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Residues of Methyl Bromide and Sulfuryl Fluoride in Manufacturer-Packaged Household Foods Following Fumigation

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Methyl bromide (MB) and sulfuryl fluoride (SF) are the only compounds currently registered as structural fumigants in the United States. MB and SF are used primarily to control drywood termites (Osbrink et al. 1987; Scheffrahn and Su 1992). Because ambient atmosphere acts as a medium for passive diffusion of fumigants to target sites, the surfaces of all structural matrices and building contents are exposed to these toxicants. If matrices are sorptive, then latent residual desorption follows (Scheffrahn et al. 1987a).

The potential for residue formation in foods as a result of fumigant exposure (Meikle and Stewart 1962) prompted SF and MB registrants to provide special food handling directions (Anonymous 1986, 1989). The use of sealed plastic containers in contemporary food packaging and the variable residue potential of different commodities invites investigation of fumigant residue formation in packaged foods. Certain polymeric films are excellent fumigant barriers (Kolbezen and Abu-El-Haj 1977; Scheffrahn et al. 1990) suggesting that some plastic food packaging may be resistant to fumigant diffusion. This study assesses MB and SF residues in 23 manufacturer-packaged household foods fumigated at approximate maximum labeled rates.

MATERIALS AND METHODS

Packages of food, beverage, or medicinal commodities (Table 1) were purchased from a local supermarket. Name-brand foods were chosen for their availability, variety, and container type. Duplicate packages of five commodities were opened and reclosed using existing closures. Corked wine bottles were fumigated upright and on sides. Four replicates of each commodity were independently fumigated with SF and MB at target concentrations of 9288 and 8640 ppm v/v

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Table 1. Methyl bromide (MB) and sulfuryl fluoride (SF) residues in consumer foods packaged in manufacturers' brand containers and exposed to 8751 ppm MB or 8810 ppm SF for 20 h at 22 °C (n=4)

Brand, Commodity, and Container Type[b]	Mean residue, ppm w/w ±SD[a] MB	SF
Campbell's vegetable soup		
10.5 oz metal can	0 ±0	0 ±0
Coca-Cola soda		
2-L HDPE bottle	0 ±0	0 ±0
open[c]	0 ±0	0 ±0
Spice Island black pepper		
2.3 oz glass, no vacuum	0.719 ±0.337	0.137 ±0.095
Ragu spaghetti sauce		
14 oz glass jar, vacuum	0 ±0	0 ±0
Oscar Meyer bologna[d]		
8 oz Barex rack package	0 ±0	0 ±0
Folger's coffee		
13 oz alum. foil vacuum	0 ±0	0 ±0
Alka Seltzer antacid[d]		
aluminum foil packets	0 ±0	0 ±0
Crisco veg. oil		
16 oz PETE bottle	0 ±0	0 ±0
open[c,e]	0 ±0	0.001 ±0.001
Breyer's yogurt		
8 oz PP tub	0 ±0	0 ±0
open[c]	0 ±0	0 ±0
Skippy peanut butter		
18 oz PETE jar	0.734 ±0.082	0 ±0
open[c,e]	106.065 ±28.240	7.660 ±2.531
M & M's chocolate candy[d]		
8 oz plastic bag	3.987 ±1.187	0.014 ±0.007
Sutter Home wine		
750 mL glass w/ cork	0.027 ±0.011	0.002 ±0.002
on side	0.027 ±0.009	0 ±0
Hershey's choc. syrup		
26 oz HDPE bottle	0.038 ±0.029	0 ±0
Log Cabin syrup		
12 oz PP bottle	0 ±0	0 ±0
open[c]	0 ±0	0 ±0
Sudafed decongestant		
foil-backed blister pk.	0 ±0	0 ±0
Jell-O pudding		
4 oz PP cup, foil lid	0.108 ±0.080	0 ±0
Kudos granola bar[d]		
1.25 oz PU wrap	20.178 ±4.083	0.374 ±0.087

(Table 1 continued)

