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Toxic Effects and Residues in Six Nectarine Cultivars following Methyl Bromide Quarantine Treatment

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Abstract. **Residues and the toxic effects of methyl bromide (MB) were determined in fumigation tests with six cultivars of nectarine *[Prunus persica* (L.) Batsch. var. nectarina (Ah.) Maxim.]. 'Fantasia', 'Firebrite', and 'Summer Grand' were treated in wooden field bins in a commercial facility, whereas 'May Fire', 'May Glo', and 'May Diamond' were fumigated in smaller fiberglass chambers. The treatment of 48 g MB/m^3 for 2 hours at 21C and normal atmospheric pressure with a load factor of 50% (179 kg·m^{-3}) was that proposed for quarantine eradication of the codling moth *(Cydia pomonella* L.). The appearance of the fruit, as well as the soluble solids content, were not affected by the MB fumigation; however, ripening of 'May Grand' and 'Firebrite' was delayed slightly. Sorption of MB was 55%. Desorption rates of organic bromide were not significantly different among the six treated cultivars; all fruits contained <0.001 µg·g^{-1} after 7 days of storage at 2.5C. Inorganic bromide residues in all treated fruits were <8.0 µg·g^{-1}.**

Since 1988, six cultivars of fresh California nectarines have been approved for export to Japan. Export was made possible by the development of a quarantine treatment using methyl bromide (MB) fumigation to disinfest early to midseason cultivars of the codling moth (Yokoyama et al., 1987). The cultivars initially permitted entry were: 'Fantasia', 'Firebrite', 'May Grand', 'Red Diamond', 'Spring Red', and 'Summer Grand'.

The efficacy of MB to treat fruit infested with 1-day-old codling moth eggs, the stage least susceptible to the fumigant in early to midseason cultivars, was reported by Yokoyama et al. (1987, 1988). Fumigation with MB at 48 g·m^{-3} for 2 h at 21C and normal atmospheric pressure with a 50% load (v/v) was accepted as a quarantine treatment by the Japanese Ministry of Agriculture Forestry and Fisheries (MAFF) in 1988. Harvey et al. (1989) reported that efficacious rates of MB were not injurious to nectarines when the fruit was fumigated before packinghouse handling and packaging and that MB residues were not excessive. They also indicated (Harvey et al., 1982) that fruit prepared for packaging, i.e., fruit that was graded, sorted, and waxed, was more susceptible to MB injury than unprocessed fruit, and that more injury was found after fumigation at 4.5C than at 26.5C. Warm fruits require less fumigant for efficacy than do cold fruit and have lower MB residues than fruit fumigated at lower temperatures (Hartsell et al., 1986a). Based upon the data available, we decided to fumigate in field bins to avoid the complications inherent with fumigating fibrous packaging material. Desorption was shown to have an influence on dosage requirements when fumigating packaged citrus with ethylene dibromide (Hartsell et al., 1986b).

Reported here are the quality of nectarines that have undergone MB fumigation and the residues of the chemical after cold storage. These fumigation tests, required by MAFF, serve to demonstrate the integrity of the proposed quarantine treatment. The results of these tests were critical for determining final approval of the treatment. All tests were conducted on fruit taken directly from the field, before sorting, packing, or cooling,

A 3.12-m^3 commercial-type fumigation chamber (Yokoyama et al., 1987) was used for studies with 'Fantasia', 'Firebrite', and 'Summer Grand' nectarines. These were loaded into commercial-type wooden bins, and for each test, two fully loaded bins (≈467 kg fruit) plus six full wooden picking boxes (≈90 kg fruit) for a total of 179 kg·m^{-3} were placed within the chamber to provide ≈50% load (v/v), which is the maximum allowed by MAFF. The loaded chamber was then fumigated with the dosage of MB specified for the quarantine treatment, which was 48 g·m^{-3} for 2 h at 21C and at normal atmospheric pressure. After fumigation, the fruit was aerated for 2 h by rerouting the chamber circulation system so that fresh air was drawn through the fruit load from bottom to top and out the exhaust.

During fumigation, MB concentrations were determined by use of a gas-liquid chromatograph with a flame ionization detector at four locations in the chamber: inside the bins at the bottom front and top back, middle center (between the bins), and in the air circulation return duct. Concentrations were determined after 5 min and after 0.5, 1.0, and 2 h of exposure. The percentage of MB sorption was calculated from initial and final chamber concentrations. After aeration, fruit were randomly selected from all areas of the fumigated load and kept for quality evaluation and residue determinations. Equal amounts of unfumigated fruit were held as controls. All fruit were held at 2.5C for 1 week to simulate commercial conditions.

