

A Statistical Model of Fungicide Deposition on Potato Foliage

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ABSTRACT

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The amount of chlorothalonil deposited on potato foliage was monitored via gas-liquid chromatography to develop a mathematical description of fungicide deposition under a variety of application conditions. The effects of canopy density, potato cultivar, application method, and application dosage on the initial deposition of chlorothalonil were assessed. More fungicide was deposited on foliage at the top of the canopy than on foliage near the ground. The amount of fungicide deposited on leaves was highly variable throughout the potato canopy. The relative frequency distribution of residue levels was skewed; there were greater frequencies of low than high

concentrations. These characteristics were accurately described by a model in which the amount of fungicide deposited on potato foliage was described by a separate gamma probability distribution for each of four canopy strata. This model was appropriate under a broad range of application conditions, but factors such as plant growth, potato cultivar, application method, and application dosage affected the magnitude of the parameters. Fungicide models that ignore the variability in fungicide residue levels will overestimate the impact of fungicides on pathogen development, even when accurate plant disease models are used.

Protectant fungicides are essential for the profitable production of many crops. These pesticides were very effective, inexpensive, and readily available, so growers relied heavily on them. With the increased costs and regulations associated with fungicide use, however, there is now a need for a more comprehensive understanding of how fungicides can be used more efficiently. Because most plant disease management systems are very complex, results from field experiments can provide only a limited understanding of such problems. Mathematical models can provide the simplification necessary to obtain a more complete assessment of the impact of plant disease control measures on the crop production system and thus to identify profitable programs for fungicide deployment (9,12,21,22).

An accurate and thorough mathematical description of how fungicides are deposited, redistributed, degraded, or lost within a crop canopy is required before the role of protectant fungicides in crop production systems can be reliably assessed. Because the detailed data necessary for the development of such a model were not available, experiments were undertaken to provide a quantitative understanding of the spatial and temporal dynamics of foliage residue levels of a protectant fungicide (chlorothalonil) within a potato plant canopy. In this paper, we describe the effect of various factors on the vertical distribution of chlorothalonil residues within a potato canopy shortly after application.

MATERIALS AND METHODS

Field plot design. Chlorothalonil was applied from either a tractor- or helicopter-mounted boom sprayer. Applications were made sequentially throughout the 1979 and 1980 seasons. For experiments with the tractor-mounted sprayer, plots of potatoes consisted of four rows 4.6 m long and 0.9 m apart. In both seasons, plots were separated by fallowed areas 4.6 m wide. For tests of application by helicopter, plots of the same size separated by guard rows of potatoes were located in a commercial potato field.

Cultural practices. Foundation or certified potato seed pieces (*Solanum tuberosum* var. *tuberosum* 'Katahdin,' 'Monona,' or 'Frito Lay 774') were planted at approximately 23-cm spacings on 10 May 1979 and on 10 May, 16 May, and 6 June 1980. Seed pieces consisted of small whole tubers or pieces of tubers, each weighing about 50 g. Small whole tubers were planted without fungicide treatment, but pieces of tubers were dusted with zinc ion-maneb complex (Manzate 200, DuPont Chemical Co., Wilmington, DE 19898). Fertilizer (177 kg/ha each of N, P, and K) was applied at planting time. The herbicide 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron, 50 W, 1.7 kg a.i./ha, DuPont Chemical Co.) was applied after planting, but before plant emergence. Aldicarb (2-methyl-2-(methylthio) propionaldehyde *O*-(methylcarbonyl) oxime; 3.3 kg a.i./ha, Union Carbide, Salinas, CA 93901) was applied at planting in both years. Plants were not hilled. Similar cultural practices were followed in the helicopter application experiments, but the plants were hilled 7 wk after planting.

Fungicide applications. Chlorothalonil (Bravo 500, formulated 500 g a.i./L, Diamond Shamrock Corp., Painesville, OH 44114) was used in all treatments. Fungicide was applied either with a

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tractor-mounted hydraulic sprayer or with a helicopter-mounted sprayer at a rate of 1.34 kg a.i./ha. For ground application, fungicide was applied in 936 L of water per hectare at 10.5 kg/cm² pressure and at a ground speed of 0.143–2.0 km/hr. Fifteen nozzles (¼ T-D3-23 TeeJet, Spraying Systems Co., Wheaton, IL 60187) were mounted 0.3 m apart on a 4.9-m boom. The boom was supported 15–23 cm above the canopy. For helicopter application, chlorothalonil was applied in 37 L of water per hectare at a pressure of 1.0–1.8 kg/cm², a ground speed of 89–97 km/hr, and an altitude of 1.8–2.4 m. Twenty-nine nozzles (D5-45 TeeJet, Spraying Systems Co.) were spaced 0.3 m apart on an 8.8-m boom.

