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

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

APR 12 1985

MEMORANDUM

SUBJECT PP#5F3198 [RCB No. 623]. Methyl Bromide in/on R.A.C.'s of Crop Groups:
I (Root and Tuber Vegetables),
II (Leaves of Root and Tuber Vegetables).
III (Bulb Vegetables),
IV (Leafy Vegetables except Brassica),
V (Brassica (cole) Leafy Vegetables),
VI (Legume Vegetables),
VIII (Fruiting Vegetables except Cucurbits),
IX (Cucurbit Vegetables),
XIII (Small Fruits and Berries),
XIX (Herbs and Spices).
and in/on Okra (Accession Numbers 073147 and 073275).

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The petitioner, The Methyl Bromide Industry Panel, requests establishment of permanent tolerances for residues of the methyl bromide metabolite inorganic bromide, resulting from soil fumigation with methyl bromide, in or on the following raw agricultural commodities by crop grouping:

COMMODITY	CROP GROUP	(#)	Inorganic Bromide Proposed Tolerance (ppm) R.A.C.	Crop Group
Beans (dry)	Legume Vegetables	(VI)	25	400
Beans (succulent)			300	
Peas (green)			275	
Southern peas			25	
Southern peas (dry)			---	
Beets (root)	Root & Tuber Vegetables	(I)	200	300
Carrots			50	
Radish			200	
Sweet potato			75	
Turnip (root)			175	
Rutabaga			20	
Potato			125	
Brussels sprouts	Brassica (cole) Leafy Vegetables	(V)	25	750
Cabbage			50	
Chinese cabbage			25	
Collard (green)			500	
Kale			50	
Mustard (green)			650	
Cauliflower			---	
Broccoli			---	
Cucumbers	Cucurbit Vegetables	(IX)	75	250
Squash (several varieties)			150	
Watermelon			25	
Cantaloupe			---	
Endive	Leafy Vegetables (except Brassica)	(IV)	350	500
Lettuce			400	
Celery			50	
Okra	Misc. commodity	(---)	150	250
Turnip (green)	Leaves of Root and Tuber Vegetables	(II)	175	225
Onion	Bulb Vegetables	(III)	125	125

COMMODITY	CROP GROUP	(#)	Inorganic Bromide Proposed Tolerance (ppm) R.A.C.	Crop Group
Eggplant	Fruiting Vegetables		25	30
Green tomato	(except Cucurbits)	(VIII)	20	
Peppers (several varieties)			20	
Red tomato			25	
Spices	Herbs and Spices	(XIX)	600	600
Raspberries	Small Fruits & Berries	(XIII)	10	10

The petitioner, the Methyl Bromide Industry Panel, also requests establishment of tolerances of 50 ppb for residues of methyl bromide resulting from soil fumigation with methyl bromide in or on the followinc agricultural commodities by crop group.

COMMODITY	VEGETABLE GROUP
Beans (dry)	Legume vegetables
Beans (succulent)	
Peas (green)	
Southern peas	
Southern peas (dry)	
Beets (root)	Root & tuber vegetables
Carrots	
Radish	
Sweet Potato	
Turnip (root)	
Rutabaga	
Potato	
Brussels sprouts	Brassica (cole) leafy vegetable
Cabbage	
Chinese cabbage	
Collard (green)	
Kale	
Mustard (green)	
Cauliflower	
Broccoli	
Cucumbers	Cucurbit vegetables
Squash (several varieties)	
Watermelon	
Cantaloupe	

COMMODITY	VEGETABLE GROUP
Endive Celery Lettuce	Leafy vegetables (except Brassica)
Okra	Miscellaneous commodity
Turnip (green)	Leaves of root and tuber vegetables
Onion	Bulb vegetables
Eggplant Green tomato Peppers (several varieties) Red tomato	Fruiting vegetables (except cucurbits)
Spices	Herbs and Spices
Raspberries	Small fruits and berries

Tolerances were previously established for inorganic bromides under 40 CFR 180.126 (resulting from soil treatment with ethylene dibromide), 40 CFR 180.146 (resulting from fumigation with ethylene dibromide), 40 CFR 180.123 (resulting from fumigation with methyl bromide), 40 CFR 180.197 (resulting from soil treatment with 1,2-dibromo-3-chloropropane), and 40 CFR 180.199 (resulting from soil treatment with combinations of chloropicrin, methyl bromide, and proparagyl bromide). When tolerances for inorganic bromides in or on the same r.a.c. are set in two or more of the above 40 CFR 180 sections, the overall level of inorganic bromide residues to be tolerated from use of two or more pesticides for which tolerances are established is the highest of the separate applicable tolerances (see 40 CFR 180.3(c)1).

Recently, the Agency has revoked most uses of ethylene dibromide (EDB) and dibromochloropropane (DBCP). Thus, the prime pesticide sources of inorganic bromide residues in the r.a.c.'s on which methyl bromide uses are proposed in this petition would be from methyl bromide preplant soil fumigation (see 40 CFR 180.199) and methyl bromide postharvest fumigation (see 40 CFR 180.123).

Inorganic bromide tolerances established under 40 CFR 180.123 and 180.199 for the individual crops cited in Section F submitted with the subject petition include the following:

R.A.C.	Inorganic Bromide Tolerance (ppm) 180.123	180.199
beans, (green), (lima), (snap)	50	--
peas/black-eyed peas	50	--
carrots	30	--
beets (roots)	50	--
radishes	30	--
sweet potatoes	75	--
turnips (roots)	30	--
rutabagas	30	--
potatoes	75	--
cabbage	50	--
cauliflower	--	25
broccoli	--	25
cucumbers	30	--
summer squash	30	--
winter squash	20	--
zuccini squash	20	--
watermelons	20	--
cantaloupe	30	--
lettuce	--	300
okra	30	--
onions	30	--
onions (dry bulb)	--	300
eggplants	20	60
tomatoes	20	40
peppers	--	25

At the current time, no tolerances are established for the parent compound, methyl bromide, on any commodities. This petition represents the first time that tolerances are proposed for both methyl bromide and inorganic bromide resulting from the proposed use of methyl bromide.

