Effects of Conventional and Reduced-Volume, Charged-Spray Application Techniques on Dislodgeable Foliar Residue of Captan on Strawberries

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An air atomization, electrostatic charging spray system was used for reduced-volume (80 L/ha) applications of captan onto commercial strawberry plantings. Initial dislodgeable foliar residue from the charged reduced-volume application was higher (7.03 vs 5.33 $\mu g/cm^2$) and the first-order decay time constant was longer (9.07 vs 6.65 days) than from a conventional, high-volume (1870 L/ha) application. Comparison of charged vs uncharged reduced-volume sprays found the addition of electrostatic charging to increase spray deposit but not to increase the time constant of the decay. Pesticide deposition and decay curves for conventional application of 2.24 kg of ai/ha and reduced-volume, charged-spray application of 1.12 kg of ai/ha were found to be coincident. Implications for fruit-harvester exposure to foliar residue are discussed.

INTRODUCTION AND RATIONALE FOR STUDY

Commercial production of strawberries often involves frequent pesticide applications and continuous worker reentry for harvesting and cultural operations. The high crop value and susceptibility to pest damage require highly effective pesticide application. While development of integrated and biological pest control strategies has reduced the prophylactic and routine application of insecticides and acaricides, fungicide application is very common during the production season. Captan [*N*-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide] is one of several commonly used fungicides for control of *Botrytis* species in commercial strawberry production. Captan is generally applied prophylactically at 14-day intervals throughout the fruit production season. Fruit are typically hand-harvested at 3–5-day intervals; therefore, harvesters are continually exposed to captan (and other foliar-applied pesticides) residue on the plant foliage. Currently, the California worker re-entry interval for captan-treated fields is 4 days unless harvesters wear long-sleeved shirts and chemically resistant gloves in addition to normal work clothing.

Worker Exposure in Strawberries. Recent studies on strawberry harvester exposure to benomyl, captan, and carbaryl have shown mean dermal exposures in the range 2–39 mg/h (Zweig et al., 1983, 1984, 1985; Winterlin et al., 1984; Maddy et al., 1989). Workers wearing long-sleeved shirts and gloves had dermal exposures of <2 mg/h for captan (Maddy et al., 1989). Dermal exposures were strongly correlated with the level of dislodgeable (i.e., removable by surface extraction using surfactant solutions) foliar captan residues. This relationship led to the development of empirical foliar transfer factors (Popendorf and Leffingwell, 1982) of 2000–8500 cm^2/h for ungloved strawberry harvesters (Zweig et al., 1983, 1984, 1985), and 250–650 cm^2/h for gloved workers (Maddy et al., 1989). The practical significance of valid transfer factors is that they allow estimation of worker exposure to be based upon measurement of foliar dislodgeable residue levels.

Potential Changes in Spray Application Techniques. The previous studies of strawberry-harvester exposure have been conducted after pesticide applications were made by using conventional, high-volume (1500–2000 L/ha) and large droplet size (200–500-μm diameter) spraying techniques. While such application techniques have been commonly used in agriculture for the past decades, alternative approaches for improving the efficiency of pesticide application (Young, 1986) and use (Hislop, 1987) have been investigated. Hislop reviewed numerous studies of droplet size and concentration that indicated increased pest-control efficacy with decreasing droplet size and increased concentration. The early work of Himel (1969), who indicated desirable insecticide droplet diameters of 50 μm, has continued to be confirmed. Munthali and Wyatt (1986) investigated the effects of droplet size on efficacy of dicofol against *Tetranychus urticae* eggs. At optimal concentrations, decreasing the droplet size from 100 to 20 μm resulted in 10-fold increases in efficacy. These general trends have also been reported by Hall (1987) and Hall and Reichard (1978).

The biologically desirable small droplets discussed by Hislop can be difficult to successfully deposit due to increased aerodynamic drag and poor retention of kinetic energy. Law (1983, 1987) described the rationale for addition of electrical forces for management of small droplets in agricultural pesticide spraying and the engineering development of an embedded-electrode agricultural spray charging system which also employed a turbulent air carrier for droplet transport (Law, 1978). Adams and Palmer (1986) reported that air assistance was necessary for foliar penetration and deposition of charged droplets.

