

Effects of the post-harvest application of methyl bromide alternatives on storage pests and quality of dried fig

Fatih ŞEN^{1,*}, Kamer Betül MEYVACI¹, Uygun AKSOY¹, Mevlüt EMEKÇİ², Ahmet Güray FERİZLİ²

¹Ege University, Faculty of Agriculture, Department of Horticulture, 35100 İzmir - TURKEY

²Ankara University, Faculty of Agriculture, Department of Plant Protection, 06110, Ankara - TURKEY

Received: 05.09.2008

Abstract: Storage insect pests, microbial deterioration, and mycotoxins are major threats to dried fruit. Methyl bromide (MeBr) was the fumigant used to control pests until it was banned. The present study compared the use of MeBr (60 g m⁻³ for 24 h) and alternatives—magnesium phosphide (1 and 2 g of phosphine (PH₃) per ton of dried fig for 5 days), and carbon dioxide (CO₂) at atmospheric pressure (in gas tight cubes for 5 days) and high pressure (2 h in pressurized tanks at 25 bars)—in controlling major pests (*Ephesia cautella* (Zell.) and *Carpoglyphus lactis*) of dried fig and in respect to dried fig quality. Fruit quality was investigated before exposure and after 2 months of storage at ambient conditions by analyzing moisture content, water activity, surface color, firmness, total soluble solids, titratable acidity, pH, and sugaring index. The effect on fruit surface was examined under a scanning electron microscope. The results show that the tested methods effectively controlled storage pests without any major adverse effects on quality, and each had an advantage for the implementation stage. Magnesium phosphide treatment of 1 g t⁻¹ for 5 days is recommended due to its low investment and operational costs, CO₂ in pressurized tanks is recommended due to its short exposure period, and CO₂ under atmospheric pressure in gas-tight cubes is recommended due to its low cost and suitability for organic production.

Key words: Dried fig, magnesium phosphide, CO₂, storage pests, quality

Hasat sonrası metil bromür alternatifi uygulamaların kuru incirde depo zararlıları ve kalitesine etkileri

Özet: Kuru meyve sektöründe depo zararlıları, mikrobiyal bulaşmalar ve mikotoksinler önemli riskler olarak ortaya çıkmaktadır. Metil bromür (MeBr) yasaklanıncaya kadar sektörde etkin olarak kullanılan tek fumigant olmuştur. Çalışma, MeBr (24 saat süreyle 60 g m⁻³) ve alternatifleri olan magnezyum fosfit (5 gün süreyle ton kuru incir başına 1.0 g ve 2.0 g PH₃) ve atmosferik (gaz geçirmez küplerde 5 gün süreyle) ve yüksek basınç altında (25 bar altında 2 saat süreyle) karbondioksit (CO₂) uygulamalarının önemli kuru incir zararlılarına (*Ephesia cautella* ve *Carpoglyphus lactis*) ve ürün kalitesine olan etkilerini araştırmak üzere yürütülmüştür. Uygulama öncesinde ve 2 aylık normal depo koşullarında saklanan kuru incirlerde meyve kalitesi, su miktarı, su aktivitesi, yüzey rengi, sertlik, suda çözünür kuru madde, titre edilebilir asitlik, pH ve şekerlenme indeksi ölçülerek değerlendirilmiştir. Uygulamaların meyve yüzeyine etkisi ise tarayıcı elektron mikroskobu yardımı ile incelenmiştir. Elde edilen sonuçlar, uygulamaların zararlıların kesin kontrolünü sağlarken, kalite üzerinde önemli düzeyde olumsuz etkileri olmadığını ve uygulama açısından farklı avantajlar taşıdığını ortaya koymuştur. Beş gün süreli magnezyum fosfit (ton kuru incir başına 1.0 g PH₃) uygulaması, maliyetinin düşük olması; basınç tanklarında CO₂ uygulama süresinin kısıtlılığı; gaz geçirmez küplerde atmosferik basınç altında CO₂ uygulaması ise düşük maliyet ve organik tarıma uygunluğu açısından önerilmektedir.

Anahtar sözcükler: Kuru incir, magnezyum fosfit, CO₂, depo zararlıları, kalite

* E-mail: fatih.sen@ege.edu.tr

Introduction

Turkey is known as the major producer and exporter of dried fruits and nuts. A common problem in the trade of these commodities is damage caused by storage pests. The incidence and severity of the pest problem varies according to the product. Additionally, standards valid in producer/importer countries vary regarding tolerance limits for insect parts or damage, and maximum residue limits for the chemicals used in treating these commodities.

Annual Turkish dried fig production is about 55-60,000 t and comes from a single cultivar (*Ficus carica* Sarilop [= Calimyrna]) grown in the western Aegean region. Nearly 90% of the production is for the export market; the main period of marketing is between the end of September and December (Aksoy et al., 2008). Storage pest infestation, especially during over-ripening, drying, and storage, may cause significant problems for dried fig producers. A number of storage pests, especially the fig moth (*Ephesia cautella*; Lepidoptera: Pyralidae) and fig mite (*Carpoglyphus lactis*, Acari: Carpoglyphidae), affect the quality and consequent trade volume of dried fig (Turanlı, 2003). The fig moth reduces fruit quality by feeding on and damaging the fruit, and contaminating the fruit with excrement and other residues, such as silky net weaves (Damarlı et al., 1997). Large populations can develop before being discovered and severe damage may occur (Jarratt, 2001). Following a series of studies in the 1970s (Erakay and Ozer, 1979) a code of practice was developed to reduce infestation, and a decree was issued that made methyl bromide (MeBr) fumigation compulsory for every fig prior to exportation.

