The Retention and Redistribution of Captan on Apple Foliage

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ABSTRACT

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Residue levels of captan were monitored on apple foliage during the 1980 and 1981 growing seasons. The residues did not build up on matured leaves sprayed at 7- or 14-day intervals because the captan deposits decreased rapidly between sprays. When captan was applied to runoff at 1.2 g a.i. (active ingredient) per liter, initial deposits on matured leaves were 5–13 μg a.i./cm^2. The greatest deposits occurred early in the season when foliage was sparse and penetration of the spray into the tree canopy was greater. Captan residues rapidly decreased to ~ 20% of the initial deposit as apple seedlings were subjected to 0.5–0.8 cm of simulated rain. The remaining 20% of the initial deposit was more tenacious, ie, the rate of captan loss decreased as rainfall increased. Captan residues decreased exponentially as the duration of simulated rainfall increased in laboratory studies. In the orchard, captan residues decreased linearly as the amount (ie, duration and/or intensity) of rainfall increased, but >25 mm of rain was required to reduce the captan deposit to 20% of the initial level. Seven days after captan was applied to runoff at 1.2 g a.i./L, leaves that were mature (fully expanded), immature (expanding), or not emerged at the time of application (emergent) bore captan deposits of 2.0, 1.5, and 1.2 μg/cm^2, respectively. A captan concentration threshold of 1–2 μg/cm^2 is proposed for protecting apple leaves from infection by *Venturia inaequalis*.

Additional key words: apple scab, fungicide.

Control of fungal diseases of apple with protectant fungicides requires repeated applications to maintain a chemical barrier between the surface of expanding foliage or enlarging fruit and pathogenic fungi. The protectant fungicides are usually applied at a fixed recommended rate and at intervals set by apple phenophases or by calendar dates, ie, every 7, 10, or 14 days. This strategy provides excellent control of the major fungal diseases such as apple scab, black rot, and powdery mildew, but at times excessive amounts of fungicides may be applied. Unnecessary protectant sprays may be applied during periods of weather unfavorable for disease development. Also, fungicides may be applied at the recommended rate when a lesser rate would suffice to restore the fungicide residue to an acceptable level on the surface of susceptible tissue.

One strategy to improve fungicide efficiency in current apple

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scab management programs is to time fungicide applications according to the distribution of scab infection periods (6). No strategies incorporate estimations of fungicide residue in the decision-making process for determining the rate and timing of fungicide applications perhaps because so little is known of fungicide retention and redistribution. Captan, the most commonly used protectant fungicide in New Hampshire, has been studied extensively in the laboratory (2–4,8,11–15), but only Nordby and Steinberg (9) have reported quantitative assessments of captan retention in an apple orchard. No studies on captan retention and redistribution have been designed specifically to provide data for establishing criteria to estimate residues of captan on susceptible tissue.

The objective of the present study was to quantify the relationships between rainfall and time elapsed since spraying on the retention and redistribution of captan on mature (fully expanded), immature (expanding), and emerging foliage.

MATERIALS AND METHODS

Measurement of captan residue on leaf surfaces. The formulation of captan (*N*-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide) used in all parts of our study was Captan 50 WP (Stauffer Chemical Co., Westport, CT), but all fungicide weights reported in this paper refer to the active ingredient. Residues were determined by a spectrophotometric assay (1) in which captan was removed from the leaf surfaces in benzene. A portion of the extract was reacted with resorcinol at 135 C, which resulted in an orange color. Absorbance of this extract was determined at 425 nm and the value was compared to those of a standard curve for known amounts of captan.

Captan residue on fully expanded leaves. *Laboratory experiments.* McIntosh seedlings were cut to a height of ~ 30 cm and were precision-sprayed in the laboratory with captan at 1.2 or 2.4 g/L with an apparatus similar to Szkolnik's (16). The seedlings were allowed to dry overnight and were then subjected to measured amounts of simulated rain at a rate of 60 mm/hr as described by Burchfield and Goenaga (2). The pH of the laboratory water supply varied from 6.5 to 7.0. A treatment replication consisted of the top four leaves collected from three seedlings. The areas of the adaxial leaf surfaces were recorded with a portable area meter (model LI-3000, Lambda Instrument Corp., Lincoln, NE), and the captan residue was measured as previously described. The initial fungicide deposit was measured as above on sprayed seedlings that were not subjected to simulated rain. Each treatment was replicated three times and the experiment was repeated twice.

