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SCIENTIFIC DATA REVIEWS
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OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

July 17, 2001

MEMORANDUM

Subject: Reregistration of **Methyl Bromide**: Fruit and Nut Magnitude of Residue Data; Chemical No. 53201; DP Barcode D275389; MRID No.: 43885001 and 43885002

From: Christine L. Olinger, Chemist
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To: Joseph Nevola
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The Methyl Bromide Industry Panel has submitted magnitude of residue studies to support the reregistration of the dried fruit and nut fumigation uses for methyl bromide. These studies have been reviewed by Dynamac Corporation under supervision of HED, and the review has been revised to reflect Division policies.

The submitted studies are adequate; no additional data are required to support methyl bromide fumigation of nuts and dried fruits.

cc: COlinger, Reg. Std. File,
7509C:RRB1:CLOlinger:clo:CM#2:Rm 722J:305-5406:6/13/01
RDI: FFort: 7/17/01; WPhang: 07/17/01

METHYL BROMIDE
PC Code 053201; Case 0335
DP Barcode D275389

Registrant's Response to Residue Chemistry Data Requirements

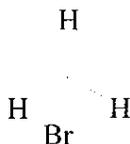
April 12, 2001

Contract No. 68-W-99-053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

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METHYL BROMIDE



PC Code 053201; Case 0335

DP Barcode D275389

Registrant's Response to Residue Chemistry Data Requirements

BACKGROUND

In response to outstanding residue chemistry requirements, the Methyl Bromide Industry Panel (MBIP) has submitted methyl bromide residue data from fumigation studies on tree nuts (1995, MRID 43885001) and dried fruits (1995, MRID 43885002). Previous studies on tree nuts and dried fruits were judged inadequate by EPA because of irregularities in the analytical method, inadequate duplication of samples, and excessive sampling-to-analysis storage intervals (DP Barcode D200922, 7/21/94).

Tolerances for residues of inorganic bromides in/on plant raw agricultural commodities (RACs) and processed foods that have been fumigated with methyl bromide have been established under 40 CFR §180.123. Tolerances for residues of inorganic bromides in/on plant RACs grown in soil fumigated with combinations of chloropicrin, methyl bromide, and propargyl bromide have been established under 40 CFR §180.199. The EPA has determined that soil fumigation uses of methyl bromide are classified as non-food uses (S. Irene, 1/31/97). The Agency has also approved the replacement of inorganic bromide tolerances with tolerances for methyl bromide *per se*, as supported by residue chemistry data (Letter to MBIP, A. Lindsay, 7/7/89).

Subsequently, in conjunction with acceptance of plant metabolism data, HED recommended that methyl bromide *per se* is the residue to be regulated (DP Barcode D168913, R. Perfetti, 9/24/91). An adequate analytical method, the head-space method of King, et al., is available for data collection and tolerance enforcement. This method has been forwarded to FDA for inclusion in PAM, Vol. II.

CONCLUSIONS

GLN 860.1460: Food Handling

1. Processed foods. An adequate residue study with dried fruits was submitted. Raisins, prunes, dried dates, and dried figs were fumigated with methyl bromide for 24 hours at a rate equivalent to 1.5 lb ai/ft³. An aeration period of ~4 hours followed the fumigation to allow chamber methyl bromide concentration to reach ≤ 5 ppm. Samples were collected immediately following aeration and at 24 and 72 hours posttreatment. Samples were analyzed on the day of sampling or after a maximum of 24 hours frozen storage in sealed containers. Maximum methyl bromide residues in 24-hour posttreatment samples were 5.91 ppm. These data support the 10 ppm tolerance for residues of methyl bromide *per se* recommended previously for processed foods, excluding chocolate products (DP Barcode D215044, 8/15/95, B. Cropp-Kohlligian,).

GLN 860.1500: Crop Field Trials

2. Tree nuts group. An adequate residue study with tree nuts was submitted. Almonds, pecans, pistachios, and walnuts were fumigated with methyl bromide for 24 hours at a rate equivalent to 1.5 lb ai/ft³. An aeration period of ~4 hours followed the fumigation to allow chamber methyl bromide concentration to reach ≤ 5 ppm. Samples were collected immediately following aeration, at 24 and 72 hours posttreatment, and 9-16 days after treatment. Samples were analyzed on the day of sampling or after a maximum of 24 hours frozen storage in sealed containers. Maximum methyl bromide residues in 24-hour posttreatment samples were 137.5 ppm. These data support a tolerance of 150 ppm for residues of methyl bromide *per se* in on tree nuts.

