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Effects of box liner perforation area on methyl bromide diffusion into table grape packages during fumigation☆

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ABSTRACT

Plastic liners are used inside boxes of table grapes to retard moisture loss from the grapes and to contain sulfur dioxide gas released inside the packages to control postharvest decay. However, to control organisms of quarantine concern, regulators specify exported packages must be fumigated with methyl bromide (MB), and to enable adequate diffusion of the fumigant into the packages they specify the liners must be perforated. The percentage of the area of the liner that is perforated, formerly stipulated to be not less than 0.3%, was recently increased to not less than 0.9%. Two MB fumigation schedules specified for control of the Chilean mite, *Brevipalpus chilensis*, were applied to grape packages with a high-density polyethylene liners with perforated areas of 0.9% or with a SO_2-releasing liners with perforated areas of 0.3, 0.6, or 0.9%. Package and chamber concentrations were measured repeatedly for up to three hours during MB fumigation at 4.4 or 6.0 °C with a dosage 64 mg L^{-1} or at 26.7 °C with a dosage 56 mg L^{-1}. Diffusion was similar and rapid into the packages among all perforated areas. MB concentrations inside the packages were not less than 95% of those of the chamber atmosphere within 15 min. After fumigation with an MB dosage 64 mg L^{-1} at 4.4 °C and subsequent storage at 2.0 °C, mean MB residue content in grapes from most packages 48 h after MB fumigation was below the limit of quantitation of 0.002 mg kg^{-1}. After fumigation with an MB dosage 56 mg L^{-1} at 26.7 °C and subsequent storage at 2.0 °C, mean MB residue content in grapes from most packages 24 h after MB fumigation was below the limit of quantitation.

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1. Introduction

Chilean plant products imported into the United States are required by the United States Department of Agriculture – Animal Plant Health Inspection Service (USDA-APHIS) to be fumigated with methyl bromide (MB) to control the Chilean false red mite, *Brevipalpus chilensis* Baker, 1949 (U.S. Department of Agriculture (2013)). Table grapes generally tolerate MB fumigation with little injury (Leesch et al., 2008; Nelson and Spitler, 1982; Nelson, 1985; Phillips et al., 1984; Smilanick et al., 2000). An additional treatment with sulfur dioxide (SO_2) is done to control postharvest fungal diseases (Nelson, 1985; Boersig et al., 2003) on grapes that are packed in Chile and elsewhere. Typically, grapes are packed in the boxes with SO_2 emitting generator sheets and, more recently, with SO_2 emitting liners (Gabler et al., 2007; Cantín and Crisosto, 2008). Plastic liners are used inside boxes of table grapes to retard moisture loss from the grapes and to contain SO_2 released inside the packages. However, to control organisms of quarantine concern, regulators specify exported packages when fumigated with MB must have adequate diffusion of the fumigant into the packages. Because the number and size of vents and composition of packaging materials can influence the diffusion of fumigants (Boersig et al., 2003; Harris et al., 1984; Harvey et al., 1988; Leesch et al., 2008), regulators specify the liners must be perforated. The percentage of the area of the liner that is perforated, formerly stipulated to be not less than 0.3%, was recently increased to not less than 0.9%. This is to assure the rapid diffusion and uniformity of MB concentrations within the clusters for pest control purposes.

Our objectives were to evaluate the influence of the perforated area of box liners on the diffusion of MB into grapes packed in cartons by measurement of MB concentrations (expressed at concentration times time products or CxT products) and MB residues in grapes.

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2. Materials and methods

2.1. Packaging

The grapes (*Vitis vinifera*) used in this study were freshly harvested 'Thompson Seedless' table grapes containing 14–17% soluble solids. Components of the packaging included an uncoated paper corrugate box (vent area approximately 6%, external dimensions of 12.7 cm H × 59.7 cm W × 40.6 cm D), various liners inside the box, and finally within the liners nine HDPE grape bags (vent area approximately 5%) containing one to three grape clusters and weighing approximately 900 g each. This box and grape bag combination, with a total weight of 8.6 kg, is among the most commonly used commercially. The liners characterized included three versions of a low density polyethylene SO_2-releasing liner ("Smartpac", Quimas S.A., Santiago, Chile, model PTCAM016, 40 × 50 cm, 0.05 mm in thickness, 7 g sodium metabisulfite, http://www.quimas.cl): 1) 0.3% vent area (0.6 cm round holes spaced 10 cm apart); 2) 0.6% vent area (0.8 cm round holes spaced 10 cm apart); and 3) 0.9% vent area (1.0 cm round holes spaced 10 cm apart). Activated to release SO_2 by moisture when the grapes are packaged, the SO_2 releasing liner is composed of a three layer laminate of low-density polyethylene films; an outer layer relatively impervious to SO_2 diffusion, and middle layer containing sodium metabisulfite crystals, and an inner layer that permits SO_2 diffusion into the liner contents. In addition, standard, high-density polyethylene (HDPE) liners (95 × 60 cm, 0.01 mm in thickness) with 0.3 or 0.9% vented areas and a commercial dual release SO_2 pad (Fresca Dual Release, Quimetal Industrial SA, Santiago, Chile) were also characterized in some tests. This is the standard packaging used by the Chilean Industry and similar to that used by grape exporters worldwide.

