Comparative Methyl Bromide Residues in Florida Citrus: A Basis for Proposing Quarantine Treatments against the Caribbean Fruit Fly

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Grapefruit and six other citrus cultivars were fumigated with methyl bromide (MB) for 2 h at dosages of 24–48 g/m³. Grapefruit was included in the same chamber in the fumigation of each of the cultivars so a direct comparison of MB sorption could be made. Fruits fumigated with 24 g/m³ MB were stored at 15.6 °C and residues determined each day for 5 days to determine the rate of residue loss. After 5 days, the residues were all <5 mg/kg. Oranges, tangerines, and tangors sorbed 1.4–1.9 times more MB compared to grapefruit. On the basis of the assumption that the amount of residual MB found in fumigated citrus fruits is a measure of, and is proportional to, the level of exposure to MB during fumigation, we propose a schedule of 30 g/m³ for 2 h for oranges, tangors, and tangerines. This schedule should provide concentrations of MB comparable to the 40 g/m³ schedule currently used against Caribbean fruit flies infesting grapefruit.

Oranges, tangerines, and tangors are hosts of several tropical fruit flies (*Tephritidae*), and appropriate quarantine treatments are often required by regulatory agencies for the shipment of the fruits from an infested area to areas where the *Tephritidae* fly pests are not established. Japan and several U.S. states require citrus fruit imported from Florida to be treated to achieve a security level of probit 9 (99.9968%) kill. Suggestions have been made that this requirement be reduced for fruit in areas with low insect populations or for fruit that is a marginal host (Landolt et al., 1984), but no changes in requirements have been made. To develop a treatment that satisfies the probit 9 security level at a 95% confidence level requires treatment of sufficient infested fruit (usually in the thousands) to kill 100 000 flies (Baker, 1939). Attempts were made by us over a period of several years to infest cultivars of oranges, tangerines, and tangors by placing fruit in an infesting cage with thousands of Caribbean fruit flies (CFF). Typically 1000–2000 fruits were exposed to about 100 000 adult gravid fruit fly females for a period of 2 weeks. Oranges, tangerines, and tangors were poor hosts of Caribbean fruit flies, and insufficient numbers of infested fruits made our efforts to experimentally develop a treatment difficult. In most cases no larvae or pupae were recovered from any exposed fruit.

Substantial information is available on the dosages of methyl bromide (MB) required to kill CFF in grapefruit (Benschoter, 1979) and on the corresponding residue levels of this fumigant in grapefruit (King et al., 1981). Insect mortality in fumigated fruit is dependent on the concentration of the fumigant in the fruit and time of exposure of the pest. To augment these data, we determined and compared MB residue levels in grapefruit and other citrus cultivars at various dosages. For each test, grapefruit and one other citrus cultivar were fumigated simultaneously in the same chamber to eliminate possible variability due to dosage measurement error, gastightness of different chambers, small differences in fruit and air temperatures, etc. The amount of MB residues remaining after various storage times was also determined to establish the rate of loss of MB from these fruits. By confirming the presence of equal or greater MB residues in oranges, tangerines, or tangors, compared to grapefruit, we developed the data required to allow us to recommend a MB treatment schedule for these fruits. The schedule should provide quarantine security equivalent to that of the presently used MB schedule for grapefruit infested with CFF.

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MATERIALS AND METHODS

During the 1984–1985 citrus season in Florida, six citrus cultivars were compared to grapefruit on the basis of their sorption and retention of MB following fumigation. The cultivars consisted of Pineapple, Hamlin, and Valencia oranges; Dancy tangerines; and Temple and Murcott tangors. The nomenclature used here is based on a recent discussion of the horticultural varieties of citrus (Hodgson, 1967). Prior to fumigation, all fruits were placed in boxes in a single layer and left in a room maintained at 21–23 °C for at least 16 h for temperature equilibration. Fruits of each cultivar were fumigated for 2 h at 21–23 °C simultaneously with grapefruit so that a direct comparison of residue values could be made. The load factor in a 0.8-m³ chamber was 20% and consisted of two boxes of grapefruit and one box of one other citrus cultivar. Dosages of 24, 32, 40, and 48 g/m³ MB were applied, and each dosage was replicated twice. After fumigation, the chamber was aerated mechanically for 15 min, and then three fruits were removed from each box for assay as described below. One sample from each fruit was immediately assayed for MB residues. Fruits fumigated at a dose level of 24 g/m³ were held in storage at 15.6 °C for a period of 5 days. At 24-h intervals three fruits were removed and each was assayed for MB residues.

