US EPA ARCHIVE DOCUMENT

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

APR 7 1994

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Response to the Methyl Bromide Reregistration Standard: Residue Data. (MRID #'s 42949601 and 42963801, CBRS Nos. 12,733 and 12,751, Barcode Nos.: D196317 and D196312).

FROM: R. B. Perfetti, Ph.D., Chemist
Reregistration Section 2
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C)

THRU: E. Zager, Chief
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C)

TO: Lois Rossi, Chief
Reregistration Branch
Special Review & Reregistration Division (H7508W)

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. 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 use rates and the use rates supported by the submitted residue data. 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 (Note: The recommended tolerance levels have been normalized to account for a 1X rate. Therefore, in those cases where the residue data did not reflect the 1X rate, the revised label may include that rate.).

2. The submitted root and tuber vegetable data are adequate. These data will support a crop group tolerance for root and tuber vegetables (Crop Group 1). The available data indicate that an appropriate tolerance for residues of methyl bromide

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is 3 ppm.

3. The submitted bulb vegetable data are adequate and indicate that 2 ppm is an appropriate tolerance for residues of methyl bromide in/on bulb vegetables (Crop Group 3).

4. The submitted leafy vegetable data are adequate and indicate that 0.5 ppm is an appropriate tolerance for residues of methyl bromide in/on leafy vegetables (Crop Group 4).

5. The submitted data on broccoli, cabbage, and cauliflower are adequate and indicate that 1 ppm will be an appropriate tolerance for residues of methyl bromide in/on Brassica leafy vegetables (Crop Group 5).

6. The submitted legume vegetable data are adequate and indicate that 3 ppm is an appropriate tolerance for residues of methyl bromide in/on legume vegetables (Crop Group 6).

7. The submitted fruiting vegetable data are adequate and indicate that 7 ppm is an appropriate tolerance for residues of methyl bromide in/on fruiting vegetables (Crop Group 8).

8. The submitted cucurbit vegetable data are adequate. The available data indicate that a tolerance of 5 ppm will be appropriate for residues of methyl bromide in/on cucurbit vegetables (Crop Group 9), based on a 3.0 lb ai/1000 ft^3 fumigation rate.

9. The submitted citrus data are adequate. The available data indicate that 6 ppm is an appropriate tolerance for residues of methyl bromide in/on citrus fruits (Crop Group 10).

10. The submitted pome fruit data are adequate and indicate that 10 ppm is an appropriate tolerance for residues of methyl bromide in/on pome fruits (Crop Group 11).

11. The submitted stone fruit data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on stone fruits (Crop Group 12).

12. The submitted blackberry, blueberry, grape, and strawberry data are adequate and indicate that a crop group tolerance is appropriate. The registrant should propose a crop group tolerance of 4 ppm for residues of methyl bromide in/on small fruits and berries (Crop Group 13).

13. The submitted cereal grain data are adequate and indicate that 10 ppm is an appropriate tolerance for residues of methyl bromide in/on cereal grains (Crop Group 15).

14. The submitted asparagus data are adequate and indicate that 0.05 ppm is an appropriate tolerance for residues of methyl bromide in/on asparagus, based on a 3.5 lb ai/1000 ft^3 fumigation rate.

15. The submitted kiwi fruit data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on kiwi fruit.

16. The submitted pineapple data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on pineapples.

17. The submitted corn grain processing study is adequate. Residues of methyl bromide do not concentrate in corn grain dust or in grits, meal, and flour dry-milled from corn 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 milled corn 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. 12733 & 12751, DP Barcodes D196317 and D196312)

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
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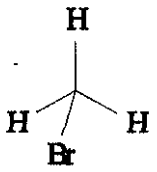
Rockville, MD 20850-3268

METHYL BROMIDE



Shaughnessy No. 053201; Case 0335

(CBRS No. 12733; DP Barcode D196317)

(CBRS No. 12751; DP Barcode D196312)

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 of crop groups having post-harvest fumigation uses for methyl bromide. Residue data were also required depicting the concentration of methyl bromide in processed commodities that are not dried or exposed to elevated temperatures during processing. In response, the Methyl Bromide Industry Panel (MBIP) submitted residue data (1993; MRID 42949601) depicting residues of methyl bromide in/on several miscellaneous commodities and representative commodities from numerous crop groups following post-harvest fumigation with methyl bromide. The registrant also submitted a corn grain processing study (1993; MRID 42963801) depicting residues in dry-milled 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 plants and plant processed commodities.

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. 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 use rates and the use rates supported by the submitted residue data. 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 (Note: The recommended tolerance levels have been normalized to account for a 1X rate. Therefore, in those cases where the residue data did not reflect the 1X rate, the revised label may include that rate.).

Root and Tuber Vegetables Group

2. The submitted root and tuber vegetable data are adequate. These data will support a crop group tolerance for root and tuber vegetables (Crop Group 1). The available data indicate that an appropriate tolerance for residues of methyl bromide is 3 ppm.