MeBr is frequently used as a fumigant for disinfestation of other stored agricultural commodities, such as nuts, cereals, and fruits, because it kills the insects rapidly, has a wide spectrum of activity, and is relatively inexpensive (Fields and White, 2002). Nonetheless, it was banned in developed countries in 2005 and scheduled for worldwide withdrawal from routine use as a fumigant in 2015, under the directive of the Montreal Protocol on Substances that Deplete the Ozone Layer (Schneider et al., 2003), except for quarantine, laboratory, and pre-shipment purposes. As a consequence, development of environmentally sound,

user-friendly, effective, and economic alternatives to MeBr became a must.

Various alternatives for integrated pest management—chemical (phosphine, carbonyl sulfide, sulfuryl fluoride, ozone, cyfluthrin, iodomethane, etc.) and non-chemical treatments (modified atmospheres, high pressure, heat/cold treatments, sanitation, radio frequency, long-wave energy, irradiation)—have been tested (Desmarchelier et al., 1998; Zettler et al., 1999; Johnson et al., 2000; Fields and White, 2002; Schneider et al., 2003; Aksoy et al., 2004; Cetinkaya et al., 2006). Although there are a large number of suggested potential chemical and non-chemical alternatives to MeBr, each has limitations in terms of efficiency, cost, penetration, or residues that prevent it from becoming a direct replacement for MeBr.

Dried fruits are rather durable commodities due to low water activity levels and are thus traded generally under ambient conditions. The parameters of dried fruit quality include color, visual appeal, porosity, texture, rehydration properties, flavor, water activity, chemical stability, taint, off-odors, microbial load, pests and contaminants (safety), and healthiness (Perera, 2005). The ban on MeBr has created an urgent necessity to develop environmentally sound, user-friendly, effective, economic, and applicable alternatives for the dried fruit sector, mainly the dried fig industry. The 4 main issues in the search for new fumigants for foodstuffs are the control of pests, effect on quality, registration, and application (Desmarchelier, 1998).

The objective of the present study was to assess the potential use of magnesium phosphide ($MgPH_3$) and CO_2 , applied under atmospheric and high pressure conditions, for disinfestation of *Ephesia cautella* and *Carpoglyphus lactis*, and to determine their effects on the major quality parameters of dried fig. Thus, it recommends applicable and efficient MeBr alternatives for the dried fig sector.

Materials and methods

The study was conducted with sun-dried fruit of the Sarilop (= Calimyrna) fig variety harvested during the 2003 season and delivered to the TARIŞ Farmers' Sales Cooperative (İzmir, Turkey), as part of a multi-

year research program that was conducted between 2000 and 2005. The treatments were administered under commercial conditions at the TARIŞ fig processing plant. Dried fruits delivered to the processing plant were fumigated with magnesium phosphide, or CO₂ at atmospheric or high pressure conditions on 25 September 2003, and each treatment was compared with MeBr-treated control samples.

MeBr application

MeBr 60 g m⁻³ for 24 h was applied in fumigation chambers holding 15 t of dried fig, as widely used by the sector.

Magnesium phosphide application

Phosphine (PH₃) (Fumi-Cel®, Degesch, Germany) used in fumigation is formulated as a solid magnesium phosphide plate that reacts with water vapor in the air to form PH₃ gas and magnesium hydroxide (Fields and White, 2002). Dried figs were exposed to magnesium phosphide at the rates of 1 g (~600 mg L⁻¹) and 2 g (~1000 mg L⁻¹) t⁻¹ of dried fig for 5 days, based on the results of previous experiments in which PH₃ was tested at concentrations ranging between 200 and 1200 mg L⁻¹ for various durations (Aksoy et al., 2004; Ferizli et al., 2004; Aksoy et al., 2007). PH₃ application was carried out under atmospheric pressure conditions in stacks under 0.50-mm thick tarpaulin placed under a shed. Nearly 50 t of dried figs in 25-30 kg perforated plastic boxes were stacked and then covered with an 18 × 12 m tarpaulin. The tarps were firmly attached with sand-snakes directly to the concrete floor. During the experiments, temperature and relative humidity were recorded by data loggers (Hobo, Onset Co., USA). Mean daily temperature under the stack ranged between 23 and 28 °C, and mean relative humidity was between 48% and 56%. PH₃ concentrations were monitored by sensors (Bedfont EC80, England) placed at the bottom, middle, and top of the stack. Maximum PH₃ concentration was achieved 24 h after Fumi-Cel® application (Figure 1).

Carbon dioxide application

CO₂ was applied under atmospheric pressure in a 36 m³ flexible PVC storage unit (Volcani Cube™ or GrainPro Cocoon®) (capacity: 15 t of dried figs) for 5 days. The cube provides a gas tight condition. CO₂ from steel cylinders was flushed in the liquid phase

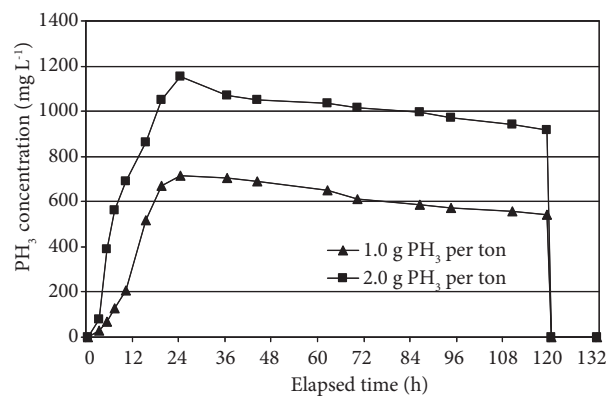


Figure 1. Change in phosphine gas (mg L⁻¹) concentration under tarpaulin following PH₃ treatment applied as 1.0 or 2.0 g t⁻¹ of dried figs for 5 days.

into the PVC storage unit. The atmospheric gas composition was increased to 94% CO₂. During the experiments 3 different levels of CO₂ and O₂ gas concentrations were monitored daily with an analyzer equipped with a thermal conductivity detector (CO₂ analyzer Model 20-600, Gow-Mac Inst, USA) and with an electrochemical detector (O₂ analyzer Model OxyCheck 2, David Bishop Ins., UK) throughout the entire 5-day exposure period (0.8 ± 0.4% O₂, 94 ± 3% CO₂). Mean temperature during the application was 26 ± 2 °C and mean relative humidity as 53 ± 3% inside the cube.

