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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

Date: 6/13/06

Subject: Glyphosate: Coffee; Summary of Analytical Chemistry and Residue Data. Request to Amend WeatherMAX® Label to Lower the PHI to One Day.

DP Numbers: 314255, 327313 Decision: 364666
PC Code: 103601 MRID Numbers: 00051980 - 00051982
40 CFR 180.364 Chemical Class: Herbicide

From: J. R. Tomerlin, Ph.D., Plant Pathologist
Fungicide Branch
Registration Division (7505P)

W. Cutchin for

Through: P. V. Shah, Ph.D., Branch Senior Scientist
Registration Acton Branch 1
Health Effects Division

P. V. Shah

and

W. Cutchin *William Cutchin*
Technical Review Branch
Registration Division (7505P)

To: V. Walters/D. Kenny PM 25
Herbicide Branch
Registration Division (7505P)

Executive Summary

A major glyphosate registrant, Monsanto, has submitted field trial and processing data for glyphosate (N-(phosphonomethyl)glycine) on coffee. The data have been submitted to support a request to amend a label to lower the pre-harvest interval (PHI) from 28 days to 1 day. In all trials, Roundup® Herbicide was applied to postemergence weeds growing among trees in tropical coffee plantations. The only difference between the test substance (Roundup® Herbicide) and the registered product (Roundup WeatherMAX®) is the percent active ingredient

JUN 22 2006

in the formulated product. A total of 4 or 8 lbs a.i./A (4.5 or 9 kg a.i./hectare) of compound was applied coffee trials, approximately 83% of the current maximum seasonal label application rate for WeatherMAX®. Therefore, the supplemental label specifying a 1 day PHI for coffee should also stipulate a maximum seasonal application rate of 8 lbs a.i./A (9 kg a.i./hectare). The treatment interval ranged from 49 to 56 days. The number and locations of coffee field trials are not in accordance with OPPTS Guideline 860.1500. Two trials were conducted in Region 13, one trial was conducted in Cali, Columbia, and two trials were conducted in San Jose, Costa Rica. TRB concludes that the field trials adequately represent potential geographic variation.

In previously submitted studies in plants and rotational crops, residues of glyphosate were not detectable in crops planted 30 days after treatment. For purposes of this petition, the residue of concern for tolerance setting and risk assessment purposes is glyphosate *per se*. Amino-methylphosphonic acid (AMPA) is no longer of toxicological concern and is not included in either the tolerance expression or the risk assessment. No impact is expected on the dietary burdens to dairy or beef cattle, poultry or hogs since coffee is not an animal feedstuff.

Adequate enforcement methods are included in the Food and Drug Administration's Pesticide Analytical Methods, Volume II (PAM II). These methods include GLC (Method I in PAM II) and HPLC with fluorometric detection. However, recoveries are not likely for glyphosate under FDA Multiresidue Methods.

The method used for the analysis of glyphosate residues in coffee samples, *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975, is adequate for data collection. The method sensitivity was 0.05 ppm.

Glyphosate residues were quantitated in sample extracts of green coffee beans and processed commodities using the method cited. Glyphosate was extracted from aqueous ammoniacal extracts of green coffee beans, roasted coffee beans, and instant coffee by elution from appropriate ion exchange resins. Following additional purification and conversion of the parent molecule to the corresponding N-trifluoroacetyl-methyl ester compounds, extracts of green coffee beans, roasted coffee beans, and instant coffee were analyzed using gas-liquid chromatography with a phosphorus-specific flame photometric detector. Untreated control green coffee beans were fortified at 0.05, 0.1, 0.2 and 0.4 ppm for recovery spikes. Mean recoveries for green coffee beans were $64 \pm 11\%$.

Tolerances for the residues of glyphosate (N-(phosphonomethyl)glycine) are established on a wide range of crops (40 CFR 180.364). The proposed reduction in PHI to one day will not have an impact upon the existing tolerance level. The residue field trial studies were adequate in number and geographic location, conducted in accordance with the proposed uses, and supported by appropriate storage stability data. There are adequate analytical methods available for tolerance enforcement. The analytical method used for data gathering is acceptable for that purpose. The residue chemistry data support the proposed in PHI from 28 days to 1 day for the use of glyphosate in coffee plantations. A glyphosate confined rotational crop study has previously been submitted and reviewed. The registrant should reinstate the 30-day PBI for crops on which use of glyphosate is not registered.

Regulatory Recommendations and Residue Chemistry Deficiencies

The petitioner should submit a revised supplemental label for the proposed uses on coffee including a 30-day plant back restriction for rotational crops. The revised supplemental label must limit the maximum total seasonal application rate on coffee to 8 lbs a.i./A (9 kg a.i./hectare).

Pending submission of a revised supplemental label, TRB recommends for the label amendment, reducing the PHI from 28 days to one day. This action has no impact on the existing tolerance level, and a human health risk assessment is not required.

Background

Glyphosate is an herbicide used to control a broad spectrum of weed species in a wide range of crop plants. The coffee growers in Hawaii have asked Monsanto to lower the PHI on the WeatherMAX® label to one day, to provide growers additional flexibility in weed control and coffee harvest. PHI values currently on the WeatherMAX® label from other Shrub and Tree Crops include one day on citrus and pome; three days on nuts; 14 days on berries, vines, and tropical fruits; and 17 days on stone fruits. The test material was Roundup®, the isopropylamine salt. Roundup® is 4 lb a.i./gal, or 3 lb/gal of acid equivalent. The nomenclature of the test substance is shown in Table 1. The physical and chemical characteristics of glyphosate are shown in Table 2.

TABLE 1. Test Compound Nomenclature	
Compound	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ \text{HOCCH}_2\text{NHCH}_2\text{P(OH)}_2 \end{array}$
Common name	Glyphosate
Company experimental name	Not Available
IUPAC name	N-(phosphonomethyl)glycine
CAS name	Glycine, N-(phosphonomethyl)
CAS #	1071-83-6
End-use product/EP	Roundup® Herbicide

TABLE 2. Physical and Chemical Properties of Glyphosate Technical Grade Active Ingredient	
Color	White
Physical State	Crystalline solid
Odor	Odorless
Melting Point	184.5°C
pH ^a	2.5, 1% solution
Specific Gravity ^b	1.7 @ 20°

Solubility in water ^b	10,100 mg/L @ 20°C
Solvent solubility ^c	Insoluble in most organic solvents
Vapor Pressure ^b	< 1 x 10 ⁻³ Pa @ 25°C
Dissociation Constant ^b	<2, 2.6, 5.6, 10.6
Octanol/Water Coefficient ^b	-2.8
Absorption coefficient ^c	12,000
^b Value obtained from International Programme on Chemical safety from data provided by Monsanto	
^c Extoxnet	

860.1200 Directions for Use

Table 3 summarizes the label directions for the use of glyphosate on coffee. Not that the maximum seasonal application rate indicates the current values. As shown in Section 860.1500, the residue data support a maximum seasonal application rate of 8 lbs a.i./A (9 kg a.i./hectare), the maximum rate in the residue trials. This value is indicated in the table as the revised rate and should be followed when the label is amended to permit a one-day PHI. Likewise, the column for the PHI indicates the current PHI of 28 days, but also indicates the PHI of one day following the amending of the label.

Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate lb ai/A (kg ai/ha)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate lb ai/A (kg ai/ha)	PHI (days)	Use Directions and Limitations
<p>Preplant (Site Preparation) Broadcast Sprays, General Weed Control, Middles (between rows of trees), strips (within rows of trees), Selective Equipment (shielded sprayers, wiper applications) Directed Sprays, spot treatment, Perennial Grass Suppression, Cut Stump.</p> <p>Applications may be made with boom equipment, CDA equipment, shielded sprayers, hand-held and high-volume wands, lances, orchard guns or with wiper applicator equipment, except as directed.</p>	524-537	0.95 – 4.5 (1.0 – 5.1)	Not specified	9.6 - Current (10.8) - Current 8 - Revised (9) - Revised.	28 – Current 1 – Proposed	Delay applications 3 months after transplanting to allow the new coffee plant to become established.

The label is adequate to allow evaluation of the residue data relative to the proposed use.

860.1300 Nature of the Residue - Plants

PP# 2E04118 (formerly 2H05650), DNums: 242628, 245591, T. Bloem, 11/30/98

PP#s 0F06130, 0F06195 and 0F06273. DNum: 280831, W. H. Donovan, W.G. Dykstra and J. T. Swackhammer, 2/20/02

SF04555, DNums: 217539 and 217541, G. Kramer, 3/14/96

Memorandum, R. B. Perfetti, 10/19/92

Memorandum, R. B. Perfetti, 10/27/92

Memorandum, R. B. Perfetti, 3/17/94

The qualitative nature of the residue in plants is adequately understood. Studies with a variety of plants including corn, cotton, soybeans, and wheat indicate that the uptake of glyphosate or its metabolite, aminomethylphosphonic acid (AMPA), from soil is limited. The material that is taken up is readily translocated. Foliar-applied glyphosate is readily absorbed and translocated throughout the trees or vines to the fruit of apples, coffee, dwarf citrus (calamondin), pears and grapes. Metabolism via N-methylation yields N-methylated glycines and phosphonic acids. For the most part, the ratio of glyphosate to AMPA is 9 to 1 but can approach 1 to 1 in a few cases (e.g., soybeans and carrots). Much of the residue data for crops reflects a detectable residue of parent (0.05 - 0.15 ppm) along with residues below the level of detection (<0.05 ppm) of AMPA (Memo, R. B. Perfetti, 10/27/92). In an 8/19/92 meeting, the HED Metabolism Committee determined that, based on toxicological considerations, AMPA need not be regulated and should be dropped from the tolerance expression (Memo, R. B. Perfetti, 10/19/92). Furthermore, in a 3/17/94 meeting, the HED Metabolism Committee discussed whether uses that result in significantly higher residues of AMPA in plants and livestock commodities in the future would require that AMPA be reintroduced into the tolerance expression of glyphosate. The Committee determined that, based on toxicological considerations, AMPA need not be regulated regardless of levels observed in foods or feeds (Memo, R. B. Perfetti, 3/17/94).

Metabolism studies submitted for genetically engineered glyphosate-tolerant canola (242628 and 245591, T. Bloem, 11/30/98) and glyphosate-tolerant corn (217539, G. Kramer, 3/14/96) have indicated that metabolism in glyphosate-tolerant plants is essentially the same as that in normal plants. Thus, the terminal residue to be regulated in plants is glyphosate *per se*.

860.1300 Nature of the Residue – Livestock

PP#s 0F06130, 0F06195 and 0F06273, DNum: 280831, W. H. Donovan, W.G. Dykstra and J. T. Swackhammer, 2/20/02

Memorandum, R. B. Perfetti, 10/19/92

Memorandum, R. B. Perfetti, 10/27/92

Memorandum, R. B. Perfetti, 3/17/94

The qualitative nature of glyphosate residues in livestock is adequately understood. Studies with lactating goats and laying hens fed a mixture of glyphosate and AMPA indicate that the primary route of elimination was by excretion (urine and feces). These results are consistent with metabolism studies in rats, rabbits, and cows. The terminal residues in eggs, milk, and livestock tissues are glyphosate and its metabolite AMPA; there was no evidence of further metabolism (Memo, R. Perfetti, 10/27/92). The conclusions of the HED Metabolism Committee on 10/19/92 and 3/17/94 apply to plant and livestock commodities. Thus, the terminal residue to be regulated in livestock is glyphosate *per se*.

860.1340 Residue Analytical Methods

0F06130, 0F06195, and 0F06273, DNums: 265970, 275014, and 275015, W. Donovan, 1/31/02

5F04555, DNums: 217539 and 217541, G. Kramer, 3/14/96

Memorandum, R. B. Perfetti, 10/27/92

MRID# 00051980, 00051981, DNums: 314255, 327313, J. R. Tomerlin, @.@

Adequate enforcement methods are available for analysis of residues of glyphosate in or on plant and livestock commodities. These methods include GLC (Method I in Pesticides Analytical Manual (PAM) II; the limit of detection is 0.05 ppm) and HPLC with fluorometric detection. Use of the GLC method is discouraged due to the lengthiness of the experimental procedure. The HPLC procedure has undergone successful Agency validation and was recommended for inclusion in PAM II (Memo, R. Perfetti, 10/27/92). A GC/MS method for glyphosate in crops has also been validated by EPA's Analytical Chemistry Laboratory (ACL) (PP#5F04555, G. Kramer, 3/21/95). Thus, adequate analytical methods are available for residue data collection and enforcement of the proposed tolerances of glyphosate in/on the green coffee beans, roasted coffee beans and instant coffee.

The gas-liquid chromatography method was used to analyze residues in coffee (*Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975). In summary, in the method, glyphosate was extracted from aqueous ammoniacal extracts of green coffee beans by elution from appropriate ion exchange resins. Following additional purification and conversion of the parent molecule to the corresponding N-trifluoroacetyl-methyl ester compounds, extracts of green coffee beans were analyzed using gas-liquid chromatography with a phosphorus-specific flame photometric detector.