Bulb Vegetables Group

3. The submitted bulb vegetable data are adequate and indicate that 2 ppm is an appropriate tolerance for residues of methyl bromide in/on bulb vegetables (Crop Group 3).

Leafy Vegetables (Except Brassica) Group

4. The submitted leafy vegetable data are adequate and indicate that 0.5 ppm is an appropriate tolerance for residues of methyl bromide in/on leafy vegetables (Crop Group 4).

Brassica Leafy Vegetables Group

5. The submitted data on broccoli, cabbage, and cauliflower are adequate and indicate that 1 ppm will be an appropriate tolerance for residues of methyl bromide in/on Brassica leafy vegetables (Crop Group 5).

Legume Vegetables Group

6. The submitted legume vegetable data are adequate and indicate that 3 ppm is an appropriate tolerance for residues of methyl bromide in/on legume vegetables (Crop Group 6).

Fruiting Vegetables (Except Cucurbits) Group

7. The submitted fruiting vegetable data are adequate and indicate that 7 ppm is an appropriate tolerance for residues of methyl bromide in/on fruiting vegetables (Crop Group 8).

Cucurbit Vegetables Group

8. The submitted cucurbit vegetable data are adequate. The available data indicate that a tolerance of 5 ppm will be appropriate for residues of methyl bromide in/on cucurbit vegetables (Crop Group 9), based on a 3.0 lb ai/1000 ft^3 fumigation rate.

Citrus Fruits Group

9. The submitted citrus data are adequate and indicate that a crop group tolerance is appropriate. The registrant should propose a crop group tolerance of 6 ppm for residues of methyl bromide in/on citrus fruits (Crop Group 10).

Pome Fruits Group

10. The submitted pome fruit data are adequate and indicate that 10 ppm is an appropriate tolerance for residues of methyl bromide in/on pome fruits (Crop Group 11).

Stone Fruits Group

11. The submitted stone fruit data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on stone fruits (Crop Group 12).

Small Fruits and Berries Group

12. The submitted blackberry, blueberry, grape, and strawberry data are adequate and indicate that a crop group tolerance is appropriate. The registrant should propose a crop group tolerance of 4 ppm for residues of methyl bromide in/on small fruits and berries (Crop Group 13).

Cereal Grains Group

13. The submitted cereal grain data are adequate and indicate that 10 ppm is an appropriate tolerance for residues of methyl bromide in/on cereal grains (Crop Group 15).

Miscellaneous Commodities

14. The submitted asparagus data are adequate and indicate that 0.05 ppm is an appropriate tolerance for residues of methyl bromide in/on asparagus, based on a 3.5 lb ai/1000 ft^3 fumigation rate.

15. The submitted kiwi fruit data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on kiwi fruit.

16. The submitted pineapple data are adequate and indicate that 5 ppm is an appropriate tolerance for residues of methyl bromide in/on pineapples.

Corn Grain Processed Commodities

17. The submitted corn grain processing study is adequate. Residues of methyl bromide do not concentrate in corn grain dust or in grits, meal, and flour dry-milled from corn 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 milled corn grain fractions.

DETAILED CONSIDERATIONS

Residue Analytical Methods

In conjunction with the methyl bromide residue data, MBIP submitted method descriptions (1993; MRID 42949601) for analysis of methyl bromide residues in/on numerous crops. Residues of methyl bromide were determined using a modified King headspace GC/ECD procedure (Method #93-001), which is based on the King et al. GC/EC method [*J. Agric. Food Chem.*, 29(5), 1003-1005, 1981]. 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. The stated limit of detection is 0.01 ppm.

Briefly, frozen samples are blended with water (0.05 M NaOH for peaches, radishes, and turnips) in a sealed container equipped with a sampling port. Residues are released by heating in a water bath to 25 C. The headspace is sampled and residues are determined by GC/ECD. The residues are quantified by comparison with a matrix standard curve,

which is generated through the analysis of fortified control samples of each commodity. A solvent standard curve is also generated to monitor instrument performance.

Method validation data were submitted by Bolsa Research Associates and ABC/Del Monte Laboratories, CA for representative commodities from the following crop groupings: root and tuber vegetables, bulb vegetables, leafy vegetables, Brassica vegetables, fruiting vegetables, cucurbit vegetables, citrus fruits, stone fruits, small fruits and berries, and cereal grains. For each crop matrix, up to 15 fortified control samples were analyzed. Fortification levels and method recoveries are presented in Table 1. In addition, concurrent recovery data from 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/on all control samples. Residues in/on treated samples were quantified by comparison to a matrix standard curve. These recoveries were inherently corrected for matrix effects, as residue levels were not quantified against a solvent standard curve.

The reported limits of detection (LOD) in each commodity are listed in Table 3. The LOD'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 asparagus, kiwi fruit, pineapples, and commodities from the following crop groups: root and tuber vegetables, bulb vegetables, leafy vegetables, brassica vegetables, legume vegetables, cucurbit vegetables, citrus fruits, pome fruits, stone fruits, small fruits and berries, and cereal grains.