CO₂ treatment under high pressure was performed at a commercial scale in 2 × 20 m³ pressurized tanks (BuseGastek Company, Badhönigen, Germany), each with a capacity of ca. 5 t. The dried figs were placed in boxes and exposed to 98% CO₂ under 25 bar pressure for 2 h.

Storage conditions

The fruits treated with PH₃, CO₂, or MeBr were then stored at ambient conditions for 2 months. Mean temperature and mean relative humidity in the storage room were 19.8 °C and 53.8% in October and 13.2 °C and 56.7% in November, respectively.

Test insects

Test organisms included *E. cautella* (0-24, 24-48, and 48-72-h-old eggs, 7-10 and 17-20-day-old [from egg stage] larvae, 0-72-h [from pupation]-old pupae, and 24-48-h [from emergence]-old adults) and mixed stages of *C. lactis*. Test species in 100 mL perforated plastic containers containing food were placed at

various locations of the stack prior to sealing. After each treatment, 5 containers of test insects were transferred to the laboratory and kept at 25 °C and 65% RH in a controlled room. Mortality of the active stages was determined 14 days after each exposure. Egg and pupa mortality was determined as the failure to hatch or lack of adult emergence, respectively, 10 days after the end of each exposure period.

Quality attributes

Quality parameters were checked as 4 replicates before treatment and after 2 months of storage under ambient conditions. Each treated lot was sampled as 10 randomly selected boxes, and then 4 kg aggregate samples were analyzed for each replicate.

Moisture content was measured by drying samples in a vacuum oven to a constant weight (AOAC, 1990) calculated based on the percentage of weight loss. A water activity meter (Novasina TH 500, Pfaeffikon, Switzerland) was used to measure water activity values at 25 °C.

The surface color of dried figs was measured on opposite sides of 25 dried figs with a colorimeter (Minolta CR-300, Japan). The colorimeter had an 8 mm diameter viewing area and was calibrated with a white tile ($L^* = 97.26$, $a^* = + 0.13$, and $b^* = + 1.71$). Measurements were recorded in L^* (lightness), $+ a^*$ (redness), and $+ b^*$ (yellowness) CIE (Commission Internationale de l'Éclairage) color co-ordinates. Chroma (C^*) and hue angle (hue°) were calculated from a^* and b^* values using the following equations:

$$C^* = (a^{*2} + b^{*2})^{1/2} \quad \text{hue}^\circ = \tan^{-1} (b^*/a^*)$$

A Nippon FHR-1 penetrometer equipped with a conical tip (base: 12 mm wide × 10 mm long) was used to measure firmness, and the results are expressed in Newtons (N). Total soluble solids content (TSS) was determined with a refractometer (Atago ATC-1, Japan) and is expressed in g 100 g⁻¹ of dry matter. Titratable acidity (TA) was determined by titration with 0.1 N NaOH, up to pH 8.1, and expressed in g of citric acid 100 g⁻¹ of dry matter. pH was measured with a pH meter (Mettler Toledo MP220, Switzerland).

Sugaring was assessed visually on a scale of 1-5, describing the fruit surface area covered by white sugar crystals (1 = no sugaring, 5 = total surface covered with sugar). The sugaring index of each

sample was calculated using the following formula: (sugaring class value (scale) × number of fruit within each class)/total number of fruit.

Scanning electron microscopy (SEM) analysis

Four dried fig sub-samples were randomly selected from each treatment. Disks 10 mm in diameter were incised (Guimond et al., 1998). After gold sputtering with Polaron CA7625 carbon accessory gold coating, the surfaces were examined in a scanning electron microscope (SEM, JEOL, JSM-6060, Japan) at 25 kV.

Statistical analysis

Quality assessment was conducted with a completely randomized design, using 4 replicates. As the treated lots were of commercial size, each application was designed separately. Therefore, each tested alternative fumigation application was statistically analyzed and compared with the MeBr-treated control after 2 months of storage. Significant differences between the treatments were determined using Duncan's multiple range test at $P \leq 0.05$. Standard deviation of the mean (SD) of the replicates was also calculated. SPSS v.16.0 (SPS Inc., Chicago, IL, USA) was used for all computations and statistical analyses.

Results

Effect on mortality of storage pests

All MeBr alternative treatments—magnesium phosphide for 5 days at 1.0 g and 2.0 g t⁻¹, and CO₂ at atmospheric pressure for 5 days or at 25 bar pressure for 2 h—resulted in complete mortality of all life stages of *E. cautella* and *C. lactis* (Table 1). Similarly, 100% mortality of the tested insects was obtained with MeBr treatment.

Effect on dried fig quality

Magnesium phosphide treatment, and CO₂ application at atmospheric or high pressure did not have any adverse effects on dried fig fruit color, determined as b^* , C^* , and hue° values. Among the measured color parameters, lightness (L^*) decreased due to darkening by magnesium phosphide application at 2.0 g t⁻¹ for 5 days and by CO₂ treatment under high pressure, as compared to MeBr-treated control fruits (Table 2). The darkening rate was

Table 1. Mortality of *Ephestia cautella* and *Carpoglyphus lactis* exposed to magnesium phosphide (MgPH₃) at dosages of 1.0 g and 2.0 g of PH₃ t⁻¹ of dried figs for 5 days, 94% CO₂ at atmospheric pressure (AP) for 5 days, and CO₂ at 25 bar high pressure (HP) for 2 h.