RCB has previously discussed the requirements for future methyl bromide tolerances (see J. Worthington memo of February 29, 1984).

In addition, a methyl bromide Data Call-In is currently underway (see E. Zager memo of April 4, 1984).

Finally, a registration standard for methyl bromide is also currently underway and is expected to be completed by the fall of 1985.

Conclusions

1a. The petitioner (Methyl Bromide Industry Panel) will need to submit letters of authorization from all methyl bromide producers whose products (16 formulations) are listed in Section A so that RCB can discuss any pertinent confidential data previously submitted to EPA concerning methyl bromide.

1b. Descriptions of the manufacturing processes, detailed listings of all components in the technical material of all methyl bromide manufactures at levels of >0.1%, and Confidential Statements of Formula for all 16 formulations cited in Section A, must be submitted in a future amendment or cited from previous submissions to EPA.

1c. The lack of product chemistry data has previously been indicated by RCB (see E. Zager memo of April 4, 1984, and M. Loftus memo of February 15, 1985 re: Methyl Bromide Data Call-In).

1d. Several of the 16 formulations cited in Section A contain chloropicrin at up to approximately 65% by weight.

2a. There are no feeding restrictions for crops grown on soils treated with methyl bromide. The petitioner will either need to revise Section B/label to include restrictions against feeding/grazing treated cover crops and bean/pea vines and hay, or submit residue data generated on these treated r.a.c.'s.

2b. Since the residue data submitted with this petition reflect only 1 application, Section B/label will need to be revised in more precise terms so that only one (1) application per year is allowed.

3a. The nature of the residue resulting from the soil application of methyl bromide is considered adequately understood at this time, although a review of all available methyl bromide data currently underway in conjunction with the reregistration process may lead to a new conclusion. The terminal residues in plants consist of methyl bromide and its metabolite inorganic bromide ion.

3b. Via uptake of inorganic bromide ions ubiquitously present in untreated soil, plants may also have naturally high levels (e.g., residue data submitted in this petition reportedly demonstrate inorganic bromide levels in untreated (control) turnip greens grown in the state of Indiana of greater than 550 ppm).

Since inorganic bromide ions (iBr) are ubiquitous to the environment, RCB defers to TOX as to the toxicological significance of iBr residues in plants resulting from the proposed use as well as the need for regulating the use of methyl bromide in terms of iBr residues.

3c. Currently, no iBr tolerances have been established for animal commodities (presumably because iBr residues are naturally present in animals due to the consumption of plants containing ubiquitous iBr residues). RCB now also defers to TOX as to the toxicological significance of iBr residues in animals resulting from the proposed use, and the need to regulate the use of methyl bromide in terms of iBr residues.

3d. Should additional postharvest uses of methyl bromide be contemplated in the future, it should be noted that the petitioner has already been informed about the requirement for metabolism/degradation studies (in-plants) using radiolabeled methyl bromide through a Data Call-In Notice (3/8/85).

3e. If significant residues of methyl bromide, per se, are found to persist in animal feed items as a result of the proposed preplant use, appropriate radiolabeled animal metabolism studies will be required in conjunction with this petition.

4a. The petitioner will need to submit a detailed description of the method utilizing neutron activation analysis which determines residue of inorganic bromides (iBr) as it was applied to generate the iBr residue data submitted in this petition. Also, fortification/recovery data will need to be submitted for all crops analyzed by this procedure before RCB can reach any conclusion regarding the adequacy of this method for iBr residue quantitation.

4b. Another method used to analyze for iBr also quantitates residues of chloropicrin (CP) and methyl bromide (MB) (WIL Research Project, Analytical Method 84:7 - dated September 17, 1984). A capillary GLC column was eventually used in the analysis of MB residues since the use of a packed column resulted in detection of false positive values.

The petitioner will need to submit fortification/recovery data for iBr, CP and MB using the WIL Method 84:7 on all crops analyzed by this procedure.

4c. In an addendum to Section D (Accession Number 073275), iBr residue data were reportedly generated on treated potatoes by an X-ray diffraction method. However, the only method cited in the addendum for iBr residues involves analyzing total bromide by ashing, oxidation to bromate ion, followed by sodium thiosulfate titration. This method does not involve X-ray diffraction. The petitioner will need to clarify/describe the actual procedure used to generate the iBr data on treated potatoes presented in Accession Number 073275, and also submit fortification/recovery data.

4d. Another method cited for MB residue analysis is that of King, et al. (J. Agric. Food Chem., 29, 1003-1981), which is a headspace assay utilizing GLC (packed column) quantitation. The petitioner will need to submit fortification/recovery data for MB in potatoes (the only crop analyzed by this method).

4e. At some future time, following the submission of all requested fortification/recovery data and information relating to detailed descriptions of all methods employed to generate the residue data presented in this petition, methods for methyl bromide and possibly chloropicrin will need to undergo a method trial. The petitioner should indicate whether the headspace assay or the capillary GLC technique for quantitation of methyl bromide residues should be submitted to EPA method trial.

