

A Mathematical Model of the Spatial and Temporal Dynamics of Chlorothalonil Residues on Potato Foliage

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ABSTRACT

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The spatial and temporal dynamics of the protectant fungicide chlorothalonil on potato foliage in the greenhouse and field were described with a mathematical model. In this study, the average half-life of chlorothalonil residues for the entire potato plant canopy was 6.60 days, but half-life values ranged from 1.23 to 7.50 days depending upon weather conditions. Rainfall on the day of fungicide application had the greatest impact on the removal of chlorothalonil from potato foliage, but the effect of rain declined with aging of the fungicide deposit. The logarithmic rate at which chlorothalonil was lost from potato foliage increased linearly with increasing average daily temperature from 15 to 27 C. Chlorothalonil was lost most rapidly from foliage in the top of the plant (average half-life, 3.6 days) and least rapidly from potato leaves nearest the ground (average half-life, 21.3 days). The slower decline of fungicide from the bottom of the canopy was attributed to increased protection there and to the redistribution of fungicide from top leaves onto lower foliage.

Chlorothalonil was redistributed from top to bottom foliage more effectively by light than heavy rains. No redistribution was observed in the absence of rainfall. The magnitude of initial fungicide deposit had no effect on the rate of fungicide removal, but rates of fungicide loss differed with potato cultivar. The variability of fungicide levels within a potato canopy was generally described by a gamma probability distribution under all conditions encountered in this study. A model was developed from these data to describe the day-to-day change in both average residue levels and the variability in residue levels of chlorothalonil on potato foliage located within each of four canopy strata. In the model, a gamma probability distribution accounts for the variability in fungicide residue levels, and mean residue levels decline exponentially over time as a function of rainfall, time since application, temperature, and position within the canopy. The change in average residue levels and in the associated variability observed over time in field plots of potatoes were accurately described by the model.

Protectant fungicides are essential in disease management programs for controlling a wide variety of foliar plant pathogens. Because inoculum densities cannot be predicted accurately, these fungicides routinely are applied as protectants throughout the growing season. Increasing fungicide costs and increasing concern about the environmental impact of fungicides have produced a need for more efficient approaches to maintaining this protection.

Although mathematical models are useful for understanding how plant disease can be controlled efficiently, their effectiveness depends upon the existence of detailed information describing the essential components of the plant disease management system. Complex and accurate pathogen models have been developed, but little attention has been given to models that describe the initial deposition, redistribution, and loss of protectant fungicides. In a previous study on fungicide deposition (4), the pattern of vertical distribution of foliage residue levels immediately following application of chlorothalonil to potatoes was determined and the variation among leaves within a canopy layer was analyzed.

The purpose of the studies reported here was to examine the redistribution and loss of chlorothalonil residues on potato plants and to develop a model to account for the effects of time and weather on the spatial and temporal dynamics of that system.

MATERIALS AND METHODS

Chlorothalonil applications to Katahdin and Monona potato plants were made sequentially throughout the 1979 and 1980 seasons. Potato plots were four rows wide and were separated by fallowed areas 3.7 and 4.6 m wide. Rows were 4.6 m long and 0.9 m

apart. Cultural practices were described earlier (3).

Chlorothalonil (BRAVO 500, formulated 500 g a.i./L; Diamond Shamrock Corp., Painesville, OH 44114) was used in all treatments. Fungicide was applied with a tractor-mounted hydraulic sprayer at a rate of 1.34 kg a.i./ha in 936 L of water per hectare at 105 kg/cm² pressure and at a ground speed of 1.7–2.0 km/hr. Fifteen nozzles (1/4 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 maintained at 15–23 cm above the canopy.

Foliage residue levels were monitored by removing three 1.35-cm-diameter leaf disks 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. Leaf position within the canopy was recorded as height above ground level. The amount of chlorothalonil on foliage was determined by soaking the leaf disks in acetone and analyzing the acetone solution with gas-liquid chromatography as described previously (4).

Greenhouse experiments were conducted to measure the impact of rainfall on the removal of chlorothalonil from potato leaves. For those experiments, potato plants (*Solanum tuberosum* L. 'Norchip') were grown in the greenhouse (16–26 C) in clay pots (volume 1,040 cm³) containing peat-vermiculite mixture (1:1, v/v) with 0.4 kg each of N, P, and K per cubic meter of mixture. For all experiments, plants were 30–40 days old and had four to eight fully expanded leaves.

A 10- μ l drop of an aqueous solution of chlorothalonil (0.5 g a.i./L) was applied to the terminal leaflets of potted potato plants. The fungicide deposit was allowed to dry for 3 hr before plants were moved. Simulated rainfall was applied immediately after drying for experiments conducted on the day of fungicide application. For experiments in which rain was not applied on the same day as the fungicide, plants were stored at 20 C under artificial lighting (12-hr photoperiod).

Rain was simulated with an overhead sprinkler system, which

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employed two hollow-cone nozzles (Delavan RD 'Raindrop,' orifice no. 5, Delavan-Delta, Inc., 20 Industry Drive, Lexington, TN 38351). Water pressure was maintained at 2.67 kg/cm². Potato plants were placed on a 2.44-m-diameter turntable that rotated beneath the water spray at a speed of 10 rpm. The water droplet size distribution generated by this method closely mimicked that of a light rain shower.