Assays were performed by using a previously reported GC-ECD headspace method (King et al., 1981) with the following salient features: For each assay a 50-g sample of fruit was weighed into a 500-mL Eberbach blending container, 50 mL of water was added, and the container was quickly sealed with a Teflon-lined cap that had been modified to incorporate a silicone rubber septum. The sample was blended, and after ≥10 min, 5 mL of headspace gas was removed with a 10-mL syringe and injected, via a 0.5-mL loop, onto a 1-m glass column (4 mm i.d.) packed with 100–120-mesh Porapak Q (Waters Associates). A Hewlett-Packard Model 5700A gas chromatograph equipped with a nickel-63 linear electron capture detector and a 0.5-mL sampling loop was used under the following conditions: detector, 300 °C; oven, 140 °C; carrier gas, argon–5% methane at 60 mL/min flow. Nonfumigated fruit samples were spiked with MB at various levels to serve as standards.

RESULTS AND DISCUSSION

The residue data obtained immediately after the fumigation of grapefruit, oranges, tangors, and tangerines

Table I. Methyl Bromide Residues in Citrus Fruit after Fumigation for 2 h at Various Dosages[a]

		citrus cultivar					
dose, g/m^3	grapefruit	Valencia	Temple	Pineapple	Hamlin	Dancy	Murcott
24	5.87	8.83	7.92	8.99	9.17	9.59	6.99
	(1.09)	(0.00)	(0.04)	(0.55)	(0.52)	(0.75)	(0.60)
32	7.72	9.48	13.57	12.81	13.24	16.54	10.43
	(2.20)	(0.02)	(1.54)	(0.35)	(0.09)	(0.87)	(0.43)
40	9.27	11.20	17.36	16.80	18.21	19.18	12.03
	(1.91)	(1.16)	(1.00)	(0.43)	(1.27)	(4.52)	(1.90)
48	11.78	19.00	15.62	19.09	17.90	20.74	18.28
	(3.48)	(0.10)	(2.16)	(0.38)	(1.61)	(2.26)	(2.54)
ratio[b]	1.00	1.40	1.57	1.67	1.69	1.91	1.38
corr[c]	0.995	0.887	0.846	0.994	0.937	0.945	0.919
slope[c]	3.86	6.45	5.38	6.86	6.23	7.22	7.09

[a] Three individual fruit were assayed from each of two fumigation repilcations at each dose level for the citrus cultivars. The grapefruit data is an average from 12 fumigations. Means (standard deviations shown in parentheses) are expressed in milligrams per kilogram. [b] The average of the ratios at the four dose levels of MB residue in each orange, tangerine, or tangor to that in grapefruit. [c] Correlation coefficients and slopes are based on a linear regression of average residue levels as a function of dose.

with various dosages of MB are shown in Table I. The areas from replicate injections from the headspace of the same sample into the GC typically differed less than 5%, and the areas obtained from fortified control standards were reproducible. The correlation coefficients obtained by linear regression analysis indicate a linear relationship between the applied dose and the resulting residue levels. Applying Student's t-test to the data for grapefruit and each other citrus cultivar (fumigated at the same time in the same chamber) indicated that (at the 95% confidence level) at any dose tested the residues are greater in oranges and tangerines than in grapefruit. This may be due to the greater surface area to volume, and hence to weight, ratio of the smaller fruits rather than differences in absorptivity between fruits. From the data in Table I the calculated ratio of the average MB residue in grapefruit to the residue in tangerines or oranges ranges from 0.52 to 0.72. Using recently measured fruit to estimate sizes, we note that if grapefruit average 11 cm in diameter and oranges, tangerines, and tangors average 7 cm in diameter, the ratio of the respective surface area to volume ratios (orange, tangerine, or tangor/grapefruit) is 0.64 on the basis of a spherical shape for the fruit. These results indicate that possibly the area to volume ratio is a major factor in the amount of MB absorbed.