5a. No storage stability data were submitted for residues of inorganic bromide (iBr), chloropicrin (CP), or methyl bromide (MB) in any of the approximately 40 crops upon which residue data were generated in conjunction with this petition. Storage stability data on several selected crops must be submitted in a future amendment for residues of iBr, MB and CP. These data are considered crucial for methyl bromide considering its volatility.

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5b. Information covering lengths of sample storage prior to analytical analysis will need to be submitted in a future amendment for all crop samples analyzed in conjunction with this petition.

5c. The petitioner has not indicated whether the residue data have been corrected for recovery, nor have fortification/recovery data for residues of iBr, MB, or CP been submitted (see conclusions 4a-4e). These data will be required in a future amendment.

5d. The petitioner will need to submit representative chromatograms corresponding to MB, iBr, and CP analysis by all methods utilized (Note: chromatograms have been submitted only for MB packed column analysis, and quantitation of MB residues in potatoes; i.e., no chromatograms representative of MB capillary column analysis nor iBr or CP analysis have been submitted).

5e. At this time, RCB is unable to reach any final conclusions regarding the adequacy of the residue data to support the proposed tolerances because of deficiencies involving the analytical methodologies, (including lack of fortification/recovery data); storage stability data for iBr, MB and CP; documented storage information; representative chromatograms; and correction of residue data for recoveries.

6a. The Section F submitted in this petition requests establishment of tolerances for methyl bromide and inorganic bromides in/on a number of raw agricultural commodities "...by crop grouping," although both group and individual tolerances are proposed. Thus, a revised Section F should be submitted in which either group or individual tolerances are proposed. The petitioner should be advised of Agency regulations for establishing "crop group" tolerances as cited under 40 CFR 180.34f (see also Conclusion 6b that follows).

6b. The methyl bromide, per se, residue data (no detectable MB residues, <50 ppb, in any crop) submitted to date tentatively support the notion of group tolerances for residues of methyl bromide, per se, with respect to 40 CFR 180.34f, subsection 5. (i.e., maximum MB residue levels do not vary greater than 5-fold). However, for some crop groups (i.e., II-Leaves of Root and Tuber Vegetables; III-Bulb Vegetables; XIII-Small Fruits and Berries), the amount of residue data is severely limited. For these groups, either individual tolerances should be proposed, or residue data should be generated on the representative commodities as cited under subsection 1 of 40 CFR 180.34f.

6c. If TOX concludes that iBr residues should not be regulated (see Conclusion 3b), the petitioner should rescind all proposed iBr tolerances.

Otherwise if TOX concludes that iBr residues still must be regulated, the residue data submitted to date will not support crop group tolerances for iBr residues in commodities of most crop groups. In addition, the iBr residue data are considered geographically inadequate since field trials for most crops were not conducted in the major vegetable producing states of California and New Jersey.

Pending the deference to TOX regarding the need for iBr tolerances, as well as resolution of deficiencies described in Conclusion 5(a-e), RCB will be unable to evaluate the need for revised iBr tolerances and/or additional iBr residue data on individual crops and/or crop groups.

Should iBr tolerances be required, the petitioner must consider existing tolerances established under 40 CFR 180 as well as regulations cited specifically under Section 180.3(c)1 (i.e., any new iBr tolerances established under Section 180.199 must be adequate to cover iBr residues from all established uses which result in iBr residues, including postharvest methyl bromide fumigation - Section 180.123). The petitioner should be alerted to the fact that some of the iBr tolerances already established under Section 180.199 are at higher levels than those proposed here.

6d. In RCB's review of the requirements for methyl bromide tolerances (see J. Worthington memo of February 29, 1984), it was concluded that the exemption from the requirement of a tolerance for chloropicrin (CP) under 40 CFR 180.1008 should be reconsidered despite the fact that 40 CFR 180.199 currently states that no residues of chloropicrin will remain in treated commodities as a result of methyl bromide plus chloropicrin soil application.

The regulation 40 CFR 180.1008 should now be revoked and replaced with a tolerance.

At a CP application rate of 240 lb ai/A (Note: maximum allowed application rate = 472 lb ai/A), residue levels up to 5 ppb were reported in green peas, squash and watermelon. In all other crops, CP residue levels were either <1 ppb or not reported.

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Provided the petitioner is willing to limit the amount of chloropicrin to no more than 2% of formulation, RCB could tentatively conclude (pending resolution of the deficiencies cited in Conclusion 5e) that a method sensitivity tolerance for CP would be appropriate. If concentrations of CP >2% in methyl bromide containing formulation are continued, then additional residue data for CP reflecting its maximum proposed application rate will be required to determine the maximum expected residue.

7a. Although it is known that inorganic bromide ions (iBr) transfer to meat, fat, milk, etc., EPA has not previously established iBr tolerances for animal commodities (presumably because iBr is ubiquitous in various animal feeds). Should TOX conclude that iBr residues in animal commodities must be regulated in conjunction with the proposed methyl bromide soil fumigation use (see Conclusion 3c), an animal feeding study using iBr will be required to evaluate the need for iBr tolerances in animal commodities.

7b. Currently, there are no tolerances established for methyl bromide (MB), per se, residues in animal commodities. If significant residues of MB, per se, are found to occur in any animal feeds for which tolerances have been proposed in the subject petition (i.e., bean seed, vine, cannery residue and hay; pea seed, vine and hay; cull potatoes; tomato pomace, turnip roots and greens), appropriate feeding studies will be required as well as development of appropriate analytical methodology. Until questions involving the residue data have been resolved, RCB is unable to reach any conclusions regarding the likelihood of secondary methyl bromide, per se, residues in animal commodities.

