Methyl Bromide Fumigation of Tree Fruits for Control of the Mediterranean Fruit Fly: Concentrations, Sorption, and Residues

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Test data obtained from methyl bromide (MB) fumigation of pears, plums, cherries, nectarines, and peaches at 21 °C with 48 g/m^3 for 2 h, 48 g/m^3 for 3 h, or 32 g/m^3 for 4 h show pears and plums less sorptive of MB during fumigation than the other three commodities. Postfumigation inorganic bromide residues found in all commodities, except pears, were below EPA tolerances. The tolerance set for pears is only 5 ppm and may have to be adjusted upward to 10 ppm if pears are to be fumigated with MB as described. Data show pears and plums had relatively higher organic bromide residues (residual MB) and retained the residues longer than did the cherries, nectarines, or peaches. Desorption of organic bromide from fumigated fruit is very rapid in the first 24–48 h, even when the fruit is in cold storage.

The recent introduction of the Mediterranean fruit fly [Diptera, Tephritidae, *Ceratitis capitata* (Wiedemann)] into California brought forward an urgent need for more efficient quarantine treatments. Presently approved treatments listed in the U.S. Department of Agriculture (USDA), Animal and Plant Health Inspection Service (APHIS), "Plant Protection and Quarantine (PPQ) Treatment Manual" (1976) against Medfly in deciduous fruits require 10–16 days of cold storage at 0–2.2 °C or fumigation with methyl bromide (MB) plus 4–10 days of refrigeration at 0.6–13.3 °C. The refrigeration component of these schedules cannot be met because of the very large volume of tree fruits produced and shipped from California. Due to lack of sufficient cold storage space, a marketing bottleneck would rapidly develop. Effective fumigation schedules using ethylene dibromide (EDB) or MB without refrigeration are approved for use against Medfly for other commodities including citrus, avocado, mango, pineapple, papaya, tomato, and certain other vegetables (USDA, APHIS, 1976). The objective of this research project was to develop MB fumigation treatments effective in controlling Medfly, without the refrigeration requirement for cherry, nectarine, peach, pear, and plum. This paper reports MB concentration, sorption, and residue data collected during the development of these MB treatments. Efficacy and phytotoxicity data were also developed at the USDA, Tropical Fruit and Vegetable Research Laboratory, Hilo, HI, and the USDA, Market Quality and Transportation Research Laboratory, Fresno, CA, respectively, and will be reported separately.

EXPERIMENTAL SECTION

Test fruits were obtained from production areas of the San Joaquin Valley in California. Each lot of fruit was divided into two parts, one for fumigation studies in Fresno and the other for shipment to Hilo, HI. Although the handling of the fruit before and after being fumigated was different at the two locations, the fruit was fumigated in a like manner and with the same MB treatments (Splitler and Couey, 1982).

Fruit was held for 18–24 h at 21 ± 1 °C to assure proper commodity temperature at the time of fumigation. The fruit was placed into 28-L fiberglass chambers (Labconco vacuum desiccators) without packing materials and fumigated as a bulk treatment. The chambers were equipped with air circulation fans which operated continuously during each fumigation. Estimated load factor for all commodities based on volume was 50–60% and by weight was 240–270 kg/m^3 (15–17 lb/ft^3). Using a gastight syringe, the calculated quantity of pure MB gas for each dosage was drawn from a MB gas cylinder and injected into the chamber. Methyl bromide is a highly toxic compound and should be applied only by a trained and certified operator.

Table I. Commodities and Cultivars Used in MB Fumigation Tests

commodity	cultivar (1981)	harvest date
cherry	Bing	5/19
nectarine	May Grand	6/8
	Flavor Top	7/14
	Fantasia	8/3
	Autumn Grand	8/24
peach	Spring Crest	5/25
	Redtop	6/23
	Sun Crest	7/7
	O'Henry (2)	8/11 and 8/17
	Fairtime	9/1
pear	Bartlett	7/18
plum	Red Beaut	5/31
	Santa Rosa	6/30
	Friar	7/27
	Casselman	8/18

Concentrations of MB within the chambers were monitored by GLC (Tracor 550). Gas samples were taken from chamber sampling ports with a 50-mL gas syringe. The samples were introduced into the GLC via an integral gas sampling valve containing a 0.10-mL sample loop. The column was 1.8 m by 4 mm i. d. nickel, packed with 10% DC-200 (12500 CSTK) on Gas-Chrom Q, 80–100 mesh. The oven temperature was 150 °C, the flame ionization detector temperature was 200 °C, and the gas sampling valve temperature was 150 °C. The nitrogen carrier gas flow rate was 50 mL/min. The retention time for MB was 0.72 min. Concentration sample times were 2–5 min after MB injection (referred to as "start"), 0.5 h, 1.0 h, and 2.0 h, 3.0 h, or 4.0 h, depending on treatment exposure time.