Orchard experiments. Captan residue was monitored on apple foliage at the Mast Road Research Orchard, Durham, NH, during the 1980 and 1981 growing seasons. During 1980, semidwarf (M-7 rootstock) McIntosh, Cortland, and Delicious trees were sprayed to runoff with captan at 0.6 or 1.2 g/L by using a Bean FMC hydraulic sprayer. Captan was applied weekly from 30 April to 4 June and every 2 wk from 18 June to 30 July. Leaf samples were collected immediately before and after applications and before and after selected rains. Samples were also collected 7 days after each application from 18 June to 30 July. Leaves were collected from 12 sites in each tree canopy: the interior and exterior of the canopy, on two sides of the tree at 1, 2, and 3 m above the ground. Thus, the leaf sample which comprised a treatment replication consisted of 12 mature leaves from a single tree. The leaves were fully expanded at the time of application. Treatments were replicated three times, once on each of three trees.

During 1981, semidwarf McIntosh trees were sprayed to runoff at 1.2 g/L. Applications were made weekly from 9 April to 4 June and every 2 wk from 18 June to 30 July. Three leaf samples consisting of 12 leaves from each of three trees were collected by following the sampling technique and schedule used in 1980. Thus, although the sample composition remained constant, three leaf samples were collected from each tree in 1981, whereas only one leaf sample per tree was collected in 1980.

Temperature, duration of leaf wetness, and rainfall (amount and intensity) were recorded at the orchard by a modified hygrothermograph, tipping-bucket rain gauge, and leaf wetness indicator (7).

Captan residue on immature leaves. McIntosh seedlings were precision-sprayed in the laboratory with captan at 2.4 g/L. A treatment replication consisted of the upper three leaves of seven seedlings. The leaves were traced in situ and tagged before fungicide application, and the area of the tracings was measured with the portable area meter. After 7 days of growth in the greenhouse (21 C and ambient RH), the tagged leaves were removed, the captan residues were measured, and the increase in leaf area was calculated. Leaves that were fully expanded at the time of application were assayed immediately after spraying and 7 days later to determine the percentage of captan loss due to factors other than leaf expansion. The treatment was replicated three times.

On 17 June 1981, immature leaves in the lower-interior canopy of three McIntosh trees were tagged and the area of each leaf was traced and measured as before. The trees were then sprayed to runoff with captan at 1.2 g/L. Captan residue was assessed on the day of application and 7 days later when the tagged leaves were removed and the final areas were measured. A treatment replication consisted of a sample of 15 randomly selected tagged leaves from a single tree. Captan residue was determined as before and the decrease in captan due to leaf expansion was recorded. Leaves that were fully expanded at the time of application were also sampled to determine the decrease in captan due to factors other than leaf expansion. The treatment was replicated three times. The experiment was repeated on 1 July with one modification: the tagged leaves were located in the upper-exterior tree canopy.

Captan residues on emergent leaves. In 1980, McIntosh trees were sprayed to runoff at 7- to 14-day intervals with captan at 0.6 and 1.2 g/L. The youngest leaves on a total of 20 terminal shoots on three trees were tagged on the day of application. Seven days after each spray application, leaves that had emerged distally to the tagged leaves were removed and analyzed as a single sample for captan residue.

