; Year (Trial ID#)	EP <sup>1</sup>	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume	Rate (lb ai/A)	RTI <sup>2</sup> (days)	Total Rate (lb ai/A)	
Williamson, NY; 2006 (TCI-06-151-01)	0.063% G	1. Soil broadcast; BBCH 85	NA <sup>3</sup>	0.004	NA	0.004	NA
Dundee, NY; 2006 (TCI-05-151-02)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Comstock Park, MI; 2006 (TCI-06-151-03)	0.063% G	1. Soil broadcast; BBCH 85	NA	0.004	NA	0.004	NA
Marengo, IL; 2006 (TCI-06-151-04)	0.063% G	1. Soil broadcast; mature	NA	0.004	NA	0.004	NA
St Catherines, ON; 2006 (TCI-06-151-05)	0.063% G	1. Soil broadcast; BBCH 85-89	NA	0.004	NA	0.004	NA
Porterville, CA; 2006 (TCI-06-151-06)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
		1. Soil broadcast; BBCH 89	NA	0.02	NA	0.02	
Dinuba, CA; 2006 (TCI-06-151-07)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Lindsay, CA; 2006 (TCI-06-151-08)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Richgrove, CA; 2006 (TCI-06-151-09)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	MA	0.004	NA
Hughson, CA; 2006 (TCI-06-151-10)	0.063% G	1. Soil broadcast; BBCH 85	NA	0.004	NA	0.004	NA
Hickman, CA; 2006 (TCI-06-151-11)	0.063% G	1. Soil broadcast; BBCH 85	NA	0.004	NA	0.004	NA
Ephrata, WA; 2006 (TCI-06-151-12)	0.063% G	1. Soil broadcast; BBCH 87	NA	0.004	NA	0.004	NA

<sup>1</sup> EP = end-use product; BAS 320 04 I.

<sup>2</sup> RTI = retreatment interval.

<sup>3</sup> NA = not applicable for the granular formulation.



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 Crop Field Trial/Residue Decline - Grape

NAFTA Growing Zones	Grape	
	Submitted	Requested <sup>1</sup>
1	2	2
2	--	--
3	--	--
4	--	--
5	3	--
6	--	--
7	--	--
8	--	--
9	--	--
10	6	8[5]
11	1	2
12	--	--
13	--	--
<b>Total</b>	<b>2</b>	<b>2</b>

<sup>1</sup> As per OPPTS 860-1500, Tables 1 and 5 for grape. The numbers in brackets reflect a 25% reduction in the required number of trials due to the pesticidal use resulting in no quantifiable residues.

## B.2. Sample Handling and Preparation

Samples of mature grape fruit were harvested by hand 5 days following application. Single untreated and duplicate treated samples were collected. All grape samples were placed on dry ice or in freezer storage within 2.5 hours of collection, maintained frozen at the field site, and shipped 0-51 days later by ACDS freezer truck or by FedEx on dry ice to the analytical laboratory, BASF Agro Research (Research Triangle Park, NC). At the laboratory, samples were stored frozen (<-10 °C) prior to homogenization and analysis; samples were homogenized in the presence of dry ice.

## B.3. Analytical Methodology

Samples of grape fruit were analyzed for residues of (E)- and (Z)-metaflumizone and metabolites M320I04 and M320I23 using the LC/MS/MS BASF analytical method 531/0, the enforcement method for plant commodities. A brief description of the method was included in the submission; for a complete description of the method, refer to D308394 (T. Bloem, 30-Nov-2005).

Briefly, samples of grape were extracted with methanol:water (70:30, v:v) and centrifuged. The supernatant was diluted with saturated sodium chloride solution and partitioned against dichloromethane (DCM). The DCM phase was evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC/MS/MS analysis. The validated LOQ was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively, based on molecular weight conversion factors of 1.7507 for M320I04 and 0.97312 for M320I23. The limit of detection (LOD), defined as ~20% of the LOQ, was ~0.002 ppm for each analyte in grapes.



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 Crop Field Trial/Residue Decline - Grape

## C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2. Grape samples were stored frozen from harvest to analysis for 9-147 days (0.3-4.8 months). Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to grape, storage stability data specific to grape are required.

Concurrent method recovery data are presented in Table C.1. Samples were analyzed for residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 using the LC/MS/MS Method 531/0. The method was adequate for data collection based on acceptable concurrent method recovery data. Concurrent method recoveries were generally within the acceptable range of 70-120% for grapes fortified with each analyte at 0.01 and 0.10 ppm. Apparent residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were each below the method LOQ in/on all samples of untreated grape.

Residue data from the grape field trials are reported in Table C.3. A summary of the residue data is presented in Table C.4. Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of grapes; total metaflumizone residues (sum of E and Z isomers) were <0.02 ppm. Residues of M320I04 and of M320I23 were also each below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on all samples of grapes. Total residues [metaflumizone (E+Z isomers) and M320I04] were <0.038 ppm in/on all samples of grapes harvested 5 days following soil treatment with the 0.063% G at 0.004 lb ai/A or 0.02 lb ai/A. M230I23 is not a residue of concern and, therefore, not included in the totals.

Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean $\pm$ Std. Dev. <sup>1</sup> (%)
Grape, fruit	(E)-Metaflumizone	0.01	3	75, 86, 97	86 $\pm$ 11
		0.10	1	84	84
	(Z)-Metaflumizone	0.01	3	70, 82, 86	79 $\pm$ 8
		0.10	1	95	95
	M320I04	0.01	3	89, 99, 106	98 $\pm$ 9
		0.10	1	79	79
	M320I23	0.01	3	63, 80, 81	75 $\pm$ 10
		0.10	1	103	103

<sup>1</sup> Standard deviation is only applicable for sample sizes of n $\geq$ 3 samples.

Matrix	Storage Temp.	Actual Storage Duration <sup>1</sup>	Interval of Demonstrated Storage Stability
Grape, fruit	<-10 °C	9-147 days (0.3-4.8 months)	Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to grape, storage stability data specific to grape are required.

<sup>1</sup> Actual storage duration from sampling to analysis; samples were analyzed within 0-4 days of extraction.

