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Captan Residues on Strawberries and Estimates of Exposure to Pickers

G. Ritcey,[1,*] R. Frank,[2] F. L. McEwen,[1] and H. E. Braun[2]

[1]Department of Environmental Biology, University of Guelph, Guelph, Ontario, Canada, N1G 2W1 and [2]Agricultural Laboratory Services Branch, Ontario Ministry of Agriculture and Food, Guelph, Ontario, Canada, N1G 2W1

The fungicide captan is widely used in Ontario to control fruit rot on strawberries (OMAF 1983). This disease is caused by the gray mould fungus (Botrytis cinerea Pass.) that infects throughout the season from blossom to ripe fruit spreading rapidly during warm wet conditions. Captan has been recommended since 1954 as the major fungicide for controlling Botrytis fruit rot of strawberries and especially since the development of resistance of this fungus to the fungicide benomyl (OMAF 1983).

In recent years concerns have been raised about the safety of captan to exposed field workers. The major route of exposure is via dermal absorption (Gunther et al. 1977) when contact is made with surface residues of any pesticide. The prime consideration in assessing exposure is therefore the disappearance rate of a pesticide from a treated plant (Nigg 1980). Field studies have been reported that assess the persistence and the rate of degradation of pesticides on different crops and the potential uptake of the residual pesticide by the field worker in terms of dermal, oral and respiratory exposure (Gunther et al. 1977, Gunther 1980; McEwen et al. 1980; Wojeck and Nigg 1980). The California Dept. of Agriculture have established guidelines on reentry intervals for 21 organophosphorus insecticides on vines and fruit trees (Knaak 1980). In 1980 the Department adopted regulations on foliar residues which required growers to test foliage for toxic residues prior to allowing entry of workers for harvesting and other activities that resulted in substantial contact with foliage (Knaak 1980).

Several workers have determined residues and assessed exposure to captan when this fungicide is applied to some vegetable and fruit crops (Hansen et al. 1978; Stevens and Davis 1981; Zweig et al. 1983). To supplement these findings field tests were conducted to determine captan disappearance from strawberries and estimate the amount of surface captan transferred to pickers harvesting the fruit. Cotton clothing was used because of its high absorbancy and minimum of penetration (Freed et al. 1980; Lillie et al. 1981). Culinary procedures were investigated to determine the loss of captan in preparation of fresh strawberries and cooked

* Correspondence and reprint requests.

strawberry products.

MATERIALS AND METHODS

In 1982 and 1983, field tests were carried out in an experimental plot of strawberries (var. Redcoat), at the Cambridge Research Station. Captan (80 WP) was applied to strawberries at the rate of 3.4 kg AI/ha using a tractor-mounted sprayer delivering 600 L/ha. Samples of leaves and ripe fruit were taken as soon as the fungicide had dried and at 1, 2, 5, 10 and 15 days after application. Sample contained 50 trifoliate leaves and 12 to 15 strawberries, each treatment was replicated four times. In the second year samples of mulch straw were taken from between the treated rows of strawberries. Foliage, fruit and straw samples were collected in polyethylene bags, sealed and forwarded immediately to the laboratory for analysis.

For the reentry study in 1982, workers were provided with the following protective clothing: cotton gloves, cotton sleeves (covering the arm from the top of the arm to wrist) and cotton leggings (covering the leg from the top part of the thigh to the ankle). Sleeves and leggings were made of factory cotton. The protective clothing was washed prior to use. On each sampling date, two workers in a kneeling position harvested strawberries for 10, 20 and 30 min on 0 day, at 24 hr (wet with dew), at 24 hr (dry) and at 48 hr after application. In 1983, two workers provided with cotton gloves harvested strawberries for 20 min 24 hr after application. After each picking interval the pieces of clothing were placed into separate bottles, covered with dichloromethane, and sealed. The samples were forwarded to the laboratory for analysis.

In 1982, freshly picked strawberries, three days after captan application, were analyzed for residues following various culinary treatments. These procedures consisted of removal of calyx, cool water rinse (10°C), warm water rinse (20°C) followed by cool water rinse, cool water rinse followed by drying, cooking, cool water rinse followed by cooking and freezing (-20°C) for three months.