Canopy development. To assess the role of canopy density on initial deposition, canopy development was measured by estimating the percent ground surface covered by the canopy and by estimating the total leaf area per plant at various times throughout the season. To measure percent ground cover, each plot was divided into 15 contiguous 0.6–1.5-m blocks. The percent ground cover was visually assessed for each block. These assessments were averaged to form a measure of percent coverage for the total plot. Two plants located in the center of the plot were destructively sampled to assess total leaf area per plant for each cultivar on each sample date. All foliage was removed from each plant. Leaves were separated into one of four leaf surface area groups (GI = 155, GII = 77, GIII = 39, GIV = 19 cm² per leaf) by comparison with standardized leaf area diagrams. The total number of leaves in each size class was used to estimate the total leaf area per plant. Leaf area index was calculated as total canopy leaf area divided by total plot surface area.

Pesticide residue monitoring. Foliage residue levels were monitored by removing three 1.35-cm-diameter leaf disks 4 hr after fungicide application from the terminal leaflet of leaves within the potato canopy. Twenty to 40 leaves were sampled from each of two to four plots of potatoes per treatment. Leaf position within the canopy was recorded as height above ground level or as height above the top of the hill. Chlorothalonil was extracted from leaves by soaking the three disks in 3 ml of acetone for 45 min. One milliliter of the acetone solution was used for gas-liquid chromatography analysis. For samples not analyzed immediately, the acetone was allowed to evaporate from the sample vial and the

dried residue sample was sealed and stored at 0 C. Stored samples were resuspended in 1 ml of acetone for gas chromatographic analysis. Samples could be stored for up to 6 wk without measurable loss of chlorothalonil. The efficiency of the extraction procedure was 98.5 ± 2.1% ($P = 0.05$, $n = 25$).

Gas-liquid chromatographic analysis. For gas-liquid chromatographic analysis, vials were sealed with Teflon rubber laminated disks and open-top screw caps to minimize solvent volatilization and to facilitate extraction of the sample. The gas chromatograph was equipped with a 0.6 cm × 1.8 m (0.25 in. × 6 ft) column packed with 10% SP on 100/120 Supelcoport (Supelco, Inc., Supelco Park, Bellefonte, PA 16823). The argon-methane (95:5) carrier gas flow rate was 60 ml/min, the column temperature was 220 C, the inlet and transfer temperatures were 250 C, and the detector (³⁵Ni electron capture) temperature was 300 C. Under these conditions, chlorothalonil was detected 2.0–2.5 min after sample injection. The amount of chlorothalonil was computed from peak area comparisons with that of standard solutions of analytical grade (99.9% pure) chlorothalonil (Diamond Shamrock Corp.). The sensitivity of the procedure was less than 10⁻⁴ µg. Peak area was linearly related to chlorothalonil amount over the range of 10⁻⁴ to 2.0 × 10⁻² µg chlorothalonil.

Parameter estimation and statistical analysis. The gamma probability distribution was used to describe fungicide residue levels. The probability density function associated with a gamma random variable, y , is described by two parameters, α and β , according to the following:

$$f(y) = \frac{\beta^{-\alpha}}{\Gamma(\alpha)} y^{\alpha-1} e^{-y/\beta} \quad \alpha > 0, \beta > 0, y > 0,$$

in which α is a shape parameter, β is a scale parameter, and Γ is the gamma function (23).

Estimation of the shape parameter was calculated via an asymptotic approximation to the maximum likelihood estimate according to:

$$\hat{\alpha} = [1 + (1 + 4A/3)^{0.5}] / 4A - \Delta\hat{\alpha},$$

in which

$$A = \ln(\bar{y}) - 1/n \left[\sum_{i=1}^n \ln(y_i) \right],$$

and in which $\Delta\hat{\alpha}$ was obtained from a table published in Thom (23). Bias associated with the maximum likelihood estimate (13) was corrected by

$$\begin{aligned} \tilde{\alpha} &= [(n-3)/(n-1.452)]\hat{\alpha} && \text{for } n \geq 4, \hat{\alpha} < 1.0, \text{ and} \\ \tilde{\alpha} &= [(n-3)\hat{\alpha} + 2/3]/n && \text{for } n \geq 4, \hat{\alpha} \geq 1.0. \end{aligned}$$

The scale parameter, β , of the gamma distribution was estimated by the following:

$$\tilde{\beta} = \bar{y} / \tilde{\alpha}.$$

To determine goodness of fit, the Kolmogorov-Smirnov (K-S) test of maximum deviations was used to compare cumulative frequency distributions (16). K-S tests involving the gamma distribution were evaluated with tables from Schneider and Clickner (20). The cumulative frequency distribution associated with the gamma distribution was approximated with tables from Harter (10).