RESULTS AND DISCUSSION

Captan residue on fully expanded leaves: Laboratory and orchard experiments. Captan applied to apple seedlings at 1.2 or 2.4 g/L provided absolute fungicide deposits that differed by nearly 50% (Table 1). When the two deposits were subjected to specified amounts of simulated rain, the relative decrease of each deposit was always similar, suggesting that the relative decrease of the fungicide residue is not a function of the density of the initial deposit when captan is applied at rates approximating those used under orchard conditions. The effects of particle size on retention of captan may explain this phenomenon. Somers and Pring (11) found that small particles (0.5–4.5 μm) of captan were more tenacious than larger particles. In our study, the density of small particles deposited from spraying was directly proportional to the concentration of captan, because the ratio of small (more tenacious) to large (less tenacious) particles was a property of the formulation of the fungicide Captan 50 WP and not the concentration of the spray mixture. Both before and after rain, one would expect the density of small, more tenacious particles on leaf surfaces that were precision-sprayed at 2.4 g/L to be approximately twice that of leaves sprayed at 1.2 g/L.

TABLE 1. Effect of simulated rain on retention of captan deposits on apple seedlings sprayed with captan at 1.2 or 2.4 g/L and subjected to simulated rain

Simulated rain (mm)	Captan (μg/cm^2)[a] 1.2 g/L	Captan (μg/cm^2)[a] 2.4 g/L	Percentage of initial deposit[b] 1.2 g/L	Percentage of initial deposit[b] 2.4 g/L
0.0	10.4	18.5	100	100
3.8	2.0	4.8	23	21
8.9	2.1	4.2	21	26
14.0	1.2	3.3	12	20

[a]Differences between treatment means within rows are significant at $P=0.05$.
[b]Differences between treatment means within rows are not significant at $P=0.05$.

However, when both residues were expressed as a percentage of the initial deposit, they were equal (Table 1).

The relationship between captan retention and simulated rainfall was not linear (Fig. 1A). Captan deposits decreased rapidly when seedlings received simulated rain ranging from 0.5 to 3.8 mm, but the rate of loss slowed as rain continued. The $\log_{10}$ of the percentage of the initial deposit was regressed against the square root of rainfall (Fig. 1B). This yielded the equation $Y = 2.11 - 0.30X$, in which $Y = \log_{10}$ of the percentage of the initial deposit, and $X =$ the square root of rainfall (mm). This equation was used to generate the curve shown in Fig. 1A. Residue estimates generated by this equation approximated values reported by Chancogne (3), who sprayed grape, bean, potato, and tomato leaves with captan and then exposed them to simulated rain. Chancogne reported that the percentage of the initial deposit that remained after 3, 5, or 11.5 mm of simulated rain was 57, 28, and 20%, respectively. Our model would predict residues of 39, 28, and 12% after similar amounts of simulated rain.

When captan was applied in the orchard at 0.6 g/L, initial deposits ranged from 2.5 to 7.5 $\mu g/cm^2$ (Fig. 2). Captan deposits following application at 1.2 g/L ranged from 5 to 13 $\mu g/cm^2$ (Fig. 2). Fungicide residues did not increase with sequential applications, because residues decreased rapidly between applications. The highest deposits were measured in early spring when foliage was sparse and penetration of the fungicide spray into the canopy was greater. Lewis and Hickey (5) demonstrated that fungicide sprays passed more easily through the canopy to cover the foliage on the side away from the sprayer when the foliage was sparse. In our study, the foliage of trees sprayed from two sides in early spring received the equivalent of two late-season applications (Fig. 2). The density of the initial deposit decreased as the growing season progressed, probably due to the development of terminal leaves that decreased spray penetration into the canopy.

