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

MAY 6 1994

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Response to the Methyl Bromide Reregistration Standard: Residue Data. (MRID #'s 43025801, 43025701, 43029801, 43025101, 43025202, 43023601 and 43025301, CBRS Nos. 12,896, 12,946, 12,948, 12,951, 12,952, 12,953 and 12,955, Barcode Nos.: D197515, D197516, D197517, D197518, D197519, D197520 and D197228).

FROM: R. B. Perfetti, Ph.D., Chemist
Reregistration Section 2
Chemistry Branch II: Reregistration Support
Health Effects Division (7509C)

THRU: W. J. Hazel, Ph.D., Section Head
Reregistration Section 2
Chemistry Branch II: Reregistration Support
Health Effects Division (7509C)

TO: Lois Rossi, Chief
Reregistration Branch
Special Review & Reregistration Division (7508W)

Attached is a review of residue data submitted in response to the methyl bromide Reregistration Standard. This review was completed by Dynamac Corporation under supervision of CBRS, HED. It has undergone secondary review in the branch and has been revised to reflect Agency policies.

1. There are numerous discrepancies between the current label-specified fumigation rates (100% PrGs, EPA Reg. Nos. 5785-11 and -41) and the rates used to generate the submitted residue data. Prior to proposing new tolerances, the registrant must revise end-use product labels to reflect the fumigation rates, number of fumigations, and retreatment intervals supported by the residue data.

Imported Fruits

2. The submitted data on methyl bromide fumigation of imported lemons, stone fruits, and grapes at ≤8.4 C are

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adequate. The data indicate that crop group tolerances of 6, 5, and 4 ppm are appropriate for the citrus, stone fruit, and small fruit and berry crop groups, respectively, and support the previously submitted residue data (CBRS Nos. 12751 and 12733, DP Barcodes 196312 and 196317, R. Perfetti) for these crop groups.

Herbs and Spices

3. The submitted data on methyl bromide fumigation of dried herbs and spices are adequate. The available data indicate that a tolerance of 35 ppm is appropriate for residues of methyl bromide in/on the dried herbs and spices, including mustard seeds. The individual tolerance for cumin of 100 ppm should be revoked. In addition, the registrant must revise all pertinent labels to specify a maximum of two 12-hour fumigations each at 3.5 lb ai/1000 ft^3, with a minimum retreatment interval of 24 hours, and in-chamber aeration.

Cocoa Beans

4. The submitted data on cocoa beans are adequate. The data indicate that 8 ppm is an appropriate tolerance for residues of methyl bromide in/on cocoa beans. The registrant must revise all pertinent labels to specify a maximum of two 24-hour fumigations each at 1.5 lb ai/1000 ft^3, with a minimum retreatment interval of 12 days, and an in-chamber aeration.

Processed Foods

5a. Data depicting residues of methyl bromide in/on representative processed foods are inadequate. Before an appropriate tolerance for processed foods can be determined, data are required depicting residues of methyl bromide in/on milled rice, popcorn, peanuts, and meats sampled 24 hours after a 24-hour fumigation at 3 lb ai/1000 ft^3 at a minimum temperature of 10 C and an in-chamber aeration. Based on the available data for processed foods (See conclusions 5b and 5c), a tolerance needs to be established for processed foods, excluding chocolate products, which would then be covered under a separate tolerance. In addition, all labels pertinent to processed foods must be revised to reflect the use pattern supported by the residue data.

5b. Data depicting residues of methyl bromide in/on flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs are adequate. At the 24-hour sampling interval, maximum residues of methyl bromide ranged from

<0.25 ppm in/on parmesan cheese to 8.25 ppm in/on flour.

5c. Data depicting residues of methyl bromide in/on chocolate products are adequate. Immediately following fumigation and an in-chamber aeration, maximum residues of methyl bromide were 3.79 in/on chocolate chips, 7.78 ppm in/on cocoa butter, and 50.4 ppm in/on chocolate liquor. The current data would support a 55 ppm tolerance for residues of methyl bromide in/on chocolate products. If the registrant wishes to support a lower tolerance, they may submit data depicting residues of methyl bromide in/on representative chocolate products sampled 0, 4, 8, 12 and 24 hours after a single fumigation at 1.5 lb ai/1000 ft^3 for 24 hours and an in-chamber aeration.

Wheat and Rice Processed Commodities

6. The submitted rice grain processing study is adequate. Residues of methyl bromide do not concentrate in rice grain dust, hulls, bran, brown rice, or polished white rice processed from rice grain bearing measurable residues of methyl bromide. No tolerance is required for residues in grain dust, and no food/feed additive tolerances are required for residues of methyl bromide in processed rice grain fractions.

7. The submitted wheat grain processing study is adequate. Residues of methyl bromide do not concentrate in wheat grain dust, bran, middlings, shorts, germ, or flour processed from wheat grain bearing measurable residues of methyl bromide. No tolerance is required for residues in grain dust, and no food/feed additive tolerances are required for residues of methyl bromide in processed wheat grain fractions.

A revised Tentative Residue Chemistry Summary sheet is included.

If you need additional input please advise.

Attachment 1: MeBr Residue Data Review.

cc (With Attachment 1): RBP, MeBr Reregistration Standard File, MeBr Subject File, RF, Circ., Richard D. Schmitt and Dynamac.