The method used for the analysis of glyphosate residues in coffee samples is adequate for data collection.

860.1360 Multiresidue Methods

0F06130, 0F06195, and 0F06273, DNums: 265970, 275014, and 275015, W. Donovan, 1/31/02

The Pesttrak database (1990) indicates that recoveries are not likely for glyphosate under FDA Multiresidue Methods. No further data regarding multiresidue methods are required for this proposed use. This conclusion is corroborated by the 2005 update of the Pesttrak database.

860.1380 Storage Stability

0F06130, 0F06195, and 0F06273, DNums: 265970, 275014, and 275015, W. Donovan, 1/31/02
DNum: 166777, R. B. Perfetti, 4/2/92
MRID# 00051980, 00051981, DNums: 314255, 327313, J. R. Tomerlin, @@

The maximum total storage intervals for grass, wheat, and alfalfa/clover samples were 11, 9.2, and 15 months, respectively. The available storage stability data indicate that residues of glyphosate are stable under frozen storage conditions (-20°C): in or on plant commodities for a period of at least 1 year, in animal commodities for at least 2 years, and in water for at least 1 year (Memo, R. Perfetti, 10/27/92). After storage for four months, average recovery from green coffee beans was $87.5 \pm 2.5\%$. There is adequate data available indicating that residues of glyphosate are stable in frozen coffee samples for the duration of the study.

860.1480 Meat, Milk, Poultry, and Eggs

DNum: 256740 W. Donovan, 6/9/00

0F06130, 0F06195, and 0F06273, DNums: 265970, 275014, and 275015, W. Donovan, 1/31/02

No impact is expected on the dietary burdens to dairy or beef cattle, poultry or hogs since coffee and coffee processed commodities are not animal feedstuffs.

860.1500 Crop Field Trials

MRID# 00051980, 00051981, DNums: 314255, 327313, J. R. Tomerlin, @@

Commodity	Total Application Rate, lb/A (kg/ha)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT ¹	Median (STMdR)	Mean (STMR)	Std. Dev.
Coffee	4 (4483)	1	2	0.08	0.11	N/A ²	0.095	0.095	0.021
Coffee	8 (8967)	1	3	0.28	0.35	N/A	0.32	0.32	0.035

¹Highest Average Field Trial
²Not Appropriate, as coffee is not an animal feedstuff

Monsanto has submitted field trial data for glyphosate on coffee. A total of three crop field trials were conducted at the proposed PHI of 1 day in Region 13 and in Cali, Columbia. In each trial, Roundup® Herbicide was applied to postemergence weeds in coffee plantations. A total of 4.0 or 8 lbs a.i./A (4.5 or 9 kg a.i./hectare) of compound was applied per treated plot. The maximum seasonal application rate of 8 lbs a.i./A is approximately 83% of the maximum seasonal application rate of 9.6 lbs a.i./A (10.8 kg a.i./hectare) on the current WeatherMAX® label. Therefore, the supplemental label amending the PHI should also stipulate a maximum seasonal application rate of 8 lbs a.i./A (9 kg a.i./hectare). The treatment interval ranged from 49 to 56 days. Green coffee beans were then picked one day, four weeks and eight weeks after the second application. The results from these trials show that glyphosate residues ranged from < 0.05 ppm to 0.67 ppm on green coffee beans picked 1 day after the last application. The number and locations of coffee field trials are not in accordance with OPPTS Guideline 860.1500.

Samples of green coffee beans were analyzed for glyphosate using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Recoveries ranged from 46% to 94% of the amount added, with an average of 65% recovery.

Samples of green coffee beans were spiked with glyphosate at 0.4 ppm and stored frozen for four months. After four months, percent recovery was 87.5 ± 2.5%. Subsequent reviews have shown that glyphosate residues remain stable in crop tissues for more than 2 years (CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92). Storage conditions are summarized in Table C.2.

860.1520 Processed Food and Feed

MRID# 00051982, DNums: 314255, 327313, J. R. Tomerlin, @@
Clifford, M. N., March 1975, Process Biochemistry
Sivetz, M. and Foote, H.E., 1963, Coffee Processing Technology, Volumes 1 and 2.

Weeds growing around the bases of coffee trees were treated with glyphosate Roundup® herbicide. Application rates ranged from 2 to 4 lbs a.i./A (2.2 to 4.5 kg a.i./hectare), with from 2 to 8 lbs a.i./A (2.2 to 9 kg a.i./hectare) applied seasonally. Green coffee beans were then picked, frozen, and shipped frozen to the laboratory for analysis. Processing samples were processed to roasted coffee beans, ground roast coffee, and instant (soluble) coffee. Samples were roasted, ground, percolator-extracted, and dried in the laboratory under conditions simulating commercial processing practice (Clifford, 1975; Sivetz and Foote, 1963). Residue concentrations demonstrate a definite reduction in processed commodities relative to the green coffee bean. The results from the processing study shows that the processing factor is 0.18 in roasted coffee bean and 0.55 in instant coffee.

Samples of green coffee beans, roasted coffee beans, and instant coffee were analyzed for glyphosate residues using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Method recovery values in green coffee beans ranged from 46% to 94% of the amount added, with an overall average of 65% recovery.

Samples of green coffee beans were spiked with glyphosate at 0.4 ppm and stored frozen for four months. After four months, percent recovery was $87.5 \pm 2.5\%$. Subsequent reviews have shown that glyphosate residues remain stable in crop tissues for more than 2 years (CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92).

A total of 4.0 or 8 lbs a.i./A (4.5 or 9 kg a.i./hectare) of compound was applied per treated plot. The maximum seasonal application rate of 8 lbs a.i./A is approximately 83% of the maximum seasonal application rate of 9.6 lbs a.i./A (10.8 kg a.i./hectare) on the current WeatherMAX® label. Therefore, the supplemental label amending the PHI should also stipulate a maximum seasonal application rate of 8 lbs a.i./A (9 kg a.i./hectare)

860.1650 Submittal of Analytical Reference Standards

Personal communication, email from C. J. Stafford to W. Cutchin and J. R. Tomerlin dated 2/22/06

Analytical reference standards are on file with the Agency.