After fumigation, the chamber was flushed with fresh air (chamber-aerated) for 2 h before opening and removing the fruit. At this time, fruit samples were taken from treated and control fruit lots for determination of inorganic bromide residues using a procedure similar to that developed by Schrader et al. (1942). Simultaneous samples were also taken to determine organic bromide residues (residual or unchanged MB) by using the method of King et al. (1981). The remaining fruit was placed into fiberboard cartons without plastic liners and held at 2.5 °C to simulate packaging and storage conditions. Additional fruit samples were taken at 24, 48, and 168 h after fumigation to determine levels of organic bromide residues.

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Table II. Concentrations, Percentage Sorption, and *CT* Products Resulting from Specified Methyl Bromide Fumigations at 21 °C for Pears and Plums (Group I) and Cherries, Nectarines, and Peaches (Group II)[a]

commodity group		MB gas concn, g/m³ start	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h	% sorption[b]	*CT* product, g·h/m³
				MB Treatment: 48 g/m³ for 2 h					
I	mean	62.7	52.1	45.7	39.6			36.8	96.6
	SD[c]	3.5	2.3	2.1	2.4			3.2	4.5
II	mean	59.2	38.6	31.7	27.6			52.8	71.7
	SD	4.8	3.3	2.2	1.4			5.2	4.4
				MB Treatment: 48 g/m³ for 3 h					
I	mean	62.4	52.2	46.0	39.4	35.3		43.4	134.6
	SD	1.8	2.0	2.2	2.4	2.7		3.4	6.4
II	mean	59.3	39.6	32.0	27.6	26.5		55.0	99.4
	SD	4.4	3.1	2.0	1.1	1.1		5.0	4.4
				MB Treatment: 32 g/m³ for 4 h					
I	mean	43.8	36.0	31.8	27.0	23.8	21.9	49.8	115.6
	SD	4.0	1.4	1.5	1.6	1.6	1.3	4.1	6.1
II	mean	41.1	27.1	21.8	18.8	18.0	17.7	56.8	85.8
	SD	2.8	2.1	1.5	0.8	0.5	0.7	4.6	3.2

[a] From concentration data. Duncan's mean separation gives the following: pear = a and plum = a (group I); cherry = b, necatarine = b, and peach = b (group II). The least significant difference (5%) was 4.81, 3.81, and 2.40 for 48 g/cm³ for 2 h, 48 g/m³ for 3 h, and 32 g/cm³ for 4 h, respectively. [b] Starting concentration minus end concentration divided by start concentration multiplied by 100. [c] Standard deviation.

Table III. Inorganic Bromide Residues in Fruits Fumigated at 21 °C with Specified Methyl Bromide Treatments and Chamber-Aerated for 2 h at 21 °C

commodity	inorganic bromide, ppm[a] (mean ± SD[b]) 48 g/m³ for 2 h	48 g/m³ for 3 h	32 g/m³ for 4 h
pear	6.4 ± 0.7	8.1 ± 1.1	7.0 ± 1.6
plum	4.8 ± 0.9	5.4 ± 1.1	5.6 ± 1.7
cherry	4.8 ± 2.8	6.4 ± 1.3	8.8 ± 2.9
nectarine	5.3 ± 1.2	6.7 ± 0.9	5.4 ± 0.9
peach	5.8 ± 1.1	6.4 ± 0.8	5.8 ± 1.0

[a] All control fruit samples had less than 2 ppm of inorganic bromide. [b] Standard deviation.

Residue analysis was replicated 3 times for each fumigation treatment, commodity, and cultivar tested. Table I lists the various cultivars tested.

On the basis of preliminary experiments and approved Medfly treatment schedules for other commodites, three MB fumigation treatments were tested: 48 g/m³ for 2 h, 48 g/m³ for 3 h, and 32 g/m³ for 4 h.

Analysis of variance (95% confidence level) and Duncan's mean separation (5%) were performed on the concentration data. Percentage sorption was calculated from start and end MB concentrations. Concentration times time (*CT*) products, i.e., the area under each resulting MB gas concentration curve, were calculated in a manner similar to that described by Monro (1969). *CT* products are expressed in gram hours per cubic meter (g·h/m³). Linear regression was used to determine the rate of desorption and half-life of the organic bromide residue from fumigated fruits. The data was fitted to $\ln C = mt + b$, where $\ln C$ is the natural logarithm of the organic bromide residue, m is the slope, t is the time in hours, and b is the intercept.