In conjunction with the methyl bromide processing study, the registrant also submitted a method description and validation data (1993; MRID 42963801) from Webb Technical Group, NC, for the analysis of methyl bromide residues in/on field corn grain and processed commodities. Residues of methyl bromide were determined using the modified King headspace procedure (Method #93-001) described above. For method validation, the laboratory fortified whole grain samples with methyl bromide at 0.212-53.0 ppm and calculated recovery data based on a solvent standard curve. Recoveries ranged from 97-111%. However, for determining concurrent method recoveries, the laboratory calculated concentrations based on a matrix fortified standard curve, as described for the other residue studies. Concurrent method recoveries ranged from 105-114% from control samples of whole grain (one sample) and grain dust (two samples) fortified at 11.2 ppm, and one control sample each of grits, meal, and flour fortified at 0.560 ppm. Residues of methyl bromide were nondetectable in/on control samples. Representative chromatograms and sample calculations were provided. The validated limit of detection in corn grain and its processed fractions is 0.05 ppm.

The modified King headspace method (Method #93-001) is adequate for collecting data on residues of methyl bromide in/on field corn grain and its processed commodities.

Table 1. Recovery of methyl bromide from fortified control crop matrices.

Crop Grouping/ Commodity	Fortification Level (ppm)	% Recovery
Root & Tuber Vegetables		
Radishes	1.19-8.89	96-109
Turnips	0.0277-0.0720	83-112
Bulb Vegetables		
Garlic	0.008-1.10	63-119 [a]
Leafy Vegetables		
Lettuce, leaf	0.0086-1.09	92-116
Brassica Vegetables		
Broccoli	0.027-1.20	83-104
Fruiting Vegetables		
Tomatoes	0.111-10.4	91-111
Cucurbit Vegetables		
Summer squash	0.008-1.10	88-100
Citrus Fruits		
Lemons	0.025-1.30	40-126 [a]
Stone Fruits		
Plums	0.0332-9.26	86-117
Small Fruits & Berries		
Blackberries	0.058-1.30	97-116
Cereal Grains		
Corn, field	0.008-1.20	63-107 [a]
Wheat	0.008-1.20	93-138 [a]

[a] Of the nine samples analyzed for each matrix, two garlic samples, four lemon samples, one corn sample, and two wheat 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
Root & Tuber Vegetables		
Carrots	1.99-36.9	86-109
Potatoes	1.32-5.95	90-109
Radishes	3.99-8.89	94-105
Sugar beets	3.98-7.38	77-108
Turnips	4.97-17.7	104-113
Bulb Vegetables		
Garlic	0.027-16.7	73-119
Onion, bulb	1.40-3.60	87-100
Onion, green	0.090-9.00	87-117
Leafy Vegetables		
Celery	0.0554-24.5	86-110
Lettuce, head	0.111-18.5	84-114
Lettuce, leaf	0.00860-5.92	95-116
Spinach	0.0277-0.995	89-106
Brassica Vegetables		
Broccoli	0.054-11.7	95-106
Cabbage	0.269-11.7	87-132
Cauliflower	0.052-4.40	91-117
Legume Vegetables		
Beans, dried	0.300-8.34	81-118
Beans, succulent	0.010-5.01	80-119
Peas, dried	1.30-4.17	91-115
Peas, succulent	0.013-3.34	92-113
Soybeans	1.00-9.18	89-106
Fruiting Vegetables		
Peppers	0.497-17.7	96-105
Tomatoes, field	4.44-22.1	92-104
Tomatoes, greenhouse	7.40-14.8	96-105

(*continued*)

Table 2 (*continued.*)

Crop Grouping/ Commodity	Fortification Level (ppm)	% Recovery
Cucurbit Vegetables		
Cantaloupes	0.375-15.8	99-118
Cucumbers	1.20-16.7	88-103
Summer squash	0.449-20.9	95-112
Citrus Fruits		
Grapefruits	1.00-4.00	81-108
Lemons	3.00-16.7	100-128
Oranges	0.026-4.00	73-112
Pome Fruits		
Apples	5.01-41.7	75-98
Pears	2.40-33.4	81-93
Stone Fruits		
Cherries	0.0115-14.8	85-113
Peaches	0.0275-37.2	92-112
Plums	22.2-22.4	100-110
Small Fruits & Berries		
Blueberries	0.305-50.1	89-110
Grapes	2.80-25.0	93-117
Blackberries	0.117-29.2	63-123
Strawberries	0.179-1.00	91-109
Cereal Grains		
Corn, field	2.50-20.0	88-116
Corn, sweet	0.054-10.0	94-113
Rice	0.600-4.17	73-106
Sorghum	4.17-16.7	104-112
Wheat	1.20-5.01	82-107
Miscellaneous Crops		
Asparagus	0.026-4.60	69-115
Kiwi fruit	2.50-33.4	91-108
Pineapples	0.500-5.01	92-105

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 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 submission (1993; MRID 42949601), commodities were analyzed within ~12 hours of sampling with the exception of summer squash, grapefruit, blackberries, and garlic. In conjunction with the methyl bromide residue data, the registrant submitted storage stability data on all samples that were not analyzed within the 12-hour interval.