7c. Provided the petitioner limits the amount of chloropicrin to a maximum of 2% of formulation, and the CP analytical method and residue data are validated, RCB tentatively concludes that secondary CP residues are not expected to pose a residue problem in meat, fat, milk, poultry and eggs.

8. An International Residue Limit Status sheet is attached to this review. Canada and Mexico have no limits/ tolerances established for methyl bromide, per se, or inorganic bromides. In Canada, inorganic bromide, when used on crops, animals or soil according to label directions, is exempt from the requirement of residue limits.

The compatibility of established Codex limits with proposed U.S. tolerances cannot be evaluated until questions concerning the residue data and proposed (Section F) tolerances are resolved. Codex sets limits on inorganic bromide resulting from the use of organic fumigants determined and expressed as total bromides from all sources.

Recommendations

At this time, RCB recommends against establishment of the proposed methyl bromide and inorganic bromide tolerances for the reasons given in Conclusions 1a, 1b, 2a, 2b, 3b, 3c, 3e, 4a-4e, 5a-5e, 6a-6d, and 7a-7c.

TOX should be alerted to RCB deferences cited in Conclusions 3b and 3c.

The petitioner should also be made aware of RCB's Comments cited in Conclusions 1c and 3d.

Detailed Considerations

Manufacture and Formulation

The petitioner, the Methyl Bromide Industry Panel (MBIP), has not submitted any information regarding the manufacturing process for methyl bromide, nor a detailed listing of all components present in the technical material at concentrations $\geq$0.1% (w/w). The petitioner may obtain this information from the manufacturers or the manufacturers must allow RCB to discuss the pertinent information if available in RCB files.

The Section A submitted in conjunction with the subject petition lists 16 different formulations containing methyl bromide for approval, but a Confidential Statement of Formula has been included for only 1 (Brom-O-Gas).

Since MBIP does not manufacture or distribute methyl bromide, authorization letters will be required from all producers of methyl bromide whose products are included in Section A so that RCB can discuss any confidential data previously submitted to EPA in conjunction with the current review.

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If information concerning the manufacturing process of methyl bromide, detailed listings of all components in the technical material of all manufactures at levels >0.1%, and Confidential Statements of Formula for all 16 formulations cited in Section A have not previously been provided to the Agency, then these must be submitted in a future amendment.

The lack of product chemistry data has previously been cited by RCB (see E. Zager memo of April 4, 1984, and M. Loftus memo of February 15, 1985 re: Methyl Bromide Data Call-In).

The information submitted in Section A of the subject petition indicates that chloropicrin can account for 0 to 64.66% of the methyl bromide-containing formulations.

Proposed Use

For control of certain soil-borne weeds, nematodes, plant diseases, and insects in the soil at time of treatment, methyl bromide is to be applied as a soil fumigant at broadcast equivalent rates between 148 and 240 lb ai/A.

Under ordinary circumstances, only one application of methyl bromide per year is required. Methyl bromide may be applied at various times during the year depending on crop production sequence and soil conditions.

There are no feeding restrictions for crops grown on soils treated with methyl bromide. The petitioner will need to either revise Section B/label to include restrictions against feeding/grazing cover crops and pea/bean vines or hay, or submit residue data generated on these r.a.c.'s.

Assuming application of Terr-O-Gas 33 (containing 33.00% methyl bromide and 64.66% chloropicrin) at 240 lb methyl bromide/A, the application rate of chloropicrin would be 472 lb/A.

Since the residue data submitted with this petition reflect only one application, Section B/label will need to be revised in more precise terms so that only one (1) application per year is allowed.

B

Nature of the Residue

No metabolism studies were submitted with the subject petition. Soil treatment with methyl bromide has been shown to result in inorganic bromide residues in plants [Pesticide Science, 1, 244 (1970)]. The nature of the residue resulting from the soil application of methyl bromide is considered adequately understood at this time, although a review of all available methyl bromide data currently underway in conjunction with the reregistration process may lead to a new conclusion. The terminal residue consists of methyl bromide, per se, and its metabolite inorganic bromide ion. It should be noted that inorganic bromide ion is ubiquitous to the environment. Plants may have naturally high levels of inorganic bromide ions: for example, the residue data submitted in this petition reportedly demonstrate inorganic bromide ion levels in untreated (control) turnip greens grown in the state of Indiana of greater than 550 ppm. Since inorganic bromide ions (iBr) are ubiquitous to the environment, RCB defers to TOX as to the toxicological significance of iBr residues in plants resulting from the proposed use as well as the need for regulating the use of methyl bromide in terms of iBr residues.

Currently, no iBr tolerances have been established for animal commodities (presumably because iBr residues are naturally present in animals due to the consumption of plants containing ubiquitous iBr residues). RCB now also defers to TOX as to the toxicological significance of iBr residues in animals resulting from the proposed use, and the need to regulate the use of methyl bromide in terms of iBr residues.

Should additional postharvest uses of methyl bromide be contemplated in the future, it should be noted that the petitioner has been informed about the requirement for metabolism/degradation studies (in plants) using radiolabeled methyl bromide through a Data Call-In Notice (3/8/85).

If significant residues of methyl bromide, per se, are found to persist in/on animal feed items as a result of the proposed preplant soil application, appropriate radiolabeled animal metabolism studies will be required in conjunction with this petition (see also Residues in Meat, Fat, Milk, Poultry and Eggs section of this review).

Analytical Methodology

The petitioner has employed several different methods to generate the residue data. One method involves neutron activation analysis of inorganic bromides (iBr). The petitioner will need to submit a detailed description of this method as it was applied to the generation of iBr residue data submitted in this petition, along with fortification/recovery data for all crops analyzed by this procedure before RCB can reach any conclusion as to the adequacy of this method for the quantitation of iBr residues.