Statistical methods. Parameters of the gamma probability distribution were estimated as presented previously (4). To determine goodness of fit the Kolmogorov-Smirnov (K-S) test of maximum deviations was used to compare cumulative frequency distributions (14). K-S tests involving the gamma distribution were evaluated with tables from Schneider and Clickner (22). The cumulative frequency distribution associated with the gamma distribution was approximated with tables from Harter (10). For tests of model performance, gamma random variates were generated according to an algorithm described by Phillips and Beitler (21). The first three quartiles were used to describe the cumulative frequency distribution associated with samples. The quartiles Q₂₅, Q₅₀, and Q₇₅ include values of the random variable that are larger in magnitude than 25, 50, and 75%, respectively, of the observations in the sample.

A simple exponential decay model was used to characterize the rate of fungicide loss over time and to provide a foundation for the development of a more complex fungicide model. The exponential decay model described the decline over time of the average fungicide residue levels (micrograms of active ingredient per square centimeter of foliage), r_t , according to the difference equation,

$$r_t = kr_{t-1} = k^t r_0,$$

in which k represents the proportion of fungicide remaining per day.

The model parameters were estimated with a least squares linear regression of $\ln(r_t)$ versus time such that

$$\ln(r_t) = a + bt,$$

in which $a = \ln(r_0)$ and $b = \ln(k)$. In this report, the value of b is referred to as the rate of fungicide loss. The half-life for a fungicide deposit was computed from the regression according to the equation, half-life = $[\ln(0.50)]/b$.

RESULTS

Model description. In this section, the basic form of the fungicide model is described to provide a frame of reference for the presentation of subsequent results. Matrix notation is used to describe the model because it provides a concise format for presenting the model and it allows for the clear depiction of the mathematical structure of the model. Variables denoted by italicized lowercase letters represent vectors or scalar values and variables denoted by uppercase letters are matrices. The i th element of the vector v is denoted by $v(i)$, while the i,j th element of the matrix G is denoted by $G(i,j)$.

The fungicide model describes daily changes in residue levels associated with the protectant fungicide chlorothalonil on potato foliage. The potato canopy is divided into four leaf height strata: stratum I, >45 cm; stratum II, >30 ≤ 45 cm; stratum III, >15 ≤ 30 cm; and stratum IV, ≤ 15 cm. Let r_t denote a vector whose elements, $r_t(i)$, represent the average fungicide residue levels on foliage in canopy level i ($i = 1, 2, 3, \text{ and } 4$) at t days after application of the fungicide. The basic fungicide model is described by the following:

$$r_t = K_t r_{t-1} = \left[\prod_{i=1}^t K_i \right] r_0 \text{ for } t > 0$$

in which r_0 represents the average amount of fungicide deposited on foliage on the day of the application and K_t denotes a 4×4 matrix that describes fungicide removal and redistribution.

In the model it is assumed that fungicide residue levels decline exponentially over time, but that redistribution can add fungicide

from upper canopy levels. The relative importance of decline and redistribution on day t is defined by the elements of K_t . The diagonal elements of K_t denote the proportion of the fungicide deposit that is retained within each canopy level, while the other elements of the matrix represent the proportion of the deposit that is redistributed to other canopy levels. Specifically, the elements $K_t(i,i)$ equal the proportion of fungicide retained in canopy stratum i for $i = 1, 2, 3, \text{ and } 4$ and the elements $K_t(i,j)$ represent the proportion of the fungicide deposit in canopy j that is redeposited onto foliage in canopy level i . We assume that fungicide removed from foliage in lower canopy levels is not redistributed onto foliage in upper canopy levels so that $K_t(i,j) = 0$ for all $i < j$. Thus, K_t is a lower triangular matrix and the four elements of r_t are given by (18)

$$\begin{aligned} r_t(1) &= K_t(1,1)r_{t-1}(1) \\ r_t(2) &= K_t(2,1)r_{t-1}(1) + K_t(2,2)r_{t-1}(2) \\ r_t(3) &= K_t(3,1)r_{t-1}(1) + K_t(3,2)r_{t-1}(2) \\ &\quad + K_t(3,3)r_{t-1}(3) \\ r_t(4) &= K_t(4,1)r_{t-1}(1) + K_t(4,2)r_{t-1}(2) \\ &\quad + K_t(4,3)r_{t-1}(3) + K_t(4,4)r_{t-1}(4). \end{aligned}$$

Thus far, the fungicide model is deterministic; however, a stochastic model (eg, a model that describes the variability associated with fungicide residue levels in each canopy level), can be derived from this deterministic formulation. Let the vector f_t denote a random variable whose elements represent the foliage residue levels in the four canopy levels at t days after application of the fungicide.

$$f_t = K_t f_{t-1} = \left(\prod_{i=1}^t K_i \right) f_0.$$

Since K_t is not random, the expected value of f_t is given by r_t in the deterministic model so that

$$E[f_t] = E\left[\left(\prod_{i=1}^t K_i \right) f_0 \right] = \left(\prod_{i=1}^t K_i \right) r_0 = r_t.$$

