Peel Injury to Citrus Fruit Fumigated with Ethylene Dibromide[1,2]

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Abstract. Peel injury in 3 citrus fruit cultivars fumigated with ethylene dibromide (EDB) was due to the persistence of resudue of the fumigant in the fruit peel. Initial resudues after fumigation were proportional to the concn and time of exposure. The desorption rate during aeration increased with temp. Incidence of peel injuries was highest in fruit stored at low temp or wrapped in polyethylene bags, probably due to prolonged action of EDB residues on the peel.

Storage of fumigated fruit in an atmosphere containing an increased concn of CO_2 delayed the appearance of damage. Susceptibility was greatest in 'Marsh' grapefruits, followed by 'Shamouti' and 'Valencia' oranges.

Fumigation of citrus fruit intended for export with ethylene dibromide (EDB) for the control of eggs and larvae of the fruit fly *Ceratitis capitata* (Wied.), has been practiced to satisfy the plant quarantine requirements of countries importing the fruit. Such treatments, while generally effective in controlling the fly, have sometimes resulted in considerable peel injury in the fumigated fruit.

Differences in tolerance to fumigation of various citrus fruit cultivars, grown under different climatic conditions and treated at different degrees of ripeness, have been noted by Lindgren and Sinclair (7), and Polacek (8). Subsequently, Grunberg et al. (6) determined the optimal fumigation conditions for Israeli-grown citrus fruit cultivars.

Proper aeration of fumigated citrus fruit has been found to reduce EDB residues in the fruit considerably. Sinclair et al. (12) and Alumot et al. (1), who found that most of the EDB residue is concd in the fruit peel while only traces appear in the fruit pulp, noted that an aeration period of about one week removes most EDB residues, leaving only inorganic bromide bound in the tissue, mostly in the fruit peel. Export of citrus fruit to remote markets often necessitates refrigerated shipment with limited ventilation. Fumigated fruit thus treated is likely to have more peel injury, partly because of a probable reduction in the diffusion rate of EDB (10).

We studied post-fumigation aeration conditions, storage temp, and EDB residues as related to peel injury in fumigated citrus fruit.

Materials and Methods

Medium-sized fruits of the Marsh, Shamouti, and Valencia cultivars were selected from a single orchard. The fruits were subjected to customary packinghouse sterilization treatment consisting of immersion in a 0.5% water solution of sodium orthophenylphenate, followed by waxing with a natural emulsion wax, wrapping in paper impregnated with 30 mg biphenyl, and packaging in standard Bruce boxes. Batches of 70-84 boxes were placed inside the fumigation room in each experiment, so that the percentage load of the fumigation room was 50-80 (2).

Eight different fumigation treatments of the 3 cultivars were performed in a fumigation room having a vol of 10.8 m^3 and an absorption when empty of 37%. The fruit temp during fumigation was 21-25, 19-22 and 16-18°C for grapefruit, 'Shamouti', and 'Valencia', respectively. The relative humidity ranged from 60-85%. EDB doses are indicated in Table 1. The fumigation procedures were those outlined in the Manual for fumigation of Mexican fruits with EDB (2).

In order to measure EDB concn in the fumigation room, the atmosphere was sampled at several points at intervals during the fumigation period, and EDB concn were determined chemically (3, 11). Similarly, EDB concn in the atmosphere of the empty fumigation room were measured.

Coggiola and Huelin (5) showed that considerable amounts of EDB are absorbed by packing materials and room structures. Assuming equal absorption by the internal surfaces in 2 fumigation rooms of different size, the EDB concn in the atmosphere will be lower in a smaller room than in a larger, due to the higher surface-to-volume ratio. Thus, room size should be considered as a factor in calculating actual EDB dose.

EDB residues in the fruit were determined by the method of Bielorai and Alumot (4) immediately following fumigation, and during aeration and storage, in duplicate 50-g peel samples prepared by chopping and mixing pieces of peel from several fruits. In large scale experiments (Table 3), EDB residues in the fruit peel were examined in fruit stored at the optimal cold storage temperature for each cultivar (9) and at 17°C.

Aeration. To study the effect of post-fumigation, pre-storage aeration periods on EDB residues and peel injury to the fruit, fumigated fruit was aerated for 3 hr and for 1, 2, and 4 days at 17°C in a large ventilated room. Thereafter, the fruit was stored at temp of 2, 5, 12, and 17°C at 88-90% relative humidity for a period of 2 weeks from the time of fumigation. A complete change of fresh air was made in the storage room every ½-hr. To obtain data on the effect of extended non-aerated storage on EDB-fumigated fruit, some of the fruit was stored at the same temp and for the same period in boxes placed inside 0.1-mm thick polyethylene bags. Thereafter, all the fruit was kept under shelf-life conditions at 17°C for 2 additional weeks. Before transferring the fruit to shelf-life, the polyethylene bags as well as the wrapping paper were removed.