Six 0-hour samples of summer squash were stored on dry ice for 12.5 to 13.5 hours prior to analysis. To determine storage stability, a 0-hour sample, which had been initially analyzed after 12.8 hours on dry ice, was stored on dry ice for an additional 6.4 hours and reanalyzed. Recovery from the stored sample was 109%.

Seven 24-hour samples of grapefruit were stored on dry ice for 15 to 17.5 hours prior to analysis. To determine storage stability, two 8-hour samples, which had been initially analyzed approximately 5 hours after sampling, were reanalyzed after 29 days of frozen storage (-20 C). Recoveries from the two stored samples were 98 and 99%.

Six 24-hour samples of blackberries were stored on dry ice for 13 to 14.5 hours prior to analysis. To determine residue storage stability, two 8-hour samples, which had been initially analyzed approximately 6 hours after sampling, were reanalyzed after 25 days of frozen storage (-20 C). Recoveries from the two stored samples were 51 and 60%.

The 24-hour garlic samples were stored on wet ice between sampling and delivery to the laboratory and had to be placed on dry ice to freeze prior to analysis. Of the eight 24-hour samples of garlic analyzed, three were analyzed within 11.5-12 hours of sampling and had residues of 0.076-0.292 ppm. Five additional samples were analyzed after 12.3-13.8 hours of storage and had residues of 0.065-0.337, indicating that the additional storage time had no effect on the recovery of methyl bromide residues.

The submitted storage stability data indicate that the amount of time elapsed before the original analysis of the 0-hour samples of summer squash and 24-hour samples of grapefruit, blackberries, and garlic did not have an adverse effect on the recoveries of methyl bromide residues.

Magnitude of the Residue in Plants

Post-harvest Fumigation

Representative Data for Crop Groupings. 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. The Update summarized protocols for generating residue data on representative commodities, which have undergone extensive review and modification by the Agency since their original submission. Based on these protocols, the MBIP submitted data (1993; MRID 42949601) depicting residues of methyl bromide in/on several miscellaneous commodities and representative commodities from numerous crop groups following a single post-harvest 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 rates are considered to be the rates listed in the approved protocols. 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.

The methyl bromide fumigations were conducted by Plant Sciences, Inc., Watsonville, CA using commercial fumigation chambers having approximately 1,175 ft^3 volumes. Commercially obtained commodities were packaged or boxed according to commercial practices and were then placed on pallets or bins within the fumigation chambers. Three replicate fumigation chambers were used for each commodity. The commodities occupied approximately 10% of the total chamber capacity. Commodities that were in relatively impermeable containers were unwrapped and a portion of the commodity was placed on trays arranged at different levels on the pallet to ensure adequate exposure. 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, chambers were forced-air vented for a specified interval or until the concentration of methyl bromide was ≤ 5 ppm. The actual in-chamber aeration interval was 2-4 hours for most commodities and ~24 hours for soybeans and cereal grains, excluding sweet corn. Following aeration, the commodities were placed in commercial storage containers at 10-18 C and were sampled at 0-, 4-, 8-, and 24-hour intervals. Three composited treated samples were collected from each chamber for a total of nine samples per commodity. Sampled commodities (except for 24-hour samples of garlic and greenhouse tomatoes) were immediately placed on dry ice and shipped to the analytical laboratories (Bolsa Research Associates or ABC/Del Monte Laboratories, CA). Garlic

and tomato samples from the 24-hour sampling interval were placed on wet ice for shipment to the analytical laboratory. All commodities, except for garlic, squash, grapefruit, and blackberries, were analyzed within approximately 12 hours of sampling. Non-fumigated control samples were stored frozen at -20 C until analysis.

Residues of methyl bromide in/on all commodities were determined using the modified King headspace method (Method #93-001) describe in the Residue Analytical Methods section. The validated limits of detection in the current studies for each commodity are presented in Table 3. Three control samples and 6-9 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 samples) and declined rapidly thereafter. With the exceptions of bulb onions, pineapples, dried legume vegetables, and dry cereal grains, methyl bromide residues declined by $\geq 80\%$ within 24 hours. The lowest rate of residue decline ($\sim 30\%$ within 24 hours) occurred in pineapples, most likely due to the colder temperatures (5 C) at which pineapples were aerated.

In the following discussions, the conclusions regarding the applicability of group crop tolerances and the appropriate levels for group or individual crop 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.

Root and Tuber Vegetables Group

Data depicting residues of methyl bromide in/on root and tuber vegetables 24 hours after a 2- to 6-hour fumigation at 2.6-4 lb ai/1000 ft^3 and in-chamber aeration are adequate. Although applications to three of the five representative commodities were below (0.9x) the application rates specified in the protocol, sufficient data are available to determine appropriate tolerances. The maximum 24-hour residues of methyl bromide ranged from 0.015 ppm in/on radishes to 2.34 ppm in/on carrots.