Test species	Stage	Age*	Treatments			Mortality (%)
			MgPH ₃	CO ₂ (AP)	CO ₂ (HP)	
			Number per replicate			
<i>Ephestia cautella</i>	Eggs	0-24 h	~ 400	~ 300	~ 100	100
		24-48 h	~ 400	~ 300	~ 100	100
		48-72 h	~ 400	~ 300	~ 100	100
	Larvae	7-10 days	~ 100	~ 50	~ 50	100
		17-20 days	~ 100	~ 50	~ 50	100
		Pupae	0-72 h	~ 50	~ 50	~ 75
	Adults	24-48 h	~100	~50	~ 50	100
<i>Carpoglyphus lactis</i>	Mixed	Mixed age	~ 200	~ 100	Uncounted	100

*Age for larval stage since eggs hatched; pupae since pupation; adults since emergence

estimated to be 5.97% in fruit treated with CO₂ at high pressure and 3.44% in fruit treated with 2.0 g of PH₃ t⁻¹, as compared to the MeBr-treated controls. As with lightness, the a* value (redness) also significantly decreased in dried figs treated with 2.0 g of PH₃ t⁻¹. At the end of 2 months of storage the L* values of fruit treated with 1.0 g of PH₃ t⁻¹, CO₂ (atmospheric pressure), and MeBr (control) were not significantly different (P ≤ 0.05) (Table 2).

At the end of the 2-month storage period, water activity (a_w) levels were lower than the initial levels. The a_w levels of fruits treated with phosphine at a higher concentration and fruit exposed to CO₂ at high pressure conditions were significantly lower when compared to control fruits fumigated with MeBr (P ≤ 0.05) (Figure 2).

During storage, sugaring, a natural process under ambient conditions, occurred on fruits exposed to all

Table 2. The effects of magnesium phosphide at dosages of 1.0 g and 2.0 g of PH₃ t⁻¹ of dried figs for 5 days, 94% CO₂ at atmospheric pressure for 5 days, CO₂ at 25 bar pressure for 2 h, and MeBr treatment on fruit color values after 2 months of storage.

Treatments		L*	a*	b*	C*	hue°
	Before treatment	61.3 ± 1.49 a	8.84 ± 0.50	31.05 ± 1.22	32.28 ± 1.29	74.11 ± 0.89
Magnesium phosphide	Control (MeBr)	58.1 ± 0.81 ab	7.66 ± 0.71 a	28.49 ± 1.14 ^{NS}	29.50 ± 1.32 ^{NS}	74.95 ± 1.16 ^{NS}
	1.0 g PH ₃ t ⁻¹	57.9 ± 1.07 a	7.53 ± 0.25 a	28.09 ± 0.65	29.08 ± 0.71	74.99 ± 1.11
	2.0 g PH ₃ t ⁻¹	56.1 ± 0.47 b	6.07 ± 0.33 b	27.42 ± 0.48	28.08 ± 0.58	77.52 ± 1.42
CO ₂ atmospheric pressure	Before treatment	62.0 ± 1.33	8.35 ± 0.43	31.63 ± 0.83	32.71 ± 0.94	75.21 ± 0.97
	Control (MeBr)	57.7 ± 1.06 ^{NS}	6.56 ± 0.36 ^{NS}	27.14 ± 0.66 ^{NS}	27.92 ± 0.75 ^{NS}	76.41 ± 0.84 ^{NS}
	94% CO ₂	56.2 ± 0.66	5.82 ± 0.29	26.01 ± 1.09	26.65 ± 1.12	77.39 ± 1.06
CO ₂ high pressure	Before treatment	62.6 ± 1.02	6.70 ± 0.48	29.19 ± 0.97	29.95 ± 1.06	77.07 ± 1.13
	Control (MeBr)	58.6 ± 1.22 a	6.00 ± 0.12 ^{NS}	26.97 ± 0.39 ^{NS}	27.63 ± 0.42 ^{NS}	77.46 ± 0.87 ^{NS}
	25 bar for 2 h	55.1 ± 0.98 b	5.77 ± 0.27	27.39 ± 0.53	27.99 ± 0.57	78.10 ± 1.02

^aResults are the mean ± SD of 4 replicate samples

^bSame lower-case letters within columns are not significantly different according to Duncan's multiple range test results (P ≤ 0.05)

^{NS}Not significant

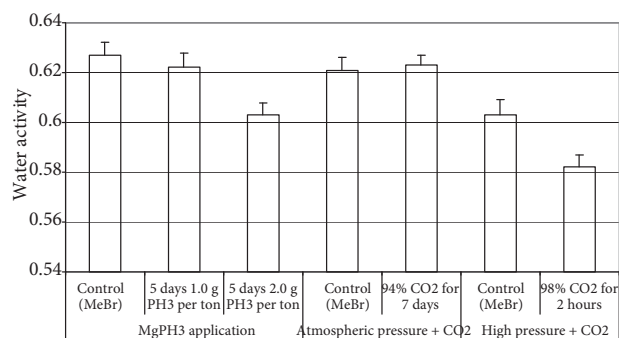


Figure 2. The effects of magnesium phosphide (at 1.0 or 2.0 g of PH₃ t⁻¹ of dried figs for 5 days), CO₂ (94% for 5 days or 25 bar for 2 h), and MeBr treatment on fruit water activity level after 2 months of storage. Results are the mean ± SD of 4 replicate samples.

treatments. Figs treated with PH₃ gas at the rate of 2.0 g t⁻¹ had a tendency to have slightly elevated moisture loss and enhanced sugaring, even if the differences were not statistically significant (P ≤ 0.05) (Table 3).