DYNAMAC CORPORATION
Environmental Services

Final Report

METHYL BROMIDE
Shaughnessy No. 053201
Case No. 0335

CBRS Nos.	DP Barcodes
12896	D197515
12946	D197516
12948	D197517
12951	D197518
12952	D197519
12953	D197520
12955	D197228

TASK 4
Registrant's Response to Residue Chemistry Data Requirements

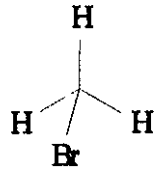
March 29, 1994

Contract No. 68-D2-0053

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
search Boulevard
Rockville, MD 20850-3268

METHYL BROMIDE



Shaughnessy No. 053201; Case 0335

(CBRS Nos. 12896, 12946, 12948, 12951, 12952, 12953, and 12955)

(DP Barcodes D197515 through D197520 and D197228)

Task 4

REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

BACKGROUND

The Methyl Bromide Reregistration Standard Update (6/91) required data depicting residues of methyl bromide in/on representative commodities having post-harvest fumigation uses for methyl bromide and in commodities processed from fumigated RACs, which are not dried or exposed to elevated temperatures during processing. Residue data were also required depicting residues of methyl bromide in processed foods that are fumigated during storage. The Methyl Bromide Industry Panel (MBIP) subsequently submitted additional magnitude of the residue protocols for the fumigation of green cocoa beans (R. Perfetti; CBRS No. 10367, DP Barcode No. 181495; 8/26/92), imported fruit from Chile (R. Perfetti; CBRS No. 10816, DP Barcode No. 184359; 11/13/92), and processed foods (S. Knizner; CBRS No. 12106, DP Barcode No. 192437; 7/29/93).

The MBIP, in conjunction with the Rice Millers Association, the Millers National Federation, the Chocolate Manufacturers of America, the Grocery Manufacturers of America, the American Spice Trade Association, and the Association of Chilean Exporters, has submitted residue data depicting residues of methyl bromide in/on imported fruits (1993; MRID 43025801), cocoa beans (1993; MRID 43025701), dried herbs and spices (1993; MRID 43029801), and representative processed food products (1993; MRIDs 43025101 and 43025201) following fumigation with methyl bromide. The registrant also submitted rice and wheat grain processing studies (1993; MRIDs 43023601 and 43025301) depicting residues in processed fractions and grain dust. These data are reviewed here to determine their adequacy in fulfilling residue chemistry data requirements. The Conclusions and Recommendations in this document pertain only to the magnitude of the residue in plant commodities and processed foods.

The qualitative nature of the residue in plants is adequately understood; the residue of

concern is methyl bromide *per se* (R. Perfetti, CBRS No. 8601, 9/24/91). The nature of the residue in animals is not adequately understood. Tolerances for residues of methyl bromide in/on food and feed commodities are currently expressed in terms of inorganic bromide [40 CFR §180.123, §180.199 and §185.3480]. However, the Agency has determined that inorganic bromide is not of toxicological concern and is requiring the registrant to propose tolerances for methyl bromide to replace the inorganic bromide tolerances. As there are no Codex MRLs for residues of methyl bromide, there are no questions with respect to Codex/U.S. tolerance compatibility.

An adequate method is available for enforcement of the current tolerances for inorganic bromide and is listed in PAM, Vol. II as Method I. For determining residues of methyl bromide *per se*, a GC/ECD headspace assay method [King et al., *J. Agric. Food Chem.*, 29(5), 1003-1005, 1981] is available for data collection and tolerance enforcement. The limit of detection for methyl bromide is 0.01 ppm. This method has been forwarded to the FDA for inclusion in PAM, Vol. II as Method A.

CONCLUSIONS/RECOMMENDATIONS

1. There are numerous discrepancies between the current label-specified fumigation rates (100% PrGs, EPA Reg. Nos. 5785-11 and -41) and the rates used to generate the submitted residue data. Prior to proposing new tolerances, the registrant must revise end-use product labels to reflect the fumigation rates, number of fumigations, and retreatment intervals supported by the residue data.

Imported Fruits

2. The submitted data on methyl bromide fumigation of imported lemons, stone fruits, and grapes at ≤ 8.4 C are adequate. The data indicate that crop group tolerances of 6, 5, and 4 ppm are appropriate for the citrus, stone fruit, and small fruit and berry crop groups, respectively, and support the previously submitted residue data (CBRS Nos. 12751 and 12733, DP Barcodes 196312 and 196317, R. Perfetti) for these crop groups.

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3. The submitted data on methyl bromide fumigation of dried herbs and spices are adequate. The available data indicate that a tolerance of 35 ppm is appropriate for residues of methyl bromide in/on the dried herbs and spices, including mustard seeds. The individual tolerance for cumin of 100 ppm should be revoked. In addition, the registrant must revise all pertinent labels to specify a maximum of two 12-hour fumigations each at 3.5 lb ai/1000 ft^3, with a minimum retreatment interval of 24 hours, and in-chamber aeration.

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Processed Foods

5a. Data depicting residues of methyl bromide in/on representative processed foods are inadequate. Before an appropriate tolerance for processed foods can be determined, data are required depicting residues of methyl bromide in/on milled rice, popcorn, peanuts, and meats sampled 24 hours after a 24-hour fumigation at 3 lb ai/1000 ft^3 at a minimum temperature of 10 C and an in-chamber aeration. Based on the available data for processed foods (See conclusions 5b and 5c), a tolerance needs to be established for processed foods, excluding chocolate products, which would then be covered under a separate tolerance. In addition, all labels pertinent to processed foods must be revised to reflect the use pattern supported by the residue data.

5b. Data depicting residues of methyl bromide in/on flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs are adequate. At the 24-hour sampling interval, maximum residues of methyl bromide ranged from <0.25 ppm in/on parmesan cheese to 8.25 ppm in/on flour.

5c. Data depicting residues of methyl bromide in/on chocolate products are adequate. Immediately following fumigation and an in-chamber aeration, maximum residues of methyl bromide were 3.79 in/on chocolate chips, 7.78 ppm in/on cocoa butter, and 50.4 ppm in/on chocolate liquor. The current data would support a 55 ppm tolerance for residues of methyl bromide in/on chocolate products. If the registrant wishes to support a lower tolerance, they may submit data depicting residues of methyl bromide in/on representative chocolate products sampled 0, 4, 8, 12 and 24 hours after a single fumigation at 1.5 lb ai/1000 ft^3 for 24 hours and an in-chamber aeration.