Motivation for the Study. Reduced-volume, charged droplet spray techniques have shown potential for reduction in pesticide use through improved pesticide deposition and pest control efficacy (Law and Giles, 1980). Clearly, the reduction of pesticide use is economically and

Table I. Application Parameters for the Spraying Techniques Investigated in the Study

appl technique	tank mix rate, L/ha	ai rate, kg/ha	droplet VMD, μm	ground speed, km/h
conv full	1870	2.24	185	4.6
charge half	80	1.12	55	3.7
charge full	80	2.24	55	3.6
no charge full	80	2.24	55	3.6

environmentally desirable. Moreover, potential mixer/loader exposure could be reduced since less material would be handled and the number of mix/load/refill cycles would be decreased. A limited study by Schneider et al. (1987) suggested that applicator exposure (dermal and inhalation) was lower for reduced-volume, electrostatic applications than for conventional air-blast, orchard applications. However, if an improved pesticide application technique achieves increased spray deposition, an immediate concern is that re-entry worker exposure to dislodgeable foliar residues may be correspondingly increased. If such a relationship exists, then an appropriate question is whether the increased exposure could be mitigated by coupling improved application efficiency with concomitant reductions in application rates of the active ingredient.

OBJECTIVE

The objective of this study was to determine the effects of reduced-volume charged and uncharged spraying techniques and conventional (typical industry) spraying techniques on dislodgeable foliar residue (DFR) of captan applied to commercial strawberry plantings. Specifically, the temporal decay of DFR from charged and uncharged reduced-volume applications was to be compared to values from conventional application. Further, the effect of spray charging was to be determined and a direct comparison of a conventional application and a 50% rate reduced-volume, charged-spray application was to be made.

EXPERIMENTAL DESIGN AND TECHNIQUES

Field Test Design. The study was conducted on a 40-ha commercial strawberry operation in Santa Cruz County, CA, during mid July, 1990. The strawberries were mature Pajaro plants grown on raised beds in rows spaced 35 cm apart with in-row spacings of 35 cm. The center area of a 0.7-ha field was partitioned into 25 plots used for the study. Each plot was three beds wide, and all foliar samples were collected from a 31 m long midsection of the center bed. The beds ran along a northeast–southwest orientation. A randomized complete block design was used to locate five replications of five treatments (four application techniques and one untreated control) in the test field.

Application Techniques. Captan applied to the test field was formulated as a commercially available 50% wettable powder (EPA Reg. No. 239-533-AA-11656). The diluent was well water. No adjuvants were used. The four spray application techniques investigated in the study are summarized in Table I. A high-volume, high-pressure spray application system, used by the commercial operation and typical of industry practice, was defined as the conventional full-rate technique. The conventional system was calibrated to deliver a liquid application rate of 1870 L/ha and a captan application rate of 2.24 kg/ha; the resulting tank mix concentration was 1.2 g/L. The sprayer boom configuration is shown in Figure 1. Eleven disk-core nozzles (no. D3-45) operating at approximately 1 MPa liquid pressure and producing a hollow-cone spray cloud with a volume median droplet diameter of 185 μm were used for each bed.

The three reduced-volume spray applications were made with a liquid application rate of 80 L/ha, representing a 23-fold decrease from the conventional application technique. The treatments were made by using the nozzle configuration shown in Figure 2. Three dual-port, air-atomizing nozzles were positioned above each bed. The nozzles used compressed air for atomization and transport of liquid droplets (with a volume