RESULTS

Initial fungicide deposition by a tractor-mounted sprayer. When chlorothalonil was applied with the tractor-mounted sprayer to a fully developed canopy of the potato cultivar Katahdin (leaf area index ≈ 4.5), the average foliage residue levels increased exponentially with leaf height within the canopy (Fig. 1). Although the relation between average residue level and canopy position was accurately described, the variability associated with foliage residue levels was large throughout the canopy.

To describe the vertical variability of foliage residue levels within

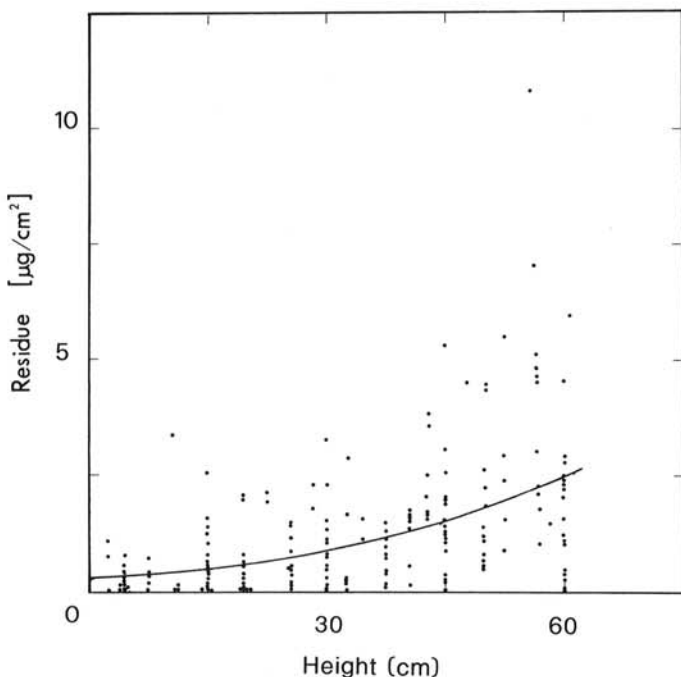


Fig. 1. Chlorothalonil residue levels on cultivar Katahdin potato foliage at various heights within the canopy 4 hr after application from a tractor-mounted sprayer. Data points indicate observed residue levels. Solid line indicates regression line (average residue = $\exp [1.10 + 0.211 (\text{leaf height})]$ $R^2 = 0.92$).

the potato canopy more completely, the relative frequency distribution of fungicide residue levels for four canopy strata (stratum I: leaf height >45 cm; stratum II: 30 < leaf height ≤45 cm; stratum III: 15 < leaf height ≤30 cm; stratum IV: leaf height ≤15 cm) were examined. For all four canopy strata, the number of residue values below the mean was greater than the number above the mean (Fig. 2). In general, the distribution of residue levels in the upper stratum of the canopy was skewed less than those of strata in the lower canopy.

Because the frequency distributions of foliage residue levels for the four canopy strata resembled gamma probability distributions, the adequacy of this family of probability distributions to describe the observed variability in foliage residue levels was tested. The samples used in this analysis were from treatments in which chlorothalonil was applied to three cultivars (Katahdin, Monona, and Frito-Lay 774) at various stages of canopy development (1.0 < [leaf area index] < 4.5) by using either tractor- or helicopter-mounted spray equipment. As measured by the K-S test, only three of the 49 empirical distributions tested differed significantly ($P = 0.05$) from the respective fitted gamma distributions. Thus, foliage residue levels followed a gamma probability distribution for all four canopy strata under a broad range of application conditions.