RESULTS AND DISCUSSION

Test results showed no consistent differences among the various cultivars tested for any one commodity. For this reason, test data are reported by commodity and not by

Table IV. Organic Bromide Residues in Fruits Fumigated at 21 °C with Specified Methyl Bromide Treatments, Chamber-Aerated for 2 h at 21 °C, and Then Stored at 2.5 °C

commodity	postfumigation sample time, h	organic bromide residue, ppm[a] (mean ± SD) 48 g/m³ for 2 h	48 g/m³ for 3 h	32 g/m³ for 4 h
pear	2	44.0 ± 10.9	37.0 ± 2.6	58.1 ± 7.2
	24	3.5 ± 2.4	5.5 ± 4.1	5.0 ± 3.1
	48	0.98 ± 0.51	1.5 ± 1.0	0.63 ± 0.29
	168	<0.01	<0.01	<0.01
plum	2	34.2 ± 13.3	49.2 ± 12.8	30.4 ± 8.8
	24	5.9 ± 3.9	7.6 ± 4.2	6.2 ± 2.7
	48	2.6 ± 1.6	3.5 ± 2.2	3.0 ± 1.9
	168	<0.01	0.02 ± 0.02	<0.01
cherry	2	18.1 ± 0.91	7.0 ± 0.21	14.0 ± 0.89
	24	0.19 ± 0.24	0.12 ± 0.17	0.16 ± 0.12
	48	0.02 ± 0.01	0.03 ± 0.01	0.02 ± 0.02
	168	<0.01	<0.01	<0.01
nectarine	2	24.4 ± 9.6	30.7 ± 16.1	24.8 ± 13.7
	24	0.19 ± 0.36	0.24 ± 0.33	0.14 ± 0.23
	48	<0.01	<0.01	<0.01
	168	<0.01	<0.01	<0.01
peach	2	24.4 ± 8.7	29.1 ± 12.1	15.8 ± 6.6
	24	0.06 ± 0.06	0.15 ± 0.24	0.05 ± 0.08
	48	<0.01	<0.01	<0.01
	168	<0.01	<0.01	<0.01

[a] All control fruit samples had less than 0.01 ppm of organic bromide.

individual cultivar. Statistical analysis of the MB gas concentrations showed pears and plums (group I) not to be significantly different but distinctly different from that for cherries, nectarines, and peaches (group II) which again were not significantly different from each other. Table II shows resultant MB gas concentrations, percentage sorption of MB, and calculated *CT* products for each MB treatment and commodity group. Pears and plums were less sorptive of MB during fumigation than cherries, nectarines, and peaches. Less sorption resulted in higher MB concentrations and, therefore, greater *CT* products.

Empty chambers were fumigated to determine sorption of MB by the chambers only. MB concentrations were measured and percentage sorption was calculated as described. Sorption of MB by the chambers was 3.1 ± 0.5, 4.2 ± 0.5, and 5.2 ± 0.4% for 48 g/m^3 for 2 h, 48 g/m^3 for 3 h, and 32 g/m^3 for 4 h, respectively. The sorption data reported in Table II are uncorrected values.

Table III shows the resultant inorganic bromide residues of the fumigated fruits. Residues are below the established EPA tolerance of 20 ppm for plum, cherry, nectarine, and peach. However, the tolerance set for pears is only 5 ppm, and the average residue levels obtained from any of the three MB treatments exceeded tolerance.

Organic bromide residues found in each commodity at various times after fumigation are shown in Table IV. Although the fruit was stored at 2.5 °C after fumigation and chamber aeration, desorption of MB was rapid in the first 24–48 h. Organic bromide residues in fumigated fruits could be detected up to 48 h or more after fumigation. Pears and plums had the highest organic bromide levels after the 2-h chamber-aeration period, and the residues were retained longer than those found in cherries, nectarines, or peaches. Harvey et al. (1982) also reported plums to have higher organic bromides and to retain the residue longer than nectarines and peaches.

Heuser (1975) discusses the occurrence and significance of bromide residues in relation to fumigation, i.e., total bromides, inorganic bromides, and organic bromide residues, the latter referring to the amount of unchanged fumigant that can be detected in fumigated produce and which is "likely to disappear in the course of normal handling or processing before consumption". Linear regression to determine the rate of desorption of organic bromides from fumigated test fruits gave the following values: for pears and plums the slopes (m) ranged from −0.949 to −0.956 and the correlation coefficients (r) from −0.974 to −0.998; for cherries, m ranged from −0.863 to −0.889 and r from −0.955 to −0.976; for nectarines and peaches, m ranged from −0.828 to −0.840 and r from −0.964 to −0.996. The calculated half-life of organic bromide in fumigated test fruits, which had been chamber-aerated 2 h at 21 °C and then stored at 2.5 °C, ranged from 13.1 to 15.5 h for pears and plums, 4.7 to 5.9 h for cherries, and 3.7 to 4.0 h for nectarines and peaches. Cherries, nectarines, and peaches, when compared to pears and plums, are more sorptive of MB during fumigation (Table II), and postfumigation desorption of organic bromide is much more rapid (Table IV).

The data herein reported for the three MB treatments, and in conjunction with efficacy and phytotoxicity data, show effective control of Medfly in the tree fruits tested (Spitler and Couey, 1982) without serious effects on marketability (Harvey and Harris, 1982).

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