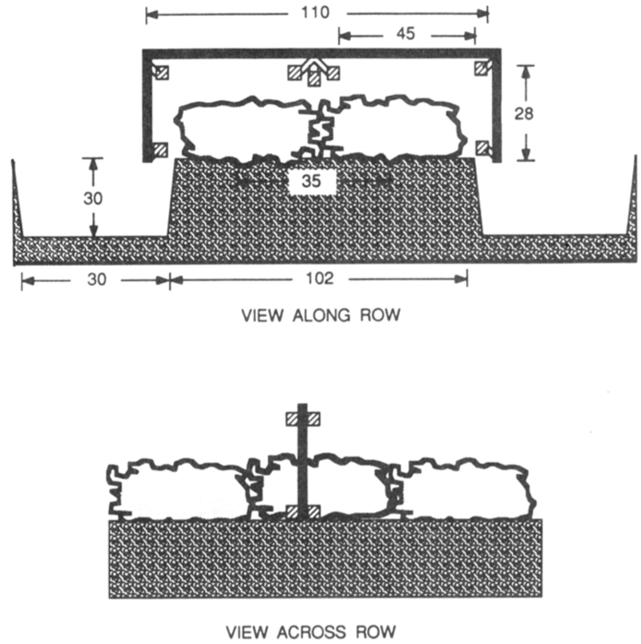

Figure 1. Strawberry bed configuration and typical position of the conventional sprayer system (11 nozzles per bed). All dimensions are in centimeters.

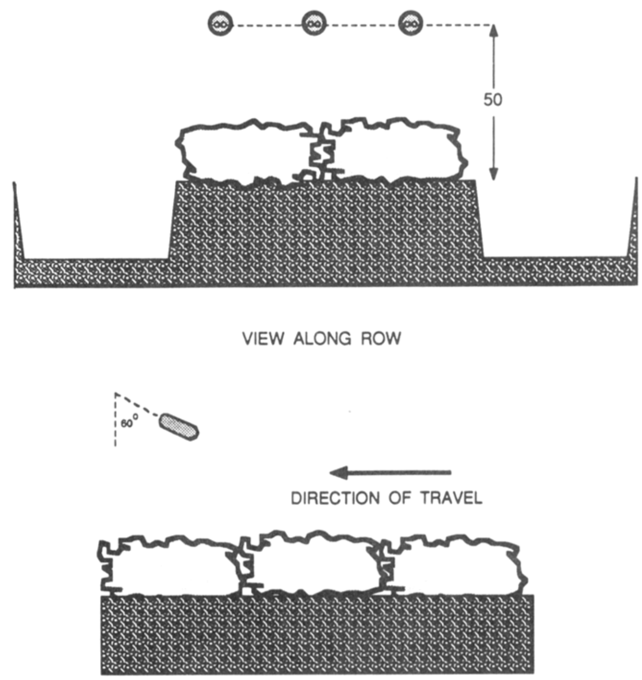

Figure 2. Typical position of the reduced-volume, air atomization spraying system (three dual-port nozzles per bed) over the strawberry bed. Bed dimensions are shown in Figure 1, and all dimensions are in centimeters.

median diameter of approximately 55 μm) into the crop canopy. An embedded electrode near the nozzle exit provided the option of electrically charging the spray droplets. The design, charging performance, and aerodynamic characteristics of the nozzle have been described by Law (1978), Frost and Law (1981), and Giles et al. (1991).

The three reduced-volume applications were selected to facilitate specific application treatment contrasts. The reduced-volume charged and uncharged full-rate treatments applied the same rate of captan, 2.24 kg/ha, as the conventional full-rate treatment. With the liquid application rate of 80 L/ha, the resulting tank mix concentration was 28 g/L or 23-fold more concentrated than the conventional tank mix. The charged full-rate application spray cloud had a charge to mass ratio of approximately −5.4 mC/kg.

Table II. Statistically Estimated Initial Deposition Values and Time Constants (with Standard Errors) for First-Order Decay of Foliar Residue from Each Application Technique

appl technique	initial deposition, Q_0, $\mu g/cm^2$	time constant, τ, days	eq r^2
conv full	5.33 (0.2)	6.65 (0.3)	0.96
charge half	5.28 (0.4)	6.81 (0.4)	0.90
charge full	7.03 (0.6)	9.07 (0.9)	0.72
no charge full	5.92 (0.6)	8.09 (1.0)	0.74
untreated	1.74 (0.2)	7.81 (0.7)	0.84

The charged half-rate application was physically identical with the charged full-rate application; however, the application rate of captan was reduced by half to 1.12 kg/ha. The tank mix concentration was correspondingly reduced to 14 g/L or 11.5-fold more concentrated than the conventional application.

Spray applications for all treatments were made during early morning (7:30–9:30 a.m.) with observed temperature and wind conditions of approximately 13 °C and 1.5 m/s (from the west), respectively. The time required for traversing the test section of each plot was observed, and proper ground speed was verified.