Wheat and Rice Processed Commodities

6. The submitted rice grain processing study is adequate. Residues of methyl bromide do not concentrate in rice grain dust, hulls, bran, brown rice, or polished white rice processed from rice grain bearing measurable residues of methyl bromide. No tolerance is required for residues in grain dust, and no food/feed additive tolerances are required for residues of methyl bromide in processed rice grain fractions.

7. The submitted wheat grain processing study is adequate. Residues of methyl bromide do not concentrate in wheat grain dust, bran, middlings, shorts, germ, or flour processed from wheat grain bearing measurable residues of methyl bromide. No

tolerance is required for residues in grain dust, and no food/feed additive tolerances are required for residues of methyl bromide in processed wheat grain fractions.

DETAILED CONSIDERATIONS

Residue Analytical Methods

In conjunction with the methyl bromide magnitude of the residue and processing studies, the registrant submitted method descriptions (1993; MRIDs 43023601, 43025101, 43025201, 43025301, 43025701, 43025801, 43029801) for analysis of methyl bromide residues in/on lemons, stone fruits, grapes, cocoa beans, wheat and rice processed commodities, and representative processed foods. Residues of methyl bromide were determined using the modified King GC/ECD headspace method #93-001. This method was reviewed by the Agency (C. Deyrup, CBRS No. 3890, 7/14/88; and CBRS No. 4399, 11/3/88) and deemed adequate as an enforcement method for analysis of methyl bromide *per se* on plants.

Briefly, frozen samples are blended with water in a sealed container equipped with a sampling port. Residues are released by heating in a water bath to 25 $\pm$ 3 C. The headspace is sampled and residues are determined by GC/ECD. The residues are quantitated by comparison with a matrix standard curve, which is generated through the analysis of fortified control samples of each commodity. A solvent standard curve was also generated to monitor instrument performance and fortification technique.

Method validation data were submitted for cocoa beans, chocolate chips, and representative commodities from the following crop groupings: citrus fruits, small fruits and berries, herbs and spices, and cereal grains. For each crop matrix, 7-19 fortified control samples were analyzed. Fortification levels and method recoveries are presented in Table 1. In addition, concurrent recovery data from 1-39 fortified control samples from each commodity were submitted. These data are presented in Table 2. Chromatograms and sample calculations were provided. Residues of methyl bromide were nondetectable in or on all control samples. Bolsa Research Associates, Hollister, CA performed the analyses of the grape, peach, plum, nectarine, lemon, green cocoa bean, and chocolate processed food samples (MRIDs 43025801, 43025701, 43025101). Webb Technical Group, Raleigh, NC analyzed the spices, the wheat and rice processed commodities, and all of the processed foods except chocolate (MRIDs 43023601, 43029801, 43025301, 43025201). Bolsa calculated method recoveries and concurrent recoveries relative to a matrix standard curve. These recoveries were inherently corrected for matrix effects, as residue levels were not quantified against a solvent curve. Webb, however, calculated method recoveries relative to a solvent curve and concurrent recoveries relative to a matrix standard curve.

The reported limits of quantitation (LOQ) for each commodity are listed in Table 3. The LOQ's are defined as (i) the lowest fortification level of any control sample analyzed during method validation or concurrently that yielded adequate recoveries (70-120%), or (ii) the lowest acceptable fortification level in any matrix standard curve generated during sample

analysis.

The modified King headspace method (Method #93-001) is adequate for collecting data on residues of methyl bromide in/on cocoa beans; commodities from the following crop groups: citrus fruits, stone fruits, small fruits and berries, cereal grains, and herbs and spices; and the following processed foods: chocolate chips, cocoa butter, chocolate liquor, flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs.

Table 1. Method recovery of methyl bromide from fortified control crop matrices.

Crop Grouping/ Commodity	Fortification Level (ppm)	% Recovery
Citrus Fruits		
Lemons	0.07-11.1	89-118
Stone Fruits		
Nectarines	0.07-18.5	52-112 [a]
Small Fruits and Berries		
Grapes	0.06-11.1	75-116
Cereal Grains		
Rice	0.21-53.0	96-111
Wheat	0.21-53.0	99-124 [a]
Herbs and Spices		
Rosemary	0.19-47.6	82-105
Sage	0.19-47.6	81-96
Oregano	0.19-47.6	82-101
Poppy Seed	0.19-47.6	74-94
Sesame Seed	0.19-47.6	30-73 [a]
Cumin	0.19-47.6	88-111
Capsicum	0.19-47.6	78-114
Black Pepper	0.19-47.6	92-102
Cassia	0.19-47.6	86-103
Garlic Powder	0.19-47.6	94-136 [a]
Onion Powder	0.19-47.6	97-119
Miscellaneous		
Cocoa Beans	0.06-11.9	91-110
Processed Foods		
Chocolate Chips	0.06-11.9	93-111

[a] One of the nineteen nectarine, one of the seven wheat, two of the seven sesame seed, and two of the seven garlic powder samples had recoveries outside of the acceptable 70-120% range.

Table 2. Concurrent method recovery of methyl bromide from fortified control samples.

