Bromide Residues from Methyl Bromide Fumigations of Fruits and Vegetables Subjected to Quarantine Schedules

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Fruits and vegetables were fumigated with methyl bromide using schedules with different dose rate, time, pressure, and chamber load, then samples were analyzed to determine bromide residues. After fumigation under atmospheric pressure most fruits and vegetables showed net residues of less than 25 p.p.m. with yams going to 29 p.p.m. Sweet corn and peas were in the range of 30 to 40 p.p.m. Cipollini fumigated under vacuum ranged from 0 to 48 p.p.m. and garlic fumigated under vacuum ranged from 2 to 11 p.p.m.

Many agricultural commodities usually of good quality enter into commercial channels in the United States by importation from foreign countries; but each is a potential source of plant pests such as insects or mites, many of which we do not now have. Every effort is being made by the U. S. Department of Agriculture to prevent such pests from gaining entry in this way. The purity of the food imported must also be assured. This includes freedom from excessive contamination by insects, their fragments or excrement, and similar evidences of rodent infestation.

Export commodities must sometimes be treated to meet the quarantine regulations of other countries. The use of methyl bromide as a fumigant in these programs has been accepted for many years.

The early Public Health studies (*2, 3, 7, 8*) indicated that bromide residues were not likely to be harmful to the consumer. However, with the passage of the Miller Amendment to the Federal Food, Drug, and Cosmetic Act in 1954, it became necessary to determine how much bromide residue resulted from fumigations of several crops. Most of the data presented here were obtained starting in 1956 for use by the Food and Drug Administration in establishing tolerances on commodities included in the study, so that practical fumigations can be carried out with the assurance that residues resulting are safe. The tolerances established are listed in the tables.

The tests involved fumigation schedules at or near those used or likely to be used in quarantine practice (*12–18*). In a few cases, some higher schedules were tested (as on yams or melons) which were near or slightly above the ability of the food to withstand the fumigation without adverse effects.

Table I. Residues of Total Bromide Found in Commodities Following Fumigations with Methyl Bromide in Dow's Laboratory

Two pounds methyl bromide per 1000 cubic feet. Temperature 70° F. Normal atmospheric pressure (NAP)

Commodity and Established Tolerance, P.P.M. Br	Amount Fumigated, No. or Wt.	Chamber Load, %	Fumigation[a] Time, Hours	Total Bromide Residues Found, P.P.M.		
				Control	Gross	Net[b]
Cherries (20)	5 lb.	50	4	0, 0	7, 9	7, 9
		50	4	0, 0	8, 9	8, 9
Grapes (20)	4 lb.	50	4	0, 0	10, 10	10, 10
		50	4	1.1, 0.9	11, 11	11, 11
		50	4	0, 0	9, 10	9, 10
Peaches (20)	40	75	4	0, 0	3, 3	3, 3
		75	4	0, 0	2, 2	2, 2
		75	4	...	3, 3	3, 3
Plums (20)	30–35	33	4	0.5, 0.4	4, 3	4, 3
		33	4	0.3, 0.2	3, 3	3, 3
Cantaloupes (20)	5	100	4	1.3, 1.5	15, 16	14, 15
		100	4	1.3, 1.5	12, 13	11, 12
Carrots (30)	42	75	4	14, 14	31, 28	19, 16
		75	4	12, 11	28, 35	16, 23
		75	4	10, 8	37, 23	25, 11
Oranges (30)	15	67	2	0.7, 0.5	14, 11	13, 10
		67	2	0.8, 0.8	13, 12	12, 11
		67	2	0.9, 0.6	12, 13	11, 12
Grapefruit (30)	10	100	2	0.3, 0.5	9, 10	9, 10
		100	2	0.0, 0.4	12, 12	12, 12
Sweet corn (50)	12	100	4	0.6, 1.4	31, 35	30, 34
		100	4	0.7, 1.3	35, 40	34, 39
		100	4	0.0, 1.0	33, 31	32, 30
Squash (summer) (30)	5	100	4	0, 0	8, 11	8, 11
		100	4	0.2, 0	6, 10	6, 10
Cucumber (30)	10	75	4	0.4, 0.6	15, 12	14, 11
		75	4	2.2, 0.3	19, 13	18, 12
		75	4	0.5, 0.4	13, 11	12, 10
Green peppers (30)	5	50	4	0.5, 0.3	21, 21	20, 20
		50	4	0.6, 0.5	23, 21	22, 20
		50	4	0.7, 0.8	22, 21	21, 20