A second method used to analyze for iBr also quantitates residues of chloropicrin (CP) and methyl bromide (MB) (WIL Research Project, Analytical 84:7 - dated September 17, 1984). In this method, a sample is processed by distillation to give three fractions which are each analyzed by gas-liquid chromatography (GLC). The analysis of MB follows a modification of a distillation procedure by Malone [JAOAC, 52, 800 (1969); JAOAC, 53, 742 (1970)], while the measurement of iBr is similar to the method of Heuser and Scudamore [Pesticide Science, 1, 244 (1970)].

In brief, a sample is blended with water prior to maceration. Following addition of isooctane, residues are fractionated by distillation to a trap at 0°C containing CP, a trap at -40°C containing MB, and a nonvolatile aqueous fraction containing iBr.

Residues of iBr are converted to 2-bromoethanol by reaction with ethylene oxide, and quantitated by GLC (10% Carbowax 20M on Chromosorb WHP 80/100) using a ^{63}Ni electron capture detector.

Residues of CP are analyzed by GLC (20% OV-101 on Chromosorb WHP 80/100) using a ^{63}Ni electron capture detector.

Two different chromatographic techniques were used to analyze for MB. Since the original procedure (referred to as Method-A) was found to detect apparent MB residues in various samples including untreated crop and soil samples, a second procedure (Method-B) was developed which allowed measurement of MB in the presence of the apparent (pseudo-) methyl bromide. Method-A employed a packed GLC column (10% Carbowax 20M on Chromosorb WHP 80/100) while Method-B employed a WCOT bonded-phase capillary column. Both methods used a ^{63}Ni electron capture detector.

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The petitioner will need to submit fortification/recovery data for iBr, CP and MB using WIL Method 84:7 on all crops analyzed by this procedure.

In an addendum to Section D (Accession Number 073275), iBr residue data were reportedly generated on treated potatoes by an X-ray diffraction method, while MB residue data were generated by the method of King, et al.

Also in the addendum, a method analyzing total bromide by ashing, oxidation to bromate ion, followed by sodium thiosulfate titration is described. This method does not involve X-ray diffraction. The petitioner will need to clarify/describe the actual procedure used to generate the iBr residue data on treated potatoes presented in Accession Number 073275, and also submit fortification/recovery data.

The King, et al. method for analysis of MB [Journal of Agricultural and Food Chemistry, 29, 1003 (1981)] is a headspace assay. In brief, a sample is macerated following addition of distilled water. After allowing the sample to stand for 15 minutes, a portion of the headspace is injected into a packed column gasliquid chromatograph (Poropak QS 100-120 mesh) and MB residues are quantitated by ^{63}Ni electron capture detection. Claimed sensitivity is <0.01 ppm. The petitioner will need to submit fortification/recovery data for MB in/on potatoes using this method.

At some future time, following the submission of all requested fortification/recovery data and information relating to detailed descriptions of all methods employed to generate the residue data presented in this petition, methods for methyl bromide and possibly chloropicrin will need to undergo a method trial. The petitioner should indicate whether the headspace assay or the capillary GLC technique for quantitation of methyl bromide residues are to undergo method trial.

At the present time, RCB is unable to reach any conclusions regarding the adequacies of the analytical methods for quantitation and enforcement of the proposed tolerances.

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Residue Data

No storage stability data were submitted for residues of inorganic bromide (iBr), chloropicrin (CP), or methyl bromide (MB) in any of the approximately 40 crops upon which residue data were generated in conjunction with this petition. Storage stability data on several selected crops must be submitted in a future amendment for residues of iBr, MB and CP. These data are crucial for MB considering its volatility.

Information concerning the lengths of sample storage prior to analytical analysis will need to be submitted in a future amendment for all crop samples analyzed in conjunction with this petition.

The petitioner has not indicated whether the residue data have been corrected for recovery, nor have fortification/ recovery data been submitted (see Analytical Methodology section of this review). This information will be required in a future amendment.

The petitioner will need to submit representative chromatograms corresponding to MB, iBr, and CP analysis by all methods utilized (Note: chromatograms have been provided only for MB packed column analysis, and quantitation of MB residues in potatoes; i.e., no chromatograms representative of MB capillary column analysis nor iBr or CP analysis have been submitted).

The residue data are presented below:

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	MB	Maximum Residue Level (ppm) iBr	iBr(C)[b]	MB	CP
beet (root)	I	IN	7	343	199	10.5	NA	NA
carrot	I	IN	7	343	48	3.8	NA	NA
potato	I	IN	240	240	118	20	<0.032	<0.0007
		WA	106	140	4.6	5.7	<0.01	NA
		CA	1.2	233	20	4	<0.01	NA
		FL	100	300	80	<2	<0.01	NA
		FL	20	80	37	37	<0.01	NA
radish (root)	I	IN	7	343	108	1.6	NA	NA
		FL	103	218	12	1.0	NA	NA
		OK	?	268	178	1.7	NA	NA
		FL	240	240	16	5	<0.004	<0.0007
		IN	240	240	268	17	<0.068	<0.0007
rutabaga	I	FL	240	240	21	4	<0.026	<0.0006
sweet potato	I	OK	?	268	57	1.8	NA	NA
		GA	240	240	8	2	<0.004	<0.0006
		GA	240	240	29	NA	<0.004	<0.0006
turnip (root)	I	IN	7	343	163	1.5	NA	NA
		FL	103	218	40	0.5	NA	NA
		GA	240	240	2	NA	<0.002	<0.0006
		FL	240	240	20	6	<0.004	<0.0007
		IN	240	240	922	122	<0.032	<0.0007