Crop Grouping/ Commodity	Fortification Level (ppm)	% Recovery
Citrus Fruits		
Lemons	0.50-37.0	81-116
Stone Fruits		
Nectarines	0.07-46.3	76-116
Peaches	0.06-37.0	45-110 [a]
Plums	0.11-37.0	58-113 [a]
Small Fruits and Berries		
Grape	0.50-21.2	85-114
Cereal Grains		
Whole Grain Rice	11.2	103
Rice Grain Dust	1.12	97
Rice Hulls	11.2	101
Brown Rice	11.2	107
Rice Bran	1.12	93
White Milled Rice	1.12	104
Whole Grain Wheat	5.60	102
Wheat Grain Dust	2.80	106
Wheat Middlings	0.56	104
Wheat Shorts	0.56	106
Wheat Patent Flour	0.56	104
Herbs and Spices		
Rosemary	0.37-10.6	97-116
Sage	0.77-10.6	79-120
Oregano	0.42-25.8	91-113
Poppy Seed	0.80-15.9	88-108
Sesame Seed	0.80-15.9	93-121
Cumin	0.80-10.6	93-115
Capsicum	0.37-10.6	81-112
Black Pepper	0.80-15.9	97-117
Cassia	0.42-25.8	77-116
Garlic Powder	0.42-25.8	77-116
Onion Powder	0.42-10.3	80-112
Miscellaneous		
Cocoa Beans	0.01-29.6	46-117 [a]
Processed Foods		
Chocolate Chips	0.01-29.6	78-111
Cocoa Butter	0.02-29.6	72-117
Chocolate Liquor	0.01-44.4	47-114 [a]
Flour	0.45-27.9	103-114
Corn Meal	0.45-27.9	104-120

(continued; footnotes follow)

Table 2 (*continued.*)

Crop Grouping/ Commodity	Fortification Level (ppm)	% Recovery
Rolled Oats	0.45-27.9	93.5-110
Dry Cake Mix	0.45-8.38	89-115
Parmesan Cheese	0.34-8.38	106-121
Dried Eggs	0.45-27.9	87-118

[a] One of the 23 peach, one of the 18 plum, two of the 68 cocoa bean, and one of the 38 chocolate liquor samples had recoveries outside of the acceptable 70-120% range.

Storage Stability Data

The Agency (N. Dodd, CBRS No. 6879, 7/30/90) has concluded that residues of methyl bromide in/on raw agricultural commodities (RACs) are stable when samples are stored on dry ice for up to 12 hours, and that storage stability data are necessary only for samples stored in excess of 12 hours.

In the current submissions (1993; MRIDs 430225101, 43025201, 43025701, 43025801, and 43029801), commodities were analyzed within ~12 hours of sampling with the exception of the 96-hour processed food samples (flour, corn meal, rolled oats, cake mix, parmesan cheese, and dried eggs) that were stored for four days after collection at <-10 C prior to analysis. To determine storage stability, the 48-hour processed food samples, which had been initially analyzed within 12 hours of collection, were reanalyzed after six days of storage at <-10 C. Recoveries from the stored samples ranged from 61.2% in dried eggs to 126.8% in corn meal.

Storage stability data are adequate.

Magnitude of the Residue in Plants and Processed Food/Feed Commodities

Fumigation of plant commodities (post-harvest) and processed foods. The Methyl Bromide Reregistration Standard Update (6/91) required data depicting residues of methyl bromide in/on representative commodities from crop groups having post-harvest fumigation uses for methyl bromide. Residue data were also required depicting residues of methyl bromide in processed foods that are fumigated during storage. The Update summarized protocols for generating residue data on representative plant commodities, which have undergone extensive review and modification by the Agency since their original submission. Based on these protocols, the MBIP submitted data (1993; MRIDs 43025801, 43025701, 43029801, 43025101 and 43025201) depicting residues of methyl bromide in/on imported lemons, stone fruits, and grapes; green cocoa beans; dried herbs and spices; and processed foods following fumigation.

The application rates and fumigation intervals for the various RACs are listed in the protocols. The two methyl bromide end-use products (100% PrGs, EPA Reg. Nos. 5785-11 and -41) currently registered for post-harvest fumigation of food/feed commodities have numerous discrepancies between the current label-specified rates and the rates listed in the protocol. For purposes of this review, the 1x application rate is considered to be the rate listed in the approved protocols. There were no approved protocols for application of methyl bromide to spices and herbs. The target application rates for each commodity are presented in Table 3, along with the actual fumigation rates and intervals. Prior to proposing new tolerances, the registrant must revise end-use product labels to reflect the fumigation rates and intervals supported by the residue data.

Commercially obtained commodities, packaged according to commercial practices, were placed on pallets within temperature controlled fumigation chambers. Two-three replicate fumigation chambers were used for each commodity. The commodities occupied approximately 1-27% of the total chamber capacity. Prior to fumigation, the commodities were equilibrated to approximate the specified target fumigation temperature. The temperature of the chambers and the commodities were monitored along with the concentration of methyl bromide. After the specified fumigation interval, the chambers were forced-air vented until the concentration of methyl bromide was ≤5 ppm. The actual in-chamber aeration interval was 2 hours for peaches, nectarines, lemons, plums, and grapes, and 24 hours for processed foods, spices and herbs. In chamber aeration intervals for cocoa beans and chocolate products were not specified. Following aeration, commodities were stored in a temperature controlled room at the following temperatures: 4.7-6.4 C (peaches, nectarines, grapes, plums, and lemons), 4.4-10 C (green cocoa beans), 10 C (herbs, spices, and processed foods), and 15.6-21 C (chocolate products). Four to six composite samples of each commodity were collected and analyzed immediately following fumigation/aeration (0-time) and at specified intervals. Treated samples were placed on dry ice and analyzed within 10-12 hours of collection except for 96-hour processed foods samples that were stored at <-10 C for four days prior to analysis. Non-fumigated control samples were stored frozen at -18 to -20 C until analysis.

Residues of methyl bromide in/on all commodities were determined using the modified King headspace method (Method #93-001) described in the Residue Analytical Methods section. The validated limits of quantitation in the current studies for each commodity are presented in Table 3. One to ten control samples and 4-6 treated samples were analyzed for each commodity. Apparent residues of methyl bromide were nondetectable in/on all control samples. Residues of methyl bromide in/on each commodity are present in Table 3.

Residues of methyl bromide were highest in all commodities immediately following the in-chamber aeration (0-hour and 0-day samples). By 24 hours after the in-chamber aeration, residues of methyl had declined by >80% in imported fruits, approximately 40-70% in dried herbs and spices, and approximately 70-80% in processed foods, excluding chocolate products.