We have shown previously (4) that the variability in foliage residue levels immediately after the application of chlorothalonil follow a gamma probability distribution so that $f_0(i) \sim \text{Gamma}(\alpha_0(i), \beta_0)$ ($i = 1, 2, 3, \text{ and } 4$). Then, if fungicide redistribution is ignored ($K_t(i,j) = 0$ for all $i \neq j$), it can be shown that f_t will follow a gamma probability distribution with shape parameter vector, $\alpha_t = \alpha_0$, and scale parameter vector,

$$\beta_t = \left[\prod_{i=1}^t K_i \right] \beta_0,$$

for all t . That is, if fungicide is not redistributed, then fungicide residue levels should follow a gamma probability distribution at all times after application, the shape parameter, α_t , should remain constant over time and the scale parameter, β_t , should decline at the same rate as does the average residue level, r_t . Thus, the deterministic fungicide model should completely specify a stochastic model.

Unfortunately, the situation in the field is not as simple as the model described above because chlorothalonil is redistributed. The following sections assess the validity of the basic dynamics implied by the model's structure, determine how weather and other factors affect the values K_t , and assess the impact of redistribution on the above theoretical stochastic results.

Adequacy of a simple exponential decay model. The average amount of chlorothalonil on potato foliage tended to decline exponentially with time (Tables 1 and 2), but a fixed-rate exponential decay model, the simplest formulation of the fungicide model, did not provide an adequate description of the data. In this simple formulation, fungicide is removed at a constant rate over time ($K_t = K$ for $t > 0$), and at the same rate in all canopy strata ($K_t(i,i) = k$ for $i = 1, 2, 3, \text{ and } 4$) with no fungicide redistribution ($K_t(i,j) = 0$ for $i \neq j$). None of these characteristics appeared appropriate for describing the change over time in foliage residue levels of

chlorothalonil on potato.

Chlorothalonil was not removed from potato foliage at the same rate in each of six field experiments. The half-life of chlorothalonil throughout the canopy was 6.60 days averaged over all experiments, but the half-life of chlorothalonil in each experiment ranged from 1.23 to 7.30 days. Because differences in weather conditions probably accounted for most of the variability in these rates, K_t should be variable over time and dependent upon weather factors.

For most experiments, chlorothalonil was removed most rapidly from foliage in canopy level I and was removed least rapidly from foliage in canopy stratum IV. The half-life of chlorothalonil in canopy levels I through IV were 3.60, 5.42, 10.31, and 21.31 days, respectively, when averaged over all experiments. The half-life of chlorothalonil in each experiment ranged from 0.66 to 4.27, 1.27 to 6.58, 1.45 to 16.98, and 2.11 days to infinity ($\hat{b} = 0$) for canopy strata I, II, III and IV, respectively. The differential rate of fungicide loss in the four canopy levels provides justification for the vertical partitioning of the potato canopy. An exponential decay model best described the loss of chlorothalonil from potato foliage in canopy level I, but the adequacy of this model declined with successively lower canopy strata: stratum I, $0.78 \leq r^2 \leq 0.99$; stratum II, $0.62 \leq r^2 \leq 0.99$; stratum III, $0.49 \leq r^2 \leq 0.89$, and stratum IV, $0.00 \leq r^2 \leq 0.97$. Evidently, a second process in addition to exponential decline was affecting fungicide loss and its effect was most important in the bottom canopy stratum. Because residue levels in the bottom of the canopy often increased with time, we concluded that fungicide redistribution contributed to the change in residue levels over time.

Impact of weather on removal of chlorothalonil from potato foliage. The change in average fungicide residue levels in canopy stratum I provided the clearest estimate of how weather affected fungicide removal since redistribution from other foliage was likely

TABLE 1. Half-life of chlorothalonil residues on potato foliage in the field

Experiment	Canopy strata ^a				Experiment average
	I	II	III	IV	
1	0.66 ^b	1.27	1.45	3.72	1.23
2	1.80	2.02	3.29	2.11	2.20
3	1.36	2.79	3.49	4.60	2.50
4	1.27	2.97	3.49	22.76	2.72
5	3.49	5.95	16.98	13.51	6.13
6	4.27	6.58	9.55	13.51	7.30
7	3.49	3.98	13.51	∞^c	6.60
8	2.94	4.27	9.55	∞	6.60

^a Canopy leaf height levels were: I, >45 cm; II, >30≤45 cm; III, >15≤30 cm; and IV, ≤15 cm.

^b Half-life in days (determined by least squares linear regression of \ln [average residue ($\mu\text{g}/\text{cm}^2$)] = $a + b$ (time since application)).

^c Half life = ∞ when $\hat{b} = 0.0$.

TABLE 2. Coefficient of determination (r^2) of the exponential decay model of chlorothalonil residue levels on potato foliage in the field

Experiment	Canopy strata ^a			
	I	II	III	IV
1	0.94	0.65	0.89	0.12 ^b
2	0.78	0.98	0.76	0.97
3	0.93	0.76	0.49	0.29
4	0.98	0.89	0.97	0.08
5	0.91	0.99	0.86	0.79
6	0.98	0.92	0.85	0.60
7	0.99	0.99	0.60	0.00
8	0.98	0.62	0.51	0.29

^a Canopy strata were: I, >45 cm; II, >30≤45 cm; III, >15≤30 cm; and IV, ≤15 cm.