These data will support a crop group tolerance for root and tuber vegetables. The available data indicate that a tolerance of 3 ppm is appropriate for residues of methyl bromide in/on the subject crop group.

Bulb Vegetables Group

Data depicting residues of methyl bromide in/on bulb vegetables 24 hours after a 4- to 6-hour fumigation at 2.5-3.2 lb ai/1000 ft^3 are adequate. The maximum 24-hour residues of methyl bromide ranged from 0.012 ppm in/on green onions to 1.19 ppm in/on bulb onions. Although application rates were below the protocol-specified rates for both garlic (0.83x) and bulb onions (0.9x), sufficient data are available to determine appropriate tolerances. The available data indicate that 2 ppm is an appropriate tolerance for residues of methyl bromide in/on bulb vegetables.

Leafy Vegetables (Except Brassica) Group

Data depicting residues of methyl bromide in/on leafy vegetables 24 hours after a 2-hour fumigation at 4 lb ai/1000 ft^3 (1x) and in-chamber aeration are adequate. The maximum 24-hour residues of methyl bromide ranged from <0.004 ppm in spinach to 0.262 ppm in head lettuce. The data indicate that a crop group tolerance of 0.5 ppm is appropriate for residues of methyl bromide in/on leafy vegetables.

Brassica Leafy Vegetables Group

Data depicting residues of methyl bromide in/on representative Brassica leafy vegetables (broccoli, cabbage, and cauliflower), 24 hours after a 2- to 4-hour fumigation at 4 lb ai/1000 ft^3 (1x) and in-chamber aeration are adequate. The maximum 24-hour residues of methyl bromide ranged from *<0.008 ppm in/on broccoli to 0.608 ppm in/on cabbage.* No data were submitted for the representative commodity, mustard greens. The registrant stated that methyl bromide is not used on leafy Brassica crops because it reacts adversely with endogenous sulfur constituents and reduces crop quality and acceptability. The available data will adequately support a crop group tolerance of 1 ppm for residues of methyl bromide in/on Brassica leafy vegetables.

Legume Vegetables Group

Data depicting residues of methyl bromide in/on legume vegetables 24 hours after a 2-hour (succulent) or 12- to 24-hour (dried legumes) fumigation at 3-4 lb ai/1000 ft^3 (0.9-1x) are adequate. The maximum 24-hour residues of methyl bromide ranged from <0.004 ppm in/on succulent legumes to 1.97 ppm in/on dried legumes. The data indicate that a crop group tolerance of 3 ppm is appropriate for residues of methyl bromide in/on legume vegetables.

Fruiting Vegetables (Except Cucurbits) Group

Data depicting residues of methyl bromide in/on fruiting vegetables 24 hours after a 2--to 4-hour fumigation at 2.5-3.9 lb ai/1000 ft^3 (0.8-1x) and in-chamber aeration are adequate. The maximum 24-hour residues ranged from 0.46 ppm in peppers to 5.33 ppm

in tomatoes. The data indicate that 7 ppm is an appropriate tolerance for residues of methyl bromide in/on fruiting vegetables.

Cucurbit Vegetables Group

Data depicting residues of methyl bromide in/on cucurbit vegetables 24 hours after a 2-4 hour fumigation at 2.1-3.3 lb ai/1000 ft^3 and in-chamber aeration are adequate. The maximum 24-hour residues of methyl bromide ranged from 0.152 ppm in/on summer squash to 3.40 ppm in/on cucumbers. Although applications rates were below the rates specified in the protocol for all three representative commodities (0.7-0.83x), sufficient data are available to determine appropriate tolerances. The available data indicate that a tolerance of 5 ppm will be appropriate for residues of methyl bromide in/on cucurbit vegetables.

Citrus Fruits Group

Data depicting residues of methyl bromide in/on citrus fruits 24 hours after a 2-hour fumigation at ~2.7 lb ai/1000 ft^3 and in-chamber aeration are adequate. The maximum 24-hour residues of methyl bromide ranged from 0.99 ppm in/on oranges to 1.55 ppm in/on lemons. Although application rates were below the rates specified in the protocol for all three representative commodities (0.9x), sufficient data are available to determine appropriate tolerances. Based on the available data, the registrant should propose a tolerance of 6 ppm for residues of methyl bromide in/on citrus fruits.

Pome Fruits Group

Data depicting residues of methyl bromide in/on pome fruits 24 hours after a 2-hour fumigation at 5 lb ai/1000 ft^3 (1x) and in-chamber aeration are adequate and indicate that a crop group tolerance is appropriate. The maximum 24-hour residues of methyl bromide were 6.77 and 3.88 ppm in/on apples and pears, respectively. The data indicate that a crop group tolerance of 10 ppm is appropriate for residues of methyl bromide in/on pome fruits.

Stone Fruits Group

Data depicting residues of methyl bromide in/on stone fruits 24 hours after a 2-hour fumigation at 4.2-5 lb ai/1000 ft^3 and an in-chamber aeration are adequate. The maximum 24-hour residues of methyl bromide ranged from 0.025 ppm in/on peaches to 2.78 ppm in/on plums. Although the application rate for plums was below (0.8x) the rate specified in the protocol, sufficient data are available for determining an appropriate tolerance. The available data indicate that 5 ppm is an appropriate crop group tolerance for stone fruits.