With the exceptions of cocoa beans and finished chocolate products, the following

conclusions regarding the appropriate levels for tolerances are based on residue data from samples held under commercial storage conditions for approximately 24 hours after completion of the in-chamber aeration period. No 24-hour samples were available for cocoa beans and chocolate products as these commodities were initially sampled at 0-, 4-, 8-, and 12-day intervals. For these commodities, the 0-day sampling interval will be used to assess appropriate tolerances.

Citrus Fruits Group

Lemon. Data depicting residues of methyl bromide in/on imported lemons 24 hours after an in-chamber aeration and a 2-hour fumigation at 4 lb ai/1000 ft^3 at $\leq$8.4 C are adequate. Residues of methyl bromide were 3.13-5.15 ppm in/on lemons after 24 hours. The current data are consistent with the previously reviewed residue data for citrus fruits (R. Perfetti, CBRS Nos. 12733 and 12751) and support the establishment of a 6 ppm tolerance for the citrus fruits crop group.

Stone Fruits Group

Peaches, nectarines, and plums. Data depicting residues of methyl bromide in/on peaches, nectarines, and plums 24 hours after an in-chamber aeration and a 2-hour fumigation at 4.0 ai/1000 ft^3 at $\leq$8.4 C are adequate. Maximum residues of methyl bromide after 24 hours ranged from 0.2 ppm in/on peaches to 4.19 ppm in/on plums. The current data are consistent with the previously reviewed residue data for stone fruits (R. Perfetti, CBRS Nos. 12733 and 12751) and support the establishment of a 5 ppm tolerance for the stone fruit crop group.

Small Fruits and Berries Group

Grapes. Data depicting residues of methyl bromide in/on imported grapes 24 hours after an in-chamber aeration and a 2-hour fumigation at 4 lb ai/1000 ft^3 at $<$8.4 C are adequate. Residues of methyl bromide were 3.11-3.57 ppm in/on grapes after 24 hours. The current data along with the previously reviewed (R. Perfetti, CBRS Nos. 12733 and 12751) residue data for strawberries, grapes, blueberries, and blackberries support the establishment of a 4 ppm tolerance for the small fruit and berries crop group.

Herbs and Spices (Dried) Group

Data depicting residues of methyl bromide in/on dried herbs and spices are adequate. Sufficient data are available to determine the appropriate crop group tolerance. Maximum residues of methyl bromide ranged from 3.27 ppm in/on rosemary to 32.0 ppm in/on sesame seeds 24 hours after an in-chamber aeration and the second of two 12-hour fumigations each at 3.5 lb ai/1000 ft^3. The available data indicate that a tolerance of 35 ppm is appropriate for residues of methyl bromide in/on the dried herbs and spices, including mustard seeds. The individual tolerance for cumin of 100 ppm should be revoked. In addition, the registrant must revise all pertinent labels to specify a maximum of two 12-hour fumigations each at 3.5

lb ai/1000 ft^3, with a minimum retreatment interval of 24 hours, and in-chamber aeration.

Miscellaneous Commodities

Cocoa beans (green). Data depicting residues of methyl bromide in/on green cocoa beans are adequate. Residues of methyl bromide in/on green cocoa beans were 1.95-6.93 ppm immediately (0-day) following an in-chamber aeration and the second of two fumigations each at 1.35 lb/1000 ft^3 (0.9x). Although the fumigation intervals were less than the maximum 24 hours and the rates were below the rates specified in the protocol, sufficient data are available to determine appropriate tolerances. The data indicate that 8 ppm is an appropriate tolerance for residues of methyl bromide in/on cocoa beans. The registrant must revise all pertinent labels to specify a maximum of two 24-hour fumigations each at 1.5 lb ai/1000 ft^3, with a minimum retreatment interval of 12 days, and in-chamber aeration.

Processed Foods

Data depicting residues of methyl bromide in/on representative processed foods are inadequate. The MBIP indicated that the magnitude of the residue study for processed foods would include milled rice, wheat flour, popcorn, parmesan cheese, and peanuts. In addition, CBRS (S. Knizner; CBRS No. 12106, DP Barcode No. 192437; 7/29/93) requested that chocolate candy, meats, dried eggs, corn meal, and rolled oats be included in the study. The current submissions contain no residue data for the fumigation of milled rice, popcorn, peanut, or meat products. Data are required depicting residues of methyl bromide in/on milled rice, popcorn, peanuts, and meats sampled 24 hours after an in-chamber aeration and one 24-hour fumigation at 3 lb ai/1000 ft^3 at a minimum temperature of 10 C. Once these data are submitted and reviewed an appropriate tolerance for processed foods can be determined. In addition, all labels pertinent to processed foods must be revised to reflect the use pattern supported by the residue data.

Flour, corn meal, cake mix, rolled oats, parmesan cheese and dried eggs. Data depicting residues of methyl bromide in/on flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs following the in-chamber aeration and the 24-hour fumigation at 3.0 lb ai/1000 ft^3 are adequate. Twenty four hours after the in-chamber aeration, maximum residues of methyl bromide ranged from <0.25 ppm in/on parmesan cheese to 8.25 ppm in/on flour. These data would support a tolerance of 10 ppm for processed foods, excluding chocolate products.

Chocolate products. Data depicting residues of methyl bromide in/on chocolate products are adequate although the commodities were fumigated at less then the specified rate for less than the maximum 24-hour interval. Immediately (0-day) following an in-chamber aeration and a 21.5-hour fumigation at 1.35 lb ai/1000 ft^3 (0.9x), maximum residues of methyl bromide were 3.79 in/on chocolate chips, 7.78 ppm in/on cocoa butter, and 50.4 ppm in/on chocolate liquor. These data could support a tolerance of 55 ppm for chocolate products. If the registrant wishes to support a lower tolerance, they may submit data depicting residues of methyl bromide in/on representative chocolate products sampled 0, 4, 8, 12 and 24 hours

after a single fumigation at 1.5 lb ai/1000 ft^3 for 24 hours and an in-chamber aeration.