860.1850 & 1900 Confined and Field Accumulation in Rotational Crops

MRID#s 41543201 and 41543202, A. Abramovitch, 10/14/92
0F06130, 0F06195, and 0F06273, DNums: 265970, 275014, and 275015, W. Donovan, 1/31/02
DNum: 200041 G. Kramer, 5/12/94

An acceptable confined rotational crop study was previously reviewed (Memo; MRIDs 41543201 and 41543202, A. Abramovitch, 10/14/92) which indicated that residues of glyphosate were not detectable in crops planted 30 days after treatment. The current label for glyphosate WeatherMAX® only addresses rotational crops in relation to use of WeatherMAX® on corn

with the Roundup Ready® gene. However, in an HED review of Monsanto's proposal to remove a 30-day plantback restriction for crops on which use of glyphosate is not registered, HED concluded that the petitioner would be required to demonstrate that significant glyphosate residues would not be present in rotational crops planted 0 days after soil treatment, and recommended against the label amendment. No rotational crop data have been submitted in support of a 0-day plantback interval (PBI) for rotational crops; therefore, the registrant should reinstate the 30-day PBI for crops on which use of glyphosate is not registered (DNum: 200041, 5/12/94, G. Kramer). This position was reiterated in a subsequent review (625970, W. Donovan, 1/31/02).

860.1550 Proposed Tolerances

The tolerance expression as stated in 40 CFR 180.364 is glyphosate (N-(phosphonomethyl)glycine). As described in the section 860.1500 – Nature of the Residue, Plants, AMPA is no longer of toxicological significance and is not included in the tolerance expression. There are currently no Codex, Canadian, or Mexican Maximum Residue Limits for residues of glyphosate on coffee, therefore there are no international harmonization issues associated with this action (Attachment 1).

Table 5. Tolerance Summary for glyphosate (N-(phosphonomethyl)glycine)			
Commodity	Established/Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments
Coffee	1	1	The requested action is a label amendment to lower the PHI to 1 day, which will have no impact upon the tolerance.

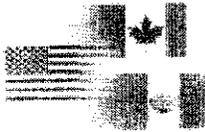
Template Version November 2003

ATTACHMENT 1

INTERNATIONAL RESIDUE LIMIT STATUS SHEET

INTERNATIONAL RESIDUE LIMIT STATUS			
Chemical Name: N-(phosphonomethyl) glycine	Common Name: Glyphosate	9 Proposed tolerance 9 Reevaluated tolerance 9 Other	Date:
Codex Status (Maximum Residue Limits)		U. S. Tolerances	
9 No Codex proposal step 6 or above ☒ No Codex proposal step 6 or above for the crops requested Residue definition (step 8/CXL): glyphosate		Petition Number: 4E6878 DP Barcode: D321667 Other Identifier: Reviewer/Branch: J. R. Tomerlin/RD-FB (ARIA Team) Residue definition: Glyphosate – N-(phosphonomethyl) glycine	
Crop (s)	MRL (mg/kg)	Crop(s)	Tolerance (ppm)
Coffee	none		
Limits for Canada		Limits for Mexico	
9 No Limits ☒ No Limits for the crops requested Residue definition: glyphosate plus AMPA		9 No Limits 9 No Limits for the crops requested Residue definition: glyphosate	
Crop(s)	MRL (mg/kg)	Crop(s)	MRL (mg/kg)
		Coffee (tree)	1.
Notes/Special Instructions: S.Funk, 06/05/2006.			

Rev. 1998



Glyphosate/103613/Monsanto
DACO 7.4.1/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 -- Coffee

Primary Evaluator J. R. Tomerlin, Ph.D.
Fungicide Branch
Registration Division

Date: 6/13/06

Peer Reviewer W. Cutchin, Chemist
Technical Review Branch
Registration Division

STUDY REPORTS:

MRID Nos.: 00051980, 00051981, Anonymous (June 1, 1976), Volume 1 of 1, Information to Support Establishment of Permanent Tolerances for Glyphosate in Coffee, R.D. 3102, Special Report 3405. The report was originally submitted by Monsanto in a single volume, linked to EPA Reg No. 524-308. The report was initially designated as EPA Acc. No. 95344 and 91677; the report included both residue data and metabolism data, in addition to information on the description of the product and similar information typical of submissions of that time. The submitted volume was subsequently broken into separate records and assigned MRIDs in the 00051977 to 00051983 series; MRID Nos. 00051980 and 00051981 contained residue data for green coffee beans.

EXECUTIVE SUMMARY:

The glyphosate registrant, Monsanto, has submitted field trial data for glyphosate (N-(phosphonomethyl)glycine) on coffee to support a request to amend the label, lowering the pre-harvest interval (PHI) to one day. Crop field trials were conducted in HI (Region 13), Brazil, Columbia and Costa Rica. In each trial, Roundup® Herbicide was applied to postemergent weeds growing among trees in a coffee plantation. Total compound applied ranged from 2 to 8 lbs a.i./A (2.2 to 9.0 kg a.i./hectare) of per treated plot. The majority of the trials at 1-day PHI were conducted at a seasonal application rate of 8 lbs a.i./A rate. The maximum seasonal rate according to the Roundup WeatherMAX® label is 9.6 lbs a.i./A. The treatment interval ranged from 49 to 56 days in trials having two applications. The number and locations of coffee field trials are not in accordance with OPPTS Guideline 860.1500.

Residues of glyphosate were quantitated using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Glyphosate was extracted from aqueous ammoniacal coffee extracts by elution from appropriate ion exchange resins. Following additional purification and conversion of the parent molecule to the corresponding N-trifluoroacetyl-methyl ester compounds, extracts of green coffee beans were analyzed using gas-liquid chromatography with a phosphorus-specific flame photometric detector. Method sensitivity was 0.05 ppm. The method is adequate for data collection.



Green coffee beans were harvested two, four and eight weeks after the first application of glyphosate. Additional samples were collected 1 day, four weeks and eight weeks after the second glyphosate application. This report is concerned with those samples having a 1-day pre-harvest interval (PHI). The results from these trials show that glyphosate residues ranged from < 0.05 to 0.67 ppm on/in treated green coffee beans, when the test substance was applied at seasonal application rates of 4 or 8 lbs a.i./A with a 1-day PHI. There is sufficient storage stability data available to support the residue chemistry data. After storage for four months, average recovery from green coffee beans was $87.5 \pm 2.5\%$.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DNums 314255 and 327313.

COMPLIANCE:

Glyphosate residue studies were completed June 1, 1976 and received by the Agency on June 3, 1976. EPA's Good Laboratory Practices guidelines were not established until 1983. Therefore, compliance of the subject study with 40 CFR 160 guidelines was not evaluated.