The effect on fruit moisture content and tissue firmness of all the treatments was not statistically significant (P ≤ 0.05) (Table 3). Similarly, phosphine and CO₂ treatment did not have a marked effect on TSS, TA content, or pH (Table 4).

Table 3. The effects of magnesium phosphide at dosages of 1.0 g and 2.0 g of PH₃ t⁻¹ of dried figs for 5 days, 94% CO₂ at atmospheric pressure for 5 days, CO₂ at 25 bar pressure for 2 h, and MeBr treatment on fruit moisture content, firmness, and sugaring index after 2 months of storage

Treatments		Moisture Content (%)	Firmness (N)	Sugaring index
Magnesium phosphide	Before treatment	22.63 ± 0.57 ^a	7.55 ± 0.41	1.00 ± 0.00
	Control (MeBr, 60 g m ⁻³)	22.07 ± 0.43 ^{NS}	8.14 ± 0.22 ^{NS}	1.58 ± 0.14 ^{NS}
	1.0 g PH ₃ t ⁻¹ for 5 days	21.63 ± 0.49	7.85 ± 0.28	1.72 ± .09
	2.0 g PH ₃ t ⁻¹ for 5 days	21.05 ± 0.27	8.34 ± 0.32	1.95 ± 0.021
CO ₂ atmospheric pressure	Before treatment	22.25 ± 0.44	7.16 ± 0.39	1.00 ± 0.00
	Control (MeBr, 60 g m ⁻³)	21.75 ± 0.28 ^{NS}	8.14 ± .031 ^{NS}	1.68 ± 0.11 ^{NS}
	94% CO ₂ for 5 days	21.39 ± 0.22	7.85 ± 0.27	1.73 ± 0.14
CO ₂ high pressure	Before treatment	21.61 ± 0.39	7.06 ± 0.34	1.00 ± 0.00
	Control (MeBr, 60 g m ⁻³)	20.98 ± 0.26 ^{NS}	7.65 ± 0.26 ^{NS}	1.86 ± 0.10 ^{NS}
	25 bar for 2 h	20.01 ± 0.27	8.04 ± 0.38	1.74 ± 0.08

^aResults are the mean ± SD of 4 replicate samples

^{NS}Not significant

Scanning electron microscopy (SEM) analysis

SEM evaluation of dried fig revealed that some surface damage occurred in fruit exposed to 2.0 g of PH₃ t⁻¹ for 5 days. The surface was intact in fruit treated with MeBr, phosphine (1.0 g of PH₃ t⁻¹ for 5 days), and CO₂ (Figure 3). Increased moisture transfer was likely a consequence of skin damage in fruits exposed to 2.0 g of PH₃ t⁻¹ for 5 days, as revealed with SEM.

Discussion

MeBr alternatives proposed for the control of stored product pests may have limitations regarding cost, residues, required exposure time, or the development of resistance. Such alternatives may also exhibit responses that vary according to the target organism or life stage(s) of the pest. In general, pre-adult insects are more tolerant to fumigants, as their respiratory rates are lower compared than those of adults. Eggs and pupae of several species are reported as the most phosphine-tolerant stages (Chaudry, 1997). Similarly, Bell (1976) stated that the egg stage of 4 species—*Ephestia elutella* (Huebner.), *E. kuehniella* Zell., *E. cautella* (Walk.), and *Plodia interpunctella* (Huebner.)—is the most tolerant developmental stage.

Table 4. The effects of magnesium phosphide at dosages of 1.0 g and 2.0 g of $\text{PH}_3 \text{ t}^{-1}$ of dried figs for 5 days, 94% CO_2 at atmospheric pressure for 5 days, CO_2 at 25 bar pressure for 2 h, and MeBr treatment on fruit TSS (% dry matter), TA (g of citric acid 100 g^{-1} of dry matter) contents, and pH value after 2 months of storage.

Treatments		TSS	TA	pH
Magnesium phosphide	Before treatment	76.6 ± 0.95^a	0.63 ± 0.05	5.23 ± 0.04
	Control (MeBr, 60 g m^{-3})	$76.5 \pm 0.82^{\text{NS}}$	$0.65 \pm 0.07^{\text{NS}}$	$5.21 \pm 0.02^{\text{NS}}$
	1.0 g $\text{PH}_3 \text{ t}^{-1}$ for 5 days	76.0 ± 0.71	0.63 ± 0.09	5.17 ± 0.08
	2.0 g $\text{PH}_3 \text{ t}^{-1}$ for 5 days	76.3 ± 0.96	0.67 ± 0.11	5.12 ± 0.01
CO_2 atmospheric pressure	Before treatment	77.2 ± 0.90	0.71 ± 0.06	4.98 ± 0.06
	Control (MeBr, 60 g m^{-3})	$77.2 \pm 0.84^{\text{NS}}$	$0.75 \pm 0.05^{\text{NS}}$	$4.90 \pm 0.02^{\text{NS}}$
	94% CO_2 for 5 days	77.2 ± 0.79	0.79 ± 0.09	4.79 ± 0.01
CO_2 high pressure	Before treatment	76.9 ± 0.91	0.69 ± 0.10	5.27 ± 0.03
	Control (MeBr, 60 g m^{-3}) 25 bar for 2 h	$76.8 \pm 1.00^{\text{NS}}$ 76.4 ± 0.92	$0.65 \pm 0.07^{\text{NS}}$ 0.63 ± 0.05	$5.16 \pm 0.04^{\text{NS}}$ 5.08 ± 0.03