^b r^2 associated with least-square linear regression of \ln [average residue ($\mu\text{g}/\text{cm}^2$)] = $a + b$ (time since application).

at a minimum. Thus, in this section an expression for K_t (1,1), the first diagonal element of K_t , dependent upon daily weather was derived.

Rainfall affected fungicide removal more than any other weather factor. In the greenhouse, chlorothalonil was readily removed by rainfall (Fig. 1), but the resistance of the fungicide deposit to removal by rainfall increased as the interval between fungicide application and rainfall increased (Fig. 2). When rainfall occurred on the same day as the application of chlorothalonil, 1 cm of rain removed 66% of the fungicide deposit. When rainfall was applied 1 and 7 days after application, however, 1 cm of rain removed 55 and 36% of the deposit that was available immediately before application of rain, respectively. The relationship between amount of rainfall, time of rainfall, and the removal of chlorothalonil from potato foliage as estimated by multiple linear regression of the transformed data was described by:

$$g_t = \exp[-1.091(p_t)^{1/3} + 0.313[p_t(t-1)]^{1/3}]$$

in which g_t represented the proportion of the fungicide deposit remaining after the rain, p_t was the amount of rain (centimeters) on day t , and t denoted the number of days since the fungicide was applied. The coefficient of determination (R^2) for this equation was 0.894 and the interaction between the effects of rain and time of occurrence was statistically significant ($P = 0.01$). Because the effect of very small amounts of rainfall on fungicide removal was probably overestimated by this equation, daily rainfall amounts less than 1.0 mm had no influence on the loss of chlorothalonil from potato foliage in the model.

Temperature was also an important weather variable for describing the loss of chlorothalonil. The rate of loss in the field increased with increasing temperature (Fig. 3). After correcting for the effect of rainfall on fungicide loss, the average rate of loss for each experiment was described by a linear function of average temperature such that

$$d_t = \exp[-0.043(\text{temp} - 15.5)] \quad 15.5 \leq \text{Temp} \leq 25.5 \text{ C}$$

$$d_t = 0.60 \quad \text{Temp} > 27.5 \text{ C}$$

$$d_t = 1.00 \quad \text{Temp} < 15.5 \text{ C}$$

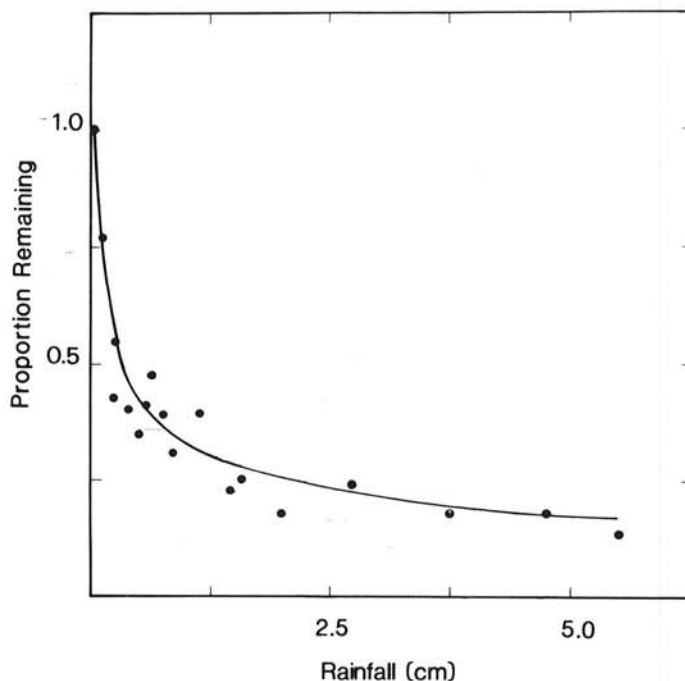


Fig. 1. Effect of simulated rainfall on removal of chlorothalonil from potato foliage. Results from greenhouse experiments in which simulated rain was applied at a constant rate to foliage of potted plants 3 hr after application of fungicide.

in which d_i was the proportion of the fungicide deposit remaining. Because temperatures above 27.5 C were not encountered experimentally, we assumed that the maximum effect of temperature on the loss of chlorothalonil occurred at 27.5 C.

A very accurate description of the change in chlorothalonil residue levels over time in the top canopy stratum was obtained by including the effects of rainfall, time since application, and temperature in the basic exponential decay process. Thus, the amount of fungicide on foliage in the top canopy level, $r_i(1)$, was described by the following:

$$r_i(1) = K_i(1,1)r_{i-1}(1) = d_i g_i r_{i-1}(1).$$

The coefficient of determination associated with using this model to predict $\ln[r_i(1)]$ was 0.914, and no significant trend in the prediction errors was observed (Predicted = $-0.075 + 1.08 \times$ Observed). The performance of this model was always superior to that of a fixed-rate exponential decay model ($r^2 = 0.422$) and to that of an exponential decay model with rainfall effects ($R^2 = 0.611$). Because fungicide redistribution was likely to be minimal in the top of the canopy and because canopy growth was also at a minimum during these experiments, the model provides an adequate description of the major processes that affected the removal of chlorothalonil from potato foliage.