DETAILED CONSIDERATIONS

GLN 860.1340: Residue Analytical Method

Methyl bromide residues in nuts and dried fruits from fumigation tests were analyzed using the head-space method of King, et al. (1981) as modified by Harvey, et al. (1989) and Hartsell et al. (1992). Fruit or nut samples are blended with water at high speed in air-tight jars for 5 minutes. After 15 minutes, the partitioned gas phase is sampled and analyzed by GC/EC. The current study included initial and ending standard curves at concentrations of 0.1-50 ppm for nuts and low and high concentration ranges of 0.01-2.0 ppm and 2-20 ppm, respectively, for dried fruits. The LOQs were 0.1 ppm for nuts and 0.01 ppm for dried fruits. Concurrent recovery data are presented in Table 1. This method is adequate for data collection.

Table 1. Recovery (percent) of methyl bromide from fortified untreated samples

Dried fruits - Standard Concentration Fortifications				
Commodity:	0.5 ppm	2.0 ppm	10.0 ppm	20.0 ppm
Raisins	100	100, 105	103, 115	101
Prunes	84, 118	82, 86, 107	96	NA ^a
Dates	90	105, 107, 118	99, 106	NA
Figs	118, 122	106, 113, 115	97	NA
Tree Nuts - Standard Concentration Fortifications				
Commodity:	5.0 ppm	10.0 ppm	20.0 ppm	50.0 ppm
Almonds	NA	103, 106, 107, 108	97, 106, 106	NA
Pecans	74, 90, 102	119, 121	120, 122	99
Pistachios	NA	117, 117, 119	92, 99, 103	118
Walnuts	82, 92, 102	98	110, 115, 115	99

^a NA = commodity not analyzed at this concentration.

GLN 860.1460: Food Handling and 860.1500: Crop Field Trials

The MBIP submitted data pertaining to methyl bromide residues in/on tree nuts (1995, MRID 43885001) and dried fruits (1995, MRID 43885002), from studies conducted by the Dried Fruit Association (DFA) of California in Fresno, CA. Fumigation chambers of 28.3 L, obtained from U.S. Department of Agriculture, were housed in 4.2 m³ walk-in boxes, where temperatures were maintained at 15.5 C for nuts or 10 C for fruits. The tested samples were almonds, pecans, pistachios, and walnuts, dried fruits tested were raisins, prunes, dates, and figs. In triplicate chambers loaded at 30% capacity, nuts or fruits in plastic-lined bulk cartons or consumer-packaged samples were fumigated with 5% methyl bromide at 56 g/m³ for nuts and 24 g/m³ for dried fruits, for 24 hours at 16 C and normal atmospheric pressure. These rates are equivalent to 3.5 and 1.5 lb ai/ft³, respectively, for nuts and fruits, 1x the maximum registered commodity fumigation rates. The methyl bromide concentrations in the chambers were monitored at regular intervals using GC with flame ionization detection. Following the exposure period, the chambers were aerated for ~4 hours until the methyl bromide concentration was ≤5 ppm.

Immediately after the aeration period (zero day), samples were collected from the top, middle, and bottom of the chamber load and mixed prior to analysis. Containers of treated nuts and dried fruits were removed from the fumigation chambers and remained in the walk-in boxes, and samples were collected for analysis after 24 and 72 hours, and in addition, for nuts, between 9 and 16 days after treatment. The samples were analyzed on the day of collection or stored in

sealed containers at frozen temperatures for up to 24 hours prior to analysis. Methyl bromide residues were analyzed using the head-space method of King, et al. described briefly above. The residue analysis results for nuts and dried fruits are presented in Tables 2 and 3, respectively.

Tree nuts: The submitted data fulfill the requirements for data on methyl bromide in/on tree nuts. Twenty-four hours following fumigation/aeration, methyl bromide residues were 35.8-137.5 ppm in almonds, pecans, pistachios, and walnuts fumigated in bulk, and 3.0-83.4 ppm in those nuts fumigated in commercial packages. By 14-16 days after treatment, residues were <LOQ in all almond samples, 0.6-3.0 ppm in pistachios, and 8.2-19.9 ppm in walnuts. These data support a tolerance of 150 ppm for residues of methyl bromide *per se* in/on members of the tree nuts group. Tolerance recommendations will be made in conjunction with Tolerance Reassessment in the Methyl Bromide RED.