[a] All samples aerated at least 24 hours before aliquots were taken for analysis. Each entry indicates separate fumigation.
[b] Increase over average untreated control.

Experimental Procedure and Results

Three types or sizes of chambers were used for the fumigations. Some cipollini and garlic samples were collected from lots fumigated in a commercial vacuum fumigation vault at dockside, Port Newark, N. J., while samples of other commodities were treated at Hoboken, N.J., in 7.4-, 19-, or 50-cubic foot laboratory vaults. The remaining fumigations

Table II. Residues of Total Bromide Found in Cipollini and Garlic Following Vacuum Fumigation in Commercial Chambers with Methyl Bromide, Port Newark, N. J.

Commodity and Established Tolerance, P.P.M.	Fumigation Data: Lb./1000 cu. ft.	Vacuum, inches	Temp., ° F.	Hours[a]	Days stored	Lot No.	Total Bromide Residue Found, P.P.M.: Control	Gross	Net[b]
Cipollini[c] bulbs (50)	3	15	75	2		11	3.8	36	34
						12	1.3	21	19
	3	15	74	2	11	30	2.3	23	21
					11	31	2.2	17	15
					11	32	2.6	20	18
	4	15	66	2	11	23	4.1	3	0
					11	24	3.5	14	11
					11	25	2.6	16	13
	4	15	46	4		13	6	54	48
					31	2	5	49	44
	4	17.5	42	4	15	1	11	47	37
					15	2	9	51	41
					15	3	10	39	29
					15	4	9	46	36
					13	5	11	55	45
					13	6	7	54	44
	4	15	38	4	35	7	4	42	38
					35	8	4	48	44
	4	15	38	4	34	9	7	54	47
					34	11	4	45	41
					34	12	5	45	40
	4	15	34	4	17	1	5	43	38
					18	3	4	41	37
					18	4	3	43	40
					18	5	3	44	41
	4	15	30	4	25	6	5	52	47
					25	10	4	42	38
Garlic[c] (50)	2	15	78	2	13	19	1.7	8	6
					13	20	1.7	9	7
					3	21	1.9	6	4
					3	22	0.7	10	8
	2	15	74	2	12	13	1.2	12	10
					12	14	3.0	7	5
					12	15	2.6	9	7
					12	16	0.6	4	2
					12	17	5.0	13	11
					12	18	2.4	8	6

[a] Each entry indicates separate fumigation.
[b] Increase over average untreated control.
[c] Aired 1 day near fumigation temperature, then stored near 75° F.

were conducted in modified 24-quart pressure cookers at Midland, Mich., as described by Getzendaner (*4*). In all cases, the vaults remained sealed until the end of the fumigation period. After removal of the samples, they were allowed to aerate 24 hours or longer before analysis or storage, and in some instances were held for analysis after the aeration period. Samples were stored, after being ground, in polyethylene bags at 0° F. Control samples of all of the commodities taken before the fumigations were handled in the same way as the fumigated samples but were not fumigated. Unless otherwise noted, all of the analyses were by the method of Shrader, Beshgetoor, and Stenger (*11*).

Data on fumigation in the Midland laboratory are given in Table I. Duplicate analytical results are given for each sample. In these, as well as the commercial fumigations (Table II), the chamber contained a normal load.

Data in Table III are from fumigations in 7.4-, 19-, or 50-cubic foot chambers. The data on honeydew melons were obtained after establishment of legal tolerances to study the effect of fumigation at low temperature, time, and fumigant concentration on residue deposition. Except for the blueberries, which were frozen, all commodities were shipped by air, in the fresh state, to Midland, Mich., for analysis.