Mott's apple juice		
8 oz foil-on-paper box	0.067 ±0.022	0.001 ±0.001
Frito's corn chips[d]		
10 oz PU bag	0.448 ±0.103	0.109 ±0.034
Ruffle's potato chips[d]		
10 oz PU bag	3.373 ±0.649	0.021 ±0.009
Kraft Parmesan cheese		
1.5 oz cardboard/foil pk	4.589 ±0.670	0.237 ±0.087
Tropicana orange juice		
16 oz cardboard carton	3.306 ±0.890	0.204 ±0.098
Fleischmann's margarine		
8 oz HDPE tub	151.308 ±13.128	5.643 ±2.503

[a] Corrected for recovery (Table 2), minimum level of detectability = 0.001 ppm.
[b] HDPE=high density polyethylene, PETE=polyethylene terephthalate, PP=polypropylene, PU=polyurethane.
[c] Duplicate container opened, ½ of commodity removed, and reclosed.
[d] Commodities subdivided prior to loading in headspace vial.
[e] Foil liner seal removed upon opening.

(36 g/m^3) for SF and MB, respectively, for 20 h at 22°C by the method of Scheffrahn et al. (1987b). Actual fumigant concentrations in the 4.2 m^3 chamber were sampled and analyzed for each fumigation (Scheffrahn et al. 1987b).

After fumigation, packages were opened and 10 g of each commodity transferred by dropper, syringe, or spatula into a headspace vial (120 mL serum bottle). Six of 23 commodities, restricted from entry by vial necks, were subdivided by hand before loading. At 2 h post-fumigation, sample vials and an empty air background vial were sealed with 20-mm Teflon-lined septa. Fumigant distribution between sample matrix and vial headspace was allowed to equilibrate for 24 h at 22 ±1 °C prior to GC analysis of MB and SF by the method of Osbrink et al. (1988). Minimum level of detection for both fumigants was 0.001 ppm w/w.

Recovery efficiency was determined by fortifying untreated commodities in vials at concentrations approximating those found in fumigated samples. Standard MB or SF dilutions (in air) were injected through vial septa 24 h prior to GC analysis. Single-level fortifications were conducted on commodities which yielded ≥ 25% recoveries at low-level (≤ 0.2 ppm) fortifications. Commodities with lower recoveries were spiked with four arithmetically spaced dilutions. Linear regression of natural logs of fortification concentrations on headspace concentrations was calculated (SAS 1988) for each multiple fortification commodity. Samples at each fortification level were replicated four times. Percent recoveries were used to correct residue values in chamber-fumigated samples.

RESULTS AND DISCUSSION

Mean exposure concentrations for packaged foods were 8751 ±911 and 8810 ±720 ppm ±SD for MB and SF, respectively. These compare with typical structural fumigation rates of ca. 2700 ppm for MB and 1700 ppm for SF for drywood termite control (Scheffrahn *unpubl.*). Recovery-corrected residues from fumigated packaged foods indicate that residue quantities are strongly matrix- and container-specific (Table 1). The affinity of MB (Daft 1988) and SF (Osbrink et al. 1988) to lipids is demonstrated by relatively high residues (> 1 ppm) in fatty commodities packaged in "leaky" containers (i.e. margarine in HDPE tub, or polyurethane bagged chips and bars). Fumigants enter containers by two routes, diffusion through air channels in closures (reclosed peanut butter jar) or porous packaging (Parmesan cheese in cardboard), and by polymer permeation (polyurethane bagged foods). Both routes contributed to high residues in margarine. Superior protection from both fumigants was given by factory sealed PETE containers of oil and peanut butter, and for bologna in the Barex (an acrylonitrile and butadiene copolymer) packaging. Decreased protection by reclosed jars of peanut butter demonstrate the added protection of untampered manufacturer seals. The cap closure on the oil bottles remained highly protective even after reclosing. As expected, vacuum-packed foods in metal (soup, coffee) or glass (sauce) containers yielded no residues, however, protection by glass is dependent on vacuum closure of lids as demonstrated by detection of MB and SF residues in black pepper jars.