Effects of canopy density on initial deposition. Chlorothalonil was applied with a tractor-mounted sprayer to plots of Katahdin and Monona four times during the growing season (Table 1). For both cultivars, the leaf area index and coverage increased with time until maxima were reached, but Monona developed more rapidly

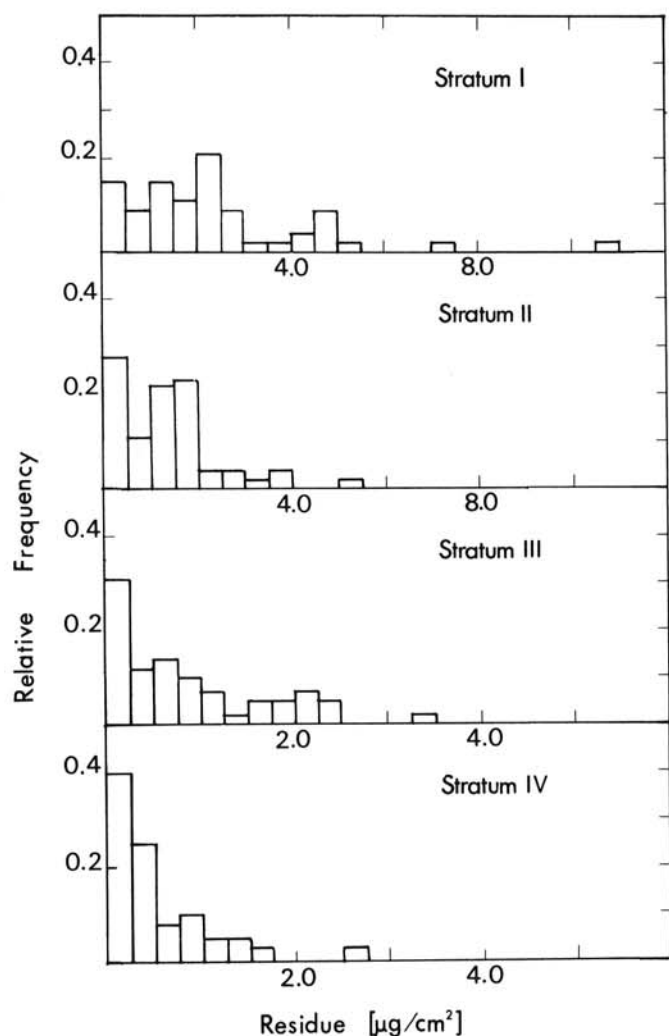


Fig. 2. Relative frequency distributions associated with foliar pesticide residues in four canopy strata of a Katahdin potato canopy. Aboveground leaf heights: stratum I, >45 cm; stratum II, >30≤45 cm; stratum III, >15≤30 cm; and stratum IV, >0≤15 cm.

than did Katahdin. The maximum leaf area index was 4.44 and 2.54 for Katahdin and Monona, respectively. The canopy of both cultivars covered 100% of the ground 74 days after planting. The total number of leaves per plant increased over time, but the relative proportion of each of the four leaf area classes was constant with time and similar for both cultivars ($G_I = 0.10$, $G_{II-IV} = 0.30$) except at the first sampling date. When plants were very small (49 days after planting) both cultivars had a high proportion of small leaves and the relative proportions of the leaf area classes differed with cultivar (for Katahdin these were $G_I = 0.15$, $G_{II} = 0.20$, $G_{III} = 0.30$, and $G_{IV} = 0.35$ and for Monona they were $G_I = 0.13$, $G_{II} = 0.12$, $G_{III} = 0.18$, and $G_{IV} = 0.57$).

For both cultivars, chlorothalonil residue levels were largest and were most evenly distributed throughout the canopy when fungicide was applied 49 days after planting (Tables 2 and 3). At this time, only 50% of the ground was covered by the canopy. By 60 days after planting, the canopy covered 83% of the ground, and further increases in total plant leaf area had very little impact on either the median fungicide residue level or the empirical frequency distribution of residue levels in any canopy level. Only the distribution of foliage residue levels obtained when chlorothalonil was applied 49 days after planting was significantly different ($P =$

TABLE 1. Canopy development during 1980 for potato cultivars Katahdin and Monona

Parameters	Days since planting			
	49	60	74	84
Growing degree days ^a	647	837	1,063	1,217
Leaf area index				
Katahdin	1.11	1.49	2.81	4.44
Monona	1.23	1.76	2.54	2.21
Percent cover ^b				
Katahdin	54	86	100	100
Monona	48	81	100	100
Total leaves per plant				
Katahdin	46	74	122	190
Monona	63	89	140	109

^aGrowing degree days since planting (base temperature = 10 °C).