A. BACKGROUND INFORMATION

Glyphosate is an herbicide currently registered for use on coffee, and the registrant is requesting that the Roundup WeatherMAX® label be amended, reducing the PHI to 1 day. The test material was Roundup SL® (Reg. No. 524-308). Roundup SL® is 4 lbs a.i./gal, or 3 lbs/gal of acid equivalent, whereas Roundup WeatherMAX® is 5.5 lbs a.i./gal, or 4.5 lbs/gal of acid equivalent. The residue data is the same data that has supported the existing tolerance of 1 ppm on coffee. The nomenclature of the test substance is shown in Table A.1. The physical and chemical characteristics of glyphosate are shown in Table A.2.

TABLE A.1. Test Compound Nomenclature	
Common name	Glyphosate
Company name	Not applicable
Chemical Class	Herbicide
IUPAC name	N-(phosphonomethyl)glycine
CAS name	Glycine, N-(phosphonomethyl)
CAS #	38641-94-0



Glyphosate/103613/Monsanto
 DACO 7.4.1/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 - Coffee

End-use product/EP	Roundup® Herbicide
Chemical Structure	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ \text{HOCCH}_2\text{NHCH}_2\text{P(OH)}_2 \end{array}$

Color ¹	White
Physical State	Crystalline powder
Odor ¹	Odorless
Melting Point ¹	184.5°C
pH ¹	2.5, 1% solution
Specific Gravity ¹	1.7 @ 20°
Solubility in water ¹	10,100 mg/L @ 20°C
Solvent solubility ²	Insoluble in most organic solvents
Vapor Pressure ¹	< 1 x 10 ⁻³ Pa @ 25°C
Dissociation Constant ¹	<2, 2.6, 5.6, 10.6
Octanol/Water Coefficient ¹	-2.8
Absorption coefficient ²	12,000
¹ Value obtained from International Programme on Chemical safety from data provided by Monsanto	
² Data from Extoxnet	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Trial Identification (City, State Year - Trial ID)	Soil characteristics				Meteorological data	
	Type	%OM ¹	pH ¹	CEC ¹ (meq/g)	Overall Daily/Monthly Rainfall Range	Overall Temperature Range (°C)
Sao Paulo, Brazil	NA ²	NA	NA	NA	NA	NA
Cali, Columbia	Lateritic	NA	NA	NA	NA	NA
Kona Branch Station, Hawaii	Silty Clay Loam	10	NA	NA	NA	NA
San Jose, Costa Rica	NA	NA	NA	NA	NA	NA
¹ These parameters are optional except in cases where their values affect the use pattern for the chemical.						
² Not Available						

Residue trials were conducted on coffee plantations in four tropical coffee production areas, Brazil, Columbia, Costa Rica and Hawaii. Weather conditions in Sao Paulo, Brazil and Kona Branch Station, Hawaii resulted in low coffee yields so that sampling was not conducted at



all times planned for.

TABLE B.1.2. Study Use Patterns							
Location	EP ¹	Application					Tank Mix Adjuvants
		Method/Timing Directed foliar postemergent spray	Volume (GPA) ²	Rate lbs a.i./A (g a.i./ha)	RTI ³ (Days)	Total Rate lbs a.i./A (g a.i./ha)	
Sao Paulo, Brazil	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA ⁴	4 (4483)	NA	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	56	8 (8967)	None
Cali. Columbia	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA	2 (2242)	NA	2 (2242)	None
		Method/Timing Directed foliar postemergent spray	NA	2 (2242)	49	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	NA	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	49	8 (8967)	None
Kona Branch Station, Hawaii	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA	2 (2242)	NA	2 (2242)	None
		Method/Timing Directed foliar postemergent spray	NA	2 (2242)	54 to 55	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	NA	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	54 to 55	8 (8967)	None
San Jose, Costa Rica	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA	4 (4483)	NA	4 (4483)	None



TABLE B.1.2. Study Use Patterns							
Location	EP ¹	Application				Tank Mix Adjuvants	
		Method/Timing Directed foliar postemergent spray	Volume (GPA) ²	Rate lbs a.i./A (g a.i./ha)	RTI ³ (Days)		Total Rate lbs a.i./A (g a.i./ha)
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	56	8 (8967)	None

¹End-use Product
²Gallons per acre
³Retreatment Interval
⁴Not Available

Roundup® herbicide was applied as a directed foliar postemergent spray to the undesirable vegetative growth among the trees. Up to two applications may be made during the season to eliminate plant pests. Roundup® was applied at seasonal rates of 2 to 8 lbs a.i./A, although the minimum rate employed in trials at a 1-day PHI was 4 lbs a.i./A; the majority of the trials at 1-day PHI were conducted at the 8 lbs a.i./A rate. The maximum seasonal rate according to the Roundup WeatherMAX® label is 9.6 lbs a.i./A.

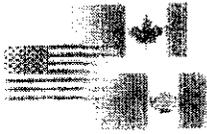
According to the Residue Chemistry Test Guidelines (OPPTS 860.1500: Crop Field Trials), five coffee trials are required, all in Region 13, Hawaii and Puerto Rico. Five trials were conducted at the proposed PHI of 1 day; two in Cali Columbia, two at Kona Branch Station, Hawaii, and one in San Jose, Costa Rica.

B.2. Sample Handling and Preparation

For each coffee trial, controls and treated samples of seed were collected 7-days following the final application. In addition, control and treated samples of coffee bean were picked at two, four and eight week intervals. After the 8-week sampling, a second application of the same rate as the first application was made. Samples were picked after 1 day and at four and eight week intervals following the second application. As stated in Section B1, coffee yields were too low because of weather conditions to permit all the sampling to be performed. Samples of green coffee beans were frozen, extracted, and prepared for residue analysis.

B.3. Analytical Methodology

Samples of green coffee beans were analyzed for glyphosate using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Samples for analysis were ground with dry ice in a Waring blender, after which the dry ice was allowed to evaporate. Aliquots of ground green coffee beans were diluted with NH₄OH, shaken, and centrifuged under refrigeration. The supernatant was decanted through a powder funnel plugged with a glass wool mat. After removing as much of the residual aqueous layer as



possible, a second volume of NH_4OH was added to the centrifuge bottle, the sample was shaken, and again centrifuged under refrigeration. This procedure was followed a third time, after which the extract was diluted with deionized water.

Aliquots of sample extract were transferred to a pre-washed A-101D ion-exchange column and flushed through the column with several deionized water rinses. The recovered glyphosate was eluted from the column with six rinses of ammonium bicarbonate.