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**Crop Field Trial/Residue Decline - Grape**

**TABLE C.3. Residue Data from Crop Field Trials with Metaflumizone.**

Trial: City, State; Year (Trial ID#)	Zone	Grape Variety	PHI <sup>1</sup> (days)	Total Rate (lb ai/A)	Residues (ppm, parent equivalents)					
					(E)- Metaflumizone	(Z)- Metaflumizone	Metaflumizone (E+Z) <sup>2</sup>	M320104	M320123	Total <sup>3</sup>
Williamson, NY; 2006 (TCL-06-151-01)	1	Cayuga White	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Dundee, NY; 2006 (TCL-05-151-02)	1	DeChaunac	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Comstock Park, MI; 2006 (TCL-06-151-03)	5	Concord	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Marengo, IL; 2006 (TCL-06-151-04)	5	Seedless Concord	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
St Catharines, ON; 2006 (TCL-06-151-05)	5	Seyval	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Porterville, CA; 2006 (TCL-06-151-06)	10	Thompson Seedless	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Dinuba, CA; 2006 (TCL-06-151-07)	10	Ruby Red	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Lindsay, CA; 2006 (TCL-06-151-08)	10	Crimsons	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Richgrove, CA; 2006 (TCL-06-151-09)	10	Ruby Seedless	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Hughson, CA; 2006 (TCL-06-151-10)	10	Thompson Seedless	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Hickman, CA; 2006 (TCL-06-151-11)	10	Carrignane	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Ephrata, WA; 2006 (TCL-06-151-12)	11	White Riesling	5	0.004	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038

<sup>1</sup> PHI = pre-harvest interval.

<sup>2</sup> Total of metaflumizone E and Z isomers.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320104, M320123 residues are presented for informational purposes and are not included in the totals.

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Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Analyte	Residues (ppm)						
				n	Min.	Max.	HAFT <sup>1</sup>	Median	Mean	Std. Dev. <sup>2</sup>
Grape, fruit	0.004	5	(E)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	24	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	24	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	24	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
	0.02	5	(E)-Metaflumizone	2	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	2	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	2	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	2	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	2	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	2	<0.01	<0.01	<0.01	<0.01	<0.01	--

<sup>1</sup> HAFT = highest average field trial.

<sup>2</sup> Standard deviation not applicable as all residues were below the LOQ.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320I04.

#### D. CONCLUSION

The submitted field trial data on grape reflect the use of a 0.063% G formulation applied as a single soil broadcast application at a rate of 0.004 lb ai/A or 0.02 lb ai/A, with a 5-day PHI. An acceptable method was used for the quantitation of residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23. Supporting storage stability data are required. Residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23 were <LOQ in/on all of the samples.

#### E. REFERENCES

D308394, T.Bloem, 30-Nov-2008

#### F. DOCUMENT TRACKING

RDI: RAB1 Chemists (18-Mar-2008)

T. Bloem:S10945:Potomac Yard 1:703-605-0217:7509P:RAB1

Template Version June 2005



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 Crop Field Trial/Residue Decline - Citrus Fruit Group 10

Primary Evaluator	 Tom Bloem, Chemist Risk Assessment Branch 1 (RAB1) Health Effects Division (HED, 7509P)	26-January-2010
Approved by	 George F. Kramer, Ph.D., Senior Chemist RAB1/HED (7509P)	26-January-2010

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 04/18/2008). The DER has been reviewed by the HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

### STUDY REPORT:

47235703 Carringer, S. (2007) Magnitude of the Residue of Metaflumizone and its Metabolites in or on Citrus Raw Agricultural and Processed Commodities Following One Application of BAS 320 04 I. Project Number: TCI/06/150, 254485, 7001662. Unpublished study prepared by BASF Agro Research and University of Idaho, Cooperative Extension and Carringers, Inc. 316 p.

### EXECUTIVE SUMMARY:

BASF Corporation submitted field trial data for metaflumizone on orange, grapefruit, and lemon, the representative commodities of the citrus fruit group 10. Twelve orange field trials in Zones 3 (FL; n=8), 6 (TX; n=1), and 10 (CA; n=3), six grapefruit field trials in Zones 3 (FL; n=3), 6 (TX; n=1), and 10 (CA; n=2), and five lemon field trials in Zones 3 (FL; n=1) and 10 (CA; n=4), were conducted during the 2006 growing season.

Each citrus fruit field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% granular (G) formulation of metaflumizone at 0.004 lb ai/A. The application was made when citrus fruits were at BBCH 83-89 or mature growth stage using ground equipment; no adjuvant was used with the granular formulation. Mature fruits were harvested 5 days after application. At three FL trial sites, additional orange samples were collected where the fruit was harvested from trees and then dropped on the orchard floor under and around the trees where the test substance had been applied; this dropped fruit was then collected for analysis.

Samples of orange, grapefruit, and lemon were analyzed for residues of (E)- and (Z)-metaflumizone, and metabolites M320I04 and M320I23 using the liquid chromatograph/mass spectrometer/mass spectrometer (LC/MS/MS) BASF analytical method 531/0, the enforcement method for plant commodities. Based on the lower limit of method validation (LLMV), the limit of quantitation (LOQ) was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively. The method was adequate based on acceptable concurrent recoveries.



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Crop Field Trial/Residue Decline – Citrus Fruit Group 10

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Citrus fruit samples were stored frozen for up to 171 days (5.6 months). Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit are required.

Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of orange, grapefruit, and lemon (including the dropped fruit); total metaflumizone residues (sum of E and Z isomers) were <0.02 ppm. Residues of M320I04 and of M320I23 were also below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on all samples of orange, grapefruit, and lemon (including the dropped fruit). Total residues [metaflumizone (E+Z isomers) and M320I04] were <0.038 ppm in/on all samples of orange, grapefruit, and lemon harvested 5 days following soil treatment with the 0.063% G at 0.004 lb ai/A. M230I23 is not a residue of concern and, therefore, not included in the totals. No residue decline data have been submitted.

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the field trial residue data are tentatively classified as scientifically acceptable pending submission of storage stability data demonstrating the stability of metaflumizone (E and Z isomers) and M320I04 in citrus fruit stored frozen for up to 6 months. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 345540.

#### **COMPLIANCE:**

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



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 Crop Field Trial/Residue Decline – Citrus Fruit Group 10

## A. BACKGROUND INFORMATION

Metaflumizone is a voltage-dependent, sodium-channel-blocker insecticide (Group 22B) which leads to inhibited feeding and paralysis in susceptible insects (Lepidoptera and Coleoptera). Metaflumizone is a mixture of the E and Z stereoisomers which are present at a ratio of  $\geq 9:1$  (E:Z). The chemical structure and nomenclature of metaflumizone, and the physicochemical properties of the technical grade of metaflumizone are presented in Tables A.1 and A.2.