Small Fruits and Berries Group

Data depicting residues of methyl bromide in/on blueberries, blackberries, and strawberries 24 hours after a 4-hour fumigation at 2-3 lb ai/1000 ft^3 (0.9-1x), and grapes 24 hours after a 2-hour fumigation at 4 lb ai/1000 ft^3 (1x) are adequate. The maximum 24-hour residues of methyl bromide ranged from 0.017 ppm in/on strawberries to 2.14 ppm in/on grapes. The registrant should propose a crop group tolerance of 4 ppm for residues of methyl bromide in/on small fruits and berries.

Cereal Grains Group

Data depicting residues of methyl bromide in/on cereal grains 24 hours after a 4-hour (sweet corn) or 12- to 24-hour (dry grains) fumigation at 3-4 lb ai/1000 ft^3 (1x) and an in-chamber aeration are adequate and indicate that a crop group tolerance is appropriate. The maximum 24-hour residues of methyl bromide ranged from 0.187 ppm in sweet corn to 8.74 ppm in sorghum. The data indicate that a crop group tolerance of 10 ppm is appropriate for residues of methyl bromide in/on cereal grains.

Miscellaneous Commodities

Data depicting residues of methyl bromide in/on asparagus 24 hours after a 2-hour fumigation at 3.4 lb ai/1000 ft^3 and an in-chamber aeration are adequate although methyl bromide was applied at 0.85x the rate specified in the protocol. The data indicate that 0.05 ppm is an appropriate tolerance for residues of methyl bromide in/on asparagus, based on a fumigation rate of 3.5 lb ai/1000 ft^3.

Data depicting residues of methyl bromide in/on kiwi fruit 24 hours after a 3-hour fumigation at 4 lb ai/1000 ft^3 (1x) and an in-chamber aeration are adequate. The data indicate that a tolerance of 5 ppm is appropriate for residues of methyl bromide in/on kiwi fruit.

Data depicting residues of methyl bromide in/on pineapples 24 hours after a 2-hour fumigation at 4 lb ai/1000 ft^3 (1x) and an in-chamber aeration are adequate. The data indicate that a tolerance of 5 ppm is appropriate for residues of methyl bromide in/on pineapples.

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

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Root & Tuber Vegetables Carrot	4.0 (4)[c]	4.0	10	0 4 8 24	46.3 - 52.3 18.4 - 25.5 10.3 - 16.2 0.586 - 2.34	0.297
Potato	3.2 (3)	6.0	10	0 4 8 24	6.83 - 8.75 3.50 - 5.07 2.84 - 5.60 1.08 - 1.56	0.092
Radish	2.6 (3)	4.0	13	0 4 8 24	5.54 - 14.6 0.523 - 2.13 0.155 - 0.340 0.006 - 0.015	0.006
Sugar Beet	2.7 (3)	2.0	10	0 4 8 24	14.0 - 16.4 4.77 - 9.68 3.78 - 5.21 0.796 - 1.10	0.587
Turnip	2.6 (3)	4.0	12	0 4 8 24	30.9 - 41.3 8.73 - 13.2 1.79 - 5.46 0.118 - 0.357	0.017
Bulb Vegetables Garlic	2.5 (3)	4.0	14	0 4 8 24[d] 48	15.9 - 23.8 9.75 - 11.6 3.52 - 6.97 0.054 - 0.337 <0.008 - 0.049	0.008
Onion, bulb	2.7 (3)	6	9	0 4 8 24	1.29 - 4.33 2.20 - 3.58 0.837 - 2.73 0.347 - 1.19	0.054
Onion, green	3.2 (3)	6	16	0 4 8 24	4.92 - 11.6 0.780 - 2.28 0.019 - 0.226 <0.008 - 0.012	0.008

(continued; footnotes follow)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Leafy Vegetables						
Celery	4.1 (4)	2.0	10	0 4 8 24	21.1 - 37.5 3.20 - 6.43 1.03 - 3.78 0.027 - 0.071	0.006
Lettuce, head	3.9 (4)	2.0	8	0 4 8 24	13.6 - 27.7 3.39 - 7.31 2.57 - 3.86 0.083 - 0.262	0.028
Lettuce, leaf	3.9 (4)	2.0	12	0 4 8 24	5.74 - 8.40 0.373 - 2.02 0.041 - 0.667 0.002 - 0.011	0.005
Spinach	3.9 (4)	2.0	9	0 4 8	0.668 - 0.899 <0.004 <0.004	0.004
Brassica Vegetables						
Broccoli	3.9 (4)	2	13	0 4 8 24	10.8 - 22.5 1.78 - 2.12 0.548 - 0.932 <0.008	0.008
Cabbage	4.0 (4)	4	13	0 4 8 24	12.5 - 16.6 4.56 - 7.43 3.38 - 4.81 0.159 - 0.608	0.054
Cauliflower	3.9 (4)	2	13	0 4 8 24	4.32 - 7.96 0.282 - 0.824 0.116 - 0.380 0.015 - 0.027	0.008
Legume Vegetables						
Beans, dried	4.1 (4)	24.3	18	0 4 8 24	7.52 - 11.6 1.77 - 5.48 1.64 - 2.35 0.343 - 0.646	0.045