The averages of the ratios of MB residues in the orange, tangerine, and tangor cultivars to the corresponding residues in grapefruit are shown in Table I. The values for all four dose levels were averaged to decrease variability by including more data. This approach is valid because of the linear relationship between dose and residue. The ratios ranged from 1.38 to 1.91 for Murcott tangors and Dancy tangerines, respectively. The results of a time study based on tests made at a dose level of 24 g/m^3 are shown in Table II. Linear regression was applied to the time after fumigation vs the log (base 10) of the concentration, and correlation coefficients ranged from 0.96 to 0.99, which indicates a good fit of the data. This pseudo-first-order kinetics relationship for the dissipation of MB was previously reported for grapefruit (King et al., 1981), for cherries (Sell et al., 1988), and for cherries, nectarines, peaches, pears, and plums (Tebbets et al., 1983). MB residues decreased rapidly in all fruits tested. The rate of loss was greatest for Temple tangors and least for Valencia oranges and Murcott tangors. The significance of the low parts per billion residues of MB remaining in the fruit depends ultimately on future decisions of regulatory agencies. Extrapolation of the data in Table II indicates that, by present analytical methodology, no detectable residues would remain after 1 week of storage at 15.6 °C (60 °F).

Table II. Methyl Bromide Residues in Oranges, Tangerines, and Tangors after Fumigation and Storage at 15.6 °C[a]

time,[b] days	citrus cultivar					
	Hamlin	Pineapple	Temple	Valencia	Dancy	Murcott
1	1.46	1.46	1.96	1.74	1.65	1.51
	(0.31)	(0.25)	(0.21)	(0.09)	(0.22)	(0.31)
2	0.29	0.51	0.32	0.46	0.28	0.34
	(0.16)	(0.10)	(0.11)	(0.08)	(0.02)	(0.08)
3	0.039	0.18	0.046	0.19	0.106	0.073
	(0.016)	(0.09)	(0.017)	(0.04)	(0.069)	(0.045)
4	0.005	0.010	0.008	0.063	0.016	0.018
	(0.002)	(0.003)	(0.003)	(0.009)	(0.006)	(0.008)
5	0.003	0.003	0.002	0.004	0.004	0.004
	(0.000)	(0.000)	(0.001)	(0.001)	(0.001)	(0.001)
corr	0.9868	0.9812	0.9983	0.9730	0.9966	0.9999
slope	−0.714	−0.708	−0.758	−0.647	−0.647	−0.613
int	0.82	1.045	1.008	0.947	0.841	0.815

[a] Means (standard deviations shown in parentheses) are expressed in milligrams per kilogram and based on three replicates. The slopes, intercepts, and correlation coefficients are based on linear regressions of time (days) and the log (base 10) of the residue concentration means. Fumigation dose: 24 g/m^3. [b] Samples were taken at 24-h intervals.

It is probable that equal concentrations of fumigant will produce the same level of fly kill in both kinds of fruits. Therefore, the amount of MB used to fumigate grapefruit is excessive when used for oranges, tangerines, and tangors. A dosage of 30 g/m^3 (rounded up from 29.0 g/m^3), based on the data for Murcot tangors, i.e., the least sorptive fruit tested, excluding grapefruit, would give the same or greater concentrations of MB in oranges, tangerines, and tangors as the currently required 40 g/m^3 for grapefruit. This substantially reduced dose would help alleviate the low tolerance problem exhibited by oranges, tangerines, and tangors. In view of the low (near zero) infestation of oranges and tangerines by the CFF this reduced dosage should be adequate for quarantine treatment of these fruit.

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