<b>Table A.1. Metaflumizone Nomenclature.</b>	
Chemical structure	
Common name	Metaflumizone
Company experimental name	BAS 320 I
IUPAC name	(E/Z)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-4-(trifluoromethoxy)carbanilohydrazide
CAS name	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide
CAS registry number	139968-49-3
End-use product (EP)	Altrevin Fire Ant Bait Insecticide (0.063% G formulation; EPA Reg. No. 7969-###)
Metabolite M320I04	<p>4-[2-oxo-2-[3-(trifluoromethoxy)phenyl]ethyl]-benzonitrile</p>
Metabolite M320I23	<p>4-[5-hydroxy-3-oxo-4-[4-(trifluoromethoxy)phenyl]-6-[3-(trifluoromethyl)phenyl]-2,3,4,5-tetrahydro-1,2,4-triazin-5-yl]benzonitrile</p>



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Table A.2. Physicochemical Properties of Metaflumizone.			
Melting point	Two melting points observed at approximately 127 °C and 186 °C.		MRID 46264204
pH	6.48 at 25 °C (1% aqueous suspension)		MRID 46264524
Density (20 °C)	1.461 g/cm <sup>3</sup>		MRID 46264204
Water solubility (20 °C)	D.I. water	1.79 µg/L	MRID 46264208
	pH 5	1.35 µg/L	
	pH 7	1.81 µg/L	
	pH 9	1.73 µg/L	
Solvent solubility (20 °C)	Acetone	142.7 mg/L	MRID 46264212
	Acetonitrile	60.3 mg/L	
	DCM	92.7 mg/L	
	EtOAc	159.7 mg/L	
	Heptane	0.0084 mg/L	
	Methanol	13.95 mg/L	
	Toluene	3.96 mg/L	
Vapor pressure	1.24 x 10 <sup>-8</sup> Pa at 20 °C		MRID 46264206
Dissociation constant, pK <sub>a</sub>	None in pH range 2-12		MRID 46264217
Octanol/water partition coefficient, Log(K <sub>ow</sub> )	Log P <sub>ow</sub> = 5.1 (Z isomer)		MRID 46264213
	Log P <sub>ow</sub> = 4.4 (E isomer)		
UV/visible absorption spectrum	Molar absorptivity: 3.81×10 <sup>4</sup> L/Mcm at 234 nm; 1.93×10 <sup>4</sup> L/Mcm at 280 nm.		MRID 46264207

## B. EXPERIMENTAL DESIGN

### B.1. Study Site Information

Twelve orange field trials in Zones 3 (FL; n=8), 6 (TX; n=1), and 10 (CA; n=3), six grapefruit field trials in Zones 3 (FL; n=3), 6 (TX; n=1), and 10 (CA; n=2), and five lemon field trials in Zones 3 (FL; n=1) and 10 (CA; n=4), were conducted in the United States during the 2006 growing season.

Each citrus fruit field site included one untreated plot and one treated plot. The treated plots received a single soil broadcast application of a 0.063% G formulation of metaflumizone at 0.004 lb ai/A (4.48 g ai/ha). The application was made when citrus fruits were at BBCH 83-89 or mature growth stage. Applications were made using commercial or simulated commercial ground-based granular application equipment; no adjuvant was used with the granular formulation. The study use pattern is presented in Table B.1.2. At two orange trial sites, an additional plot received one application at 0.02 lb ai/A (22.4 g ai/ha) to generate samples for processing; refer to the processing DER for MRID 47235703.

The test crops were grown and maintained according to typical agricultural practices for each region; maintenance pesticides and fertilizers were used. Trial site conditions are presented in Table B.1.1, and the crop varieties grown are identified in Table C.3. Rainfall amounts during the trial period, mean monthly temperature minimums and maximums, and ten-year historical averages of rainfall and temperatures were provided. Overall the trials experienced normal weather, but the FL and CA trials generally experienced a drier than normal season. There was no irrigation between the application and harvest.



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<b>TABLE B.1.1. Trial Site Conditions.</b>				
Trial Identification: City, State; Year (Trial ID#)	Soil characteristics			
	Type	%OM <sup>2</sup>	pH	CEC <sup>2</sup> (meq/100 g)
<b>Orange Trials</b>				
Oviedo, FL; 2006 (TCI-06-150-01)	Mucky sand	<4	6.5-7.0	NR <sup>1</sup>
Clermont, FL; 2006 (TCI-06-150-02)	Sand	<1	6.5-7.0	NR
Fellsmere, FL; 2006 (TCI-06-150-03)	Organic layer with sandy clay loam subsoil	<5	6.5-7.0	NR
Oviedo, FL; 2006 (TCI-06-150-04)	Sand	2.7	3.7	5.0
Mims, FL; 2006 (TCI-06-150-05)	Sand	1	6.5	4.5
Clermont, FL; 2006 (TCI-06-150-06)	Sand	<1	6.5-7.0	NR
Bithlo, FL; 2006 (TCI-06-150-07)	Sand	>1	6.5	NR
Holopaw, FL; 2006 (TCI-06-150-08)	Sand	<1	6.5	NR
Raymondville, TX; 2006 (TCI-06-150-09)	Fine sandy loam	1.1	7.7	17.3
Richgrove, CA; 2006 (TCI-06-150-10)	Loam	NR	NR	NR
Strathmore, CA; 2006 (TCI-06-150-11)	Loam	0-2	7.6	NR
Porterville, CA; 2006 (TCI-06-150-12)	Loam	0-2	7.9	NR
<b>Grapefruit Trials</b>				
Oviedo, FL; 2006 (TCI-06-150-13)	Sand	0.7	4.9	1.8
Mims, FL; 2006 (TCI-06-150-14)	Sand	2.6	7.3	11.7
Holopaw, FL; 2006 (TCI-06-150-15)	Sand	<1	6.5	NR
Raymondville, TX; 2006 (TCI-06-150-16)	Fine sandy loam	1.1	7.7	17.3
Porterville, CA; 2006 (TCI-06-150-17)	Loam	0-2	7.9	NR
Terra Bella, CA; 2006 (TCI-06-150-18)	Loam	0-2	7.8	NR
<b>Lemon Trials</b>				
Clermont, FL; 2006 (TCI-06-150-19)	Sand	2.1	7.1	9.6
Somis, CA; 2006 (TCI-06-150-20)	Clay	0-1	6-8	11-19
Santa Paula, CA; 2006 (TCI-06-150-21)	Clay loam	0-1.5	6-8	13-24
Porterville, CA; 2006 (TCI-06-150-22)	Clay loam	2.8	6.9	28.4
Ivanhoe, CA; 2006 (TCI-06-150-23)	Loam	0-2	6-8	16-24

NR = not reported.

<sup>2</sup> %OM = percent organic matter; CEC = cation exchange capacity.