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Beans, succulent	3.6 (4)	2.0	10	0 4 8 24	2.88 - 6.28 0.035 - 0.099 0.021 - 0.028 ≤0.007	0.007
Peas, dried	4.1 (4)	25.0	14	0 4 8 24	6.53 - 8.92 4.34 - 6.77 3.27 - 4.57 1.29 - 1.91	0.108
Peas, succulent	3.1 (3)	2.0	9	0 4 8 24	1.92 - 4.40 0.02 - 0.067 0.009 - 0.014 <0.004	0.004
Soybean	4.0 (4)	12.0	12	0 4 8 24	1.51 - 8.69 1.01 - 3.74 1.24 - 4.04 0.306 - 1.97	0.179
Fruiting Vegetables Pepper	3.9 (4)	2.0	12	0 4 8 24	22.0 - 30.3 9.43 - 12.9 4.12 - 7.52 0.332 - 0.459	0.055
Tomato, field	3.0 (3)	4.0	13	0 4 8 24	20.9 - 34.3 15.2 - 18.1 11.5 - 14.6 4.02 - 5.33	1.58
Tomato, greenhouse	2.5 (3)	4.0	13	0 4 8 24 48	11.3 - 25.4 10.3 - 14.7 6.21 - 12.6 1.39 - 2.38 0.282 - 0.555	0.067
Cucurbit Vegetables Cantaloupe	2.5 (3)	2.0	8	0 4 8 24	8.69 - 14.8 5.49 - 9.86 4.07 - 7.74 1.27 - 1.90	0.072

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Cucumber	2.1 (3)	4.0	9	0 4 8 24	15.0 - 36.9 11.3 - 27.6 8.83 - 14.9 1.97 - 3.40	0.269
Summer squash	3.3 (4)	2.0	9	0 [d] 4 8 24	33.6 - 47.6 1.91 - 13.7 1.26 - 5.11 0.067 - 0.152	0.008
Citrus Fruits Grapefruit	2.6 (3)	2.0	14	0 4 8 24 [d]	3.89 - 6.00 2.50 - 5.13 1.48 - 3.61 0.335 - 1.16	0.117
Lemon	2.6 (3)	2.0	17	0 4 8 24	12.0 - 16.3 6.64 - 8.82 4.44 - 7.07 1.03 - 1.55	0.117
Orange	2.7 (3)	2.0	10	0 4 8 24	5.33 - 7.81 3.59 - 5.95 2.66 - 4.03 0.716 - 0.989	0.117
Pome Fruits Apple	5.1 (5)	2.0	13	0 4 8 24	19.0 - 37.9 14.9 - 18.9 12.2 - 16.7 3.46 - 6.77	0.135
Pear	5.1 (5)	2.0	12	0 4 8 24	15.6 - 36.1 18.4 - 23.4 13.0 - 15.6 2.53 - 3.88	0.135
Stone Fruits Cherry	5.0 (5)	2.0	12	0 4 8 24	19.6 - 29.4 2.20 - 7.32 1.39 - 2.47 0.009 - 0.058	0.006

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Peach	5.1 (5)	2.0	13	0 4 8 24	16.2 - 31.9 4.91 - 6.25 1.31 - 2.33 0.019 - 0.025	0.009
Plum	4.2 (5)	2.0	11	0 4 8 24	28.8 - 36.2 17.7 - 23.0 10.5 - 13.4 1.89 - 2.78	0.005
Small Fruits & Berries Blueberry	2.1 (2)	4.0	13	0 4 8 24	33.2 - 44.0 8.30 - 11.6 3.59 - 7.64 0.067 - 0.380	0.054
Grape	4.1 (4)	2.0	16	0 4 8 24	28.7 - 32.5 16.1 - 20.1 9.63 - 11.5 1.20 - 2.14	0.269
Blackberry	2.7 (3)	4.0	11	0 4 8 24 [d]	17.5 - 33.2 5.03 - 8.16 1.76 - 2.53 0.234 - 0.362	0.058
Strawberry	2.6 (3)	4.0	14	0 4 8 24	1.61 - 5.82 0.178 - 0.882 0.074 - 0.239 0.009 - 0.017	0.008
Cereal Grains Corn, field	4.0 (4)	24.7	12	0 4 8 24 48 72	7.77 - 18.5 8.36 - 13.1 5.42 - 13.2 2.98 - 8.20 3.24 - 5.24 2.26 - 3.63	0.008
Corn, sweet	3.0 (3)	4.0	15	0 4 8 24	17.0 - 22.3 3.31 - 5.53 1.09 - 1.74 0.045 - 0.187	0.027