Fruit of 'May Diamond', 'May Fire', and 'May Glo' received treatment identical to that above. These fumigations, however, were conducted in 28-liter fiberglass chambers

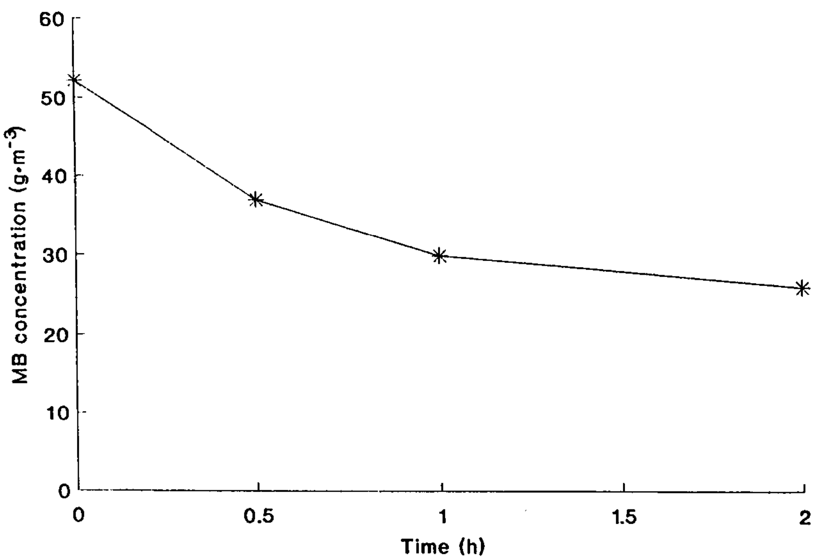

Fig. 1. Mean methyl bromide concentrations from chambers during fumigations of 'May Fire', 'May Glo', and 'May Diamond' (small-scale tests) and 'May Grand', 'Firebrite', and 'Fantasia' (large-scale tests) when exposed to the quarantine treatment of 48 g·m^{-3} for 2 h at 21C and atmospheric pressure with a 50% load (v/v), which produced a concentration × time product (C × T; grams per cubic meter per hour) of 66.9 ± 3.3 and the sorption was 49.8% ± 6.4%.

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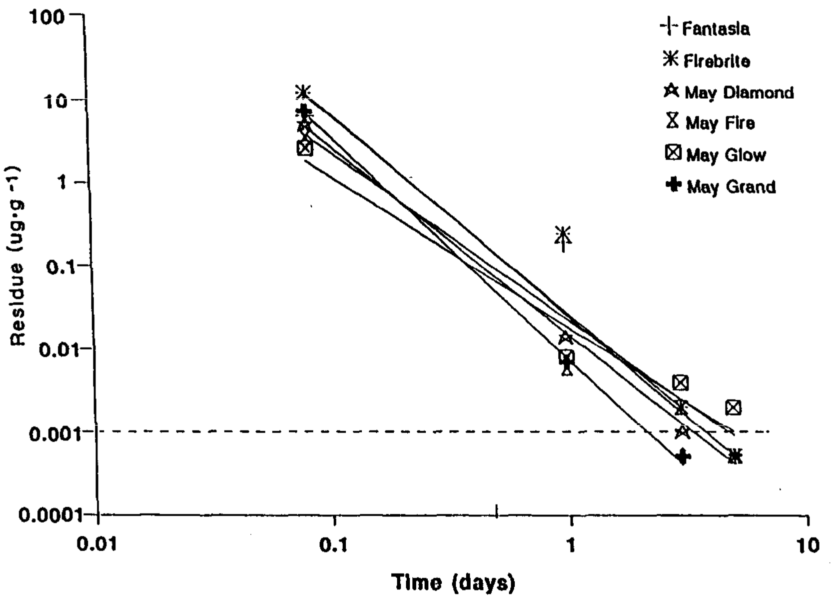

Fig. 2. Methyl bromide desorption rates, determined by organic bromide residue analysis, from six cultivars of nectarines following quarantine fumigation of 48 $g \cdot m^{-3}$ for 2 h at 21C and atmospheric pressure with a 50% load (v/v) and 2 h aeration then stored at 2.5C. Values were not significantly different (F = 0.04; df = 5,15; $P > 0.05$).

Table 1. Firmness of California nectarines after fumigation with methyl bromide at 48 $g \cdot m^{-3}$ for 2 h at 21C at normal atmospheric pressure and storage for 1 week at 0C.