Foliage Sampling and Analytical Techniques. Foliage sampling and analysis techniques were similar to those used by Gunther et al. (1973) and Iwata et al. (1977). Forty leaf punches, each 2.52-cm diameter (400 cm^2 total surface area), were randomly taken throughout the plant canopy from the center section of each plot. Sample jars were sealed with aluminum foil, capped, and stored on ice during transport. All samples were extracted within 24 h after collection. Samples were collected at 2 h and 1, 3, 4, 7, and 14 days after application. Pretreatment samples were taken approximately 14 h prior to spray application; mean and standard deviation values of pretreatment foliar residue were 1.58 and 0.23 $\mu g/cm^2$, respectively. No rainfall occurred, and all irrigation water was supplied by subsurface emitter tape during the 14-day posttreatment period.

Captan was surface-extracted from the leaf disks by using two 20-min washes with 80 ppm of sodium dioctyl sulfosuccinate solution. Ethyl acetate was added to extract captan from the aqueous solution by filtering the solvent through anhydrous Na_2SO_4. Aliquots were directly analyzed for captan on a Hewlett-Packard 5880A gas chromatograph (recovery for 10 μg of captan in the aqueous extractant was 98%).

Data Analysis. The dislodgeable foliar residue (DFR) values (expressed as micrograms of captan per square centimeter of leaf area) were used to fit a first-order decay equation for each spray application technique. The form of the decay relationship was

$$Q(t) = Q_0 e^{(-t/\tau)} \qquad (1)$$

where $Q(t)$ is the quantity of DFR present on the foliage at time t, Q_0 is the initial deposition or the DFR present at time zero, and τ is a characteristic time constant. The half-life of DFR is equal to 0.693τ. Equation 1 was fitted to the observed data from each application technique by using linear, least-squares analysis on log-transformed DFR data.

RESULTS

Decay Curves. The estimated Q_0 and τ parameters representing the decay curves for each spray application technique and the fitted equation r^2 values are shown in Table II. The DFR data were well described by the fitted decay curves as indicated by the relatively high r^2 values and low standard errors of the parameter estimates. Observed data and the fitted decay curves for the conventional full-rate and reduced-volume, charged full-rate applications methods are plotted in Figure 3. Similar comparisons of the conventional full-rate and charged half-rate techniques and the effect of spray charging (charged and uncharged full-rate, reduced-volume applications) are shown in Figures 4 and 5, respectively.

Statistical Comparisons of Decay Curves. The effects of application technique on the deposit and decay of the captan were rigorously quantified through statistical comparison of the fitted decay curves. If the decay curves for two application techniques were found to be statistically coincident, it could be concluded that there was no difference between the two techniques. If coincidence was rejected, further analysis was used to determine whether initial deposition, Q_0, the time constant, τ, or both parameters differed for the two application techniques being compared.

Separate hypotheses regarding initial deposition and

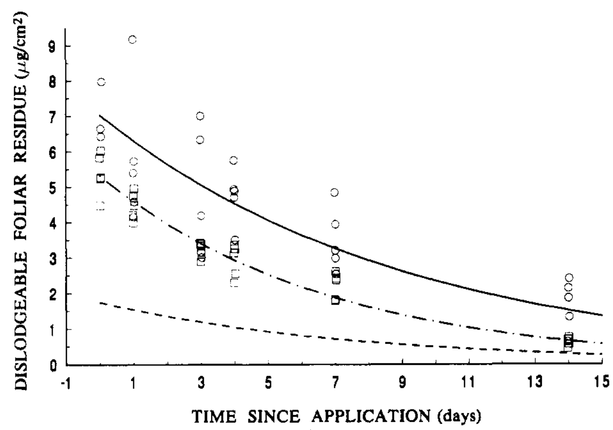

Figure 3. Observed DFR data and fitted decay curves for the conventional (□, -·-) and charged, reduced-volume (○, —) full-rate spray applications. Background DFR levels (- - -) are also shown.