Dried fruit: Twenty-four hours following fumigation/aeration, methyl bromide residues were 1.26-3.9 ppm in bulk raisins, prunes, dates, and figs, and 0.1-5.91 ppm in corresponding packaged samples. These data support the 10 ppm tolerance suggested previously by HED (DP Barcode D215044, 8/15/95, B. Cropp-Kohlligian,) for residues of methyl bromide *per se* in processed foods. Tolerance reassessments will be made in the Methyl Bromide RED.

Table 2. Methyl bromide residues in/on tree nuts following fumigation at 3.5 lb ai/1000 ft³ for 24 hours at 15.6 C.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
Almonds, bulk	0	136.8, 129.6, 130.8 138.3, 134.7, 121.0	132.4, 131.3
	1	67.5, 69.3, 78.6 73.7, 64.3, 73.8	71.8, 70.6
	3	10.2, 10.2, 10.0 15.2, 12.2, 13.5	10.1, 13.6
	15	<0.1	<0.1
Almonds, packaged	0	2.6, 3.6, 3.6 3.9, 4.5, 3.9	3.3, 4.1
	1	14.9, 11.1, 13.8 3.2, 3.0, 2.7	13.3, 3.0
	3	6.7, 5.0, 6.0 9.9, 9.7, 9.4	5.9, 5.7
	15	<0.1	<0.1

Table 2. Continued.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
Pecans, bulk	0	220.6, 200.5, 196.3 198.7, 225.9, 203.9	205.8, 209.5
	1	124.7, 134.5, 102.9 96.9, 74.6, 92.3	120.7, 87.9
	3	25.8, 24.4, 22.1 23.4, 28.6, 25.2	24.1, 25.7
	9	1.7, 1.2, 1.3 4.7, 4.6, 4.1	1.4, 4.5
Pecans, packaged	0	54.9, 48.8, 57.9 27.8, 34.4, 35.3	53.9, 32.5
	1	39.2, 34.7, 29.6 24.8, 22.8, 26.4	34.5, 24.7
	3	17.5, 15.3, 15.2 23.9, 20.4, 18.7	16.0, 21.0
	9	0.7, 0.9, 0.8 7.9, 3.0, 6.1	0.8, 5.7
Pistachios, bulk	0	197.6, 189.4, 198.7 185.9, 185.3, 179.9	195.2, 183.7
	1	36.0, 36.9, 34.5 37.9, 37.1, 43.8	35.8, 39.6
	3	14.6, 15.2, 16.0 17.9, 17.3, 16.2	15.3, 17.1
	16	0.6, 0.6, 0.5 1.1, 1.0, 1.1	0.6, 1.1
Pistachios, packaged	0	206.2, 200.3, 236.3 251.8, 235.8, 242.5	214.3, 243.4
	1	14.5, 16.3, 14.6 13.8, 14.9, 15.8	15.1, 14.8
	3	33.4, 34.6, 31.8 43.9, 42.3, 44.6	33.3, 43.6
	16	2.8, 2.7, 2.8 3.0, 3.1, 2.9	2.8, 3.0

Table 2. Continued.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
Walnuts, bulk	0	171.9, 213.1, 232.9 224.6, 259.4, 251.1	206.0, 245.0
	1	126.1, 119.4, 137.0 140.9, 134.3, 137.4	127.5, 137.5
	3	67.3, 79.4, 66.6 78.5, 93.2, 75.6	71.1, 82.4
	14	7.9, 8.5, 8.1 8.4, 8.8, 7.9	8.2, 8.4
Walnuts, packaged	0	103.9, 85.3, 80.9 115.9, 112.0, 110.2	90.0, 112.7
	1	86.8, 81.6, 81.9 70.1, 68.7, 77.9	83.4, 72.2
	3	94.4, 95.2, 82.6 72.8, 74.4, 67.4	71.5, 90.7
	14	18.2, 20.9, 20.6 18.1, 16.2, 16.4	19.9, 16.9

Table 3. Methyl bromide residues in/on dried fruits following fumigation at 1.5 lb ai/1000 ft³ for 24 hours at 10 C.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
Raisins, bulk	0	5.00, 4.67, 4.97 6.56, 5.86, 5.26	4.88, 5.89
	1	1.47, 1.76, 1.62 1.19, 1.34, 1.26	1.62, 1.26
	3	0.66, 0.66, 0.64 0.77, 0.77, 0.77	0.65, 0.77
Raisins, packaged	0	6.43, 6.76, 7.33 6.62, 6.24, 5.98	6.84, 6.28
	1	5.30, 4.50, 4.80 4.88, 3.66, 4.06	4.87, 4.20
	3	1.53, 1.74, 1.27 1.45, 1.40, 1.48	1.51, 1.44
Prunes, bulk	0	4.29, 3.43, 3.97 4.29, 4.90, 3.21	3.90, 4.13
	1	1.43, 1.22, 1.49 2.55, 2.28, 2.59	1.38, 2.47

Table 2. Continued.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
	3	1.01, 1.05, 1.33 0.94, 1.18, 1.03	1.13, 1.05

Table 3. Continued.