^aResults are the mean \pm SD of 4 replicate samples

^{NS}Not significant

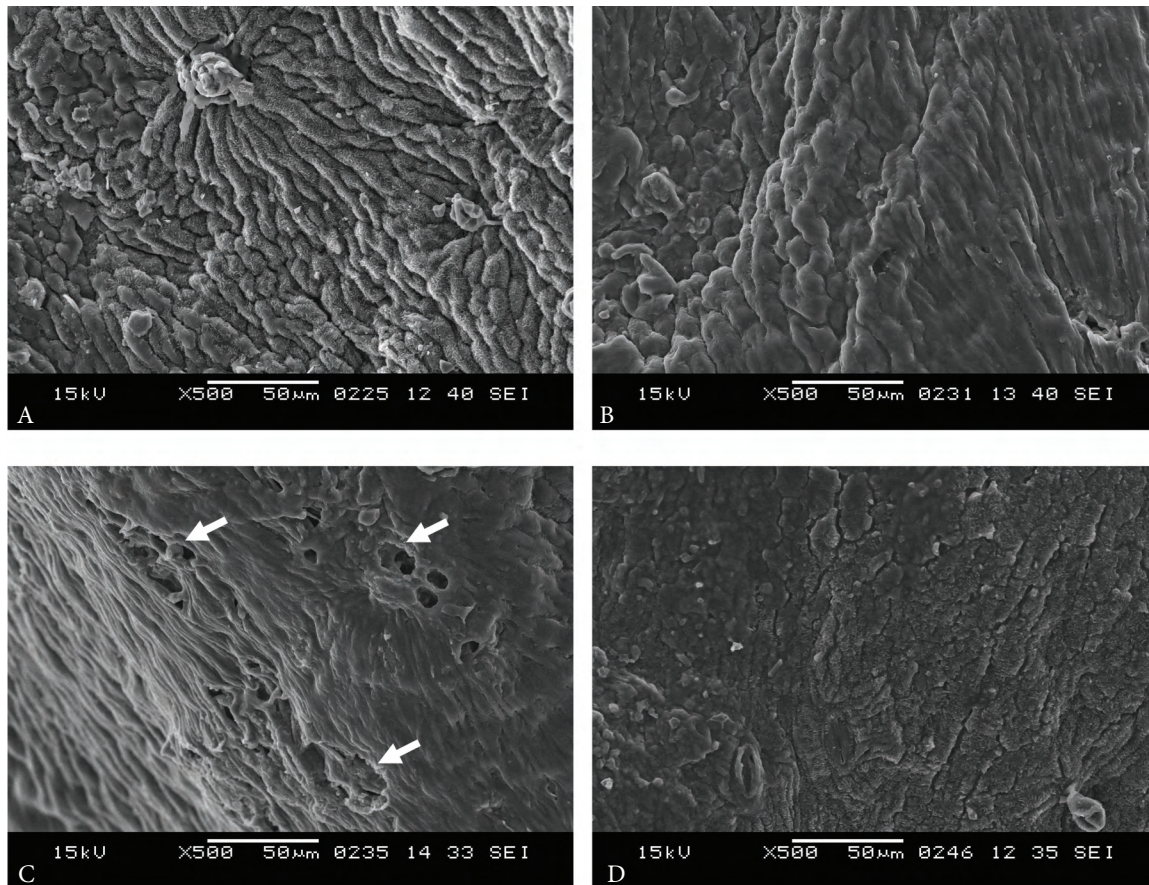


Figure 3. SEM images of dried figs treated with (A) the control (MeBr), (B) 1.0 g of $\text{PH}_3 \text{ t}^{-1}$ of dried figs for 5 days, (C) 2.0 g of $\text{PH}_3 \text{ t}^{-1}$ of dried figs for 5 days, (D), and CO_2 at 25 bar pressure for 2 h (C, arrows point to damaged fruit skin).

Navarro and Donahaye (1990) reported that greater insect mortality could be obtained with comparatively short exposure times at high CO₂ conditions than at low oxygen conditions. In the present study the MeBr alternatives we tested were effective against all stages of the test species known as the most tolerant. The results presented herein, therefore, can be transferred to other relevant sectors and other producing countries, especially where these pests are identified as major pests.

Phosphine, a highly effective fumigant used for disinfestation of bulk grain and other durable commodities, is already applied to dried fruits as an MeBr alternative (Bell, 2000); however, its activity is slow (3-15 days), it is flammable above concentrations of 1.8% by volume, it is corrosive to copper, silver, and gold (Bond et al., 1984), and it is associated with a rapid increase in insect resistance (Price and Mills, 1988; Zettler et al., 1989). In the dried fig sector, longer exposure periods restrict its use during the early season, when every hour is crucial. Fig processors are usually under time constraints to transport figs to the destined markets, especially during the Christmas season.

Phosphine is currently accepted as the most immediate and cost-effective alternative for use with dried fruits. Exposure for 5 days at 1.0 g of PH₃ t⁻¹ of dried fig was adequate to achieve complete control of all stages of the test insects. Longer exposure to MgPH₃ at concentrations surpassing 2.0 g of PH₃ t⁻¹ resulted in increased darkening and sugaring of fruits during storage due to skin damage, as was confirmed by SEM. In addition, high concentrations may trigger resistance against phosphine (Bell and Wilson, 1995; Chaudhry, 1997; Collins et al., 2005). Previous research has shown that under gas-tight conditions, e.g. cubes, 1.0 g of PH₃ t⁻¹ of dried figs for 3 days can be adequate to control these pests if ambient temperatures are high, as they are between June and October (Meyvacı et al., 2003b; Aksoy et al., 2004; Ferizli et al., 2004).