^bPercentage of ground surface covered by potato canopy.

TABLE 2. Shape ($\hat{\alpha}$) and scale ($\hat{\beta}$) parameters for the gamma probability distribution estimated from chlorothalonil residue levels on foliage in canopy level for plants of potato cultivar Katahdin

Canopy stratum	Postplanting residue levels ^a							
	49 ^b		60		70		84	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$
I	5.79	0.29	1.34	1.81
II	4.91	0.42	0.46	1.76	1.09	0.60	1.19	1.14
III	0.96	1.78	1.52	0.65	0.78	0.84	0.83	1.03
IV	1.16	0.49	0.75	0.52	1.44	0.10	0.53	1.08

^aMicrograms of chlorothalonil per square centimeter of foliage.

^bDays since planting.

TABLE 3. Shape ($\hat{\alpha}$) and scale ($\hat{\beta}$) parameters for the gamma probability distribution estimated from chlorothalonil residue levels on foliage in canopy levels for plants of potato cultivar Monona

Canopy stratum	Residue levels ^a at three different periods during the season					
	49 ^b		60		74	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$
I
II	3.41	0.79	1.21	1.23	1.45	1.23
III	3.12	0.94	0.81	0.94	0.98	0.74
IV	1.39	1.08	0.59	0.29	0.61	0.53

^aMicrograms of chlorothalonil per square centimeter of foliage.

^bDays since planting.

0.01) from that obtained when chlorothalonil was applied at other stages of canopy development. Additionally, the distribution of residue levels for Monona was significantly different from that of Katahdin only at the first time period (49 days after planting). These results suggest that changes in ground coverage had a more direct influence on the efficacy of chlorothalonil coverage than did changes in total plant leaf area.

Effect of rate of application on initial deposition. To determine the effect of fungicide application rate on the distribution of foliage residues, chlorothalonil was applied at two concentrations, 1.34 and 2.68 kg a.i./ha, to plants of the cultivar Katahdin. Canopy development had stabilized and the leaf area index was approximately 4.5. For the lower half of the canopy (strata III and IV) the cumulative frequency distribution of foliage residue levels associated with the 1.34 kg a.i./ha rate of application was not significantly different ($P > 0.20$) from that of the 2.68 kg a.i./ha application rate (Table 4). The distributions of residue levels in the upper canopy levels for the two rates of application were significantly different ($P = 0.05$). Doubling the concentration of chlorothalonil resulted in a twofold increase in the amount of chlorothalonil on foliage in the top half of the potato canopy (strata I and II).

Effects of application method on initial deposition. Applications of fungicide by a helicopter-mounted sprayer and a tractor-mounted sprayer were compared with respect to the amount and distribution of fungicide on foliage of two potato cultivars, Frito Lay 774 (helicopter) and Katahdin (tractor). When the plants were small (50 and 49 days after planting for Frito Lay 774 and Katahdin, respectively), the mean foliar residue levels were greater for the helicopter than for the tractor application, especially in the upper strata of the canopy (Table 5). When the plants were older (85 and 84 days after planting for Frito Lay 774 and Katahdin, respectively), the canopy was dense and closed. Helicopter

application of chlorothalonil resulted in significantly larger residue levels in canopy strata II and III, but significantly smaller residue levels in canopy stratum IV than was obtained by ground application (Table 5). Significant differences due to application method were not observed for canopy stratum I.

DISCUSSION

Three features characterized the deposition of chlorothalonil on potato foliage under all conditions encountered in this study. First, more fungicide was deposited on leaves in the top of the canopy than was deposited on foliage near the ground. Second, the amount of fungicide deposited was highly variable at all points within the canopy. Third, the relative frequency distribution associated with foliage residue levels was skewed so that residue levels below the mean occurred more frequently than those that exceeded the mean. These characteristics were accurately described by a model in which the amount of chlorothalonil deposited on potato foliage was described by a separate gamma probability distribution for each of the four canopy strata. This model was appropriate under a wide range of application conditions, but factors such as plant growth, application method, potato cultivar, and application dosage affected the magnitude of the parameters associated with the model.