For analytical procedure, strawberries were extracted by blending with an acetonitrile: water (2:1) mixture according to the multi-residue procedure described in the Pesticide Analytical Manual (1973). The extracts were filtered and a measured aliquot was diluted with four volumes of 2% sodium chloride in water and partitioned by shaking three times for 60 sec with 50 ml-portions of dichloromethane. The dichloromethane extracts were dried and combined by percolation through anhydrous sodium sulfate, evaporated to dryness with rotary vacuum at 45°C, and re-dissolved in 5 ml hexane. Cotton sleeves and leggings were allowed to soak for a minimum of two days in dichloromethane and then filtered quantitatively using dichloromethane rinse. The combined extract and rinsings were then evaporated just to dryness and re-dissolved in hexane as described above. All samples were cleaned up on activated Florisil(R) according to the procedure of Mills et al.

(1972); only the third elution fraction was collected and analyzed.

Analysis was carried out by gas-liquid chromatography, using ^{63}Ni-electron capture detection and a 1.8 m x 2 mm i.d. column packed with 1.5% OV-17/2% OV-210 on 100-120 mesh Gas Chrom Q at an isothermal column temperature of 190°C. Recoveries from blank samples of strawberry tissue fortified with captan ranged from 84% to 97%. Detection limits approximated 0.01 µg/g in strawberry tissue and 0.1 µg per clothing sample.

RESULTS AND DISCUSSION

Initial captan residues on the berries were 2.38 µg/g in 1982 and 4.05 µg/g in 1983 and declined slowly to 0.31 and 0.26 µg/g, respectively, on the 15th day after application (Table 1). Initial foliar residues were near 20 µg/g in 1982 and 28 µg/g in 1983 and declined only slightly during the first 10 days. However foliar residues on the 15th day had markedly declined for no apparent reason since there had been no irrigation or rainfall during that period. Residues on the foliage were about ten times higher (weight/weight basis) than on the berries. Initial residues on berries with or without calyx were similar and the residues on berries plus calyx showed a slow decline more

Table 1. Captan residues on strawberry foliage, berries, berries plus calyx and straw mulch[a].

Days after application	Accumulative rainfall (mm)		Captan residue (µg/g)[b]					
			berries without calyx		berries with calyx	foliage		straw mulch
	1982	1983	1982	1983	1983	1982	1983	1983
0	0.0	0.0	2.38a[c]	4.05a	4.15bc	17.2a	28.0a	97.0a
1	0.6	0.0	1.78ab	4.05a	2.48bc	23.8a	22.8ab	51.5ab
2	0.0	1.2	0.87cd	3.00a	7.05a	19.0a	20.8ab	30.0b
5	6.0	1.2	1.29bc	0.91b	5.00ab	21.2a	15.2bc	45.2ab
10	23.9	16.0	0.93cd	0.76b	3.00bc	17.2a	19.0b	3.5b
15[d]	25.5	16.0	0.31d	0.26b	1.85c	1.0b	8.7c	20.5b

[a]Treated June 22, 1982 and June 29, 1983, at the rate of 3.4 kg AI/ha.
[b]Mean of 4 replicates.
[c]Means followed by the same letter are not significantly different at the 0.05 level of probability, by Duncan's multiple range test.
[d]1982 - 14 days after application.

comparable to the decline on foliage. Residue decline was slow from both foliar and fruit surfaces, with the rate of decline being much slower on foliage. A similarly slow decline for surface residue on corn foliage was reported by Annapura (1982). Initial residues on the straw mulch were high at 97 µg/g and declined to 20 µg/g after 15 days.

Residues of captan transferred from the foliage and fruit to the garments of the worker showed no significant difference between 10, 20 and 30 min picking exposure; therefore these time exposures have been combined and presented in Tables 2 and 3, and expressed as µg/g and µg/cm^2 on gloves, sleeves and leggings. Examination of these data show that when residues are calculated in relation to surface area, the gloves accumulated three times as much captan per unit area as did the sleeves and 5 times as much as the leggings.

Table 2. Captan pick up on garments as a result of harvesting treated strawberries[a].