Storage in an atmosphere containing high CO_2 concentration. An elevated CO_2 concn in the storage room atmosphere, particularly during shipments, often results from inadequate air exchange. To study the possible effects of such conditions on the degree of EDB injury to fruit peel, fumigated fruit was stored at 5-6°C for 2 weeks in a non-aerated storage room in which the CO_2 concn was maintained at 8-12% by flushing from pressurized CO_2 cylinders. The O_2 concn decreased to 15%. The CO_2 and O_2 concn were measured twice daily with an Orsat apparatus. Fumigated fruit stored under

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[6]Unpublished data.

Table 1. Injured oranges and grapefruits, 4 weeks after fumigation, as a function of ethylene dibromide (EDB) dose and storage conditions.

Treatment	Storage temperature (°C)	Aeration period (days)	EDB dose (g/m³) 10.0	19.5		22.1		10.0		14.7		19.5[c]	
			Percent of Shamouti oranges showing damage					Percent of Marsh grapefruit showing damage				Percent of Valencia oranges showing damage	
			Slight[a]	Slight	Severe	Slight	Severe	Slight	Severe	Slight	Severe	Slight	Severe
Fumigation	2	1/8	0	4.2	2.4	7.9	1.2	0	0	18.2	11.5	0	0
		1	3.0	6.0	0.6	9.7	3.6	0	0	13.4	3.8	0	0
		2	0	2.4	0	0	0	1.9	0	3.8	0	0	0
		4	0	0	0	0	0	1.9	0	4.8	3.8	0	0
Fumigation + polyethylene bags		1/8	3.0	22.4	9.6	0	22.4 70.3[b]	42.3	34.6	12.5	40.3	8.7	3.7
		1	0	0.6	0.6	8.5	2.4	0	0	25.0	12.5	0	0
		2	0	0	0	0.6	0	1.9	0	2.8	0	0	0
		4	0	0	0	0.6	0	1.9	0	1.9	0	0	0
Fumigation	5	1/8	1.8	6.6	0.6	23.0	10.9	5.7	0	20.2	15.3	3.7	1.3
		1	1.2	10.9	0	13.3	3.6	5.7	1.0	10.5	6.7	0	0
		2	0	3.0	0	9.7	1.8	2.8	1.0	5.7	1.0	0	0
		4	0	1.2	0	1.8	1.2	0	0	2.8	0	0	0
Fumigation + polyethylene bags		1/8	0	20.0	4.2	12.7	11.5 69.7[b]	17.3	17.3	5.7	56.7	28.1	11.9
		1	0	1.2	0.6	7.3	1.8	0	0	8.6	2.8	4.4	0
		2	0	0.6	0	3.0	0	0	0	1.0	0	0	0
		4	0	0	0	1.8	0.6	2.8	0	2.8	0	0	0
Fumigation	12	1/8	0	0	0	0	0	1.9	0	0	0	0	0
		1	0	0	0	1.8	1.2	0	0	0	0	0	0
		2	0	0	0	0	0	0	0	1.9	0	0	0
		4	0	0	0	3.0	0.6	0	0	2.8	0	0	0
Fumigation + polyethylene bags		1/8	0	13.9	12.1	15.2	11.5	4.8	1.9	40.3	27.0	9.4	1.8
		1	0	0.6	0	1.2	3.6	0	0	1.0	1.0	0	0
		2	0	0	0	0	0	0	0	2.8	1.9	0	0
		4	0	0	0	0	0	0	0	2.8	1.0	0	0
Fumigation	17	1/8	0	0	0	0	0	1.0	0	2.8	1.0	0	0
		1	0	0	0	0	0	1.9	0	0	0	0	0
		2	0	0	0	0	0	0	1.9	0	0	0	0
		4	0	0	0	0	0	1.0	0	1.0	0	0	0
Fumigation + polyethylene bags		1/8	0	14.5	14.5	8.4	13.9	1.0	0	24.0	14.4	0	0
		1	0	0	0	0	0	0	0	1.0	0	0	0
		2	0	0	0	0	0	0	0	0	0	0	0
		4	0	0	0	0	0	0	0	0	0	0	0

a. No severe damage developed.
b. Rotted fruit. This fruit probably suffered severe damage.
c. At a dose of 14.0 g/m³, no damage developed in Valencia oranges except for 13.1 percent slight damage found in polyethylene wrapped fruit 1/8 day after fumigation at 5°C.

normal aeration conditions, and non-fumigated fruit stored in a high-CO_2 atmosphere, served as controls.