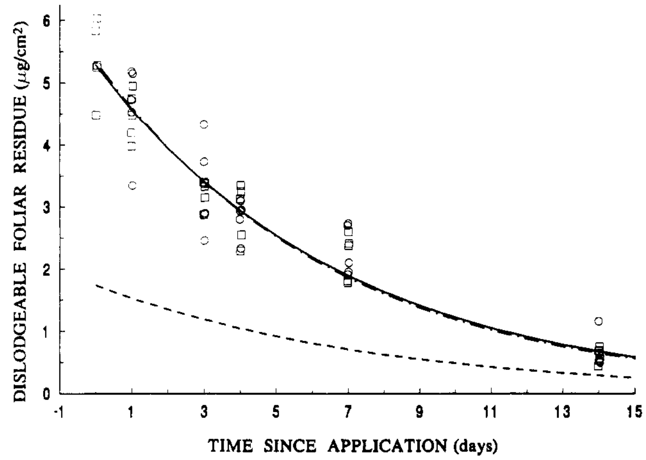

Figure 4. Observed DFR data and fitted decay curves for the conventional full-rate (□, -·-) and charged, reduced-volume, half-rate (○, —) spray applications. Background DFR levels (- - -) are also shown.

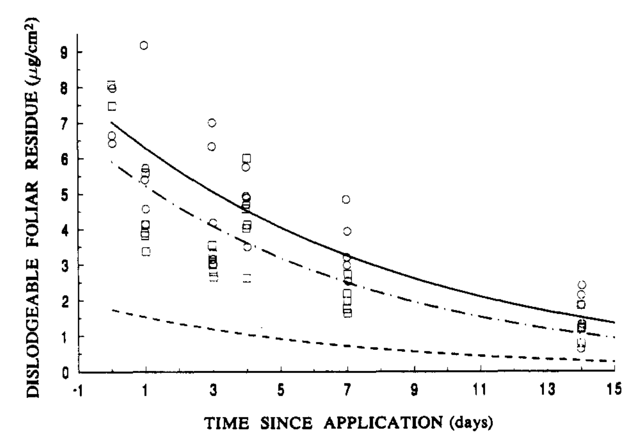

Figure 5. Observed DFR data and fitted decay curves for the charged (○, —) and uncharged, reduced-volume (□, -·-) full-rate spray applications. Background DFR levels (- - -) are also shown.

Table III. Statistical Contrasts of Hypotheses Regarding Initial Deposition and Time Constants for First-Order Decay of Foliar Residue from Each Application Technique[a]

treatment pair A	treatment pair B	H: ($Q_{0A} = Q_{0B}$)	H: ($\tau_A = \tau_B$)	H: ($Q_{0A} = Q_{0B}$ and $\tau_A = \tau_B$)
conv full	charge half	ns	ns	ns
conv full	charge full	**	**	**
conv full	no charge full	**	ns	**
charge half	charge full	**	*	**
charge half	no charge full	**	ns	**
charge full	no charge full	**	ns	*

[a] Key: ns denotes failure to reject hypothesis; * denotes rejection of hypothesis at $\alpha < 0.05$; ** denotes rejection of hypothesis at $\alpha < 0.01$.

time constant and the joint hypothesis of curve coincidence for each treatment pair were tested as shown in Table III. Each hypothesis was tested by computation of the lack of fit sum of squares produced by imposing the particular hypothesis under test. The mean lack of fit sum of squares was divided by the mean error sum of squares of the unconstrained model to produce an f statistic for the hypothesis. The hypothesis was rejected if the f value exceeded central F values for the appropriate degrees of freedom and α values. Coincidence of the decay curves was rejected for all treatment pairs except the conventional full-rate vs the charged half-rate contrast.

Decay curves for the conventional full-rate and charged half-rate application techniques were found to be statistically coincident. The coincidence was intuitively apparent from examination of the results in Figure 4. Contrasts between the conventional full-rate and charged full-rate techniques indicated highly significant differences in both initial deposition and decay time constant for the techniques. The charged application technique achieved higher initial deposition (7.03 vs 5.33 $\mu g/cm^2$) which decayed more slowly (τ of 9.07 vs 6.65 days). Coincidence of decay curves and initial deposition for the conventional full-rate and the uncharged, reduced-volume full-rate application techniques was rejected; however, the time constants were not found to differ.