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	MB	Maximum Residue Level (ppm) iBr	iBr(C)[b]	MB	CP
turnip (greens)	II	IN	7	343	108	14	NA	NA
		FL	103	218	12	0.9	NA	NA
		OK	?	268	178	2.1	NA	NA
		GA	240	240	102	NA	<0.013	<0.0006
		FL	240	240	25	11	<0.026	<0.0006
		IN	240	240	3229	556	<0.012	<0.0006
onion (dry, bulb or green?)	III	IN	240	240	112	10	<0.012	<0.0007
celery	IV	CA	72	151	22	29	NA	NA
endive	IV	OK	?	268	341	4.8	NA	NA
lettuce (variety?)	IV	IN	7	343	376	9	NA	NA
(variety?)		FL	103	218	14	0.4	NA	NA
(variety?)		IN	240	240	461	12	<0.032	<0.0007
(bibb)		IN	240	240	307	236	<0.032	<0.0007
broccoli	V	FL	240	240	10	1.0	<0.026	<0.0006
		FL	?	268	18	NA	<0.026	<0.0006
		GA	240	240	54	NA	<0.013	<0.0006
brussels sprouts	V	FL	103	218	13	0.2	NA	NA
		FL	240	240	25	1.0	<0.026	<0.0006

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	MB	Maximum Residue Level (ppm) iBr	iBr(C)[b]	MB	CP
cabbage	V	FL	103	218	44	0.7	NA	NA
		FL	240	240	41	2.0	<0.004	<0.0007
		GA	240	240	6	NA	<0.004	<0.0006
cauliflower	V	GA	240	240	2	NA	NA	<0.0006
		FL	240	240	19	4	<0.026	<0.0006
Chinese cabbage	V	FL	103	218	15	0.2	NA	NA
		FL	240	240	17	5	<0.004	<0.0007
collard greens	V	OK	?	268	454	15	NA	NA
		GA	240	240	71	NA	<0.013	<0.0006
		FL	240	240	77	12	<0.004	<0.0007
kale	V	FL	103	218	35	0.6	NA	NA
		FL	240	240	66	12	<0.004	<0.0007
		GA	240	240	12	NA	<0.004	<0.0006
mustard greens	V	FL	103	218	43	1.1	NA	NA
		OK	?	268	648	7.2	NA	NA
		GA	240	240	20	NA	<0.013	<0.0006
		FL	240	240	39	6	<0.004	<0.0007
		IN	240	240	1360	112	<0.032	<0.0007
beans (dry)	VI	OK	?	268	4	0.2	NA	NA
snap beans (dry)		GA	240	240	35	NA	<0.013	<0.0006
lima beans (dry)		GA	240	240	24	NA	<0.013	<0.0006

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	MB	Maximum Residue Level (ppm) iBr	iBr(C)[b]	MB	CP
beans (succulent)	VI	IN	7	343	300	5.7	NA	NA
beans (succulent)		CA	?	285	13	7	NA	NA
snap beans (succulent?)		GA	240	240	4	2	<0.004	<0.0006
snap beans (succulent?)		GA	240	240	11	NA	<0.004	<0.0006
Southern peas (succulent?)	VI	OK	?	268	17	1.0	NA	NA
		MS	?	268	8	8	NA	NA
Southern peas (dry)	VI	GA	240	240	19	NA	<0.013	<0.0006
peas (English)	VI	IN	7	343	261	3.9	NA	NA
peas (green)		IN	240	240	280	74	<0.032	0.004
soybeans	VI	IN	240	240	728	71	<0.012	<0.0006
eggplant	VIII	GA	240	240	6	2	NA	<0.0006
		GA	240	240	17	NA	<0.004	<0.0006
tomato (variety?)	VIII	GA	240	240	6	<1	<0.004	<0.0006
(variety?)		GA	240	240	3	NA	<0.004	<0.0006
(variety?)		IN	240	240	119	32	<0.012	0.004
pepper (variety?)	VIII	GA	240	240	9	13	NA	<0.0006
bell pepper		GA	240	240	6	NA	<0.013	<0.0006
Hungarian sweet wax pepper		GA	240	240	2	NA	<0.004	<0.0006
pepper (variety?)		IN	240	240	48	11	<0.012	<0.0006

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	MB	Maximum Residue Level (ppm) iBr	iBr(C)[b]	MB	CP
cantaloupe	IX	GA	240	240	59	14	<0.003	<0.0006
cucumber	IX	IN	7	343	76	7.2	NA	NA
	IX	FL	103	218	25	0.3	NA	NA
		OK	?	268	51	1.4	NA	NA
		MS	?	268	84	3.7	NA	NA
		GA	240	240	5	1.0	<0.003	<0.0006
		GA	240	240	7	NA	<0.002	<0.0006
		IN	240	240	123	114	<0.012	<0.0006
squash (variety?)	IX	IN	7	343	130	4.0	NA	NA
squash (summer)		FL	103	218	13	1.3	NA	NA
squash (winter)		FL	103	218	4.2	3.0	NA	NA
squash (variety?)		MS	?	268	49	4.4	NA	NA
squash (variety?)		GA	240	240	10	3.2	<0.003	<0.0006
butternut squash		GA	240	240	4.0	NA	<0.004	<0.0006
spaghetti squash		GA	240	240	19	NA	<0.004	<0.0006
acorn squash		GA	240	240	2.0	NA	<0.002	<0.0006
zucchini		GA	240	240	9.0	NA	<0.002	<0.0006
yellow summer squash		GA	240	240	11	NA	NA	<0.0006
squash (variety?)		IN	240	240	59	14	<0.012	0.0042
pumpkin	IX	GA	240	240	20	NA	<0.002	<0.0006
watermelon	IX	MS	?	268	14	11	NA	NA
		OK	?	268	1.8	0.02	NA	NA
		IN	240	240	75	NA	<0.012	0.0046
		GA	240	240	6	1.0	NA	<0.0006