Discussion

Methyl bromide per se is rapidly dissipated from nearly all foods when they are removed from the fumigation atmosphere. Dudley (*3*) fumigated commodities, including some fruits and vegetables, and found that the bromide content drops rapidly during the first 48 hours after fumigation. Roehm, Stenger, and Shrader (*8*) showed that methyl bromide aired from cheese almost completely within 48 hours, and from butter completely after 96 hours. Lindgren, Gunther, and Vincent (*6*) found that essentially all of the bromide in wheat after 6 hours of aeration was fixed and not lost by further aeration. Desbaumes (*1*) found only traces of methyl bromide in foods after aeration for one day. Laug (*5*) concluded that within one hour after exposure, approximately 85 to 95% of the volatile residue disappears from the foodstuff. He also showed a continuing decrease in concentration at 24 hours.

These findings indicate that all the commodities fumigated here were allowed to aerate long enough to remove all of the methyl bromide. The bromide residue content would not have been significantly different with different periods of aeration as long as 24 to 48 hours elapsed between fumigation and analysis. The analyses for total bromide were, in fact, a determination of inorganic bromide, as Winteringham (*19*) has shown this to be the residue remaining.

Residue content could increase if appreciable dehydration occurred, as it is proportional to the loss in weight of the sample. In the work reported here, time lapses which could result in dehydration were no greater than might occur in good marketing practice.

Actual conditions for fumigation of commodities with methyl bromide are many and varied. It was not practical to obtain samples fumigated under all conditions which might be used in practice. Rather, replicated fumigations were carried out under somewhat

Table III. Bromide Residues Found in Various Fruits and Vegetables Following Fumigation in 7.4-, 19-, or 50-Cubic Foot Experimental Chambers in Hoboken, N. J.

Commodity and Established Tolerance, P.P.M.	Rate, Lb./1000 Cu. Ft. MeBr	EDB	Pressure	Chamber load	Hours[a]	° F.	Days Stored	Variety[b]	Bromide Found, P.P.M. Control	Gross	Net[c]
Apples[d] (5)	2		NAP	Full	3	72	45	G	2, 1	4, 4	3, 3
	2		NAP	Full	3	72	45	L	0, 0	2, 4	1, 3
	2		NAP	Full	4½	53	45	G		5, 5	4, 4
	2		NAP	Full	4½	53	45	L		2, 4	1, 3
	4		NAP	Full	2	41	45	G		5, 4	4, 3
	4		NAP	Full	2	41	45	L		2, 2	1, 1
	5[e]		NAP	Small	2	34	7	G		3, 3	2, 2
	5[e]		NAP	Small	2	34	7	L		2, 3	1, 2
	1½ +	½	NAP	Full	3	72	45	G		5, 5	4, 4
	1½ +	½	NAP	Full	3	72	45	L		2, 3	1, 2
	1½ +	½	NAP	Full	4½	53	45	G		3, 4	2, 3
	1½ +	½	NAP	Full	4½	53	45	L		5, 4	4, 3
Blueberries[f]	2		NAP	66%	2¼	74	10	W	1, 1	11, 9	9, 7
	2		NAP	66%	2¼	74	8	J	3, 2	13, 12	11, 10
	2		NAP	Small	4½	52	9	W		10, 10	8, 8
		1½	NAP	66%	2½	74	10	W		2, 3	0, 1
		1½	NAP	66%	2¼	74	8	J		3, 4	1, 2
		1½	NAP	Small	4½	52	9	W		4, 4	2, 2
		1½	NAP	66%	2¼	74	10	W		10, 9	8, 7
	1½ +	½	NAP	66%	2½	74	8	J		12, 11	10, 9
	1½ +	½	NAP	Small	4½	52	9	W		9, 9	7, 7
Cabbage[g] (50)	2		NAP	20%	2	75	29		1, 2	15, 20	13, 18
	3		NAP	20%	2	51	30			17, 22	15, 20
	3		15″ vac.	5%	2	51	30			26, 30	24, 28
	4		NAP	20%	2	41	30			19, 19	17, 17
	4		NAP	20%	3	34	29			19, 17	17, 15
	4		15″ vac.	5%	3	34	29			31, 23	29, 31
	5		NAP	20%	3	51	30			28, 30	26, 28
Yams, Cuban[h]	3		NAP	15%	4	87	21		5.1	18	15
(*Dioscorea*) (30)	4½		NAP	15%	4	87	21			32	29
	3		NAP	15%	4	86	27		2.4	32	29
	4½		NAP	15%	4	86	27		2.4	26	23
	3		15″ vac.	15%	4	80	23			26	23
	3		NAP	15%	4	67	3			10	7
	4½		NAP	15%	4	55	21		2.7	13	10
	6		NAP	15%	4	55	21			16	13
	3		NAP	15%	4	55	28		2.8	19	16
Peas[i] (in pods) (50)	3		NAP	Small	2	70	21		23	49	31
	3		NAP	Small	2	70	8		20	53	35
	4		NAP	Small	2	70	8		10	59	41
	3½		NAP	Small	1¾	55	8			54	36
	4		NAP	Small	2	55	8			48	30
	3		NAP	Small	2	55	21			45	27
Honeydew[j] melons (20)	3		NAP	15%	2	56	39		<5	<5	0
	4		NAP	15%	2	56	39			<5	0
	5		NAP	15%	4¾	46	13			<5	0
	4		NAP	15%	2	42	40		<5	<5	0
	4		NAP	15%	3	42	40			<5	0
	4		NAP	15%	3½	42	40			<5	0
	4		NAP	15%	2	46	13			<5	0
	4		NAP	15%	3	46	13			<5	0