<b>TABLE B.1.2. Study Use Pattern.</b>							
Trial Identification: City, State; Year (Trial ID#)	EP <sup>1</sup>	Application					Tank Mix/ Adjuvants
		Method/Timing	Volume	Rate (lb ai/A)	RTI <sup>2</sup> (days)	Total Rate (lb ai/A)	
<b>Orange Trials</b>							
Oviedo, FL; 2006 (TCI-06-150-01)	0.063% G	1. Soil broadcast; BBCH 83/ mature fruit	NA <sup>3</sup>	0.004	NA	0.004	NA
Clermont, FL; 2006 (TCI-06-150-02)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Fellsmere, FL; 2006 (TCI-06-150-03)	0.063% G	1. Soil broadcast; BBCH 83/ mature fruit	NA	0.004	NA	0.004	NA
Oviedo, FL; 2006 (TCI-06-150-04)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Mims, FL; 2006 (TCI-06-150-05)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA



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<b>TABLE B.1.2. Study Use Pattern.</b>							
Trial Identification: City, State; Year (Trial ID#)	EP <sup>1</sup>	Application					Tank Mix/ Adjuvants
		Method/Timing	Volume	Rate (lb ai/A)	RTI <sup>2</sup> (days)	Total Rate (lb ai/A)	
Clermont, FL; 2006 (TCI-06-150-06)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Bithlo, FL; 2006 (TCI-06-150-07)	0.063% G	1. Soil broadcast; BBCH 89/ mature fruit	NA	0.004	NA	0.004	NA
Holopaw, FL; 2006 (TCI-06-150-08)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Raymondville, TX; 2006 (TCI-06-150-09)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Richgrove, CA; 2006 (TCI-06-150-10)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Strathmore, CA; 2006 (TCI-06-150-11)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Porterville, CA; 2006 (TCI-06-150-12)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
<b>Grapefruit Trials</b>							
Oviedo, FL; 2006 (TCI-06-150-13)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Mims, FL; 2006 (TCI-06-150-14)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Holopaw, FL; 2006 (TCI-06-150-15)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Raymondville, TX; 2006 (TCI-06-150-16)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Porterville, CA; 2006 (TCI-06-150-17)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Terra Bella, CA; 2006 (TCI-06-150-18)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
<b>Lemon Trials</b>							
Clermont, FL; 2006 (TCI-06-150-19)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.004	NA	0.004	NA
Somis, CA; 2006 (TCI-06-150-20)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Santa Paula, CA; 2006 (TCI-06-150-21)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Porterville, CA; 2006 (TCI-06-150-22)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA
Ivanhoe, CA; 2006 (TCI-06-150-23)	0.063% G	1. Soil broadcast; BBCH 89	NA	0.004	NA	0.004	NA

<sup>1</sup> EP = end-use product; BAS 320 04 I.

<sup>2</sup> RTI = retreatment interval.

<sup>3</sup> NA = not applicable for the granular formulation.



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NAFTA Growing Zones	Orange		Grapefruit		Lemon	
	Submitted	Requested <sup>1</sup>	Submitted	Requested <sup>1</sup>	Submitted	Requested <sup>1</sup>
1	--	--	--	--	--	--
2	--	--	--	--	--	--
3	8	8	3	3	1	1
4	--	--	--	--	--	--
5	--	--	--	--	--	--
6	1	1	1	1	--	--
7	--	--	--	--	--	--
8	--	--	--	--	--	--
9	--	--	--	--	--	--
10	3	3	2	2	4	4
11	--	--	--	--	--	--
12	--	--	--	--	--	--
13	--	--	--	--	--	--

As per OPPTS 860.1500, Tables 2 and 5 for orange, grapefruit, and lemon as the representative crops of citrus fruit group 10.

## **B.2. Sample Handling and Preparation**

Single untreated and duplicate treated samples of mature citrus fruit were harvested by hand 5 days following application. At three FL trial sites, additional orange samples were collected where the fruit was harvested from trees and then dropped on the orchard floor under and around the trees where the test substance had been applied; this dropped fruit was then collected for analysis.

Samples were either frozen at the field site (within 2.6 hours after collection from the field) or shipped overnight at ambient temperatures, on the day of collection, to the analytical laboratory, BASF Agro Research (Research Triangle Park, NC). Except for those samples shipped at ambient temperatures, samples were maintained frozen at the field facilities and shipped 1-35 days later by ACDS freezer truck or by FedEx on dry ice to the analytical laboratory. At the laboratory, samples were stored frozen at <-5 °C until homogenization and analysis. Samples were homogenized in the presence of dry ice, and then milled in the presence of liquid nitrogen to a fine powder.

## **B.3. Analytical Methodology**

Samples of citrus fruit were analyzed for residues of (E)- and (Z)-metaflumizone and metabolites M320I04 and M320I23 using the LC/MS/MS BASF analytical method 531/0, the enforcement method for plant commodities. A brief description of the method was included in the submission; for a complete description of the method, refer to D308394 (T. Bloem, 30-Nov-2005).



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Briefly, fruit samples were extracted with methanol:water (70:30, v:v) and centrifuged. The supernatant was diluted with saturated sodium chloride solution and partitioned against dichloromethane (DCM). The DCM phase was evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC/MS/MS analysis. Based on the LLMV, the LOQ was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively, based on molecular weight conversion factors of 1.7507 for M320I04 and 0.97312 for M320I23. The limit of detection (LOD), defined as ~20% of the LOQ, was ~0.002 ppm for each analyte in orange, grapefruit, and lemon.

### C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2.1. Fruit samples were stored frozen from harvest to analysis for 8-171 days (0.3-5.6 months) for oranges, 17-79 days (0.6-2.6 months) for grapefruit, and 50-171 days (1.6-5.6 months) for lemon. Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit are required.

Concurrent method recovery data are presented in Table C.1. Samples were analyzed for residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 using the LC/MS/MS Method 531/0. The method was adequate for data collection based on acceptable concurrent method recovery data. Concurrent method recoveries were generally within the acceptable range of 70-120% for orange, grapefruit, and lemon fortified with each analyte at 0.01 and 0.10 ppm; however, a single very low recovery (37%) was obtained for M320I04 from orange fortified at the LOQ. Apparent residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were each below the method LOQ in/on all samples of untreated orange, grapefruit, and lemon.

Residue data from the citrus fruit field trials are reported in Table C.3. A summary of the residue data for citrus fruits is presented in Table C.4. Residues of (E)- and (Z)-metaflumizone were each below the LOQ (<0.01 ppm) in/on all samples of orange, grapefruit, and lemon (including the dropped fruit). Residues of M320I04 and of M320I23 were also below the LOQ (<0.018 or <0.01 ppm parent equivalents, respectively) in/on all samples of orange, grapefruit, and lemon (including the dropped fruit). No residue decline data have been submitted.