Fungicide loss in canopy strata II, III, and IV. Fungicide was lost most rapidly from the top canopy level and was lost at successively slower rates downward in the canopy. Two separate processes produced this effect. First, fungicide removal was most rapid from the top canopy level because it was most weathered. Second, net removal from the lower canopy strata was reduced further because fungicide removed from top leaves was redeposited onto lower foliage. These processes were best described by the model when the rate of fungicide loss in canopy strata II, III, and IV equaled 0.471 times that of canopy strata I (eg, $K_i(i,i) = [K_i(1,1)]^{0.471}$ for $i = 2, 3,$ and 4) and when the redistribution of chlorothalonil was used to

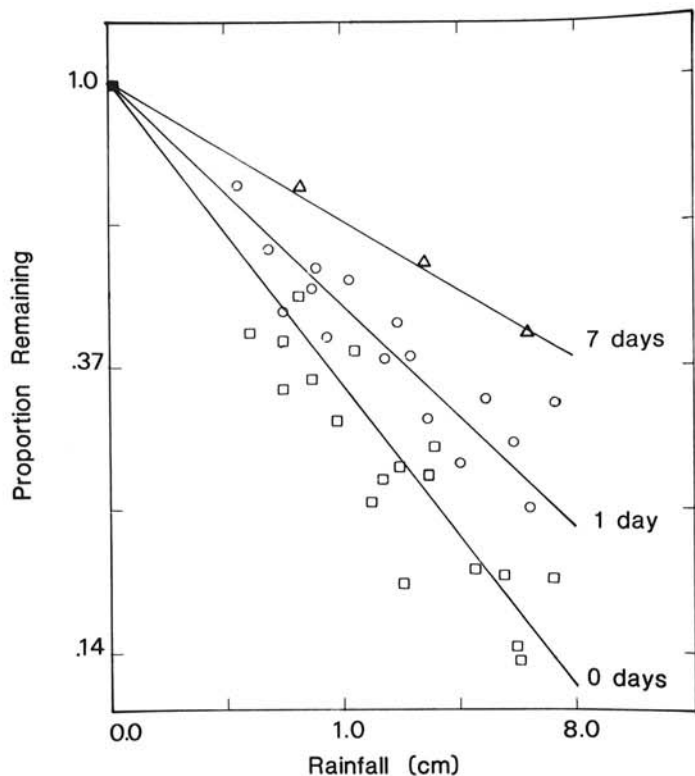


Fig. 2. Results of greenhouse experiments to assess the interaction of rain and time since application on the removal of chlorothalonil from potato foliage. Symbols: \square , rain applied same day of application; \circ , rain applied 1 day after application; Δ , rain applied 7 days after application. Proportion remaining = (the amount of fungicide on leaves after rainfall)/(amount present immediately prior to application of rainfall).

account for remaining differences in the rate of fungicide removal between the canopy strata.

Rainfall was the only weather variable that clearly affected redistribution. Redistribution was absent or sporadic when rainfall did not occur or when rainfall exceeded 1.0 cm. The parameter z_{i-j} was used to describe the redistribution of chlorothalonil on potato foliage. In the model, z_{i-j} was defined as the proportion of fungicide that had been removed from canopy level j and redeposited onto foliage in canopy level $(i-j)$. For Katahdin, z_{i-j} equaled 0.05, 0.20, and 0.20 for $(i-j) = 2, 3,$ and 4. In the model, z_{i-j} equals zero if $p_i = 0.0$ or if $p_i > 1.0$.

Other factors affecting the rate of fungicide loss. Besides weather and canopy position, potato cultivars also affected the rate of chlorothalonil loss from potato foliage (Table 3). The half-life of chlorothalonil on Katahdin when averaged over the entire canopy was 8.80 days, while that on Monona was 37.47 days over the same period. Canopy density was constant over time, but differed with cultivar (leaf area index, 4.4 and 2.7 for Katahdin and Monona, respectively) and probably accounted for the different rates of fungicide loss between the two cultivars. The ratio between the proportion of fungicide remaining per day for Monona relative to that of Katahdin was nearly constant for all canopy levels and averaged 1.06. Thus, the effect of cultivar on fungicide removal, cv , was incorporated into the model by

$$r_i = cv (K_i r_{i-1}),$$

in which cv is a scalar and equals 1.06 for Monona and 1.00 for Katahdin.

TABLE 3. Half-life of chlorothalonil from foliage of potato cultivars Katahdin and Monona

Canopy strata ^a	Katahdin	Monona
I	3.50 ^b	5.06
II	7.15	57.76
III	13.86	∞
IV	∞^c	∞
Canopy average	8.80	37.47

^a Canopy strata were: I, >45 cm; II, >30 ≤ 45 cm; III, >15 ≤ 30 cm; and IV, ≤ 15 cm.

^b Half-life in days.

^c No decline in fungicide residue levels. Half life = ∞ when $\hat{b} = 0.0$.