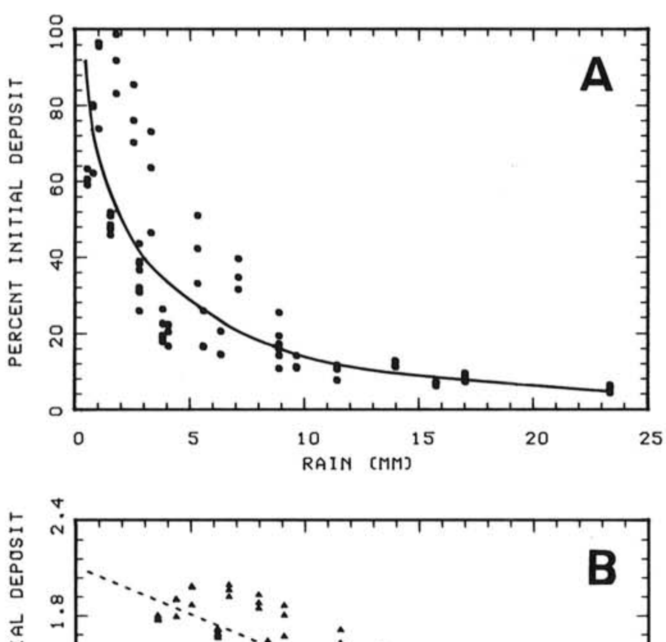

Fig. 1. A, Effect of simulated rain on retention of captan. Apple seedlings were sprayed with captan at 1.2 g/L and were then subjected to simulated rain. Residues were measured by a spectrophotometric assay. **B,** Transformed estimation of captan residue on apple seedlings exposed to simulated rain. Linear regression analysis was used to develop an equation that described the relationship between simulated rainfall and loss of captan.

To compare the removal of captan residues by simulated rain in the laboratory and natural rain in the orchard, rainfall that fell within 48 hr of a fungicide application in the orchard was plotted against the corresponding residue values (Fig. 3). These data were chosen to lessen variation in fungicide loss due to leaf wetness (caused by dew), relative humidity, and light. The amount of captan removed from leaf surfaces in the orchard was directly proportional to the amount of rain, but the relationship between retention and rainfall was not curvilinear as in the laboratory studies (Fig. 1A). More than 2.5 cm of rain was required to reduce the initial deposit of captan to 20% of the original level in the orchard, compared to only 0.8 cm of simulated rain in the laboratory. In the laboratory, there was an exponential loss of captan during simulated rain. This exponential loss of captan was not observed under orchard conditions. However, all leaves on the seedlings used in the laboratory studies were exposed directly to rain and the entire fungicide deposit was exposed to rain since only the adaxial leaf surface was sprayed. In the orchard, all leaves did not receive the same amount of rain because tree canopies sheltered some of the leaves from rain. Captan was deposited on both leaf surfaces, but the abaxial surface was exposed to less rain than was the adaxial surface. Also, redistribution of captan from the upper to the lower canopy may have occurred during rain.

Captan deposits were reduced even in the absence of rain. Rain did not occur within the 7-day interval after two fungicide applications, but the residues on leaves that were mature at the time of application were reduced by 59 and 78%. Thus, although rain is the major environmental variable that removes captan from apple foliage, other variables also reduce the residue level. These variables were considered collectively in this study by regressing the percentage of the initial deposit remaining after 2.3–2.5 cm of rain against days after application. The removal of the initial deposit increased with time (Fig. 4), suggesting that the time elapsed since application should be considered with rain in determining captan residues.

Captan residues on immature, emergent, and mature leaves. Redistribution of captan to immature leaves was dependent on location of the leaves in the canopy. The area of immature leaves collected from the upper-exterior portion of the canopy increased by 118% between the day of fungicide application and 7 days later.

TABLE 2. Actual and expected decreases in captan residue on immature apple leaves following leaf expansion after spray application

	Area	Captan decrease (%)	
Canopy location	increase[a] (%)	Actual[b]	Expected[c]
Orchard study[d]			
Lower-interior	246	26*[e]	71
Upper-exterior	118	46	54
Greenhouse study[f]			
Seedlings	210	48	68

[a] Percent area increase = (final area − initial area)/initial area × 100.
[b] Actual captan decrease was calculated as: 100 × (deposit on mature leaves on the final day − deposit on immature leaves on the final day)/deposit on immature leaves on the day of application.
[c] Expected captan decrease based on percent area increase.
[d] Trees were sprayed to runoff with captan at 1.2 g/L at 14-day intervals. Leaves were collected from terminals in the upper-exterior or lower-interior of the tree canopy. Six to 8 days elapsed between the initial and final leaf collection.
[e] Asterisk indicates difference between expected and actual residue is significant at $P = 0.05$.
[f] Seedlings were sprayed with captan at 2.4 g/L. The area of immature leaves was determined immediately after spraying and 7 days later. Difference between expected and actual residue is significant at $P = 0.05$.