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**TABLE C.1. Summary of Concurrent Recoveries of (E)- and (Z)-Metaflumizone, M320I04, and M320I23 from Citrus Fruits.**

Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean $\pm$ Std. Dev. (%) <sup>1</sup>
Orange	(E)-Metaflumizone	0.01	8	62, 75, 77, 84, 87, 97, 98, 116	87 $\pm$ 17
		0.10	2	98, 115	107
	(Z)-Metaflumizone	0.01	8	89, 91, 91, 92, 95, 97, 98, 111	96 $\pm$ 7
		0.10	2	98, 102	100
	M320I04	0.01	8	37, 67, 74, 75, 84, 87, 88, 101	76 $\pm$ 19
		0.10	1	100	100
M320I23	0.01	8	59, 67, 70, 79, 83, 84, 98, 100	80 $\pm$ 14	
	0.10	2	94, 99	97	
Grapefruit	(E)-Metaflumizone	0.01	3	78, 90, 115	94 $\pm$ 19
		0.10	1	72	72
	(Z)-Metaflumizone	0.01	3	98, 106, 107	104 $\pm$ 5
		0.10	1	86	86
	M320I04	0.01	3	89, 89, 103	94 $\pm$ 8
		0.10	1	99	99
M320I23	0.01	3	69, 101, 102	91 $\pm$ 19	
	0.10	1	54	54	
Lemon	(E)-Metaflumizone	0.01	2	78, 144	111
		0.10	1	109	109
	(Z)-Metaflumizone	0.01	2	87, 111	99
		0.10	1	120	120
	M320I04	0.01	2	83, 92	88
		0.10	1	126	126
M320I23	0.01	2	93, 101	97	
	0.10	1	71	71	

Standard deviation is only applicable for sample sizes of  $n \geq 3$  samples.

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

Matrix	Storage Temperature	Actual Storage Duration <sup>1</sup>	Interval of Demonstrated Storage Stability
Orange, fruit	<-5 °C	8-171 days (0.3-5.6 months)	Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit are required. <sup>2</sup>
Grapefruit, fruit		17-79 days (0.6-2.6 months)	
Lemon, fruit		50-171 days (1.6-5.6 months)	

<sup>1</sup> Actual storage duration from sampling to analysis; samples were analyzed within 0-2 days of extraction.

<sup>2</sup> Previously submitted storage stability data; refer to D308394 (T. Bloem, 30-Nov-2005).

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**TABLE C.3. Residue Data from Crop Field Trials with Metaflumizone.**

Trial: City, State; Year (Trial ID#)	Zone	Variety	Total Rate (lb ai/A)	PHI' (days)	Commodity	Residues (ppm; parent equivalents)					
						(E)- Metaflumizone	(Z)- Metaflumizone	Metaflumizone (E+Z) <sup>2</sup>	M320104	M320123	Total <sup>3</sup>
<b>Orange Trials</b>											
Oviedo, FL; 2006 (TCI-06-150-01)	3	Valencia	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
					Dropped fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Clermont, FL; 2006 (TCI-06-150-02)	3	Valencia	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
					Dropped fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Fellsmere, FL; 2006 (TCI-06-150-03)	3	Valencia	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Oviedo, FL; 2006 (TCI-06-150-04)	3	Navel	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
					Dropped fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Mims, FL; 2006 (TCI-06-150-05)	3	Hamlin	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Clermont, FL; 2006 (TCI-06-150-06)	3	Mid Sweet	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Bithlo, FL; 2006 (TCI-06-150-07)	3	Hamlin	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Holopaw, FL; 2006 (TCI-06-150-08)	3	Mid Sweet	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Raymondville, TX; 2006 (TCI-06-150-09)	6	N-33 Navels	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Richgrove, CA; 2006 (TCI-06-150-10)	10	Valencia	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Strathmore, CA; 2006 (TCI-06-150-11)	10	Washington	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Porterville, CA; 2006 (TCI-06-150-12)	10	Newhall	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038

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**TABLE C.3. Residue Data from Crop Field Trials with Metaflumizone.**

Trial: City, State; Year (Trial ID#)	Zone	Variety	Total Rate (lb ai/A)	PHI <sup>1</sup> (days)	Commodity	Residues (ppm; parent equivalents)					
						(E)- Metaflumizone	(Z)- Metaflumizone	Metaflumizone (E+Z) <sup>2</sup>	M320104	M320123	Total <sup>3</sup>
<b>Grapefruit Trials</b>											
Oviedo, FL; 2006 (TCI-06-150-13)	3	Flame	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Mims, FL; 2006 (TCI-06-150-14)	3	Marsh	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Holopaw, FL; 2006 (TCI-06-150-15)	3	White -- Marsh	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Raymondville, TX; 2006 (TCI-06-150-16)	6	Rio Red	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Porterville, CA; 2006 (TCI-06-150-17)	10	Mellogold	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Terra Bella, CA; 2006 (TCI-06-150-18)	10	Oro Blanco	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
<b>Lemon Trials</b>											
Clermont, FL; 2006 (TCI-06-150-19)	3	Meyers	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Somis, CA; 2006 (TCI-06-150-20)	10	Eureka	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Santa Paula, CA; 2006 (TCI-06-150-21)	10	Lisbon	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Porterville, CA; 2006 (TCI-06-150-22)	10	Pryor	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038
Ivanhoe, CA; 2006 (TCI-06-150-23)	10	Lisbon	0.004	5	Fruit	<0.01	<0.01	<0.02	<0.018	<0.01	<0.038

<sup>1</sup> PHI = pre-harvest interval.

<sup>2</sup> Total of metaflumizone E and Z isomers.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320104; M320123 residues are presented for informational purposes and are not included in the totals.



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 Crop Field Trial/Residue Decline - Citrus Fruit Group 10

Commodity	Total Applic. Rate (lb ai/A)	PHI (days)	Analyte	Residue Levels (ppm)						
				n	Min.	Max.	HAFT <sup>1</sup>	Median	Mean	Std. Dev. <sup>2</sup>
Orange, fruit	0.004	5	(E)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	24	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	24	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	24	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	24	<0.01	<0.01	<0.01	<0.01	<0.01	--
Grapefruit, fruit	0.004	5	(E)-Metaflumizone	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	12	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	12	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	12	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	12	<0.01	<0.01	<0.01	<0.01	<0.01	--
Lemon, fruit	0.004	5	(E)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			(Z)-Metaflumizone	10	<0.01	<0.01	<0.01	<0.01	<0.01	--
			<b>Metaflumizone (E+Z)</b>	10	<0.02	<0.02	<0.02	<0.02	<0.02	--
			M320I04	10	<0.018	<0.018	<0.018	<0.018	<0.018	--
			<b>Total Residues<sup>3</sup></b>	10	<0.038	<0.038	<0.038	<0.038	<0.038	--
			M320I23	10	<0.01	<0.01	<0.01	<0.01	<0.01	--

HAFT = highest average field trial.

<sup>2</sup> Standard deviation not applicable as all residues were below the LOQ.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320I04.

#### D. CONCLUSION

The submitted field trial data on citrus fruit reflect the use of a 0.063% G formulation applied as a single soil broadcast application at a rate of 0.004 lb ai/A, with a 5-day PHI. An acceptable method was used for the quantitation of residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23. Supporting storage stability data are required. Residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23 were <LOQ in/on all of the samples.