When chlorothalonil was applied with a tractor-mounted sprayer to potatoes in various phases of canopy development, the average residue level on foliage declined exponentially with increasing distance from the canopy top. The application of chlorothalonil to a dense potato canopy with a helicopter sprayer resulted in a fairly uniform coverage of foliage throughout the upper half of the canopy, but rather poor coverage in the lower canopy levels so that a sigmoidal relationship between average foliage residue levels and distance from the top of the canopy was observed. These results are consistent with those of other investigators who have reported that pesticide coverage of leaves in the top of the canopy is generally better than that of leaves near the ground (5,7,11,15). The results obtained with a tractor-mounted sprayer confirm Courshee's (4) suggestion that foliage residue levels would decline exponentially with distance from the top of the canopy when a pesticide is applied to a uniformly dense canopy, such as that of potatoes. The differences in the patterns of fungicide deposition obtained with the two application methods probably resulted from differences in droplet size spectra or in the relative importance of impaction and sedimentation to fungicide deposition (4,7,17) with the two application methods.

Fungicide coverage depends on a number of plant characteristics in addition to leaf position, including growth habit, canopy density, and leaf shape, surface texture, and pubescence (4,5,7,8,19). Differences between the cultivar Katahdin and Monona in these characteristics did not significantly affect the distribution of foliage residue levels. The greater deposition of fungicide on foliage of young plants than on foliage of older plants was more closely associated with differences in percentage of the ground covered by the canopy rather than with differences in total plant leaf area or with differences in leaf area index.

When the application dosage of chlorothalonil was doubled from 1.34 kg a.i./ha, the foliage residue levels in the upper half of the canopy were also doubled, but residue levels in the lower half of the canopy remained unchanged. Courshee (4) reported similar results on cotton and suggested that leaves in the bottom part of the canopy were more likely to be concealed from the fungicide spray than were leaves located near the top of the canopy.

These studies provide the basis for an accurate fungicide model that, when combined with models of other components of a plant disease management system, will be used to examine the efficiency and effectiveness of various approaches to disease control. Because the amount of fungicide deposited on potato foliage is highly variable and because the relationship between fungicide dosage and fungicide effect is generally not linear (2,4,6), estimates of the average efficacy of residue levels will probably differ from estimates of the efficacy of average residue levels. Thus, a stochastic fungicide model should assess the efficacy of disease control programs

TABLE 4. Shape ($\hat{\alpha}$) and scale ($\hat{\beta}$) parameters for the gamma probability distribution estimated from fungicide residue levels 4 hr after application of chlorothalonil at two dosages to foliage of plants of potato cultivar Katahdin

Canopy stratum	Application dosage			
	1.34 kg (a.i.)/ha		2.68 kg (a.i.)/ha	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$
I	1.34 ^a	1.81	1.09	4.72
II	1.19	1.14	1.11	3.10
III	0.83	1.03	0.77	1.52
IV	0.53	1.08	0.86	0.56

^aParameter estimates based on foliage residue levels measured in micrograms of chlorothalonil per square centimeter of foliage.

TABLE 5. Shape ($\hat{\alpha}$) and scale ($\hat{\beta}$) parameters for the gamma probability distribution estimated from potato foliage residue levels when chlorothalonil was applied with a helicopter-mounted sprayer to plants of potato cultivar Frito Lay 774 or with a tractor-mounted sprayer to plants of potato cultivar Katahdin

Canopy stratum	Early application ^a				Late application ^a			
	Helicopter ^b		Tractor ^c		Helicopter		Tractor	
	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\alpha}$	$\hat{\beta}$
I	4.05	0.53	1.34	1.81
II	1.21 ^d	4.53	4.46	1.76	4.25	0.64	1.19	1.14
III	0.93	4.44	1.52	0.65	0.91	2.20	0.83	1.03
IV	0.79	2.07	0.75	0.52	0.29	0.48	0.53	1.08

^aApplications were at 48 or 50 days after planting for early application and 84–85 days after planting for the late application.

^bHelicopter application of chlorothalonil (1.34 μ g a.i./ha) to cultivar 'Frito Lay 774.'

^cTractor application of chlorothalonil (1.34 μ g a.i./ha) to cultivar 'Katahdin.'

^dParameter estimates based on foliage residue levels measured in micrograms of chlorothalonil per square centimeter of foliage.

involving fungicides more reliably than can a deterministic fungicide model. Thus far, only deterministic models have been used to evaluate the use of pesticides (1,3,14,18,22). This paper presents an accurate stochastic model of the initial deposition of chlorothalonil on potato foliage. A second report will describe the effects of rainfall, temperature, and other weathering factors on the redistribution, degradation, and loss of chlorothalonil within a potato canopy.

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