The use of modified atmospheres as alternatives to MeBr at normal ambient temperatures has limitations due to the long exposure times required for complete mortality (Navarro and Jay, 1987; Ekmekci et al., 2004), as compared with phosphine fumigation (Navarro and Donahaye, 1990). A CO₂-rich

atmosphere was reported to be suitable for the protection of dried fruits (Navarro et al., 1998; Ferizli and Emekci, 2000). The efficiency of CO₂ depends on the concentration of gas, duration of exposure, temperature, product's moisture content, and insect species and life stage (Jay, 1984). Applying a modified atmosphere under high pressure (25 bars) proved to be effective in shortening the exposure period required for complete insect mortality, as reported by Rajendran (2001). CO₂ treatment under high pressure provides rapid control of insects, but its use is limited to high-value crops because large quantities of gas are needed and the chambers are expensive (Adler et al., 2000).

Very little research has been performed on the impact of the post-harvest application of MeBr alternatives on product quality. In present study CO₂-enriched atmospheres, both under atmospheric and under high pressure conditions for 5 days and 2 h, respectively, effectively controlled the test species without any adverse effects on dried fig quality. The water activity (a_w) of dried fig is relatively low and below the critical level (0.70); thus, most chemical and biochemical reactions, as well as microbiological growth and aflatoxin formation are inhibited at low a_w (Rahman and Labuza, 1999). Even if water activity levels decreased with some of the tested treatments (Figure 2), they did not have significant effects on other related parameters, such as firmness and sugaring. Firmness and sugaring levels of the treated dried figs stored for 2 months rendered them marketable and palatable (Meyvacı et al., 2003a).

Longer exposure (4.5 months) of figs to CO₂-enriched atmospheres (60%-80%) was effective on storage pests, with no adverse effects on fruit quality (Donahaye, 1990). Previous studies showed that for dried figs long-term storage in CO₂-enriched atmospheres cannot be recommended, as the color of dried figs was darkened (Meyvacı et al., 2003a) during longer exposures. Therefore, for the dried fig sector, a CO₂-enriched atmosphere can be utilized only for short-term application. Shorter exposure periods required by high pressure CO₂ treatment seem to be a benefit, especially at the beginning of the season; however, pressurized tanks necessitate a large investment. The results obtained in the present study show that CO₂ application at high concentrations in

the flexible, gas-tight Volcani Cube™ could be effective for dried fruits for short exposure periods and yields results comparable to magnesium phosphide treatment. Atmospheric CO₂ provides an advantage over MgPH₃ in the case of organic production and has no deleterious effect on product quality, even with long exposure periods.

CO₂ under atmospheric pressure and phosphine applications are inexpensive practical alternative methods to MeBr for dried fruit disinfestation. They do not require a sophisticated technology, which is usually not available in small scale dried fruit processing plants in Turkey. Even so, these alternatives require longer exposures than MeBr and shorter

exposures can only be obtained by CO₂ application under high pressure, which requires a large investment. Therefore, there is still a need for effective low-cost chemical and non-chemical methods with short exposure periods.

Acknowledgments

This research was a part of the “Project to Phase-out Methyl Bromide in the Dried Fig Sector in Turkey” (TTGV-P2/30m) and was funded by the World Bank through the Multilateral Funds for the Implementation of the Montreal Protocol on Substances that Deplete the Ozone Layer.

References

- Adler, C., H.G. Corinth and C.H. Reichmuth. 2000. Modified atmospheres. In: Alternatives to Pesticides in Stored Product IPM (Eds.: B.H. Subramanyam and D. Hagstrum). Kluwer Academic Publ. Group, pp. 105-146.
- Aksoy, U., K.B. Meyvacı, F. Sen and A. Altindisli. 2004. Impact of fumigants applied to control storage pests on fruit quality of dried figs. IOBC WPRS Bulletin. 27: 203-209.
- Aksoy, U., H.Z. Can, K.B. Meyvacı and F. Şen. 2008. Türk Sultanları. In: Kuru İncir (Ed.: U. Aksoy), Can Dijital Baskı Merkezi, İzmir, pp. 61-62. (In Turkish)
- AOAC. 1990. Official Method of Analysis, 15th ed., Association of Official Analytical Chemists, Washington DC, USA, p. 760.
- Bell, C.H., 1976. The tolerance of developmental stages of four stored product moths to phosphine. J. Stored Prod. Res. 12: 77-86.
- Bell, C.H. and S.M. Wilson. 1995. Phosphine tolerance and resistance in *Trogoderma granarium* Everts (Coleoptera: Dermestidae). J. Stored Prod. Res. 31: 199-205.
- Bell, C.H. 2000. Fumigation in the 21st century. Crop Protection. 19: 563-569.
- Bond, E.J., T. Dumas and S. Hobbs. 1984. Corrosion of metals by the fumigant phosphine. J. Stored Prod. Res. 20: 57-63
- Cetinkaya, N., B. Ozyardimci, E. Denli and E. İc. 2006. Radiation processing as a post-harvest quarantine control for raisins, dried figs and dried apricots. Radiation Physics and Chemistry. 75: 424-431.
- Chaudhry, M.Q. 1997. A review of the mechanisms involved in the action of phosphine as an insecticide and phosphine resistance in stored-product insects. Pestic. Sci. 49: 213-228.
- Collins, P.J., G.J. Darglish, H. Pavić and R.A. Kopittke. 2005. Response of mixed-age cultures of phosphine-resistant and susceptible strains of lesser grain borer, *Rhyzopertha dominica*, to phosphine at a range of concentrations and exposure periods. J. Stored Prod. Res. 41: 373-385.
- Damarlı, E., H. Gün, G. Özyay, S. Bülbül and P. Oechsle. 1997. An alternative method instead of methyl bromide for insect disinfestations on dried figs: controlled atmosphere. Acta Hort. 480: 209-215.
- Desmarchelier, J.M. 1998. Potential new fumigants. In: Stored Grain in Australia: Proceedings of the Australian Postharvest Technical Conference, 26-29 May Canberra, Australia, pp. 133-137.
- Desmarchelier, J.M., S.E. Allen, Y. Ren, R. Moss and L.T. Un. 1998. Commercial scale trials on the application of ethyl formate, carbonyl sulphide, and carbon disulphate to wheat. CSIRO Entomol. Tech. Rep. pp. 75-63.
- Donahaye, E.J. 1990. Laboratory selection of resistance by the red flour beetle, *Tribolium castaneum* (Herbst), to a carbon dioxide-enriched atmosphere. Phytoparasitica. 18: 299-308.
- Emekci, M., A.G. Ferizli, S. Tutuncu, S. Navarro. 2004. The efficiency of modified atmosphere applications against dried fruit pests in Turkey. IOBC WPRS Bulletin. 27: 227-231.
- Erakay, S. and A.I. Ozer. 1979. Preliminary studies on infestation rates of dried fig pests in the Aegean region and control methods. Plant Protection Bulletin. 19: 159-173. (In Turkish)
- Ferizli, A.G. and M. Emekci. 2000. Carbon dioxide fumigation as a methyl bromide alternative for the dried fig industry. In: 2000 Annual Research Conference on Methyl Bromide Alternatives and Emissions Reductions (Eds., G.L. Obenauf and R. Obenauf), Orlando, Florida, pp. 81
- Ferizli, A.G., M. Emekci, S. Tutuncu and S. Navarro. 2004. The efficiency of phosphine fumigation against dried fruit pests in Turkey. IOBC WPRS Bulletin. 27: 265-270.
- Fields, P.G. and N.D.G. White. 2002. Alternatives to methyl bromide treatments for stored-product and quarantine insects. Ann. Rev. Entomol. 47: 331-359.