#### E. REFERENCES

D308394, T.Bloem, 30-Nov-2008

#### F. DOCUMENT TRACKING

RDI: RAB1 Chemists (18-Mar-2008)

T. Bloem:S10945:Potomac Yard 1:703-605-0217:7509P:RAB1

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 DACO 7.4.5/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5  
 Processed Food and Feed - Orange

Primary Evaluator		26-January-2010
	Tom Bloem, Chemist Risk Assessment Branch 1 (RAB1) Health Effects Division (HED; 7509P)	
Approved by		26-January-2010
	George F. Kramer, Ph.D., Senior Chemist RAB1/HED (7509P)	

This data evaluation record (DER) was originally prepared under contract by Dynamac Corporation (2275 Research Boulevard, Suite 300; Rockville, MD 20850; submitted 04/18/2008). The DER has been reviewed by the HED and revised to reflect current Office of Pesticide Programs (OPP) policies.

### **STUDY REPORT:**

47235703 Carringer, S. (2007) Magnitude of the Residue of Metaflumizone and its Metabolites in or on Citrus Raw Agricultural and Processed Commodities Following One Application of BAS 320 04 I. Project Number: TCI/06/150, 254485, 7001662. Unpublished study prepared by BASF Agro Research and University of Idaho, Cooperative Extension and Carringers, Inc. 316 p.

### **EXECUTIVE SUMMARY:**

BASF Corporation submitted a processing study for metaflumizone on orange. In two field trials conducted in FL during the 2006 growing season, the 0.063% granular (G) formulation of metaflumizone was applied to orange trees as a single soil broadcast application at 0.02 lb ai/A. The application was made when citrus fruits were at BBCH 83 or mature growth stage using ground equipment; no adjuvant was used with the granular formulation. Mature fruits were harvested 5 days after application. At one site, the orange samples were harvested from the trees and then dropped on the orchard floor under and around the trees where the test substance had been applied. This dropped fruit was collected and processed into orange oil using simulated-commercial practices (the other sample was not processed); the samples were not processed into juice.

Samples of orange fruit and oil were analyzed for residues of (E)- and (Z)-metaflumizone, and metabolites M320I04 and M320I23 using the liquid chromatograph/mass spectrometer/mass spectrometer (LC/MS/MS) BASF analytical method 531/0, the enforcement method for plant commodities. Based on the lower limit of method validation (LLMV), the limit of quantitation (LOQ) was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively. The combined LOQ for metaflumizone (E+Z isomers) and M320I04 is 0.038 ppm. The method was adequate based on acceptable concurrent recoveries.

Samples were processed within 4 days of harvest, and the raw agricultural commodity (RAC) and citrus oil samples were stored frozen for up to 8-14 days prior to analysis. Since previous



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storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit and oil are required.

Residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23, were each below the LOQ (<0.01 ppm or <0.018 ppm for M320I04) in/on all (picked and “dropped”) orange RAC samples. Following processing of dropped fruit, residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were also nonquantifiable in the orange oil. Because residues were nonquantifiable in both the RAC and citrus oil, no processing factors could be calculated. The theoretical concentration factor for citrus oil based on separation into components is 1000x (OPPTS 860.1520, Table 3).

#### **STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:**

Under the conditions and parameters used in the study, the field trial residue data are tentatively classified as scientifically acceptable pending submission of storage stability data demonstrating the stability of metaflumizone (E and Z isomers) and M320I04 in citrus fruit and oil stored frozen for up to 14 days. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DP# 345540.

#### **COMPLIANCE:**

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

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## A. BACKGROUND INFORMATION

Metaflumizone is a voltage-dependent, sodium-channel-blocker insecticide (Group 22B) which leads to inhibited feeding and paralysis in susceptible insects (Lepidoptera and Coleoptera). Metaflumizone is a mixture of the E and Z stereoisomers which are present at a ratio of  $\geq 9:1$  (E:Z). The chemical structure and nomenclature of metaflumizone, and the physicochemical properties of the technical grade of metaflumizone are presented in Tables A.1 and A.2.

Table A.1. Metaflumizone Nomenclature.	
Chemical structure	
Common name	Metaflumizone
Company experimental name	BAS 320 I
IUPAC name	(EZ)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-4-(trifluoromethoxy)carbanilohydrazide
CAS name	2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]hydrazinecarboxamide
CAS registry number	139968-49-3
End-use product (EP)	Altrevin Fire Ant Bait Insecticide (0.063% G formulation; EPA Reg. No. 7969-###)
Metabolite M320I04	<p>4-[2-oxo-2-[3-(trifluoromethoxy)phenyl]ethyl]-benzotrile</p>
Metabolite M320I23	<p>4-[5-hydroxy-3-oxo-4-[4-(trifluoromethoxy)phenyl]-6-[3-(trifluoromethyl)phenyl]-2,3,4,5-tetrahydro-1,2,4-triazin-5-yl]benzotrile</p>



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Melting point	Two melting points observed at approximately 127 °C and 186 °C.		MRID 46264204
pH	6.48 at 25 °C (1% aqueous suspension)		MRID 46264524
Density (20 °C)	1.461 g/cm <sup>3</sup>		MRID 46264204
Water solubility (20 °C)	D.I. water	1.79 µg/L	MRID 46264208
	pH 5	1.35 µg/L	
	pH 7	1.81 µg/L	
	pH 9	1.73 µg/L	
Solvent solubility (20 °C)	Acetone	142.7 mg/L	MRID 46264212
	Acetonitrile	60.3 mg/L	
	DCM	92.7 mg/L	
	EtOAc	159.7 mg/L	
	Heptane	0.0084 mg/L	
	Methanol	13.95 mg/L	
	Toluene	3.96 mg/L	
Vapor pressure	1.24 x 10 <sup>-8</sup> Pa at 20 °C		MRID 46264206
Dissociation constant, pK <sub>a</sub>	None in pH range 2-12		MRID 46264217
Octanol/water partition coefficient, Log(K <sub>OW</sub> )	Log P <sub>OW</sub> = 5.1 (Z isomer)		MRID 46264213
	Log P <sub>OW</sub> = 4.4 (E isomer)		
UV/visible absorption spectrum	Molar absorptivity: 3.81 × 10 <sup>4</sup> L/Mcm at 234 nm; 1.93 × 10 <sup>4</sup> L/Mcm at 280 nm.		MRID 46264207

## B. EXPERIMENTAL DESIGN

### B.1. Application and Crop Information

In two crop field trials conducted in FL during the 2006 growing season, the 0.063% G formulation of metaflumizone was applied to orange trees as a single soil broadcast application at a rate of 0.02 lb ai/A (22.4 g ai/ha). Applications were made using simulated commercial ground-based granular application equipment. The actual study use pattern is reported in Table B.1.1.

The test crops were grown and maintained according to typical agricultural practices for each region; maintenance pesticides and fertilizers were used. Rainfall amounts during the trial period, mean monthly temperature minimums and maximums, and ten-year historical averages of rainfall and temperatures were provided. Overall the trials experienced normal weather, but the trials generally experienced a drier than normal season. There was no irrigation between the application and harvest.