Captan residue decreased by 46%, which was not significantly different ($P = 0.05$) from the expected decrease of 54% based on the increase in leaf area (Table 2). The area of immature leaves collected in the lower-interior portion of the canopy increased by 246% between the day of fungicide application and 8 days later. However, the captan residue decreased by only 26% during this interval compared to the expected decrease of 71% (Table 2). The captan residues that exceeded the expected levels in the lower tree canopy can be attributed to redistribution of fungicide from the upper to lower canopy during rain. Expanding leaves in the upper canopy received few or no splashed rain droplets containing captan. In the greenhouse study, no opportunity was provided for redistribution by rain, and there was no significant difference ($P = 0.05$) between actual and expected decrease of captan residues on expanding leaves (Table 2). Work by Szkolnik (12,16) supports the occurrence of redistribution of captan by rain in the orchard. Redistribution of captan to unsprayed foliage occurred when potted Rome Beauty trees were placed under sprayed trees in an

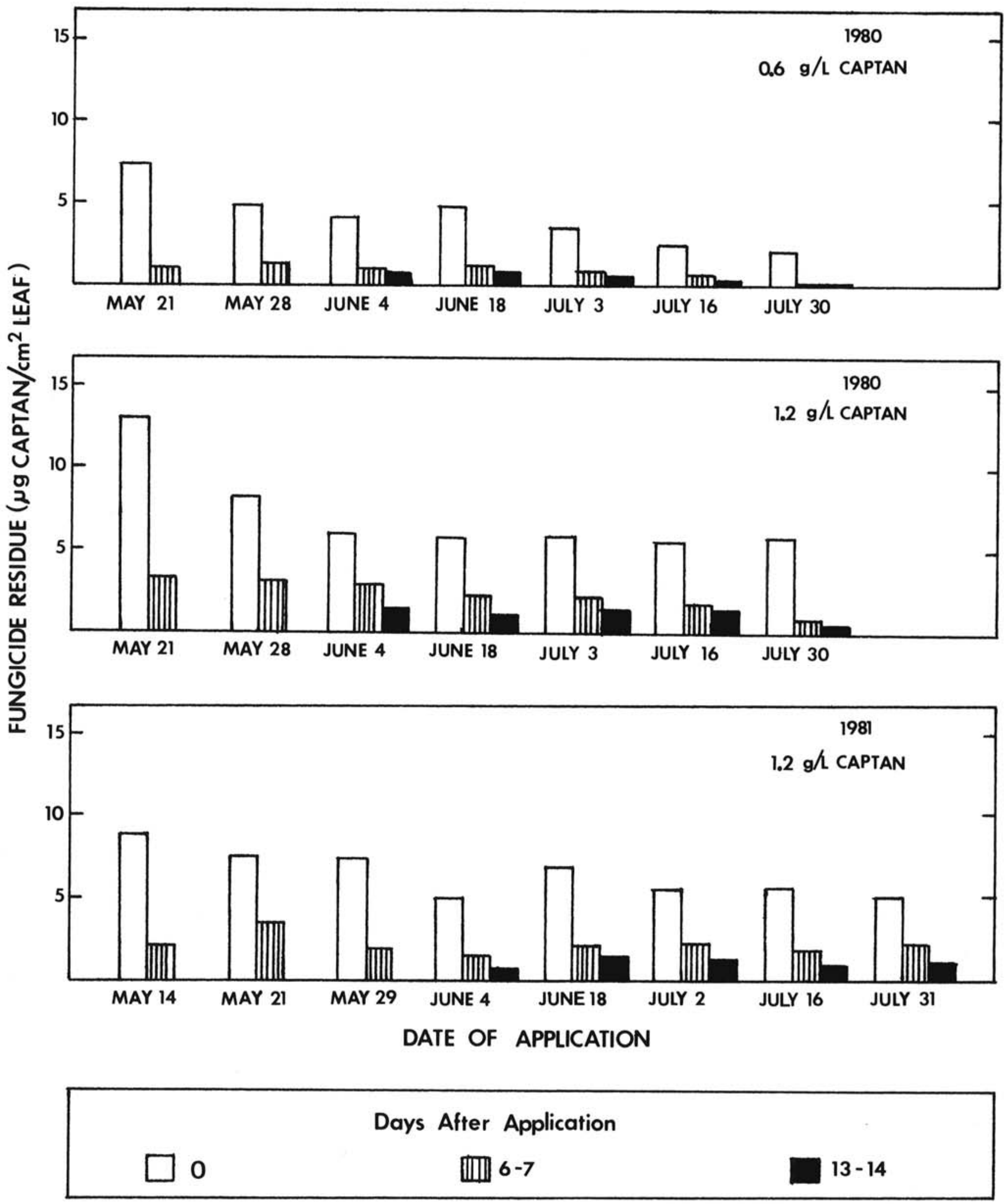