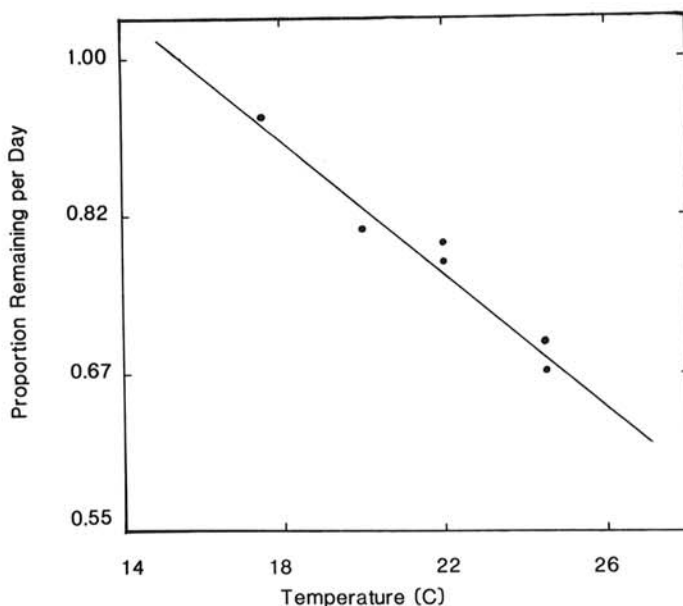


Fig. 3. The effect of temperature on the loss of chlorothalonil from potato foliage in the field. (Temperature is the average temperature during the experiment; proportion remaining is the average proportion of fungicide retained on leaves during experiment).

The amount of chlorothalonil initially deposited on foliage did not have a clearly identifiable effect on the rate of fungicide loss (Table 4). Repeated applications of chlorothalonil to Katahdin one, two, and three times in the same day resulted in average canopy residue levels of 5.07, 9.24, and 17.79 g/cm², respectively, while the respective half-lives for these deposits were 6.27, 7.49, and 7.24 days. Therefore, in the model, the rate of fungicide loss or redistribution is assumed independent of the amount of fungicide deposited on foliage.

For chlorothalonil on potato foliage the elements of the matrix K_t are defined by

$$\begin{aligned} K_t(1,1) &= g_d d_t c v \\ K_t(i,i) &= [K_t(1,1)]^{0.471} \quad i = 2, 3, \text{ and } 4 \\ K_t(i,j) &= [1 - K_t(j,j)] z_{i-j} \quad i > j \\ K_t(i,j) &= 0.0 \quad i < j. \end{aligned}$$

Stochastic considerations. The variability in chlorothalonil residue levels at various times after application was accurately described by a gamma probability distribution. Of 124 samples of foliage residue levels from all four canopy strata, the cumulative frequency distribution of 119 samples was not significantly different ($P = 0.05$) from an empirically fitted gamma probability distribution. Thus, fungicide residue levels, f_t , retained gamma distributions over time in accordance with the theory derived earlier.

Fungicide redistribution influenced the way that the parameters of the gamma distribution changed over time. The shape parameter vector, α_t , declined over time causing the scale parameter vector, β_t , to decline at a rate slower than that of the mean, r_t . These results were used to describe the variability associated with chlorothalonil residue levels on potato foliage as a function of the deterministic model that describes r_t . Since residue levels in $f_t(i)$ in each canopy stratum, $i = 1, 2, 3, \text{ and } 4$, follow a gamma probability distribution with parameters $\alpha_t(i)$ and $\beta_t(i)$ for $t \geq 0$, the expected value of $f_t(i)$, which is $r_t(i)$, is equal to the product of $\alpha_t(i)$ and $\beta_t(i)$. Then since $\alpha_t(i)$ declines at a constant rate over time, the values of the shape and scale parameter vectors, α_t and β_t , respectively, can be described by the following equations:

TABLE 4. Half-life of chlorothalonil from Katahdin potato foliage as influenced by number of applications^a

Canopy strata ^b	Number of applications		
	1	2	3
I	3.47 ^c	4.39	4.47
II	4.05	6.08	6.66
III	13.08	15.75	10.04
IV	38.51	12.84	12.60
Canopy average	6.27	7.49	7.24

^aAll applications were made on the same day.

^bCanopy strata were: I, >45 cm; II, >30 ≤ 45 cm; III, >15 ≤ 30 cm; and IV, ≤ 15 cm.

^cHalf-life in days.

TABLE 5. Model performance—range in half-life values of chlorothalonil residues on potato foliage for eight time series

Canopy strata ^a	Observed range	Fixed-rate model	Complete model
	I	0.66– 4.27 ^b	3.72
II	1.27– 6.85	5.42	1.49– 6.66
III	1.45– 16.98	11.20	1.76– 8.56
IV	2.15– ∞ ^c	22.76	2.06– 12.16

^aCanopy strata were: I, >45 cm; II, >30 ≤ 45 cm; III, >15 ≤ 30 cm; and IV, ≤ 15 cm.

^bHalf-life in days.

^cNo decline in fungicide residue levels. Half life = ∞ when $\hat{b} = 0.0$.

$$\alpha_t = m' I \alpha_{t-1} = [m' I]^t \alpha_0$$

$$\beta_t = h' I r_{t-1}$$

in which r_t is described by the deterministic model and I is a 4×4 identity matrix. The elements of the 1×4 vector h' equal

$$h'_t(i) = \frac{1}{\alpha_{t(i)}} \quad i = 1, 2, 3, \text{ and } 4.$$

For Katahdin, $m'(i)$ values of 0.89, 0.90, 0.93, and 0.97 and $\alpha_0(i)$ value of 2.43, 1.57, 1.68, and 0.98 for $i = 1, 2, 3, \text{ and } 4$, respectively, provided the best fit to the data used for model development.