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RAC	Crop[a] Group	State	Application Rate (lb ai/A) CP	Application Rate (lb ai/A) MB	Maximum Residue Level (ppm) iBr	Maximum Residue Level (ppm) iBr(C)[b]	Maximum Residue Level (ppm) MB	Maximum Residue Level (ppm) CP
raspberry	XIII	OH	?	235	<0.6	<0.6	NA	NA
basil	XIX	CA	?	400	92	89	NA	<0.0004
dill	XIX	CA	?	400	568	538	NA	<0.0004
majoram	XIX	CA	?	400	3	3	<0.006	<0.0004
sage	XIX	CA	?	400	236	331	NA	<0.0010
okra	None	MS	?	268	141	12	NA	NA
		FL	103	218	20	2.1	NA	NA
		OK	?	268	87	0.8	NA	NA
		FL	?	234	30	7.4	NA	NA
		FL	?	392	39	7.4	NA	NA
		GA	240	240	6	4	<0.004	<0.0006
		GA	240	240	9	NA	<0.004	<0.0006

NA = Not analyzed
a) Crop grouping according to 40 CFR 180.34f9.
b) Inorganic bromide ion control values.

RCB's Comments/Conclusions re: Residue Data

At this time, RCB is unable to reach any final conclusions regarding the adequacy of the residue data to support the proposed tolerances because of deficiencies involving the analytical methodologies (including lack of fortification/ recovery data); storage stability data for iBr, MB and CP; documented storage information; representative chromatograms; and correction of residue data for recoveries.

The Section F submitted in this petition requests establishment of tolerances for methyl bromide and inorganic bromides in/on a number of raw agricultural commodities "...by crop grouping," although both group and individual tolerances are proposed.

EPA's requirements for establishing "crop group" tolerances are cited in 40 CFR 180.34f.

According to subsection (1), when there is an established or proposed tolerance for all of the representative commodities (as defined under 40 CFR 180.34f subsection (9)) for a specific group or related commodities, a single tolerance may be established for all commodities in the group. The representative crops are given as an indication of the minimum residue chemistry data base acceptable to the Agency for the purposes of establishing a group tolerance.

According to subsection (3), since a group tolerance reflects maximum residues expected to occur on all individual crops within a group, the proposed or registered use patterns for all crops in the group should be the same.

According to subsection (5), if maximum residues or tolerances for the representative crops vary by more than a factor of 5 from the maximum value observed for any crop in the group, individual crop tolerances, rather than group tolerances, will normally be established. Subsection (6) does state that an exception to the 5-fold rule can be made in the case when generally only one commodity in a group would be expected to have significantly lower or higher residue levels. In this case, an individual tolerance at the appropriate level for the unique commodity would be established, if necessary. Also, residue data from crops additional to the representative crops may be required for systemic residues (such as inorganic bromide).

The following discussion will consider the proposed tolerances on the basis of regulations cited under 40 CFR 180.34f:

A. Methyl Bromide, per se

The residue data (no detectable MB residues, <50 ppb, in any crop) submitted to date tentatively support the notion of group tolerances for residues of methyl bromide, per se, with respect to 40 CFR 180.34f, subsection 5, (i.e., maximum MB residue levels do not vary greater than 5-fold). However, for some crop groups (i.e., II-Leaves of Root and Tuber Vegetables; III-Bulb Vegetables; XIII-Small Fruits and Berries), the amount of residue data is severely limited. For these groups, either individual tolerances should be proposed, or residue data should be generated on the representative commodities as cited under subsection 1.

B. Inorganic Bromide Ions

RCB defers to TOX as to the need to regulate inorganic bromides. If TOX concludes that iBr residues should not be regulated, the petitioner should rescind all proposed iBr tolerances.

Otherwise if TOX concludes that iBr must still be regulated, the residue data submitted to date will not support crop group tolerances for iBr residues in commodities of most crop groups. In addition, the iBr residue data are considered geographically inadequate since field trials for most crops were not conducted in the major vegetable-producing states of California and New Jersey.

Pending the deference to TOX regarding the need for iBr tolerances, as well as resolution of deficiencies described at the outset of this Section, RCB will be able to evaluate the need for revised iBr tolerances and/or additional iBr residue data on individual crops and/or crop groups.

Should iBr tolerances be required, the petitioner must consider existing tolerances established under 40 CFR 180 as well as regulations cited specifically under Section 180.3(c)1 (i.e., any new iBr tolerances established under Section 180.199 must be adequate to cover iBr residues from all established uses which result in iBr residues including postharvest methyl bromide fumigation - Section 180.123). The petitioner should be alerted to the fact that some of the iBr tolerances already established under Section 180.199 are at higher levels than those proposed here.

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C. Chloropicrin

In RCB's review of the requirements for future methyl bromide tolerances (see J. Worthington memo of February 29, 1984) the following was concluded re: chloropicrin:

> The inclusion of chloropicrin in many of the methyl bromide formulations poses questions about possible residues of this compound remaining in/on treated commodities. Although Section 40 CFR 180.199 currently states that no residues of chloropicrin will remain in the treated commodity, it is RCB's opinion that this conclusion and the exemption of chloropicrin from the requirement of a tolerance under Section 40 CFR 180.1008 should be reconsidered.