Cultivar	Treatment	Firmness (N)
May Fire[z,y]	Control	39.2 a
	Fumigated	51.0 b
May Glo[z,y]	Control	53.0 a
	Fumigated	56.9 a
May Diamond[z,y]	Control	56.9 a
	Fumigated	57.9 a
May Grand[z,y]	Control	38.2 a
	Fumigated	56.9 b
Fantasia[z,y]	Control	49.0 a
	Fumigated	48.1 a
Firebrite[x]	Control	38.2 a
	Fumigated	64.7 b

[z]Average of three replications.
[y]Mean separation for each pair by F test, P = 0.05.
[x]Only one replication.

based on the techniques described by Tebbets et al. (1983) and Hartsell et al. (1986a) and were the same as those reported by Harvey et al. (1989).

Twenty individual fruits were randomly chosen from each cultivar and each replicated fumigation treatment and evaluated for quality. Individual fruit were rated for toxic effects, firmness, soluble solids content (SSC), and severity of surface defects. Toxic effects were determined by the percentage of fruits with obvious injury caused by the fumigation treatment. Surface defect of fruits, which measured overall external quality, included discoloration, pitting, cutting, and bruising; they were rated on a scale of 0 = none, 1 = trace, 2 = slight, 3 = moderate, 4 = severe, and 5 = extreme damage. Firmness of individual fruit was measured at the equator with a UC pressure tester (Western Ind. Supply, San Francisco) equipped with an 8-mm-diameter plunger. All firmness measurements were made after removal of a thin layer of skin. The SSC was measured with a temperature-compensated hand refractometer. The results were evaluated by analysis of variance (ANOVA), and differences between treatments were separated by F test at P = 0.05.

The desorption rate of residual MB was determined by organic bromide residue analysis in the fruit immediately after aeration and after 1, 3, 5, and 7 days of storage at 2.5C or until levels decreased to <0.001 $\mu g \cdot g^{-1}$, the level requested by MAFF. To reach this objective, several modifications were made on the head space method developed by King et al. (1981). In addition to the modifications reported by Harvey et al. (1989), we used a 30 m × 0.53 mm GS-Q (gas-solid porous polymer) open tubular megabore column, and a heated gas sampling valve with a 1-ml sample loop. The gas-solid chromatography oven was isothermal at 95C, the electron capture detector was 275C, and the gas sampling valve was 125C. The argon/methane (95:5) carrier gas flow rate was 20 $ml \cdot min^{-1}$. Due to the inertness of this column, a discernible resolved peak for MB was obtained from untreated nectarines fortified at the 0.001 $\mu g \cdot g^{-1}$ level after a column retention time of 1.9 min. Organic bromide residue data are expressed as log regression curves using the power curve: $y = ax^b$, where x = time of analysis after fumigation and y = residue value ($\mu g \cdot g^{-1}$). Analysis of covariance (Dixon and Massey, 1969: Draper and Smith, 1981) was used to compare desorption rates between the cultivars tested.

An X-ray fluorescence spectrophotometer (Spectrace 431, Tracor Northern, Middleton, Wis.) was used for determining inorganic bromide residues in the fruit, as described by Harvey et al. (1989). ANOVA was performed on the data, and means were separated by Duncan's multiple range test at P = 0.05.

There were no obvious phytotoxic responses in any of the cultivars fumigated at the schedule used. Surface defects were minor, with a rating averaging < 1 for treatments in all cultivars. No significant differences occurred due to treatment.

Fumigated 'May Fire' and 'May Grand' nectarines were significantly firmer after storage than unfumigated fruit (Table 1), indicating that fumigation may have slowed ripening of these cultivars. Fumigated 'Firebrite' nectarines were also firmer than control fruit after storage. However, since only one replication was completed on this cultivar, significance could not be determined. Firmness of the other cultivars was similar for fumigated and unfumigated fruit.

The SSC did not differ significantly among fumigated and unfumigated fruit nor among any of the cultivars tested. Average SSC for all cultivars was 11% and ranged from 9.3% for 'May Glo' to 13% for 'May Grand'.

MB sorption was 49.8% ± 6.4% for all six cultivars (Fig. 1). However, sorption was ≈10% higher in the confirmatory tests than in the nectarines treated in the 28-liter chambers, which was the result of sorption by the wood bins used in the large chambers. MB concentrations during the exposure period were similar to those found in our previous studies (Harvey et al., 1989) and the same as the values reported by Yokoyama et al. (1989), which resulted in 100% mortality of codling moth eggs.