Commodity	Sampling interval (days)	Methyl bromide residues (ppm)	Replicate chamber mean residues (ppm)
Prunes, packaged	0	4.41, 5.15, 4.43 5.57, 4.87, 5.85	4.66, 5.43
	1	6.07, 5.98, 5.68 3.74, 3.12, 3.25	5.91, 3.37
	3	1.45, 1.66, 1.60 1.84, 1.71, 1.92	1.57, 1.82
Dates, bulk	0	13.04, 14.10, 14.13 9.27, 10.87, 8.43	13.76, 9.52
	1	2.29, 2.04, 1.97 2.75, 2.83, 2.04	2.10, 2.54
	3	0.66, 0.64, 0.63 0.62, 0.64, 0.67	0.64, 0.64
Dates, packaged	0	8.58, 8.64, 8.76 8.72, 8.89, 8.51	8.66, 8.71
	1	3.25, 3.46, 3.54 3.30, 3.23, 3.55	3.42, 3.66
	3	1.23, 1.30, 1.44 1.16, 1.23, 1.36	1.32, 1.25
Figs, bulk	0	7.3, 9.7, 8.4 7.7, 10.3, 9.2	8.4, 9.1
	1	4.0, 3.5, 4.2 2.4, 2.9, 2.6	3.9, 2.6
	3	1.6, 1.6, 1.5 1.4, 1.7, 1.7	1.6, 1.6
Figs, packaged	0	0.5, 0.4, 0.4 0.4, 0.4, 0.4	0.4, 0.4
	1	2.3, 2.2, 2.3 <LOQ, <LOQ, 0.4	2.3, 0.1
	3	0.5, 1.1, 1.1 1.9, 1.7, 1.6	0.9, 1.7

MASTER RECORD IDENTIFICATION NUMBERS

43885001 Hartsell, P.; Hurley, J. (1995) Magnitude of Organic Bromide Residues on Tree Nut Meats (Shelled Almonds, Pecans, Pistachios, and Walnuts) Following Post-Harvest Fumigation: Amended Report: Lab Project Number: 2B. Unpublished study prepared by DFA of California. 90 p.

43885002 Hartsell, P.; Hurley, J. (1995) Magnitude of Organic Bromide Residues on Dried Raisins, Raisin Waste, Prunes, Figs & Dates Following Post-Harvest Fumigation: Amended Report: Lab Project Number: 2A. Unpublished study prepared by DFA of California.. 97 p.

AGENCY MEMORANDA CITED IN THIS DOCUMENT

DP Barcode: None
 Subject: Methyl Bromide Registration Standard Administrative Review of Inorganic Bromide Tolerances
 From: Anne Lindsay, RD
 To: L. V. White, Methyl bromide Industry Panel
 Dated: 7/7/89
 MRID(s): None

DP Barcode: D168913
 Subject: Methyl Bromide Industry Panel: Response to the Methyl Bromide Registration Standard: Metabolism Study
 From: R.B. Perfetti, HED
 To: W. Burnam
 Dated: 9/24/91
 MRID(s): 42137701

DP Barcode: D200922
 Subject: Response to the Methyl Bromide Reregistration Standard. Residue Data.
 From: R. Perfetti, HED
 To: E. Saito, SRRD
 Dated: 7/21/94
 MRID(s): 43166201

DP Barcode: D215044
 Subject: Methyl Bromide. Magnitude of the Residue in processed Commodities: Instant White Rice, Shelled Roasted peanuts, Unpopped Corn, and Country Ham.
 From: B. Cropp-Kohlligian, HED
 To: L. Schnaubelt/B. O'Keefe, SRRD

Dated: 8/15/95
MRID(s): 43628701

DP Barcode: None
Subject: Methyl Bromide. Food vs. Non-Food Use Status for Soil Fumigation Uses.
From: S. Irene, HED
To: S. Johnson, RD
Dated: 1/31/97
MRID(s): None