Charcoal is then added to the fraction collected from the A-101D column and shaken. The mixture was filtered, via suction, through glass fiber and washed twice with NH_4CHO_3 . The sample was then rotary evaporated under heat, washed, and re-evaporated. This procedure was followed four times, after which the sample was dissolved in deionized water and subjected to AG 50W-X8 column chromatography. Although the method describes procedures for collecting and analyzing for the aminomethylphosphonic acid (AMPA) metabolite, AMPA will not be discussed in this review because it is no longer of any toxicological or regulatory importance.

Sample aliquots were transferred to a methanol-washed XAD-2 column. The glyphosate fraction was collected and diluted with NH_4CHO_3 , after which it was rotary evaporated to dryness. The final evaporated residue from the previous step was washed in trifluoroacetic anhydride. Trifluoroacetic acid was then added to the flask and the mixture was heated. After heating, the contents of the reaction flask were evaporated under dry nitrogen. The dried residue was treated with a methanol:tetrahydrofuran:O-methyl-N,N'-dicyclohexyl pseudourea solution and heated at high temperature. After cooling, this derivatized sample was analyzed by gas-liquid chromatography with a phosphorus-specific flame photometric detector.

The method sensitivity of this method is 0.05 ppm. A limit of detection (LOD) was not reported.

C. RESULTS AND DISCUSSION

Samples of green coffee beans were analyzed for glyphosate using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Recoveries ranged from 46% to 94% of the amount added, with an average of 65% recovery. Individual method recovery results for green coffee bean are shown in Table C.1

Samples of green coffee beans were spiked with glyphosate at 0.4 ppm and stored frozen for four months. After four months, percent recovery was $87.5 \pm 2.5\%$. Subsequent reviews have shown that glyphosate residues remain stable in crop tissues for more than 2 years (CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92). Storage conditions are summarized in Table C.2.

Weeds growing around the bases of coffee trees were treated with glyphosate Roundup® herbicide. Application rates ranged from 2 to 4 lbs a.i./A, with from 2 to 8 lbs a.i./A applied seasonally. At the proposed PHI of 1 day, seasonally application rates were 4 or 8 lbs a.i./A. For



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 Crop Field Trial - Coffee

trials having multiple applications, the interval between treatments ranged from 49 to 56 days. Green coffee beans were picked two, four and eight weeks after the first application. Green coffee beans were then picked one day, four weeks and eight weeks after the second application. The results from these trials show that glyphosate residues ranged from < 0.05 ppm to 0.67 ppm on green coffee beans picked 1 day after the last application. Residue results are shown in Table C.3, and residue data summaries are shown in Table C.3.

TABLE C.1. Summary of Method Recoveries of Glyphosate from Green Coffee Beans.

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean ± std dev
Green Coffee Bean	Glyphosate	0.05	4	84.1, 72.2, 76.1, 77.2	77 ± 5 %
		0.1	16	87.1, 60.5, 67.6, 57.4, 94.0, 69.9, 56.8, 62.4, 74.9, 66.8, 68.1, 70.6, 61.8, 75.3, 68.0, 62.6	69 ± 10%
		0.2	20	78.5, 60.2, 55.0, 53.6, 49.7, 62.9, 55.8, 53.7, 64.5, 59.3, 64.7, 56.4, 55.4, 65.9, 55.3, 49.0, 47.7, 63.7, 45.9, 51.9	57 ± 8%

¹Not available

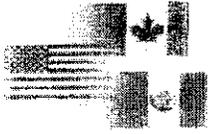
TABLE C.2. Summary of Storage Conditions

Matrix (RAC or Extract)	Storage Temperature (°C)	Actual Storage Duration (Months)	Limit of Demonstrated Storage Stability (Days)
Green Coffee Bean	Frozen, temperature range not reported	4	> 730 ¹

¹CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92

TABLE C.3. Residue Data from Crop Field Trials with Glyphosate.

Trial ID (City, State, Year)	Region	Crop/Variety	Commodity or Matrix	Total Rate/Season, lbs a.i./A/Season (kg a.i./ha/Season)	PHI (days)	Residues (ppm)
Cali, Columbia	NA ¹	Coffee	Green Bean	4 (4483)	1	0.11
Cali, Columbia	NA ¹	Coffee	Green Bean	8 (8967)	1	0.67
Kona Branch Station, Hawaii	13	Coffee	Green Bean	4 (4483)	1	0.08
Kona Branch Station, Hawaii	13	Coffee	Green Bean	8 (8967)	1	0.35



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Crop Field Trial – Coffee

Trial ID (City, State/Year)	Region	Crop/Variety	Commodity or Matrix	Total Rate/Season, lbs a.i./A/Season (kg a.i./ha/Season)	PHI (days)	Residues (ppm)
San Jose, Costa Rica	NA ¹	Coffee	Green Bean	8 (8967)	1	< 0.05
¹ Not Available						

Commodity	Total Application Rate, b/A (kg/ha)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT ¹	Median (STMdR)	Mean (STMR)	Std. Dev.
Coffee	4 (4483)	1	2	0.08	0.11	N/A ²	0.095	0.095	0.021
Coffee	8 (8967)	1	3	0.28	0.35	N/A	0.32	0.32	0.035
¹ Highest Average Field Trial									
² Not Appropriate, as coffee is not an animal feedstuff									

D. CONCLUSION

Glyphosate residues in or coffee green beans were 0.071 ppm or below when applied at a seasonal rate of 4 or 8 lb /A and harvested at 1-day PHI. In all studies, applications were made in accordance with the proposed use directions. Studies were conducted consistently with standard agricultural practices as per proposed experimental designs; the only exception was the curtailed sampling at two locations because of unfavorable weather conditions. The analytical method has been found suitable for data collection.

E. REFERENCES

CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92

F. DOCUMENT TRACKING

RDI: W. Cutchin, 6/5/06
Petition Number: None – Amend PHI
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DACO 7.4.1/OPPTS 860.1520/OECD IIA 6.5.4 and IIIA 8.5
Processed Food and Feed – Coffee, Instant and Roasted

Primary Evaluator J. R. Tomerlin, Ph.D.
Fungicide Branch
Registration Division

Date: 6/13/06

Peer Reviewer W. Cutchin, Chemist
Technical Review Branch
Registration Division

STUDY REPORTS:

MRID Nos.: 00051980, 00051981, Anonymous (June 1, 1976), Volume 1 of 1, Information to Support Establishment of Permanent Tolerances for Glyphosate in Coffee, R.D. 3102, Special Report 3405. The report was originally submitted by Monsanto in a single volume, linked to EPA Reg No. 524-308. The report was initially designated as EPA Acc. No. 95344 and 91677; the report included both residue data and metabolism data, in addition to information on the description of the product and similar information typical of submissions of that time. The submitted volume was subsequently broken into separate records and assigned MRIDs in the 00051977 to 00051983 series; MRID No. 00051982 contained residue data for processed commodities.