Thus, the spatial and temporal dynamics of chlorothalonil residue levels on potato foliage are described by the following model:

$$f_t \sim \text{Gamma}(\alpha_t, \beta_t)$$

$$E[f_t] = r_t$$

$$r_t = K_t r_{t-1}$$

$$\alpha_t = [m' I]^t \alpha_0.$$

$$\beta_t = h' I r_t.$$

Model performance. To assess model performance, chlorothalonil residue levels on potato foliage observed in the field were compared with residue levels predicted by the model when using the same weather data. The analysis was of two types. The first test determined whether the complexities incorporated into the deterministic model provided a better description of the data than could be obtained with a simple exponential decay model. This

TABLE 6. Comparisons of observed half-life of chlorothalonil on potato foliage with model predictions, an independent test of model performance

Experiment	Values that were:	Canopy strata ^a				Canopy average
		I	II	III	IV	
1	Observed	... ^b	2.30	2.94	5.42	3.12
	Predicted	...	2.20	3.49	9.55	3.55
2	Observed	...	1.12	2.79	9.55	2.22
	Predicted	...	1.09	2.94	4.27	2.01
3	Observed	2.30	2.94	3.49	13.50	3.52
	Predicted	1.80	3.72	3.98	5.95	3.21
4	Observed	1.16	2.30	2.52	2.65	1.93
	Predicted	1.09	2.65	2.94	3.72	2.10

^aCanopy strata were: I, >45 cm; II, >30 ≤ 45 cm; III, >15 ≤ 30 cm; and IV, ≤ 15 cm.

^bHalf-life in days.

TABLE 7. Comparisons of the cumulative frequency distribution of actual chlorothalonil residue levels of potato foliage in the field with those predicted by the model: an independent test of model performance

Experiment	Quartile						
	Q ₂₅ ^a		Q ₅₀ ^b		Q ₇₅ ^c		Maximum deviation ^d
	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	
1	0.06 ^d	0.22	0.20	0.36	0.41	0.56	0.325*
2	0.03	0.03	0.19	0.11	0.37	0.42	0.150
3	0.00	0.00	0.02	0.01	0.09	0.10	0.125
4	0.31	0.16	0.52	0.43	1.00	1.23	0.175
5	0.00	0.00	0.06	0.03	0.35	0.10	0.271
6	0.00	0.00	0.008	0.002	0.005	0.06	0.200

^aResidue level that exceeds 25% of the observed residue levels.

^bResidue level that exceeds 50% of the observed residue levels.

^cResidue level that exceeds 75% of the observed residue levels.

^dFoliage residue level (micrograms of chlorothalonil per square centimeter of foliage).

* $P = 0.05$.

comparison used residue data employed in model development. The second test measured the predictive capacity of the complex model and was performed with data not used in model development.

The complex fungicide model developed here was superior to that of a fixed-rate exponential decay model. As measured by the coefficient of determination, the complex model ($R^2 = 0.929, 0.895, 0.865, \text{ and } 0.741$ for canopy strata I through IV, respectively) described a greater proportion of the observed variability in the data than did a fixed-rate exponential decay model ($r^2 = 0.422, 0.523, 0.206, \text{ and } 0.024$ for canopy strata I through IV, respectively). By incorporating the effects of weather on fungicide loss, the complex model's predictions accurately reflected the observed variability in the rate at which chlorothalonil was removed from potato foliage, but the fixed-rate exponential decay model did not (Table 5).

The complex model was also an accurate predictor of fungicide residue levels when tested against data not used in model development. It predicted the change over time in both the average residue levels and the variability in foliage residue levels (Tables 6 and 7). The average canopy half-life for chlorothalonil on potatoes was 3.12, 2.22, 3.52, and 1.93 days for the four time series used in this analysis, while the fungicide model predicted half-life values of 3.55, 2.01, 3.21, and 2.10 days, respectively. In general, average residue levels predicted by the complex model agreed with observed values on both a linear scale ($R^2 = 0.820, 0.872, 0.871, \text{ and } 0.883$ for canopy strata I through IV, respectively) and a logarithmic scale ($R^2 = 0.947, 0.923, 0.724, \text{ and } 0.377$ for canopy strata I through IV, respectively). The model was least accurate when used to predict $\ln r_t$ for the bottom canopy level. This discrepancy, however, is unlikely to have a serious influence on the model's accuracy in application because the initial amount of chlorothalonil deposited on foliage in this canopy stratum was generally small. Thus, the fungicide model appeared to provide a very accurate deterministic representation of the loss and redistribution of chlorothalonil throughout a potato canopy.