Table 3. Residues in representative commodities following fumigation with methyl bromide at ~ 1x and in-chamber aeration.

Crop Grouping/ Commodity	Application Data: Rate (lb ai/ 1000 ft^3)	Application Data: Fumigation Interval (hrs)	Application Data: Commodity Temp. (C)	Sampling Interval [a] (hrs)	Methyl Bromide Residues (ppm)	LOQ [b]
Citrus Fruits						
Lemon	4 (4)[c]	2.0	≤8.4	0	18.5 - 48.3	0.07
				4	13.9 - 16.7	
				8	8.60 - 12.8	
				24	3.13 - 5.15	
Stone Fruits						
Nectarine	4 (4)	2.0	≤8.4	0	26.0 - 38.8	0.07
				4	4.45 - 7.24	
				8	2.99 - 4.77	
				24	0.10 - 0.37	
Peach	4 (4)	2.0	≤8.4	0	22.9 - 47.0	0.06
				4	5.09 - 9.41	
				8	1.40 - 4.18	
				24	0.11 - 0.20	
Plum	4 (4)	2.0	≤8.4	0	14.1 - 23.2	0.11
				4	10.7 - 13.8	
				8	7.83 - 11.4	
				24	2.49 - 4.19	
Small Fruits & Berries						
Grape	4 (4)	2.0	≤8.4	0	16.4 - 21.3	0.06
				4	13.1 - 16.3	
				8	4.75 - 10.6	
				24	3.11 - 3.57	
Herbs and Spices, Dried						
Rosemary	3.5	12 + 12	10	0	7.39 - 11.4	0.19
				6	4.59 - 6.21	
				12	3.56 - 5.22	
				24	2.70 - 3.27	
				48	1.40 - 2.66	
				72	0.93 - 1.07	
				120	0.35 - 0.54	
				192	0.21 - 0.31	
Sage	3.5	12 + 12	10	0	8.10 - 10.4	0.19
				6	3.76 - 7.08	
				12	3.61 - 6.07	
				24	3.72 - 6.12	
				48	2.96 - 4.58	
				72	2.90 - 3.94	
				120	1.06 - 2.87	
				192	1.16 - 2.25	

(continued; footnotes follow)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval [a] (hrs)	Methyl Bromide Residues (ppm)	LOQ [b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Oregano	3.5	12 + 12	10	0	6.72 - 15.4	0.19
				6	4.76 - 12.6	
				12	3.49 - 10.1	
				24 *	2.77 - 6.99	
				48	1.59 - 3.44	
				72	1.29 - 2.47	
				120	0.43 - 1.08	
				192	0.23 - 0.62	
Poppy Seed	3.5	12 + 12	10	0	13.9 - 28.4	0.19
				6	18.1 - 23.2	
				12	14.2 - 18.6	
				24	10.3 - 18.2	
				48	11.3 - 14.8	
				72	4.42 - 11.2	
				120	3.01 - 6.25	
				192	1.60 - 3.15	
Sesame Seed	3.5	12 + 12	10	0	54.4 - 57.3	0.19
				6	39.7 - 45.1	
				12	36.2 - 39.2	
				24	29.1 - 32.0	
				48	21.7 - 24.6	
				72	16.4 - 17.8	
				120	7.22 - 9.88	
				192	3.51 - 4.86	
Cumin	3.5	12 + 12	10	0	5.20 - 8.68	0.19
				6	4.17 - 6.20	
				12	3.05 - 5.54	
				24	3.06 - 4.28	
				48	2.64 - 5.16	
				72	1.99 - 3.16	
				120	2.45 - 2.85	
				192	1.49 - 2.72	
Capsicum	3.5	12 + 12	10	0	7.82 - 13.7	0.19
				6	5.76 - 7.53	
				12	3.44 - 4.34	
				24	2.58 - 5.57	
				48	2.08 - 2.42	
				72	1.29 - 1.74	
				120	0.47 - 0.74	
				192	0.17 - 0.32	

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data: Rate (lb ai/ 1000 ft³)	Application Data: Fumigation Interval (hrs)	Application Data: Commodity Temp. (C)	Sampling Interval [a] (hrs)	Methyl Bromide Residues (ppm)	LOQ [b]
Black Pepper	3.5	12 + 12	10	0	16.1 - 17.2	0.19
				6	9.47 - 12.9	
				12	9.41 - 12.1	
				24 *	6.51 - 9.86	
				48	6.52 - 6.98	
				72	5.94 - 6.83	
				120	2.95 - 3.58	
				192	1.52 - 1.82	
Cassia	3.5	12 + 12	10	0	13.5 - 34.4	0.19
				6	7.00 - 23.5	
				12	5.62 - 22.5	
				24	4.97 - 19.1	
				48	4.17 - 8.33	
				72	2.22 - 5.22	
				120	1.28 - 2.10	
				192	0.60 - 1.23	
Garlic Powder	3.5	12 + 12	10	0	3.05 - 5.30	0.19
				6	2.16 - 4.26	
				12	1.67 - 3.43	
				24	1.98 - 3.35	
				48	1.63 - 3.20	
				72	1.26 - 2.77	
				120	1.03 - 1.99	
				192	0.83 - 1.10	
Onion Powder	3.5	12 + 12	10	0	3.58 - 9.41	0.19
				6	3.26 - 7.58	
				12	3.07 - 5.57	
				24	1.96 - 5.70	
				48	2.16 - 5.02	
				72	1.68 - 3.35	
				120	1.06 - 2.56	
				192	0.81 - 1.77	
Miscellaneous Crops						
Cocoa Beans (green) 1st fumigation	1.32 (1.5)	22.5	7.2-12.3	0 days	2.22 - 5.26	0.01
				4 days	0.30 - 0.97	
				8 days	0.08 - 0.26	
				12 days	0.26 - 0.50	
2nd fumigation	1.35 (1.5)	22.0	8.6-9.7	0 days	1.95 - 6.93	0.01
				4 days	0.43 - 1.43	
				8 days	0.14 - 0.66	
				12 days	0.09 - 0.55	
				20 days	0.03 - 0.12	