EXECUTIVE SUMMARY:

The glyphosate registrant, Monsanto, has submitted field trial data for glyphosate (N-(phosphonomethyl)glycine) on green coffee beans, roasted coffee beans and instant coffee to support a request to amend the label, lowering the pre-harvest interval (PHI) to one day. Crop field trials were conducted in HI (Region 13), Brazil, Columbia and Costa Rica. In each trial, Roundup® Herbicide was applied to postemergent weeds growing among trees in a coffee plantation. Total compound applied ranged from 2 to 8 lbs a.i./A (2.2 to 9.0 kg a.i./hectare) of per treated plot. Samples of green coffee beans were processed to roasted coffee beans, ground roast coffee, and instant (soluble) coffee.

Residues of glyphosate in green coffee beans, roasted coffee beans, and instant coffee were quantitated using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Glyphosate was extracted from aqueous ammoniacal extracts of green coffee beans, roasted coffee beans, and instant coffee by elution from appropriate ion exchange resins. Following additional purification and conversion of the parent molecule to the corresponding N-trifluoroacetyl-methyl ester compounds, extracts of green coffee beans, roasted coffee beans, and instant coffee were analyzed using gas-liquid chromatography with a phosphorus-specific flame photometric detector. Method sensitivity was 0.05 ppm. The method is adequate for data collection.

The results from the processing study showed that glyphosate does not concentrate in



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either roasted coffee beans or instant coffee. The processing factors were 0.17 and 0.55 in roasted coffee beans and instant coffee, respectively. There is sufficient storage stability data available to support the residue chemistry data. After storage for four months, average recovery from green coffee beans was $87.5 \pm 2.5\%$.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the processing study residue data are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document, DNum 321667.

COMPLIANCE:

Glyphosate residue studies were completed June 1, 1976 and received by the Agency on June 3, 1976. EPA's Good Laboratory Practices guidelines were not established until 1983. Therefore, compliance of the subject study with 40 CFR 160 guidelines was not evaluated.

A. BACKGROUND INFORMATION

Glyphosate is an herbicide currently registered for use on coffee, and the registrant is requesting that the Roundup WeatherMAX® label be amended, reducing the PHI to 1 day. The test material was Roundup SL® (Reg. No. 524-308). Roundup SL® is 4 lbs a.i./gal, or 3 lbs/gal of acid equivalent, whereas Roundup WeatherMAX® is 5.5 lbs a.i./gal, or 4.5 lbs/gal of acid equivalent. The residue data is the same data that has supported the existing tolerance of 1 ppm on coffee. The nomenclature of the test substance is shown in Table A.1. The physical and chemical characteristics of glyphosate are shown in Table A.2.

TABLE A.1. Test Compound Nomenclature	
Common name	Glyphosate
Company name	Not applicable
Chemical Class	Herbicide
IUPAC name	N-(phosphonomethyl)glycine
CAS name	Glycine, N-(phosphonomethyl)
CAS #	38641-94-0
End-use product/EP	Roundup Ultra® Herbicide



TABLE A.1. Test Compound Nomenclature	
Chemical Structure	$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{HOCCH}_2\text{NHCH}_2\text{P(OH)}_2 \end{array}$

TABLE A.2. Physical and Chemical Properties of Glyphosate Technical Grade Active Ingredient	
Color ¹	White
Physical State ¹	Crystalline powder
Odor ¹	Odorless
Melting Point ¹	184.5°C
pH ¹	2.5, 1% solution
Specific Gravity ¹	1.7 @ 20°
Solubility in water ¹	10,100 mg/L @ 20°C
Solvent solubility ²	Insoluble in most organic solvents
Vapor Pressure	< 1 x 10 ⁻⁵ Pa @ 25°C
Dissociation Constant ¹	<2, 2.6, 5.6, 10.6
Octanol/Water Coefficient ¹	-2.8
Absorption coefficient ²	12,000

¹Value obtained from International Programme on Chemical Safety from data provided by Monsanto
²Data from Extocnet

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

TABLE B.1.1 Site Conditions for Coffee.						
Trial Identification (City, State/Year - Trial ID)	Soil characteristics				Meteorological data	
	Type	%OM ¹	pH ¹	CEC ¹ (meq/g)	Overall Daily/Monthly Rainfall Range	Overall Temperature Range (°C)
Calí, Columbia	Lateritic	NA ²	NA	NA	NA	NA
Kona Branch Station, Hawaii	Silty Clay Loam	10	NA	NA	NA	NA

¹ These parameters are optional except in cases where their values affect the use pattern for the chemical.
² Not Available

Residue trials were conducted on coffee plantations in four tropical coffee production areas, Brazil, Columbia, Costa Rica and Hawaii. However, glyphosate residues in roasted coffee beans and instant coffee were determined only for samples from Columbia and Hawaii.



TABLE B.1.2. Study Use Patterns

Location	EP ¹	Application					Tank Mix Adjuvants
		Method/Timing Directed foliar postemergent spray	Volume (GPA) ²	Rate lbs a.i./A (g a.i./ha)	RTI ³ (Days)	Total Rate lbs a.i./A (g a.i./ha)	
Cali, Columbia	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA	2 (2242)	NA	2 (2242)	None
		Method/Timing Directed foliar postemergent spray	NA	2 (2242)	49	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	NA	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	49	8 (8967)	None
Kona Branch Station, Hawaii	Roundup® Herbicide	Method/Timing Directed foliar postemergent spray	NA	2 (2242)	NA	2 (2242)	None
		Method/Timing Directed foliar postemergent spray	NA	2 (2242)	54 to 55	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	NA	4 (4483)	None
		Method/Timing Directed foliar postemergent spray	NA	4 (4483)	54 to 55	8 (8967)	None

¹End-use Product
²Gallons per acre
³Retreatment Interval
⁴Not Available – one application

B.2. Sample Handling and Preparation

Samples were frozen upon harvesting in the country of production and shipped to Monsanto while still frozen. Upon receipt, samples were stored in a freezer.

An unprocessed sample for green coffee beans was collected before processing. Samples were roasted, ground, percolator-extracted, and dried in the laboratory to simulate commercial practice (Clifford, 1975; Sivetz and Foote, 1963).