Each fruit was examined twice during each experiment, after 2 weeks of cold storage and after 2 weeks under shelf-life conditions, to estimate the degree of EDB damage. The degree of EDB damage was expressed as: (a) "Slight damage" - characterized by light to shallow pittings in the peel, brownish-red in color, in a few, small, isolated spots over a small surface area. Fruit showing such "Slight damage" is marketable. (b) "Severe damage" - consisting of moderately deep to deep pittings, red to brown, usually over a large portion of the fruit surface. This fruit is not marketable.

Two boxes (about 150 fruits) were used in each treatment. Non-fumigated fruit in all treatments served as controls.

Results

Only slight damage developed in 'Shamouti' fruit fumigated at the low EDB dose (10.0 g/m³), during the 4 weeks of combined storage and shelf-life. (Table 1). Fruit fumigated at the higher EDB dose (19.5 g/m³) showed at 2 and 5°C slight damage after 2 weeks in cold storage, and severe damage at the end of the 4-week period. In fruit fumigated at the highest EDB dose (22.1 g/m^3), considerable damage was noticeable after 2 weeks of cold storage; fruit stored at 5°C developed more damage than that stored at the other temp. Non-fumigated fruit did not show any peel injuries similar to EDB damage and are therefore omitted from the table.

The most pronounced increase in percent and severity of damage during the 2-week shelf-life period took place in the polyethylene-wrapped fruit stored at 2 and 5°C (Table 1). Grapefruit fumigated at the low EDB dose (10.0 g/m^3), developed only slight damage after 2 weeks of storage, but after the 2 additional weeks under shelf-life conditions, more damage was visible, particularly in the polyethylene-wrapped fruit stored at 2 and 5°C. A heavier fumigation treatment (14.7 g/m^3EDB) caused considerable grapefruit peel injury after 2 weeks of storage. At low storage temp, the damage appeared in unwrapped as well as polyethylene-wrapped fruit, and at higher storage temp (12 and 17°C), mostly in the polyethylene-wrapped fruit.

Almost no EDB damage was found in 'Valencia' fruit fumigated at the low EDB dose (14.0 g/m^3). Most damage at the high fumigation dose (19.5 g/m^3), after the first 2 weeks cold storage period, was found in fruit stored in polyethylene bags.

A high percentage of additional injuries appeared in fruit of all 3 cultivars fumigated at the highest EDB dose and stored at low temp during the shelf-life period.

Small-scale fumigation experiments with 'Shamouti' oranges, performed in 20-liter fumigation chambers, showed that the degree of absorption of EDB in the fruit peel is approximately proportional to the CxT (concn of EDB x time of exposure) factor (Table 2).

Table 2. Residual ethylene dibromide (EDB) in the peel of 'Shamouti' orange.

EDB concn (g/m^3)	Fumigation time (hr)	CxT[1]	EDB residues[2] in peel (ppm)
10	2	20	50
15	2	30	64
30	2½	75	160

[1]Concn of EDB x time of exposure.

[2]EDB residues were determined immediately after fumigation.

Fruit containing 50 or 64 ppm EDB showed no EDB damage if aerated immediately after fumigation, but 80% damage after transfer to closed containers for 2 weeks. The fruit containing 160 ppm EDB showed 20% injuries after being kept for only 3 days under normal aeration conditions.

Storage temp clearly affected the rate of EDB desorption from the peel (Table 3). The lower the temp, the slower the desorption rate. This was clearly seen in the 'Valencia' oranges, in which the difference between the 2 storage temp (2 and 17°C) was large. However, in grapefruit in which the difference between the 2 storage temp (17 and 12°C) was smaller, the effect of temp on EDB disappearance rate was almost negligible. The peel of polyethylene-wrapped fruit contained relatively high and persistent EDB levels, particularly at low temp. The EDB concn in the peel fell to 50% in the polyethylene-wrapped fruit after 3 days, as compared with 1 day in the unwrapped fruit (Table 3). Higher levels of EDB in the peel corresponded, in most cases, with more severe damage.

In addition to reducing the EDB desorption rate, wrapping fruit in polyethylene bags caused several other changes in the fruit's environment: the relative humidity inside the bags was close to 100%, and the CO_2 concn increased up to 5%, while the O_2 concn decreased to 17%. Thus, the higher incidence of the EDB-caused peel injuries found in polyethylene-wrapped fruit could be related to all these factors.