Garments	wt (g)	Surface area (cm^2)	Captan adhering to clothing (mg)	(µg/g)	(µg/cm^2)
2 gloves	53	1018	2.17	40.8	2.13
2 sleeves	42	2508	1.79	42.8	0.71
2 leggings	102	5473	2.68	26.1	0.49

[a]Treated June 22, at the rate of 3.4 kg AI/ha.

A number of reentry studies in the field suggest that dermal exposure is the most important pathway by which pesticides enter the body. Knaak (1980) reported that 90% of dermal exposure is through the hands. In this study the amount of captan per unit area was greatest on the gloves but, because of a greater total area, the quantity of captan was greatest on the leggings.

Captan adsorption on clothing increased rather than decreased as a result of picking two days following application (Table 3). However residues picked up 48 hr after application were greater than at 0 or 24 hr after application. Residues on clothing were slightly greater when plants were wet than dry. In both years, similar captan levels were detected on the gloves (1.18 mg in 1982, 1.24 mg in 1983).

Table 3. Residues on clothing (gloves, sleeves, leggings) following harvesting of strawberries treated with captan[a].

Hours after application	Captan residue on garments (mg)	(μg/g)[b]	(μg/cm^2)[c]
0	5.29	26.7	0.59
24	5.01	25.3	0.56
24 (wet)	6.14	31.0	0.68
48	10.14	51.2	1.13

[a]Treated June 22, at the rate of 3.4 kg AI/ha.
[b]Included cotton gloves, full length cotton sleeves and leggings.
[c]Average weight of clothing per person 198 g, Average area of clothing per person 8999 cm^2.

Wolfe et al. (1975) found that dermal exposure was greater following the application of wettable powder parathion formulation than with an emulsifiable concentrate. The highest exposure to apple thinners was 24 hr after applying parathion. It was concluded that the spray deposit on the foliage did not dry thoroughly until 24 hr after application. In these studies, pick-up changed little between 0, 24 and 48 hr.

Whether or not captan poses a danger to workers in treated crops or to those picking fruit such as strawberries that have been treated with captan is not certain. These studies suggest that captan residues on berries and foliage of strawberries are dislodgeable when the treated surfaces are handled and that residues will be transferred to workers' clothing in near equal amounts whether the exposure was 0, 24 or 48 hr following application if no rain has fallen. Captan residue on the foliage did not decline in the absence of rain and appeared available for absorption into clothing. Pickers should be advised to wear arm and leg covering to reduce exposure.

Various culinary procedures have been studied to determine the reduction of captan residues in fresh fruit and cooked food products. Rinsing captan-treated strawberries in cool water removed 14% of the residue. The removal of the calyx from the strawberries increased the removal by 36%. Frank et al. (1983) reported that captan on dipped apples decreased by 43% after following a washing procedure. After various rinsing procedures of freshly picked strawberries minus calyx reductions of residues were 43 to 63%. The most efficient rinsing procedure, a warm

water rinse followed by a cool water rinse, removed 63% of the residue from fresh strawberries where the calyx had been removed. Cooking strawberries increased the removal of captan residue to 95%. Koivistoinev (1965) studied the losses of captan residues in strawberries during various steps in preservation and reported 99% removed following boiling or autoclaving. Residues did not decline by freezing the strawberries for a 3-month period.

Table 4. Removal of captan from strawberries following various post-picking culinary procedures, 72 hr after treatment[a].

Culinary treatment[b] (newly picked)	Residue of captan (mg/kg) Mean (SD)	Captan removal (%)
With Calyx		
- none	2.37 (± 0.46)	0
- cool water rinse dried on paper towel	2.05 (± 0.15)	14
Calyx Removed		
- none	1.52 (± 0.57)	36
- cool water rinse	1.35 (± 0.52)	43
- warm water rinse then cool water rinse	0.86 (± 0.29)	63
- cook (5 min)	0.11 (± 0.07)	95
- cool water rinse then cook	0.10 (± 0.07)	96
With Calyx		
- frozen (-20°C) 3 months	2.46 (± 0.46)	0

[a]Treated June 22, 1982 at the rate of 3.4 kg AI/ha.
[b]Rinse - rinsing in a colander under tap for 20 min, cool water rinse 10°C, warm water rinse 20°C.

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