Fig. 2. Captan residue levels at the Mast Road Research Orchard during 1980 and 1981. Trees were sprayed with captan at 0.6 or 1.2 g/L at 7- and 14-day intervals. Leaf samples were collected at 0, 6–7, and 13–14 days after application. Residues were measured by a spectrophotometric assay.

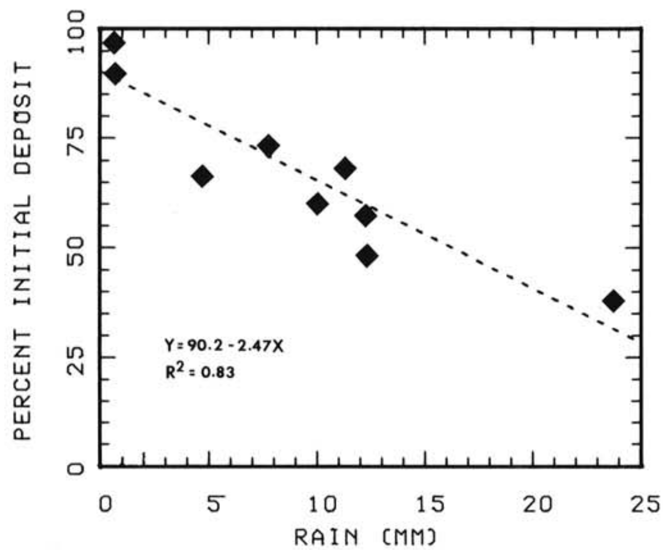

Fig. 3. Effect of rain on captan retention under orchard conditions when rain fell within 48 hr of a fungicide application. Trees were sprayed with captan at 1.2 g/L. Leaf samples were collected after rain, and the residue was measured by a spectrophotometric assay.

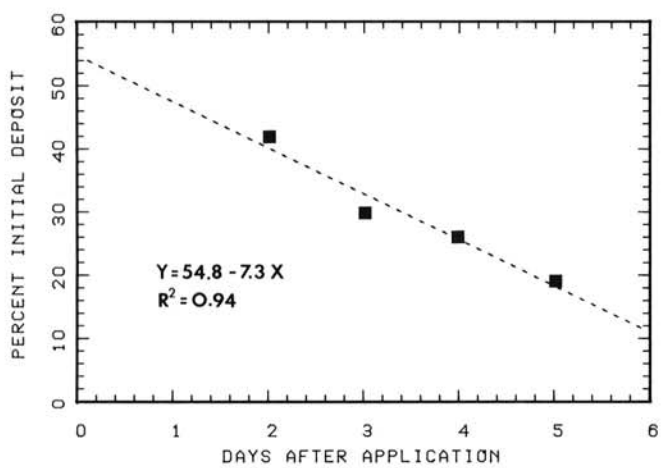

Fig. 4. The effect of time elapsed since application on the amount of captan removed by 2.3–2.5 cm of rain. Trees were sprayed to runoff with captan at 1.2 g/L. Leaf samples were collected after rain and the residue was measured by a spectrophotometric assay.

orchard during periods of rain.

Residues of from 0.5 to 1.8 $\mu g/cm^2$ (Table 3) recorded 7 days after spraying on leaves that had not emerged at the time of application suggest that captan was redistributed onto new growth. Less captan was found on emergent leaves sprayed at 0.6 g/L than at 1.2 g/L. In comparison, residue remaining on mature leaves ranged from 0.7 to 3.1 $\mu g/cm^2$ by 7 days after application (Table 3).