The slope of the log regression curve for MB residue vs. time appeared to be considerably steeper for 'May Grand' than those for the other cultivars (Fig. 2). 'May Grand' reached the organic bromide residue level of 0.001 $\mu g \cdot g^{-1}$ after 3 days of storage, whereas the other cultivars took ≥4 days to reach this level. Statistically, however, there were no significant differences in desorption rates among any of the treated cultivars.

Significant differences (P = 0.05) in the amount of inorganic bromide residue were found among 'May Diamond', 'May Fire', and 'May Grand'. For all cultivars, inorganic bromide residue ranged from 5.4 ± 0.3 to 7.8 ± 0.3 $\mu g \cdot g^{-1}$. Since the tolerance for inorganic bromide residue for nectarines in the United States is 20.0 $\mu g \cdot g^{-1}$ and is acceptable to MAFF, the differences are not important.

Yokoyama et al. (1990) showed that the efficacy of MB for killing codling moth eggs was not affected when diverse substrates (nectarines, peaches, plums, apples, and waxed paper) were subjected to equal MB concentrations. Based on Yokoyama's (1990) research, our data, and those of Harvey et al. (1989), it will not be necessary to test each new nectarine cultivar destined for the Japanese market.

Methyl bromide desorbed from the fruit at a rapid rate even though the storage temperature was 2.5C. In most cases, organic bromide residues were <0.001 $\mu g \cdot g^{-1}$ after 3 or 5 days of storage. In the future, when tolerances for organic bromide residue are established in the United States, residues could be lowered considerably by lengthening the aeration time under commercial conditions, if necessary. Under such conditions, temperature would generally remain ≥ 21C during aeration as compared with our studies, where the fruit was placed in cold storage immediately after the 2-h aeration. In addition, desorption rates would be increased because of the higher temperature.

Literature Cited

Dixon, W.J. and F.J. Massey, Jr. 1969. Introduction to statistical analysis. 3rd ed. McGraw-Hill, New York.

Draper, N.R. and H. Smith. 1981. Applied regression analyses. 2nd ed. Wiley, New York.

Hartsell, P.L., H.D. Nelson, J.C. Tebbets, and P.V. Vail. 1986a. Methyl bromide fumigation treatments for pistachio nuts to decrease residues and control navel orangeworm, *Amyelois transitella* (Lepidoptera:Pyralidae). J. Econ. Entomol. 79:1299-1302.

Hartsell, P.L., J.S. Tebbets, and J.C. Tebbets. 1986b. Ethylene dibromide fumigation of California-grown citrus: Effects of fumigating unpacked, bulk fruits, or commercially packed fruits on applied dosage and residues. J. Econ. Entomol. 79:166-171.

Harvey, J.M., C.M. Harris, and P.L. Hartsell. 1982. Commodity treatments: Responses of nectarines, peaches, and plums to fumigation with methyl bromide. U.S. Dept. Agr. Mktg. Res. Rpt. 1124, Washington, D.C.

Harvey, J.M., C.M. Harris, and P.L. Hartsell. 1989. Tolerances of California nectarine cultivars to methyl bromide quarantine treatments. J. Amer. Soc. Hort. Sci. 114:626-629.

King, J.R., C.A. Benschoter, and A.K. Burditt, Jr. 1981. Residues of methyl bromide in fumigated grapefruit determined by rapid, head-space assay. J. Agr. Food Chem. 29:1003-1005.

Tebbets, J.S., P.L. Hartsell, H.D. Nelson, and J.C. Tebbets. 1983. Methyl bromide fumigation of tree fruits for control of the Mediterranean fruit fly: Concentrations, sorption, and residues. J. Agr. Food Chem. 31:247-249.

Yokoyama, V.Y., G.T. Miller, and P.L. Hartsell. 1987. Methyl bromide fumigation for quarantine control of codling moth (Lepidoptera: Tortricidae) on nectarines. J. Econ. Entomol. 80:840-842.

Yokoyama, V.Y., G.T. Miller, and P.L. Hartsell. 1988. Methyl bromide quarantine treatment for codling moth on exported nectarines. Insecticide and Acaricide Tests, vol. 13. Entomol. Soc. Amer., Lanham, Md.

Yokoyama, V.Y., G.T. Miller, and P.L. Hartsell. 1990. Evaluation of methyl bromide quarantine treatment to control codling moth (Lepidoptera: Tortricidae) on nectarine cultivars proposed for export to Japan. J. Econ. Entomol. 83:466-471.