B.3. Analytical Methodology

Samples of green coffee beans, roasted coffee beans, and instant coffee were analyzed for glyphosate using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Samples for analysis were ground with dry ice in a Waring blender, after which the dry ice was allowed to evaporate. Aliquots of green coffee beans, roasted coffee beans, and instant coffee were diluted with NH_4OH , shaken, and centrifuged under refrigeration. The supernatant was decanted through a powder funnel plugged with a glass wool mat. After removing as much of the residual aqueous layer as possible, a second volume of NH_4OH was added to the centrifuge bottle, the sample was shaken, and again centrifuged under refrigeration. This procedure was followed a third time, after which the extract was diluted with deionized water.

Aliquots of sample extract were transferred to a pre-washed A-101D ion-exchange column and flushed through the column with several deionized water rinses. The recovered glyphosate was eluted from the column with six rinses of ammonium bicarbonate.

Charcoal is then added to the fraction collected from the A-101D column and shaken. The mixture was filtered, via suction, through glass fiber and washed twice with NH_4CHO_3 . The sample was then rotary evaporated under heat, washed, and re-evaporated. This procedure was followed four times, after which the sample was dissolved in deionized water and subjected to AG 50W-X8 column chromatography. Although the method describes procedures for collecting and analyzing for the aminomethylphosphonic acid (AMPA) metabolite, AMPA will not be discussed in this review because it is no longer of any toxicological or regulatory importance.

Sample aliquots were transferred to a methanol-washed XAD-2 column. The glyphosate fraction was collected and diluted with NH_4CHO_3 , after which it was rotary evaporated to dryness. The final evaporated residue from the previous step was washed in trifluoroacetic anhydride. Trifluoroacetic acid was then added to the flask and the mixture was heated. After heating, the contents of the reaction flask were evaporated under dry nitrogen. The dried residue was treated with a methanol:tetrahydrofuran:O-methyl-N,N'-dicyclohexyl pseudourea solution and heated at high temperature. After cooling, this derivatized sample was analyzed by gas-liquid chromatography with a phosphorus-specific flame photometric detector.

The method sensitivity of this method is 0.05 ppm. A limit of detection was not reported.

C. RESULTS AND DISCUSSION

Samples of green coffee beans, roasted coffee beans, and instant coffee were analyzed for glyphosate residues using *Analytical Method for N-Phosphonomethylglycine and Aminomethylphosphonic Acid in Green Coffee Beans*, May 1, 1975. Method recovery values ranged from 46% to 94% of the amount added, with an overall average of 65% recovery. Individual method recovery results for green coffee bean are shown in Table C.1



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Samples of green coffee beans were spiked with glyphosate at 0.4 ppm and stored frozen for four months. After four months, percent recovery was $87.5 \pm 2.5\%$. Subsequent reviews have shown that glyphosate residues remain stable in crop tissues for more than 2 years (CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92). Storage conditions are summarized in Table C.2.

Weeds growing around the bases of coffee trees were treated with glyphosate Roundup® herbicide. Application rates ranged from 2 to 4 lbs a.i./A, with from 2 to 8 lbs a.i./A applied seasonally. Green coffee beans were then picked, frozen, and shipped frozen to the laboratory for analysis. Processing samples were processed to roasted coffee beans, ground roast coffee, and instant (soluble) coffee. Samples were roasted, ground, percolator-extracted, and dried in the laboratory under conditions simulating commercial processing practice (Clifford, 1975; Sivetz and Foote, 1963). Residue concentrations demonstrate a definite reduction in processed commodities relative to the green coffee bean. The results from the processing study shows that the processing factor is 0.18 in roasted coffee bean and 0.55 in instant coffee. Residue results from the processing study are shown in Table C.3.

TABLE C.1. Summary of Method Recoveries of Glyphosate from Green Coffee Beans.

Matrix	Analyte	Spike level (mg/kg)	Sample size (n)	Recoveries (%)	Mean \pm std dev
Green Coffee Bean	Glyphosate	0.05	4	84.1, 72.2, 76.1, 77.2	77 \pm 5 %
		0.1	16	87.1, 60.5, 67.6, 57.4, 94.0, 69.9, 56.8, 62.4, 74.9, 66.8, 68.1, 70.6, 61.8, 75.3, 68.0, 62.6	69 \pm 10%
		0.2	16	78.5, 60.2, 55.0, 53.6, 49.7, 62.9, 55.8, 53.7, 64.5, 59.3, 64.7, 56.4, 55.4, 65.9, 55.3, 49.0	59 \pm %
		0.4	4	47.7, 63.7, 45.9, 51.9	52 \pm 3%
¹ Not available					

TABLE C.2. Summary of Storage Conditions

Matrix (RAC or Extract)	Storage Temperature (°C)	Actual Storage Duration (Months)	Limit of Demonstrated Storage Stability (Days)
Green Coffee Bean	Frozen, temperature range not reported	4	> 730 ¹
¹ CBRS No. 8337. DNum: 166777, R. Perfetti, 4/2/92			



RAC	Commodity or Matrix	Total Rate lbs a.i./A (kg a.i./ha)	PHI (days)	Residues (ppm)	Processing Factor
Green Coffee Bean	Green Coffee Bean	Not Reported	Not Reported	0.44	-- ¹
Green Coffee Bean	Roasted Coffee Bean	Not Reported	Not Reported	0.08	0.18
Green Coffee Bean	Instant Coffee	Not Reported	Not Reported	0.24	0.55

¹Not calculable

D. CONCLUSION

Applications of glyphosate made in accordance with the proposed use directions resulted in measurable residues in green coffee bean, roasted coffee bean and instant coffee. Glyphosate did not concentrate in either roasted coffee bean or instant coffee. Glyphosate residues were approximately 18% and 55% of the level in green coffee bean in roasted coffee bean and instant coffee, respectively.

E. REFERENCES

Clifford, M. N., March 1975, Process Biochemistry
Sivetz, M. and Foote, H.E., 1963, Coffee Processing Technology, Volumes 1 and 2.
CBRS No. 8337, DNum: 166777, R. Perfetti, 4/2/92

F. DOCUMENT TRACKING

RDI: W. Cutchin, 6/5/06
Petition Number(s): Amend PHI
DNums: 314255, 327313
PC Code: 103613

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R128709

Chemical: Glyphosate-isopropylammonium

PC Code:
103601

HED File Code: 11000 Chemistry Reviews

Memo Date: 6/13/2006

File ID: DPD314255
DPD327313

Accession #: 412-06-0192

HED Records Reference Center
7/12/2006