Rich (10) reported that applications of captan at 7-day intervals allowed only 5% leaf and fruit scab during a year that was favorable for the development of apple scab. MacHardy (*unpublished*) also applied captan at weekly intervals during the primary infection season in 1973, 1975, and 1977–1982. The highest percentage of leaves or fruit infected was 4%, and during most years fruit infection was less than 1%. Data from the present study may explain the success of a 7-day captan spray schedule and suggest a threshold level for scab control under orchard conditions. Seven days after captan was applied at 1.2 g/L, leaves that were mature, immature, or not emerged at the time of application had ~ 2.0, 1.5, or 1.2 $\mu g/cm^2$ captan, respectively. The relationship between leaf development and fungicide residue on the day of application and 7 days later is depicted diagramatically in Fig. 5. The amount of captan redistributed onto emergent and immature leaves was dependent on weather conditions and the position of the leaves in the canopy. Given that these levels of captan had provided excellent control of apple scab under conditions that were highly favorable for disease development, we propose that a captan deposit of 1–2 $\mu g/cm^2$ is the minimum level (threshold) necessary to limit scab development to commercially acceptable levels under orchard conditions. Captan residues were not assessed on fruit, but McIntosh fruit was also protected from scab development when captan residue on the foliage averaged between 1 and 2 $\mu g/cm^2$.

TABLE 3. Captan residue on emergent and mature apple leaves 7 days after application of captan at 0.6 or 1.2 g/L

Application date	Captan (g/L)	Captan residue ($\mu g/cm^2$) Emergent leaves[a]	Mature leaves[b]	Rain[c] (mm)
28 May 1980	1.2	0.7	3.1	1.0
	0.6	0.5	1.5	1.0
4 June 1980	1.2	1.6	3.1	30.5
	0.6	0.9	1.5	30.5
11 June 1980	1.2	1.8	2.8	6.6
	0.6	1.0	1.0	6.6
26 June 1980	1.2	0.8	1.6	8.4
	0.6	0.7	0.7	8.4

[a]Emergent leaves were those not present at the time of application.
[b]Mature leaves were those fully expanded at the time of application.
[c]Total rainfall in the 7-day interval between captan application and the collection of leaves for residue analysis.

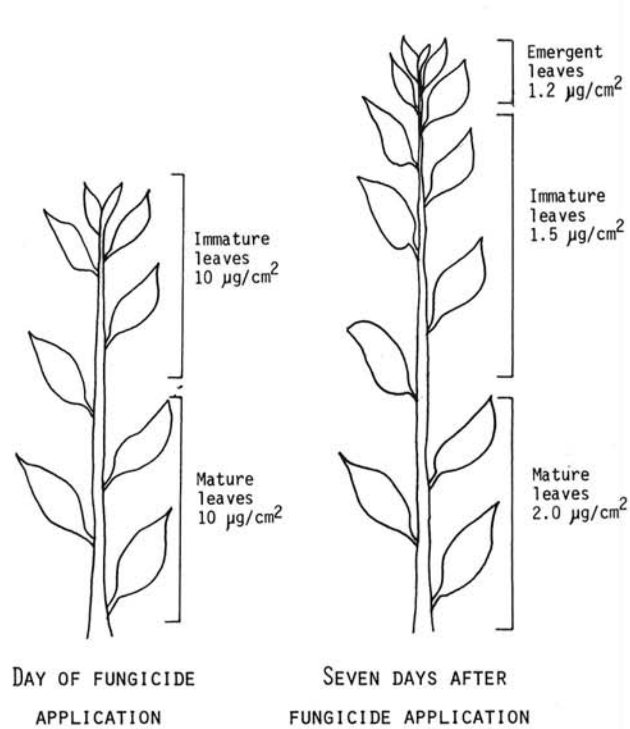

Fig. 5. Diagramatic representation of distribution of captan residue on terminal growth of apple on the day of fungicide application and 7 days later.

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