Storing fumigated fruit (22.1 g/m^3) in an artificially generated atmosphere containing 8-12% CO_2 at 5°C delayed the appearance of EDB damage. No EDB damage was detected after 2 weeks of such storage, while control fumigated fruit stored under normal aeration conditions developed, during the same period, 18% slight damage and 3% severe damage. (Non-fumigated control fruit stored at 5°C in an atmosphere of high CO_2 concn did not develop EDB - like peel injuries.) After 2 additional weeks under shelf-life conditions, fumigated fruit which had been kept in an elevated - CO_2 atmosphere, developed rots in 90% and severe damage in 10%. It can be assumed that in most of the rotted oranges rots developed on severely damaged tissues, since in the control fumigated fruit (in ordinary atmosphere), only 16% rots and 11% severe damage were found (Table 1).

Of the 3 citrus fruit cultivars tested, grapefruit was found to be the most and 'Valencia' oranges the least susceptible to EDB peel injury.

Table 3. The effect of storage temp and polyethylene wrappers on the ethylene dibromide (EDB) residues (ppm) in citrus fruit peel (EDB dose: grapefruit, 14.9 g/m^3; oranges, 19.5 g/m^3).

Aeration period (days)	Polyethylene wrappers	EDB residue: Grapefruit		Shamouti		Valencia	
		Storage temp (°C) 17	12	17	5	17	2
1/8	+	70	70	75	75	150	150
	-	70	70	75	75	150	150
1	+	--	49	59	58	140	121
	-	42	40	49	58	75	78
2	+	28	38	38	95	104	102
	-	17	17	20	42	36	65
3	+	38	29	38	46	84	–
	-	–	11	18	25	30	–
4	+	--	–	–	–	–	102
	-	9	–	--	–	16	43
8-9	+	–	–	8	75	–	55
	-	1	6	2	14	–	34

"+" with polyethylene wrappers.

"-" without polyethylene wrappers.

Discussion and Conclusions

The most important consideration in determining the optimal EDB dose for fumigation of citrus fruit, is the effectiveness of the treatment in controlling the Mediterranean fruit fly. All dosages used in these experiments were effective in this respect[6], so treatments which resulted in the least damage to the fruit are preferable.

Residues in the peel are influenced by several factors: e.g., EDB dose and time of exposure; duration of post-fumigation aeration period; and storage temp. Within the range we used residue and injury increased with the EDB dose. It should be emphasized that the actual EDB concn measured during the fumigation process, and not the dose calculated according to usual fumigation procedures (2), is related to the residues content and the resulting damage.

Our results indicate that the degree of injury to fumigated fruit is determined, to a large extent, by the amount of EDB residue and the length of time the residue persists in the fruit peel.

The residue levels depend on the length of the aeration period after fumigation. Desorption of EDB from the peel during aeration is exponential; it is slower at low than at high temp (Table 3). Thus, damage can be reduced either by post-fumigation aeration, or by storing the fruit at relatively high temp (12-17°C), or both. The higher the EDB dose and its initial residues in the peel, the more important is aeration.

The effect of aeration is also illustrated in experiments with polyethylene-wrapped fruit. This treatment, which limits aeration, caused an increase in the incidence of peel injury, particularly in fruit wrapped shortly after fumigation (following

3-hr and 1-day aeration periods), while EDB residue in the peel were still high. In this fruit the increase in incidence of peel injuries was particularly noticeable during the shelf-life period. This phenomenon was probably due to slower EDB desorption as well as to increased CO_2 concn inside the polyethylene bags. A similar phenomenon was also noted in fumigated fruit stored without polyethylene bags in a high-CO_2 atmosphere; in both cases, the relatively high CO_2 concn delayed development of injuries which appeared only after the fruit was stored under normal atmospheric conditions.

Storage at higher storage temp usually resulted in less EDB injury than storage at the lower temp, in accordance with the faster EDB desorption from the peel. The low storage temp itself could have contributed to the development of peel injuries by increasing peel susceptibility, particularly in grapefruit.

The increase in the incidence of EDB injuries after transfer from cold storage to shelf-life storage could be explained by the following hypothesis: development of EDB peel damage may be seen as a 2-step process. During the first step a chemical reaction occurs between EDB and active chemical groups in the peel cells, without visible changes. During the 2nd step localization of the damage takes place, probably by enzymatic action, leading finally to necrosis. Storage at low temp or at high CO_2 concn might inhibit only the second step. Therefore, little or no EDB injury is seen when the fruit is stored under such conditions. Only after transfer of the fruit to the high temp (17°C) of shelf-life and removal of the high CO_2 concn by stripping the polyethylene bags from the fruit do EDB injuries develop, although by this time virtually no EDB residues remain in the fruit peel.

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