- Guimond, M.C., K.P. Andrews and A.G. Lang. 1998. Scanning electron microscopy of floral initiation in sweet cherry. *J. Amer. Soc. Hort. Sci.* 123: 509-512.
- Jarratt, J.M. 2001. Pest management principles: Industrial, institutional and structural pest control, <http://msucares.com/publications/p2247ch7.pdf>
- Jay, E.G. 1984. Imperfections in our current knowledge of insect biology as related to their responses to controlled atmospheres. In: *Controlled Atmosphere and Fumigation in Grain Storages* (Eds.: B.E. Ripp, H.J. Banks, E.J. Bond, D.J. Calverley, E.G. Jay and S. Navarro). Elsevier, Amsterdam, pp. 493-508.
- Johnson, J.A., K.A. Valero, M.M. Hannel and R.F. Gill. 2000. Seasonal occurrence of postharvest dried fruit insects and their parasitoids in a culled fig warehouse. *J. Econ. Entomol.* 93: 1380-1390.
- Meyvacı, K.B., F. Sen, U. Aksoy F. Özdamar and M. Çakır. 2003a. Research on prolonging the marketing period of dried and ready-to-eat type figs (*Ficus carica*). *Acta Hort.* 628: 439-445.
- Meyvacı, K.B., F. Sen, U. Aksoy, A. Altındisli, M. Emekci and A.G. Ferizli. 2003b. Project to phase-out methyl bromide in the dried fig sector in Turkey. *Acta Hort.* 628: 73-81.
- Navarro, S. and E. Jay. 1987. Application of modified atmospheres for controlling stored grain insects. *Proc. British Crop Protection Council, No. 37 Stored Products Pest Control. Univ. of Reading.* pp. 229-236.
- Navarro, S. and E. Donahaye. 1990. Generation and application of modified atmospheres and fumigants for the control of storage insects. In: *Fumigation and Controlled Atmosphere Storage of Grain, Proceedings of an International Conference* (Eds., B.R. Champ, E. Highley and H.J. Banks), ACIAR Proceedings No. 25, Singapore, pp. 152-165.
- Navarro, S., J.E. Donahaye, M. Rindner and A. Azrieli. 1998. Storage of dates under carbon dioxide atmosphere for quality preservation. In: *Proceeding International Conference Controlled Atmosphere and Fumigation in Stored Products* (Eds., E.J. Donahaye, S. Navarro, and J.G. Leesch), Fresno, CA, pp. 231-239.
- Perera, C.O. 2005. Selected quality attributes of dried foods. *Dry. Technol.* 23: 717-730.
- Price, L.A. and K.A. Mills. 1988. The toxicity of phosphine to the immature stages of resistant and susceptible strains of some common stored-product beetles, and implications for their control. *J. Stored Prod. Res.* 24: 51-59
- Rahman, M.S. and T.P. Labuza. 1999. Water activity and food preservation. In: *Handbook of Food Preservation*, (Ed. M.S. Rahman). Marcel Dekker, NY, USA, pp. 339-382.
- Rajendran, S. 2001. Alternatives to methyl bromide as fumigants for stored food commodities. *Pesticide Outlook.* 12: 249-253.
- Schneider, S.M., E.N. Roskopf, J.G. Leesch, D.O. Chellemi, C.T. Bull and M. Mazzola. 2003. Research on alternatives to methyl bromide: pre-plant and post-harvest. *Pest Management Science.* 59: 814-826.
- Turanlı, F. 2003. Studies on infestation levels of pests on dried fig in Aydın and Izmir provinces. *Turkish J. Entomol.* 27: 171-180.
- Zettler, J.L., W.R. Halliday and F.H. Arthur. 1989. Phosphine resistance in insects infesting stored peanuts in the southeastern United States. *J. Econ. Entomol.* 32: 1508-1511
- Zettler, J.L., J.G. Leesch, R.F. Gill and J.G. Tebbets. 1999. Chemical alternatives for methyl bromide and phosphine treatments for dried fruits and nuts. In: *Proceedings of the Seventh International Working Conference on Stored Product Protection* (Eds., J. Zuxun, L. Quan, L., Yongsheng, T. Xianchang and G. Lianghua), Beijing, China, pp. 554-561.