[a] Each entry indicates separate fumigation.
[b] Varieties fumigated: G = Golden Delicious, L = Lady apple, W = Weymouth, J = Jersey.
[c] Increase over average untreated control.
[d] Aired 1 day near fumigation temperature, then stored at 42° F.
[e] These applies held 4 days after fumigation before sampling, all others held 42 days.
[f] Aired 1 day near fumigation temperature, then stored at 45° F.
[g] Aired 1 day at fumigation temperature, then stored near 35° F.
[i] Aired 1 day near 75° F., then stored at 75° F. (or 55° F. for 55° F. tests).
[j] Aired and stored at 50° F. Analyzed by x-ray fluorescence, with sensitivity of 5 p.p.m. (*4*).

limited conditions for many of the commodities. In most of the laboratory fumigations, the temperature used was near the maximum recommended. This would be likely to produce maximum residue. Most of the schedules used here have been demonstrated to be effective against insects and eggs.

The data in Table I show a very low rate of residue accumulation for peaches and plums under the experimental conditions used. Cherries, grapes, cantaloupes, oranges, grapefruit, summer squash, and cucumbers have a somewhat higher rate, although still relatively low. Carrots, peppers, and sweet corn all were higher. The residue values on replicated fumigations show generally good agreement.

Cipollini bulbs (Table II) fumigated under 15-inch sustained vacuum (approximately 380 mm. of mercury absolute pressure) show remarkably consistent residues over the temperature range of 30° to 46° F. with other factors held constant. At higher temperatures, up to 77° F. with time of fumigation cut from 4 to 2 hours and dosage reduced from 4 to 3 pounds, the residues drop markedly. The cold temperature schedules for cipollini are generally limited to 40° F. or above and are useful for shipments that arrive in winter at northern ports of entry.

Residues in garlic are somewhat lower than in cipollini even considering the lower rate of methyl bromide usage. The tolerance of cabbage, cipollini, garlic, and yams to such fumigation has been discussed by Roth and Richardson (*9, 10*).