2.2. Fumigation

The dose schedules used in this study issued by USDA-APHIS assume that the structure being fumigated is an empty chamber with boxes occupying not more than 80% of the chamber space. In this study the chamber loads were 36% and 28%. The USDA-APHIS did not specify a load factor maximum for chamber fumigations conducted to control *Brevipalpus chilensis*. A maximum load factor of 50% was indicated in a similar USDA-APHIS schedule for the control of *Lobesia botrana,* the European grapevine moth (USDA, 2013; Boersig et al, 2003). Fumigations to determine the diffusion of MB into the grape clusters were conducted at two locations. Location one (USDA-Agricultural Research Service, Parlier, CA) employed gastight steel chambers with a volume of 241.9 L. Each was equipped with a single fan (49.5 L s^{-1}) mounted at the top and center of each chamber to ensure adequate circulation and mixture of the fumigant and air throughout the chamber and packages being treated. Three chambers were used for each package type. Each chamber contained three boxes of grapes (total volume of the load = 92.35 L) constituting a load factor of 38% (v/v). For each test, the boxes of grapes were preconditioned at the fumigation temperature for 16 h prior to MB fumigation. The grapes were fumigated with an MB schedule that specified an initial dosage of 64 mg L^{-1} for a 2 h fumigation at 6 °C (USDA, 2013). MB was dispensed into chambers using a large, gastight syringe. During the fumigation, gas samples were taken using a gastight syringe from two sites inside the chamber; from the chamber atmosphere outside the containers of grapes and from inside a clamshell of grapes located near the center of the center box on the load. A 100 ml syringe, pumped ten complete strokes, was used to clear the Tygon® vacuum tubing to make concentration readings of MB throughout the chamber as described by Hartsell et al. (1986) and Tebbets et al. (1983).

Gas concentrations of MB within the chamber head space as well as the packaged grapes (top, middle and bottom) were taken through 119-cm lengths of Teflon tubing that exited the side of the chamber through Teflon-lined neoprene stoppers as described by Boersig et al. (2003). Concentrations of MB were determined using a gas chromatograph (Varian, model 3800) equipped with a 1 ml gas sampling loop and a flame ionization detector. Conditions for the gas chromatograph were as follows: 2 mm id × 2 m Teflon column packed with 10% OV-101 on Gas-Chrom Q (100/120 mesh), helium carrier gas at 20 ml/min, hydrogen (FID) at 30 ml min^{-1}, air (FID) at 250 ml min^{-1}, oven temperature at 100 °C, FID detector temperature at 250 °C, and the gas sampling loop injection temperature was 110 °C. A single gas sample (1 ml) was taken at 3-min intervals for the first 30 min of exposure followed by three replicate samples from each chamber were taken at 45, 60, 90 and 120 min. For the first 30 min of sampling, the three chambers were sampled in succession to minimize the influence of sampling on the volume of atmosphere removed on the diffusion of MB gas into the sample site inside the bag at the center of the load. MB concentrations inside chambers were expressed as mg L^{-1}.

Location two (DFA of California, Fresno CA) employed a single gastight steel commercial fumigation chamber with a volume of 554.0 L. It was equipped with a single fan (47.2 L s^{-1}) mounted at the top and center of each chamber to ensure adequate circulation and mixture of the fumigant and air throughout the chamber and packages being treated. The chamber contained five boxes of grapes (total volume of the load = 153.92 L) constituting a load factor of 28% (v/v). The fumigation chamber was inside a controlled temperature room. For each test, the boxes were preconditioned for 2 h prior to MB fumigation at the temperature subsequently used during fumigation. The grapes were fumigated according to one of two MB schedules that specified an initial dosage of 64 mg L^{-1} at 4.4 °C or an initial dosage of 56 mg L^{-1} at 26.7 °C (USDA, 2013). MB was dispensed into the chamber using a large, gastight syringe. MB atmosphere and within package sampling was as previously described. MB concentrations during fumigation at 26.7 °C were determined after 30 min, 1 h, and at the end of fumigation.

Concentrations of MB were determined using a gas chromatograph (Varian, model 3800) equipped with a 1 ml gas sampling loop and a thermal conductivity detector. The temperature of the column, detector and valve was 90, 230 and 50 °C, respectively. The helium carrier gas flow rate through the 27.0 M Porpak GS-Q column was 8 ml min^{-1} with a retention time for MB is 4.6 min. MB concentrations inside chambers were expressed as mg L^{-1}.

MB concentration × time products (CxT) using the method of Monroe and coworkers (1969). CxT products were compared using analysis of variance followed by Fisher's Protected LSD (SAS 9.2, Cary, NC).

2.3. Post-fumigation handling

After fumigation, chambers were aerated as described by Boersig et al. (2003) for at least 2 h before opening and removing the grapes. Residues of MB were determined using the procedure described by Hartsell et al. (1992). Grape samples were stored at 2 °C after fumigation and residues were determined at 1, 18, 24, and 48 h after fumigation or until residues were below the LOQ (Limit of Quantitation) of 0.002 mg kg^{-1} (King et al., 1981).

3. Results and discussion

3.1. MB concentrations and CxT products inside packages

MB concentrations in the center-most bag of grapes determined at 3-min intervals during the first 30 min of fumigation at