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval [a] (hrs)	Methyl Bromide Residues (ppm)	LOQ [b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Processed Foods	3.0 (2.5)	24	10	0	11.3 - 24.9	0.25
Flour				24	5.53 - 8.25	
				48	4.50 - 8.86	
				96 [d]	2.21 - 2.94[e]	
				192	<0.25 - 1.06	
Corn Meal	3.0 (2.5)	24	10	0	5.7 - 12.3	0.25
				24	1.38 - 2.21	
				48	0.87 - 1.23	
				96	0.35 - 0.41[e]	
				192	<0.25	
Rolled Oats	3.0 (2.5)	24	10	0	13.9 - 20.1	0.25
				24	4.33 - 5.78	
				48	2.00 - 2.80	
				96	0.90 - 1.52[e]	
				192	<0.25 - 0.34	
Cake Mix	3.0 (2.5)	24	10	0	1.00 - 1.40	0.25
				24	<0.25 - 0.33	
				48	0.26 - 0.44	
				96	0.26 - 0.94[e]	
				192	<0.25	
Parmesan Cheese	3.0 (2.5)	24	10	0	<0.25 - 0.33	0.25
				24	<0.25	
				48	<0.25	
				96	NA[f]	
				192	NA	
Dried Eggs	3.0 (2.5)	24	10	0	8.89 - 13.3	0.25
				24	1.95 - 2.79	
				48	1.01 - 1.88	
				96	<0.25 - 0.35[e]	
				192	<0.250	
Chocolate Chips	1.35 (1.5)	21.5	15.6-20	0 days	2.12 - 3.79	0.01
				4 days	1.76 - 3.07	
				8 days	1.11 - 1.76	
				12 days	0.55 - 0.87	
				27 days	0.03 - 0.11	
Cocoa Butter	1.35 (1.5)	21.5	15.5-20	0 days	<1.99 - 7.78	0.02
				4 days	0.40 - 2.85	
				8 days	0.16 - 1.11	
				12 days	0.04 - 2.55	
				27 days	<0.04 - 1.53	

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval [a] (hrs)	Methyl Bromide Residues (ppm)	LOQ [b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Chocolate Liquor	1.35 (1.5)	21.5	15.6-20	0 days	27.6 - 50.4	0.02
				4 days	5.60 - 8.47	
				8 days	1.76 - 3.09	
				12 days	0.42 - 0.70	
				27 days	0.03 - 0.06	

[a] The sampling interval represents the time that commodities were held under commercial storage conditions following the fumigation and the specified 2-hour or 24-hour in-chamber aeration.
[b] Method limit of quantitation.
[c] Values in parentheses are the target application rates specified in the protocol.
[d] Dried herbs and spices were fumigated at 3.5 lb ai/1000 ft^3 for 12 hours, aerated, and retreated 24 hours later at the same rate for 12 hours.
[e] Samples were stored frozen for 4 days prior to analysis.
[f] Not analyzed.

Rice and wheat processed commodities. The Methyl Bromide Update (7/91) required data depicting the concentration of methyl bromide in grain dust, polished rice, hulls, and bran processed from rice bearing measurable residues of methyl bromide, and in grain dust, germ, bran, flour, middlings, and shorts processed from wheat grain bearing measurable residues of methyl bromide. In response, the MBIP submitted data (1993; MRIDs 43023601 and 43025301) depicting residues of methyl bromide in/on fumigated rice and wheat grain, dust, and their respective processed commodities.

Rice and wheat grain, in polypropylene mesh bags, were fumigated in a temperature-controlled chamber (10 C) with methyl bromide at a rate of 8 lb ai/1,000 ft^3 for 24 hours (2.7x the maximum label rate). Following fumigation, the chamber was aerated until the methyl bromide concentration in the chamber reached ≤5 ppm. The chamber was then closed for an additional 24 hours. After the 24-hour aeration, treated and untreated rice and wheat grain were sampled and shipped to the processor (Engineering Biosciences Research Center, Texas A&M University) by freezer truck. Samples were in transit for 7 days. Using commercially simulated practices, the rice and wheat grain were cleaned by aspiration to remove grain dust, which was then separated by particle size. Rice was processed into hulls, bran, brown rice, and polished white rice, and wheat was processed into bran, middlings, shorts, germ, and flour. After processing, whole grain, dust, and processed fractions were sent frozen on dry ice by overnight air freight to Webb Technical Group, Inc., Raleigh, NC for analysis. From sampling to analysis, rice fractions were stored frozen for 10-16 days, and wheat fractions were stored frozen for 2-10 days. One to three control and treated samples of each commodity were analyzed for methyl bromide residues using the method described in the Residue Analytical Methods section above. Apparent residues of methyl bromide were <0.21 ppm (LOQ) in the control samples.

In the rice study, residues of methyl bromide were 9.94-10.6 ppm in/on whole grain, 4.68-6.27 in hulls, 3.15-3.48 ppm in brown rice, 0.69-0.79 in bran, and 0.49-0.52 in polished white rice. Residues of methyl bromide in/on rice grain dust fractions were: 7.30-8.28 ppm in dust particles >2540 μm; 3.78-5.11 ppm in particles ≤2540->2030 μm; 2.20-3.02 ppm in particles ≤2030->1190 μm; 2.57-2.91 ppm in particles ≤1190->840 μm; 2.22-2.46 in particles ≤840->420 μm; and 1.28 ppm in particles ≤420 μm.