Coincidence of the decay curves, initial deposition, and time constants for the charged full-rate and charged half-rate applications was rejected. The full-rate application achieved higher initial deposition (7.03 vs 5.28 $\mu g/cm^2$) and a longer time constant (9.07 vs 6.81 days). Coincidence of the reduced-volume charged half-rate and uncharged full-rate decay curves was also rejected; the full-rate application achieved a slightly higher initial deposit (5.92 vs 5.28 $\mu g/cm^2$).

Comparison of the charged and uncharged reduced-volume applications resulted in rejection of coincident decay curves. Addition of the electrical charge resulted in higher initial deposition (7.03 vs 5.92 $\mu g/cm^2$) but no significant change in the characteristic time constant of residue decay.

DISCUSSION AND WORKER EXPOSURE IMPLICATIONS

Behavior of dislodgeable foliar residue of captan was affected by the mechanical technique used for spray application. All reduced-volume application techniques investigated appeared to offer improved pesticide deposition and retention over the conventional application technique. While such benefits may be attractive from grower, economic, or environmental viewpoints, the improvements in pesticide deposition could similarly increase the potential re-entry worker exposure to the deposit.

Table IV. Potential Harvester Exposure of Gloved and Ungloved Workers to Captan Applied by Conventional and Reduced-Volume, Charged-Spray Application Techniques[a]

gloved workers: picking date days since application	exposure: conv, mg	exposure: charged, mg	ungloved workers: picking date days since application	exposure: conv, mg	exposure: charged, mg
3	17.7	26.3	4	198.6	307.4
6	11.2	18.9	7	126.5	221.0
9	7.2	13.6	10	80.9	158.4
12	4.6	9.7	13	51.0	114.2
total	40.7	68.5	total	457.0	801.0

[a] An 8-h work day and transfer factors of 8500 and 650 cm^2/h for ungloved and gloved workers, respectively, were assumed.

Comparison of the decay curves for the reduced-volume charged and no charge full-rate application techniques found the effect of electrostatic charging of the spray to be highly significant. While charging had no effect on the characteristic time constant of the decay, it significantly increased the initial deposition rate. This result was consistent with previous laboratory studies of the embedded-electrode, air atomization nozzle (Law and Lane, 1981). Since the benefit of spray charging has consistently been demonstrated, it is likely that growers would operate the reduced-volume sprayer with the spray charging system active.

Comparisons of full-rate captan applications using the conventional and reduced-volume, charged spraying techniques found higher initial pesticide deposition and a longer decay time with the charged spray application. Such behavior would suggest that potential worker exposure would be increased when the charged spray application system was used as a direct replacement for the conventional sprayer and other pest control practices such as rate and reapplication interval remained unchanged. Potential harvester exposure during the 14-day treatment period was estimated from the DFR decay curves by assuming (1) a worst-case transfer factor of 8500 cm^2/h for ungloved workers (Zweig et al., 1983), (2) a worst-case transfer factor of 650 cm^2/h for gloved workers (Maddy et al., 1989), (3) a 3-day picking interval, and (4) re-entry intervals of 3 and 4 days for gloved and ungloved workers, respectively. The results of the analysis appear in Table IV and indicate 69% and 75% increases in cumulative potential worker exposure during the four picking events.

The longer pesticide decay time characteristic of the charged application could be exploited by extending the reapplication interval of captan treatments. The typical industry practice is to apply captan at 14-day intervals. In this study, at 14 days postapplication, DFR from the conventional full-rate application was 0.64 $\mu g/cm^2$ (as calculated from the fitted decay curve). For the charged full-rate application, DFR did not decay to 0.64 $\mu g/cm^2$ until 21 days postapplication. Assuming the 0.64 $\mu g/cm^2$ DFR value is an accurate threshold point at which captan reapplication is necessary, use of the charged application technique would allow the reapplication interval to be extended to 21 days. This assumption and the following analysis are based solely on the pesticide decay results and implicitly assume that there are no other biological factors (such as growth of new target areas on the plants) which would require a 14-day interval to be maintained.