Residues in yams (Table III) from atmospheric pressure fumigation (NAP) are variable, but generally lower at 55° F. than at 80° to 86° F. The residue from the vacuum fumigation at 80° F. is about the same as would be produced by an atmospheric fumigation at that temperature. Peas show little temperature dependence in this study. The residue levels in the honeydew melons are all below the level of sensitivity of the x-ray fluorescence method used.

Fumigation of apples results in a very low rate of bromide residue accumulation (Table III), similar to peaches and plums (Table I). The residue in blueberries, slightly higher, is comparable with grapes and cherries (Table I). Cabbage accumulates residue at a significantly higher rate, comparable with carrots and peppers (Table I) and yams (Table III). Although the results are not directly comparable because of different chamber loading, the residues on cabbage after 15-inch sustained vacuum fumigation appear slightly higher than those after atmospheric pressure fumigation in two paired tests at 34° and 51° F.

The results reported here are generally in good agreement with those of Dudley (*3*), who also fumigated carrots, apples, and sweet potatoes with methyl bromide at the rate of 2 pounds for 2 hours.

This series of fumigations included some preliminary tests of ethylene dibromide (EDB) alone on blueberries and in combination with methyl bromide on apples and blueberries. The efficiency of these fumigants is being studied separately. The results given here are included merely for comparison of the residues resulting from this type of schedule. The possibility of ethylene dibromide per se remaining in the samples at the time of analysis has not been studied.

The data indicate that, on a nearly equal weight basis, there is less bromide residue from ethylene dibromide than from methyl bromide. This is not unexpected because of the relatively greater reactivity of the latter.

It is concluded from this study that no excessive residues of bromide will result from fumigation of these fruits and vegetables with methyl bromide following quarantine schedules.

Acknowledgment

The authors gratefully acknowledge help given by E. E. Kenaga, A. E. Doty, S. A. Shrader, and D. A. Mapes of The Dow Chemical Co., H. Roth and J. W. Bulger of Entomology Research Division, and R. G. Oakley, S. W. Luke, and A. E. Peters in the Plant Quarantine Division, U.S.D.A.

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Received for review July 9, 1965. Accepted October 25, 1965.

HEPTACHLOR IN ALFALFA

Distribution, Movement, and Persistence of Heptachlor and Its Epoxide in Alfalfa Plants and Soil

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The development of more sensitive analytical procedures for the detection of insecticide residues necessitates the re-evaluation of application procedures, especially where food products are concerned which traditionally are assigned a zero tolerance. Electron-capture gas chromatography revealed the presence of residues of heptachlor epoxide and dieldrin in milk produced in areas where these insecticides were being used to control the alfalfa weevil. A statewide testing program conducted by the University of Maryland involving over 1500 analyses of dairy feeds indicated that alfalfa treated the previous fall was the only significant source of the residue in milk (*5*).

Lichtenstein and coworkers have reported the translocation of chlorinated hydrocarbons from soil to a variety of plants (*9, 11*) and the epoxidation of heptachlor and aldrin by plant tissue (*6, 10*). Insecticide in the leaves and stems of pea plants was shown to be the result of absorption through the roots and not of adsorption of vapor by the aerial parts of the plants (*10*). Carrots were reported not only to absorb more insecticide than some other plants, but to concentrate it in their roots (*6, 7*). The retention of heptachlor by the soil was greater when alfalfa had been used as a cover crop (*8, 11*). Terriere and Ingalsbe (*13*) reported the translocation of heptachlor, aldrin, and dieldrin in potatoes. Traces of dieldrin in oil and meal from cottonseed produced in treated soil were reported by Randolph and coworkers (*12*). Eden and Arthur (*3*) found small residues of DDT and heptachlor in soybeans grown in soil treated at the time of planting, but concluded that there had been no translocation. Hardee and coworkers (*4*) found detectable residues of dieldrin in alfalfa 32 months after treatment with 3 to 5 pounds per acre. The soil contained most of the residual insecticide in the top 1 inch and it was concluded that the mechanism of contamination was by splashing onto the plant. Contamination of alfalfa is also considered to be the result of dust created during haymaking operations (*2*).