(*continued; footnotes follow*)

Table 3 (*continued.*)

Crop Grouping/ Commodity	Application Data			Sampling Interval[a] (hrs)	Methyl Bromide Residues (ppm)	LOD[b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)			
Rice	3.1 (3)	24.0	15	0 4 8 24 48	0.703 - 3.23 0.629 - 2.07 0.568 - 2.00 0.223 - 0.904 0.188 - 0.580	0.027
Sorghum	4.1 (4)	24.0	13	0 4 8 24 48	14.8 - 22.2 8.54 - 12.8 8.26 - 14.2 6.26 - 8.74 3.45 - 6.33	0.600
Wheat	3.1 (3)	24.0	17	0 4 8 24 48	3.38 - 6.22 1.36 - 4.88 1.59 - 4.24 1.09 - 2.10 0.579 - 1.33	0.108
Miscellaneous Crops Asparagus	3.4 (4)	2.0	12	0 4 8 24	0.780 - 4.53 0.021 - 0.219 <0.009 - 0.022 0.009 - 0.021	0.016
Kiwi fruit	4.1 (4)	3.0	9	0 4 8 24	22.7 - 29.7 15.6 - 20.1 11.4 - 12.9 3.67 - 4.19	0.013
Pineapple	3.9 (4)	2.0	5	0 4 8 24	2.08 - 5.41 2.70 - 5.00 2.48 - 3.69 2.21 - 3.86	0.027

[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 detection.

[c] Values in parentheses are the application rates specified in the protocol.

[d] Samples of garlic, summer squash, grapefruit, and blackberries were stored frozen for >12 hrs prior to analysis: 12.5-13.8 hrs for four 24-hour samples of garlic; 12.5-13.5 for 0-hr samples of summer squash; 15-17.5 hrs for six 24-hour samples of grapefruit; and 13-14.5 hrs for six 24-hour samples of blackberries.

Magnitude of the Residue in Processed Food/Feed Commodities

Corn grain processed commodities. The Methyl Bromide Update (7/91) required data depicting the concentration of methyl bromide in grits, meal, flour, and grain dust processed from corn grain bearing measurable residues of methyl bromide. As wet-milling of corn grain involves elevated temperature and extensive drying, processing data depicting methyl bromide in wet-milled fractions is not required.

In response, the MBIP submitted data (1993; MRID 42963801) depicting residues of methyl bromide in/on fumigated corn grain, dust, and processed commodities following dry-milling of corn grain bearing measurable residues. Corn grain, in polypropylene mesh bags, was 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. Following fumigation, the chamber was aerated until the methyl bromide concentration in the chamber reached $\leq$5 ppm. The chamber was then closed for an additional 24 hours. Using commercially simulated practices, the corn grain was cleaned by aspiration to remove grain dust and was then dry-milled to yield meal, grits, and flour.

Treated grain (collected 24 hours after fumigation) remained at the fumigation facility for one additional day prior to transport to the processor (Engineering Biosciences Research Center, Texas A&M University). The treated and untreated grain samples were in transit in a freezer truck for 7 days. Samples were stored at <-10 C at Texas A & M for no longer than 14 days. Samples of grain, grain dust, and processed fractions were sent frozen on dry ice by overnight air freight to Webb Technical Group, Inc., Raleigh, NC for analysis. Analyses were completed within 3 days.

To determine storage stability of frozen samples during the interval between processing and analysis, the registrant reanalyzed one each of the stored grain and dust (>2540 μm) samples 14 days after the initial analysis. The initial analysis and the 14-day reanalysis detected residues in grain of 6.47 and 6.41 ppm, respectively, and in grain dust of 5.54 and 6.06 ppm, respectively.

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 <0.25 ppm (LOQ) in the control samples.

Residues of methyl bromide were 5.53-7.39 ppm in corn grain and were non-detectable (<0.25 ppm) in grits, meal, or flour. Residues in grain dust fractions were: 5.19-5.72 ppm for dust particles >2540 μm; 2.15-2.54 ppm for particles $\leq$2540->2030 μm; 1.01-1.58 ppm for particles $\leq$2030->1190 μm; and 0.32-0.93 ppm for particles $\leq$1190 μm.

The corn grain processing study is adequate. The data indicate that methyl bromide residues do not concentrate in grits, meal, or flour processed from fumigated corn grain, or in corn grain dust. Tolerances for methyl bromide in/on grain dust and food/feed additive tolerances for methyl bromide in milled corn grain fractions are not required.

MASTER RECORD IDENTIFICATION NUMBERS

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

42949601 Slesinski, R. (1993) Magnitude and Persistence on methyl Bromide residues following fumigation of various food commodities: Laboratory Project No. MEBR 93-01. Unpublished study prepared by Technical Assessment Systems. 4171 p.

42963801 Ussary, J., Moseman, R., Nanke K. (1993) Post-Harvest Fumigation of Field Corn Grain with Methyl Bromide: Magnitude of the Residue Processing Study: Laboratory Project No. P2. Unpublished study prepared by Webb Technical Group. 169 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.