A comparison of DFR values from the fitted decay curves for such conventional and charged full-rate applications over a 42-day growing period appears in Figure 6. Within the 42-day period, three conventional applications or two reduced-volume, charged applications would be required

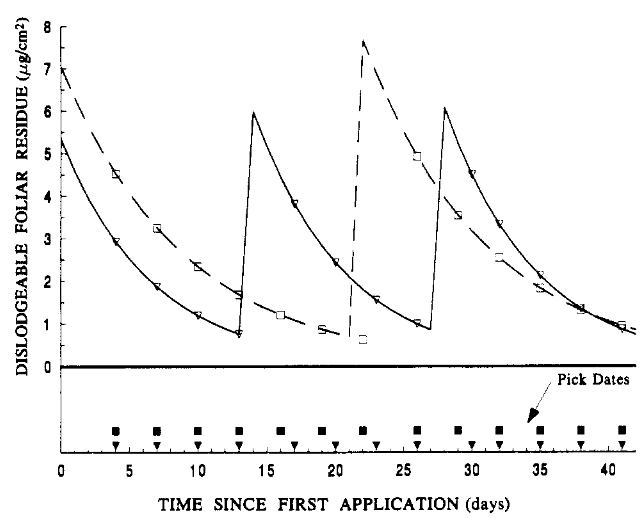

Figure 6. Dislodgeable foliar residue (from fitted decay curves) for the conventional full-rate (—) and reduced-volume charged full-rate (- -) applications over a 42-day production period. Picking dates (▼) and corresponding DFR values (▽) for the conventional and reduced-volume (■, □) applications are also shown.

to maintain the threshold DFR of 0.64 $\mu g/cm^2$. Typical fruit harvest schedules are also shown along the time axis. The schedules are for gloved workers and based on a 3-day picking interval and a 3-day re-entry interval after captan applications. Thirteen harvest days would occur for either application technique; the corresponding DFR values on the decay curves for each harvest day are indicated. As expected, the analysis showed the reduced-volume, charged spray application to result in higher DFR values (and potential worker exposure) in the periods immediately after application (viz., days 0–14 and 26). However, due to the additional application required, conventional DFR values were higher after the two later applications (viz., days 15–21 and 30–42). Over the entire 42-day period, total potential cumulative DFR exposure for harvesters was 29.5 and 27.6 $\mu g/cm^2$ for the reduced-volume charged and conventional applications, respectively. Assuming an 8-h work day and a transfer factor of 650 cm^2/h, the resulting cumulative exposures would be 153 and 144 mg for reduced-volume charged and conventional applications, respectively. A similar analysis for ungloved workers (4-day re-entry and 8500 cm^2/h transfer factor) over the 42-day period found 2.19 and 1.66 g cumulative exposure for the reduced-volume charged and conventional applications, respectively.

Since the conventional full-rate and the reduced-volume, charged half-rate application DFR decay curves were found to be coincident, potential re-entry worker exposure following each application would be expected to be similar. No evidence was found to indicate that use of the reduced-volume technique (coupled with a 50% ai rate reduction) would result in higher worker exposure during harvesting.

CONCLUSIONS

Use of a reduced-volume, charged-spray application system was found to significantly increase the initial deposition and the decay time of captan dislodgeable foliar residue as compared to those of a conventional spray application system. In contrasts of reduced-volume, air-assisted application techniques, electrostatic charging of the spray droplets was found to significantly increase the initial spray deposition (as measured by DFR). Use of the charged spray system, coupled with a 50% reduction in the captan application rate, achieved pesticide deposition and retention equivalent to the conventional, full-rate application.

Extrapolation of the study results indicated that the reduced-volume, charged-spray application technique could potentially allow a 50% reduction in applied captan and continued use of the 14-day application intervals with essentially no increase in DFR levels. However, if the application rate of active ingredient were not reduced, use of the reduced-volume system could increase potential worker exposure by approximately 70%. Alternatively, use of the reduced-volume, charged system with the full rate of captan and a longer reapplication interval could reduce the number of spray applications (and amount of applied pesticide) by one-third while increasing worker exposure to DFR by approximately 6–38% depending on worker protection practices.

The worker exposure estimates in this study were calculated by using transfer factors developed from previously reported field studies using conventional application techniques. An implicit assumption in the analysis was that transfer factors are not affected by pesticide application technique. Reduced-volume techniques characteristically use smaller, more concentrated droplets, and the addition of spray charging has been shown to alter the spatial distribution of foliar spray deposit. Such characteristics could affect the transfer factor, and the effects should be investigated.

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