In the wheat study, residues of methyl bromide were 2.81-3.21 ppm in/on whole grain and were non-detectable (<0.21 ppm) in bran, middlings, shorts, germ, and flour. Residues of methyl bromide in wheat grain dust fractions were: 0.82-1.15 ppm in dust particles >2540 μm; 0.32-0.34 ppm in particles ≤2540->2030 μm; <0.21 ppm in particles ≤2030->1190 μm; 0.38 ppm in particles ≤1190->840 μm; and <0.21 ppm in dust particles ≤840 μm.

To determine storage stability of frozen samples during the interval between processing and analysis, the registrant reanalyzed a single sample of wheat grain and dust 7 days after the initial analysis, and single samples of rice grain, hulls, bran, dust, brown rice, and white rice 15 days after their initial analysis. The results are presented in Table 4. These storage stability data adequately support the residue data for the rice and wheat processing studies.

Table 4. Storage stability of methyl bromide residues in rice and wheat fractions.

Commodity	Residues (ppm)			Percent Recovery
	0 Day	7 Days	15 Days	
Rice grain	10.2	--	8.43	82.6
Rice hulls	5.49	--	5.12	93.3
Rice bran	0.73	--	0.46	63.2
Rice dust	7.95	--	7.12	89.6
Brown rice	3.34	--	2.59	77.5
White polished rice	0.50	--	0.34	68.1
Wheat grain	3.03	2.56	--	84.5
Wheat dust	0.95	0.90	--	95.0

The wheat and rice grain processing studies are adequate. The data indicate that methyl bromide residues do not concentrate in rice and wheat grain dust, or in commodities processed from fumigated rice and wheat grain. Tolerances are not required for methyl bromide in/on rice and wheat grain dust, and food/feed additive tolerances are not required for methyl bromide in milled rice and wheat grain fractions.

MASTER RECORD IDENTIFICATION NUMBERS

The citations for the MRID documents used in this review are presented below.

43023601 Ussary, J., Moseman, R., Nanke K. (1993) Post-Harvest Fumigation of Rice with Methyl Bromide: Magnitude of the Residue Processing Study: Laboratory Project No. P3. Unpublished study prepared by Webb Technical Group. 190 p.

43025101 Lee, H.; Van Natta, K. (1993) Magnitude and Persistence of Methyl Bromide Residues Following Fumigation of Finished Chocolate Products: Project Identification Nos. BR600.2:93, BR600.3:93, and BR600.4:93. Unpublished study prepared by Churchill Nut Company and Bolsa Research Associates. 316 p.

43025201 Ussary, J., Moseman, R., Nanke K. (1993) Fumigation of Processed Foods with Methyl Bromide: Magnitude of the Residues: Laboratory Project No. P5. Unpublished study prepared by Webb Technical Group. 205 p.

43025301 Ussary, J., Moseman, R., Nanke K. (1993) Post-Harvest Fumigation of Wheat with Methyl Bromide: Magnitude of the Residue Processing Study: Laboratory Project No. P4. Unpublished study prepared by Webb Technical Group. 175 p.

43025701 Lee, H.; Van Natta, K. (1993) Magnitude and Persistence of Methyl Bromide Residues Following Fumigation of Green Cocoa Beans: Project Identification No. BR600.1:93. Unpublished study prepared by Churchill Nut Company and Bolsa Research Associates. 222 p.

43025801 Marulli, A.; Lee, H. (1993) Magnitude and Persistence of Methyl Bromide Residues Following Fumigation of Grape, Peach, Plum, Nectarine, and Lemon: Project Identification No. BR550.1,2,3,4,5:93. Unpublished study prepared by AgFume Services. Inc. and Bolsa Research Associates. 330 p.

43029801 Ussary, J., Moseman, R., Nanke K. (1993) Post-Harvest Fumigation of Spices with Methyl Bromide: Magnitude of the Residues: Laboratory Project No. P1. Unpublished study prepared by Webb Technical Group. 373 p.

AGENCY MEMORANDA CITED IN THIS DOCUMENT

CBRS No: 3890
Subject: Follow-up to Methyl Bromide Registration Standard. Post Harvest Protocol, Interim Plant Metabolism Report, Analytical Methods, and Storage Stability.
From: C. Deyrup
To: J. Kempter
Date: 7/14/88
MRID(s): 40579501, 40607801, and 40618501.

CBRS No.: 4399
Subject: Follow-up to Methyl Bromide Registration Standard. Methyl Bromide Industry Panel Response (9/22/88) to DEB Review of 7/14/88 on Postharvest Protocol, Analytical Methodology, and Storage Stability.
From: C. Deyrup
To: J. Kempter
Date: 11/3/88
MRID(s): None.

CBRS No.: 6879, 7/30/90
Subject: Methyl Bromide Reregistration Letter and Attachments from the Methyl Bromide Industry Panel Dated 5/25/90.
From: N. Dodd
To: W. Francis
Date: 7/30/90
MRID(s): None.

CBRS No.: 8601
Subject: Methyl Bromide Industry Panel: Response to the Methyl Bromide Reregistration Standard: Metabolism Study.
From: R. Perfetti
To: W. Burnam and L. Rossi
Date: 9/24/91
MRID(s): None.

CBRS No.: 10367
Subject: Methyl Bromide Industry Panel: Response to the Methyl Bromide Reregistration Standard: Magnitude of the Residue Protocol.
From: R. Perfetti
To: E. Saito and L. Rossi
Date: 8/26/92
MRID(s): None.

CBRS No.: 10816
Subject: Methyl Bromide Industry Panel: Response to the Methyl Bromide Reregistration Standard: Magnitude of the Residue Protocol.
From: R. Perfetti
To: E. Saito and L. Rossi
Date: 11/13/92
MRID(s): None.

CBRS No.: 12106
Subject: Methyl Bromide. Data Requirement for Processed Foods.
From: S. Knizner
To: B. O'Keefe
Date: 7/29/93
MRID(s): None.