Regulation 40 CFR 180.1008 should now be revoked and replaced with a tolerance.

At a CP application rate of 240 lb ai/A (Note: maximum allowed application rate = 472 lb ai/A), residue levels up to 5 ppb were reported in green peas, squash and watermelon. In all other crops, CP residue levels were either <1 ppb or not reported.

Provided the petitioner is willing to limit the amount of chloropicrin to no more than 2% of formulation, RCB could tentatively conclude (pending resolution of the deficiencies cited at the outset of this Section) that a method sensitivity tolerance for CP would be appropriate. If concentrations of CP greater than 2% in methyl bromide containing formulations are continued, then additional residue data for CP reflecting its maximum proposed application rate will be required to determine the maximum expected residue.

Residues in Meat, Fat, Milk, Poultry and Eggs

A. Inorganic Bromide Residues

Although it is known that inorganic bromide ions (iBr) transfer to meat, fat, milk, etc., EPA has not previously established iBr tolerances for animal commodities (presumably because iBr is ubiquitous in various animal feeds). Should TOX conclude that iBr residues in animal commodities must be regulated in conjunction with the proposed methyl bromide soil fumigation use (see Nature of the Residue section of this review), an animal feeding study using iBr will be required to evaluate the need for iBr tolerances in animal commodities.

B. Methyl Bromide, Per Se, Residues

Currently, there are no tolerances established for methyl bromide (MB), per se residues in animal commodities. If significant residues of MB, per se, are found to occur in any animal feeds for which tolerances have been proposed in the subject petition (i.e., bean seed, vine, cannery residue and hay; pea seed, vine and hay; cull potatoes; tomato pomace; turnip roots and greens), appropriate feeding studies will be required as well as development of appropriate analytical methodology. Until questions involving the residue data have been resolved, RCB is unable to reach any conclusions regarding the likelihood of secondary methyl bromide, per se, residues in animal commodities.

C. Chloropicrin

Provided the petitioner limits the amount of chloropicrin to a maximum of 2% of formulation, and the CP analytical method and residue data are validated, RCB tentatively concludes that secondary CP residues are not expected to pose a residue problem in meat, fat, milk, poultry and eggs.

Other Considerations

An International Residue Limit Status sheet is attached to this review.

Canada and Mexico have no limits/tolerances established for methyl bromide, per se, or inorganic bromides. In Canada, inorganic bromide, when used on crops, animals or soil according to label directions, is exempt from the requirement of residue limits.

The compatibility of established Codex limits with proposed U.S. tolerances canot be evaluated until questions concerning the residue data and proposed (Section F) tolerances are resolved. Codex sets limits on inorganic bromide resulting from the use or organic fumigants determined and expressed as total bromides from all sources.

cc:R.F, Circu, Reviewer, TOX, EAB, EEB, PP#5F3198, FDA,
Robert Thompson, M. Loftus, W. Hazel
RDI:JHOnley:3/29/85:RDSchmitt:3/29/85
TS-769:CM#2:RCB:X7484:MPFirestone:edited by:wh:4/8/85

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INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL: methyl bromide

PETITION NO.: 5F3198

CCPR NO.:

REVIEWER: Michael P. Firestone

dss 2/12/85

Codex Status

☐ No Codex Proposal Step 6 or above

Residue (if Step 9):

Crop(s) | Limit (mg/kg)

none (on given commodities)

Proposed U.S. Tolerances

Residue: inorganic bromide plus methyl bromide

Crop(s) | Tol. (ppm)

(see attached sheets for inorganic bromides)

all methyl bromide tolerances are proposed at 50 ppb

CANADIAN LIMIT

Residue:

Crop(s) | Limit (ppm)

none

MEXICAN TOLERANCIA

Residue:

Crop(s) | Tolerancia (ppm)

none

Notes:

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R. A. C.	CROP GROUP	Inorganic Bromides PROPOSED TOLERANCE (PPM) individual	group	CODE
beans (dry)		25		
beans (succulent)	legume vegetables	300	400	
peas (green)		275		
Southern peas		25		
Southern peas (dry)		—		
beets (root)		200		
carrots	root and tuber	50	300	
radish	vegetables	200		
sweet potato		75		
turnip (root		175		
rutabaga		20		
potato		125		
Brussels sprouts		25		
cabbage	Brassica (cole)	50	750	10
Chinese cabbage	leafy vegetables	25		
collard (green)		500		
kale		50		
mustard (green)		650		
cauliflower		—		
broccoli		—		
cucumbers	Cucurbit	75		50 2/
squash	vegetables	150	250	
watermelon		25		
cantaloupe		—		

1/ Inorganic bromide resulting from the use of organic fumigant determined and expressed as total bromide from all sources.

2/ Step 3

cont.

R.A.C.	CROP GROUP	Inorganic Bromides PROPOSE TOLERANCE individual	group	Codex
endive	leafy vegetables (except Brassica)	350	500	100
lettuce		400		
celery		50		30
okra	misc. commodity	150	250	
turnip (green)	leaves of root and tuber vegetables	175	225	
onion	bulb vegetables	125	125	
eggplant	fruiting vegetables (except Cucurbits)	25	30	
green tomato		20		75 2/ton
peppers (several varieties)		20		
red tomato		25		75 2/ton
spices	herbs and spices	600	600	
raspberries	small fruits and berries	10	10	30 (strawberri

Canada - Inorganic bromide, when used on crops, animals or soil according to label directions, is exempt from the requirement of residue limits.