The consistently higher residues in samples exposed to MB, compared to SF-fumigated foods (Table 1), is related to MB's greater diffusion rate through synthetic polymers (Scheffrahn et al. 1990), greater affinity for fat (Meikle and Stewart 1962), higher water/ethanol solubility (wine, orange juice; Table 1) and lower vapor pressure (i.e. slower desorption). MB is registered as a commodity fumigant for which tolerances have been established (Anonymous 1989).

Recoveries from fortified commodities are listed in Table 2. As reported previously (Osbrink et al. 1988), percent recovery of SF is generally high, even at ppb-level fortifications. MB recoveries in this study were found to be poor or sporadic with many, especially fatty, commodities as has been previously noted (Daft 1988, 1989). Poor recoveries may be due to MB dealkylation in commodities (Meikle and Stewart 1962), non-optimum equilibration time (DeVries et al. 1985), and high fat affinity (Daft 1988, 1989).

Although this study simulates worst-case conditions (maximum exposure rates and minimum commodity aeration), residues of both fumigants were lower than expected. Thirteen commodities contained no detectable residues for either fumigant, and many containers were highly resistant to fumigant penetration. However, the vast combinations of container types, closures, and commodities available to consumers prescribe that wording on fumigant labels be carefully reevaluated. The current SF label (Anonymous 1986) specifies "Food, feed, drugs and medicinals (including those items in refrigerators and freezers) must be removed from fumigation site or *sealed* in highly resistant containers such as glass, metal or plastic such as polyethylene plastic bags of at least 4 mil thickness or equivalent such as two 2-mil bags". One registrant's label for MB (Anonymous 1989) is written "Remove.... all food, animal feed and medicinals not sealed in metal or glass". This study suggest that terms such as "resistant container" and "sealed" be better defined and that food commodities be additionally protected (Scheffrahn et al. 1990) or removed from a structure prior to fumigation.

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Table 2. Recoveries of methyl bromide (MB) and sulfuryl fluoride (SF) from food products in Table 1 spiked at single or quadruple fortification concentrations (n=4)

Commodity	MB Fort. Range (ppm)	MB % recovery ±SD or regression eq.[a]	SF Fort. Range (ppm)	SF % recovery ±SD
vegetable soup	0.2	92 ±16	-	
Coca-Cola soda	0.2	97 ±7	-	
black pepper	4-16	R=0.8916F-0.5757	2	70 ±13
spaghetti sauce	0.2	43 ±2	-	
bologna	0.2	25 ±4	-	
coffee	0.2	38 ±4	-	
antacid	0.2	101 ±16	-	
vegetable oil	0.1-500[b]	R=0.9949F-1.983	0.05-0.8	R=0.914F-0.199
fruit yogurt	0.2	95 ±7	-	
peanut butter	4-16	R=0.8269F-0.02662	125	83 ±1
high range	400-3200	R=1.273F-4.728	-	
chocolate candy	20-160	R=0.9325F-0.005218	0.2	76 ±3
wine	0.4-3.2	R=0.9911F-1.407	0.05	74 ±2
chocolate syrup	0.4-3.2	R=1.010F-0.9904	-	
pancake syrup	0.2	97 ±9	-	
decongestant	0.2	102 ±5	-	
pudding	0.4-3.2	R=1.032F-1.226	-	
granola bar	100-800	R=0.9523F-0.5611	6	85 ±2
apple juice	0.4-3.2	R=0.9726F-0.7783	0.05	81 ±3
corn chips	4-16	R=1.092F-1.459	2	90 ±1
potato chips	20-160	R=0.9314F-0.9159	0.4	87 ±3
Parmesan cheese	20-160	R=1.144F-2.936	3	63 ±5
orange juice	0.1-500	R=1.065F-0.8726	3.5	91 ±6
margarine	500-4000	R=1.180F-3.666	90	81 ±3

[a] R = nat. log of recovered headspace concentration in ppm, F = nat. log of fortification concentration.
[b] Five fortification levels.

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