Trial Identification: City, State; Year (Trial ID#)	EP <sup>1</sup>	Application					Tank Mix/ Adjuvants
		Method; Timing	Volume	Rate (lb ai/A)	RTI <sup>2</sup> (days)	Total Rate (lb ai/A)	
Oviedo, FL; 2006 (TCI-06-150-01)	0.063% G	1. Soil broadcast; BBCH 83/ mature fruit	NA <sup>3</sup>	0.02	NA	0.02	NA
Oviedo, FL; 2006 (TCI-06-150-04)	0.063% G	1. Soil broadcast; BBCH 83	NA	0.02	NA	0.02	NA

<sup>1</sup> EP = end-use product; BAS 320 04 I.

<sup>2</sup> RTI = retreatment interval.

<sup>3</sup> NA = not applicable for the granular formulation.



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## B.2. Sample Handling and Processing Procedures

Bulk samples of untreated and treated oranges were harvested by hand 5 days after application. At one site (TCI-06-150-01), the orange samples were harvested from the trees and then dropped on the orchard floor under and around the trees where the test substance had been applied and collected. On the day of collection, samples were shipped at ambient temperatures by overnight courier to Englar Food Laboratories (Caldwell, ID) for processing. Subsamples of orange were reserved as RAC samples and the remaining sample (stored at  $3 \pm 3$  °C) was processed into orange oil; processing was initiated within 2 days of harvest.

Samples were processed using simulated commercial processing procedures omitting the juice extraction step. Processed oil samples were frozen ( $-17 \pm 8$  °C), and RAC and oil samples were shipped by FedEx on dry ice to the analytical laboratory, BASF Agro Research (Research Triangle Park, NC), where they were stored frozen ( $<-5$  °C) until homogenization (RAC samples only) and analysis. The orange processing procedures are summarized in the flow chart below, which was copied without alteration from MRID 42735703.

## B.3. Analytical Methodology

Samples of orange fruit and orange oil were analyzed for residues of (E)- and (Z)-metaflumizone and metabolites M320I04 and M320I23 using the LC/MS/MS BASF analytical method 531/0, the enforcement method for plant commodities. A brief description of the method was included in the submission; for a complete description of the method, refer to D308394 (T. Bloem, 30-Nov-2005).

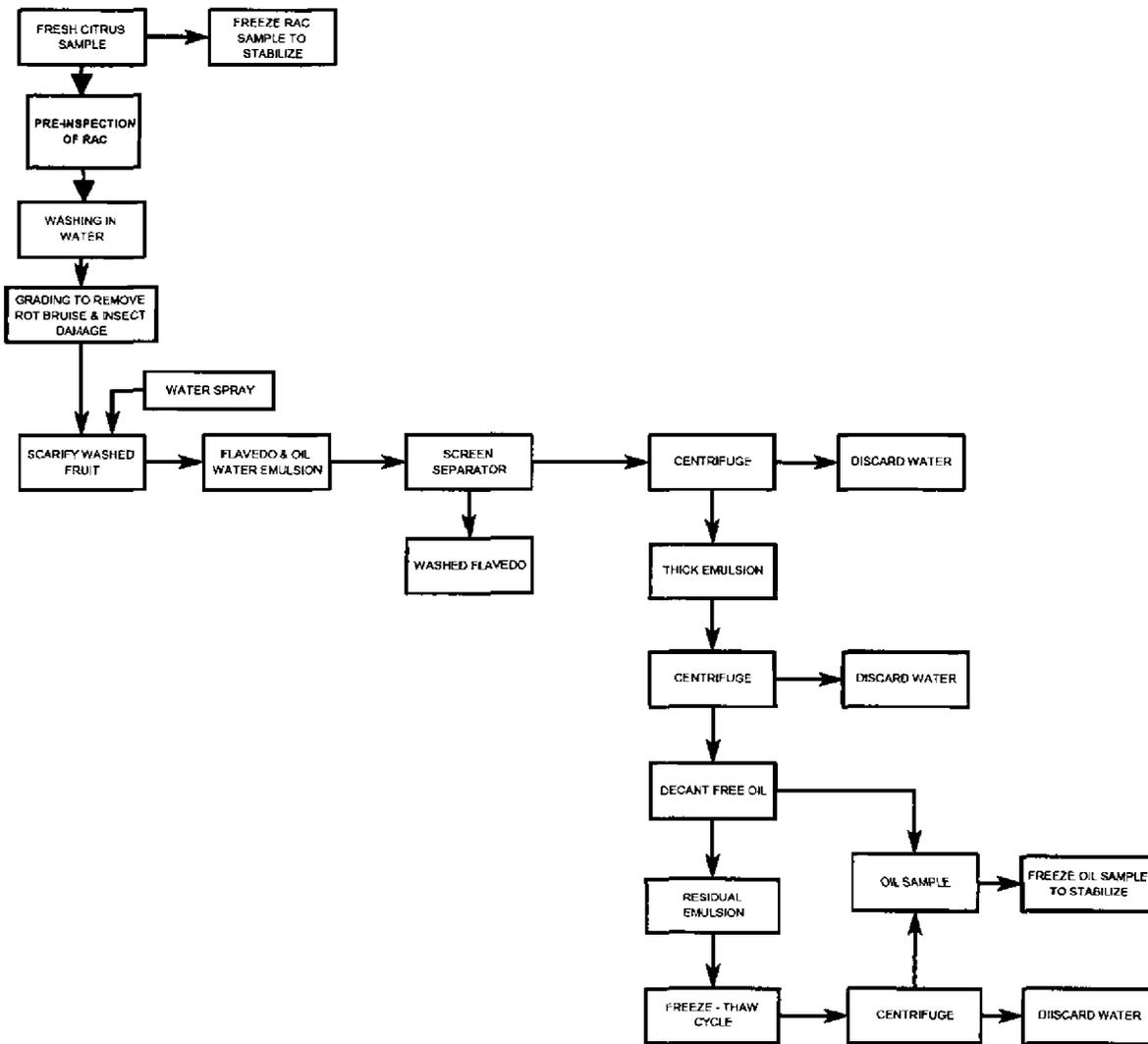
Briefly, fruit samples were extracted with methanol:water (70:30, v:v) and centrifuged. The supernatant was diluted with saturated sodium chloride solution and partitioned against dichloromethane (DCM). The DCM phase was evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC/MS/MS analysis. Oil samples were extracted with isohexane and cleaned up by liquid/liquid partitioning against acetonitrile (ACN). The extract was further purified on a silica column, eluted with ACN, and the eluate evaporated to dryness and redissolved in methanol:water (50:50, v:v) for LC-MS/MS analysis.