The variability in chlorothalonil residue levels predicted by the model was very similar to the observed variability. The predicted cumulative frequency distribution of residue levels throughout the entire potato canopy was similar to the corresponding observed cumulative frequency distribution in five of the six comparisons (Table 7). Additionally, the predicted cumulative frequency distributions for residue levels in each canopy were in close agreement with those observed in the field. As measured by the K-S test, model predictions were similar to observed cumulative frequency distributions in 18 of 22 comparisons and were significantly different from the observed in only four instances (one comparison: $P = 0.20$, three comparisons: $P = 0.05$). Thus, the fungicide model accurately depicted the impact of weather and position within the canopy on the variability associated with chlorothalonil residue levels on potato foliage.

DISCUSSION

In this report, a mathematical model that accurately depicted the quantitative changes both in average residue levels and in the variability of residue levels of chlorothalonil on potato foliage was developed and tested. The model was based upon exponential decay in which fungicide residue levels followed a gamma probability distribution. The impact of rainfall, time since application, temperature, and canopy position on fungicide loss and redistribution were needed to predict foliage residue levels reliably.

Rainfall was the most important weather variable affecting the loss of chlorothalonil from foliage. In greenhouse experiments, small amounts of rain removed a large proportion of the original deposit, but the remaining deposit was difficult to remove with more rain. A similar pattern of fungicide loss due to rainfall has been reported for chlorothalonil (12,15,27,28) and certain copper compounds (24).

In greenhouse tests, the effect of simulated rain on fungicide loss declined as the deposit aged. Because rainfall was highly correlated

with time since application, field observations could not be used to estimate the effect of rain on fungicide removal accurately. This same correlation probably explains why other workers have been unable to correlate the loss of chlorothalonil with rainfall (13,16,19). Additionally, the correlations among time and other weather variables greatly restricted the reliability and applicability of weather-dependent pesticide models that have been derived with multiple linear regression (17,18). For example, because the correlations that exist among weather variables can differ with season and geographic location, and because these correlations affect the accuracy with which the parameters of a statistically derived model can be estimated, the reliability of predictions of pesticide loss generated by these models will also differ when they are applied to different seasons and geographic locations.

The rate at which chlorothalonil was removed from foliage increased with increasing temperature. It seems likely that the temperature effect resulted from the volatilization of chlorothalonil. Volatilization is theoretically a function of the inverse of absolute temperature (25); however, for the range of temperatures encountered in our study, a linear function of temperature described the data as well as did the theoretical relationship. Since the range of temperatures used in model development was quite restricted, predictions of the impact of temperature on the loss of chlorothalonil should be interpreted cautiously if average daily temperatures are consistently below 15 C or consistently above 30 C.

To describe the initial deposition of chlorothalonil on potato, the canopy was divided into four vertical strata because more fungicide was deposited onto foliage in the top of the canopy than in the bottom (4). In this study, the horizontal partitioning of the potato canopy was also necessary because chlorothalonil was lost most rapidly from foliage in the top canopy stratum and least rapidly in the bottom canopy stratum. Lukens and Ou (13) reported a similar relationship for chlorothalonil on tomato and attributed the rapid loss of fungicide in the top canopy stratum to dilution resulting from new foliage growth. Because canopy density remained constant in our experiments, dilution by new foliage growth was not important. Instead, the differential rates of fungicide loss probably occurred because residues on foliage in lower canopy strata were protected from rainfall by foliage in the upper canopy, and because fungicide washed from foliage in the top of the canopy was redeposited onto foliage in the bottom of the canopy. As in other studies (8,20), we found that fungicide redistribution was greatest with light rains and that heavy rainfall prevented redistribution. No redistribution of chlorothalonil was found in the absence of rainfall.

We found that chlorothalonil was removed more rapidly from Katahdin than from Monona. The difference between the rate of fungicide loss for the two cultivars remained constant throughout the four canopy strata, suggesting that the basic processes described in the fungicide model affect the removal of chlorothalonil from Monona in a manner similar to that from Katahdin. Thus, the influence of cultivar on fungicide loss was included in the model by multiplying predicted residue levels by a constant. Since the canopy of Monona is quite different from that of Katahdin (4), it seems likely that this fungicide model similarly can be adjusted to predict the loss of chlorothalonil from foliage of other potato cultivars.

The loss of pesticides from plant foliage has usually been described by a simple exponential decay model with a fixed rate of decay (1,5,6,9,11,23,30). More complex pesticide models (3,17,18,26,29) have not described the variability in residue levels. The results presented here suggest that the exponential decay model provides a good theoretical foundation for understanding how residue levels decline over time. However, because weather affects the rate of fungicide loss and affects the importance of fungicide redistribution, the use of an exponential decay model alone is inappropriate for more detailed analyses. Additionally, because foliage residue levels can be highly variable and because the dosage-response relationship of pesticides is generally not linear (2,6,7,9,13), pesticide models that ignore variation in residue level are likely to predict pesticide efficacy inaccurately.

Mathematical models are useful for understanding how plant disease can be managed efficiently. In a previous report (3), a deterministic fungicide model was used with a simulation model to describe the development of *Phytophthora infestans* on potatoes and to obtain a qualitative assessment of how plant resistance and environmental variability affected the effectiveness of fixed-interval fungicide spray programs for controlling potato late blight. The use of the fungicide model developed in this report with accurate models of other components of the plant disease management system should allow for an even more thorough and accurate quantitative analysis of how protectant fungicides can best be used to control plant disease.

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