Based on the LLMV, the LOQ was 0.01 ppm for each analyte; the LOQs for M320I04 and M320I23 in parent metaflumizone equivalents are 0.018 and 0.01 ppm, respectively, based on molecular weight conversion factors of 1.7507 for M320I04 and 0.97312 for M320I23. The limit of detection (LOD), defined as ~20% of the LOQ, was ~0.002 ppm for each analyte in orange fruit and oil.



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**FIGURE 1. Processing Flow Chart for Orange.**



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**CITRUS PROCESSING FLOW CHART**

THIS FLOW CHART IS THE PROPERTY OF THE UNIVERSITY OF IDAHO FOOD TECHNOLOGY CENTER AND SHALL NOT BE DUPLICATED IN WHOLE OR IN PART OR USED FOR UNINTENDED PURPOSES WITHOUT WRITTEN CONSENT FROM THE UNIVERSITY OF IDAHO.

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## C. RESULTS AND DISCUSSION

Sample storage conditions and durations are summarized in Table C.2. Samples were processed within 2 days of harvest, and the RAC and citrus oil samples were stored frozen for up to 8-14 days prior to analysis. Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit and oil are required.

Concurrent method recovery data are presented in Table C.1. Samples were analyzed for residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 using the LC/MS/MS Method 531/0. The method was adequate for data collection based on acceptable concurrent method recovery data. Concurrent method recoveries were generally within the acceptable range of 70-120% for orange fruit and oil fortified with each analyte at 0.01 and 0.10 ppm. Apparent residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were each below the method LOQ in/on all samples of untreated orange RAC and processed oil.

Residue data from the orange processing study are reported in Table C.3. Residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23, were <LOQ (<0.01 ppm) in/on all (picked and “dropped”) orange RAC samples. Following processing of dropped fruit, residues of (E)- and (Z)-metaflumizone, M320I04, and M320I23 were also nonquantifiable in the orange oil; residues of (E)- and (Z)-metaflumizone were observed in oil at the limit of detection. Because residues were nonquantifiable in both the RAC and citrus oil, no processing factors could be calculated. The theoretical concentration factor for citrus oil based on separation into components is 1000x (OPPTS 860.1520, Table 3).

Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean ± Std. Dev. <sup>1</sup> (%)
Orange, fruit	(E)-Metaflumizone	0.01	2	75, 83	79
		0.10	2	98, 115	107
	(Z)-Metaflumizone	0.01	2	91, 98	95
		0.10	2	98, 102	100
	M320I04	0.01	2	74, 101	87
		0.10	1	100	100
	M320I23	0.01	2	70, 83	77
		0.10	2	94, 99	97
Orange, oil	(E)-Metaflumizone	0.01	1	98	98
		0.10	1	84	84
	(Z)-Metaflumizone	0.01	1	93	93
		0.10	1	89	89
	M320I04	0.01	1	67	67
		0.10	1	70	70
	M320I23	0.01	1	110	110
		0.10	1	83	83

<sup>1</sup> Standard deviation is only applicable for sample sizes of n≥3 samples.



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

Matrix	Storage Temperature	Actual Storage Duration <sup>1</sup>	Interval of Demonstrated Storage Stability
Orange, fruit (RAC)	<-5 °C	7-14 days (0.2-0.5 months)	Since previous storage stability data demonstrated some instability of the metaflumizone Z isomer and M320I04 in diverse crops (in some instance unstable for intervals of <30 days; D308394, T. Bloem, 30-Nov-2005) and since none of the employed crops are translatable to citrus, storage stability data specific to citrus fruit and oil are required.
Orange, oil		6-8 days (0.2-0.3 months)	

<sup>1</sup> Actual storage duration from field sampling or processing to sample analysis. Samples were analyzed within 0-4 days of extraction.

**TABLE C.3. Residue Data from Orange Processing Study with Metaflumizone.**

Trial: City, State; Year (Trial ID#)	Processed Commodity	Total Rate (lb ai/A)	PHI (days)	Residues (ppm; parent equivalents) <sup>1</sup>						Processing Factor <sup>4</sup>
				Metaflumizone			Metabolites		Total <sup>3</sup>	
				(E)	(Z)	Total <sup>2</sup>	M320I04	M320I23		
Oviedo, FL; 2006 (TCI-06-150-01)	Dropped fruit (RAC)	0.02	5	<0.01 <sup>3</sup> <0.01	<0.01 <0.01	<0.02 <0.02	<0.018 <0.018	<0.01 <0.01	<0.038 <0.038	--
	Oil	0.02	5	(0.0025) (0.0021)	(0.0023) (0.0025)	<0.02 <0.02	<0.018 <0.018	<0.01 <0.01	<0.038 <0.038	NC
Oviedo, FL; 2006 (TCI-06-150-04)	Fruit (RAC)	0.02	5	<0.01 <0.01	<0.01 <0.01	<0.02 <0.02	<0.018 <0.018	<0.01 <0.01	<0.038 <0.038	--

<sup>1</sup> LOQ = 0.01 ppm for all excluding M320I04 where the LOQ = 0.018 ppm; petitioner indicated a LOD of 0.002 ppm. Residues between the LOQ and LOD are reported in parentheses.

<sup>2</sup> Total of metaflumizone E and Z isomers; the LOQ (<0.01 ppm) for each isomer was used for individual values reported as <LOQ.

<sup>3</sup> Total of the residues of concern: metaflumizone (E + Z isomers) and M320I04; the LOQ was used for individual values reported as <LOQ. M320I23 residues are presented for informational purposes and are not included in the totals.

<sup>4</sup> Processing factors for total residues of metaflumizone (E + Z isomers) and M320I04 could not be calculated (NC) because residues were below the LOQ in both the RAC and processed oil.

## D. CONCLUSION

The submitted orange processing study reflect the use of a 0.063% G formulation applied as a single soil broadcast application at a rate of 0.02 lb ai/A, with a 5-day PHI (samples only processed to oil). An acceptable method was used for the quantitation of residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23. Supporting storage stability data are required. Residues of (E)- and (Z)-metaflumizone and its metabolites M320I04 and M320I23 were <LOQ in/on all of the orange RAC (picked and dropped) and oil samples (residue data for the remaining processed commodities were not provided).

## E. REFERENCES

D308394, T.Bloem, 30-Nov-2008

## F. DOCUMENT TRACKING

RDI: RAB1 Chemists (18-Mar-2008)

T. Bloem:S10945:Potomac Yard 1:703-605-0217:7509P:RAB1

Template Version June 2005



13544

# R181057

**Chemical Name:** Metaflumizone  
4-[(2Z)-2-[[4-(TRIFLUOROMETHOXY)ANILINO]CARBONYL]HYDRAZONO)-2-[3-(TRIFLUOROMETHYL)PHENYL]ETHYL]BENZONITRILE

**PC Code:** 281250

281251

**HED File Code:** 11000 Chemistry Reviews  
**Memo Date:** 1/26/2010  
**File ID:** 00000000  
**Accession #:** 000-00-0134

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