Temporal Dynamics of Chlorothalonil Residues on Peanut Foliage and the Influence of Weather Factors and Plant Growth

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ABSTRACT

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The persistence of chlorothalonil residues on foliage of peanut (*Arachis hypogaea*) cultivar Florigiant was evaluated under field conditions. Chlorothalonil (Bravo 720) was applied at 1.26 kg a.i./ha with a boom sprayer. The results of seven trials over 3 yr yielded an average decay rate of -0.051 $\mu g/cm^2$ per day, with values ranging from -0.093 to -0.036. This corresponds to a mean half-life of 13.6 days, with values ranging from 7 to 19 days. Decay rates increased with increasing rainfall. No influence of temperature on decay rates could be detected. A simulation model was developed to examine the effects of new leaf emergence on the measurement of residue dynamics. With the diluting influence of new leaf emergence, apparent residue half-life decreased from a true half-life of 13.6 days to 6.4 days. The model also demonstrated that because of new leaf emergence, significant amounts of unprotected foliage developed during the interval between successive fungicide applications.

Chlorothalonil is a protectant fungicide that is widely used to control foliar fungal diseases of peanut (*Arachis hypogaea* L.) such as early leaf spot, caused by *Cercospora arachidicola* S. Hori, and late leaf spot, caused by *Cercosporidium personatum* (Berk. & Curt.) Deighton (12). Chlorothalonil application for leaf spot control in North Carolina usually begins in mid- to late June and continues until late September. Applications generally are recommended on a 10- to 14-day schedule or according to a leaf spot spray advisory based on daily observations of relative humidity and temperature (5,10).

Effective management of leaf spot diseases with protectant fungicides such as chlorothalonil requires the maintenance of a fungicide deposit on the leaf surface sufficient to arrest a fungal pathogen prior to the establishment of infection. From a theoretical standpoint, the period of crop protection resulting from a single application depends on how quickly the fungicide deposit decays, how sensitive the fungal population is to the active ingredient, and the rate at which new unprotected foliage is produced.

A simulation model developed to evaluate fungicide management for peanut leaf spot control (6) could be used to evaluate some strategies, but its usefulness was limited because chlorothalonil persistence data developed for other crops were used in the peanut leaf spot model. A better understanding of the behavior of chlorothalonil residues on peanut foliage could assist in developing

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improved simulation models and in evaluating fungicide management strategies.

The persistence of chlorothalonil has been studied on other crops (3,7–9). Neely (8) indicated that protective levels persisted for about 20 days when evaluated on 12 species of woody plant hosts, but no half-life values could be estimated because bioassays were used. Lukens and Ou (7) reported persistence data on tomato foliage from which a half-life value (for upper canopy) of 3.8 days could be estimated. Bruhn and Fry (3), in an extensive study of chlorothalonil residue dynamics on potato foliage, reported an average half-life of 6.6 days, but half-life varied considerably with canopy position and potato cultivar, from as short as 1.2 days to longer than 30 days. They also reported that rainfall near the time of application was an important factor in chlorothalonil persistence and that chlorothalonil decayed more rapidly with higher temperatures. The persistence data reported for other plants may not be applicable for peanuts because chlorothalonil retention can vary with the species of plant under consideration (8,9) or between cultivars of a crop (3). Furthermore, these investigations were conducted with earlier formulations of chlorothalonil.

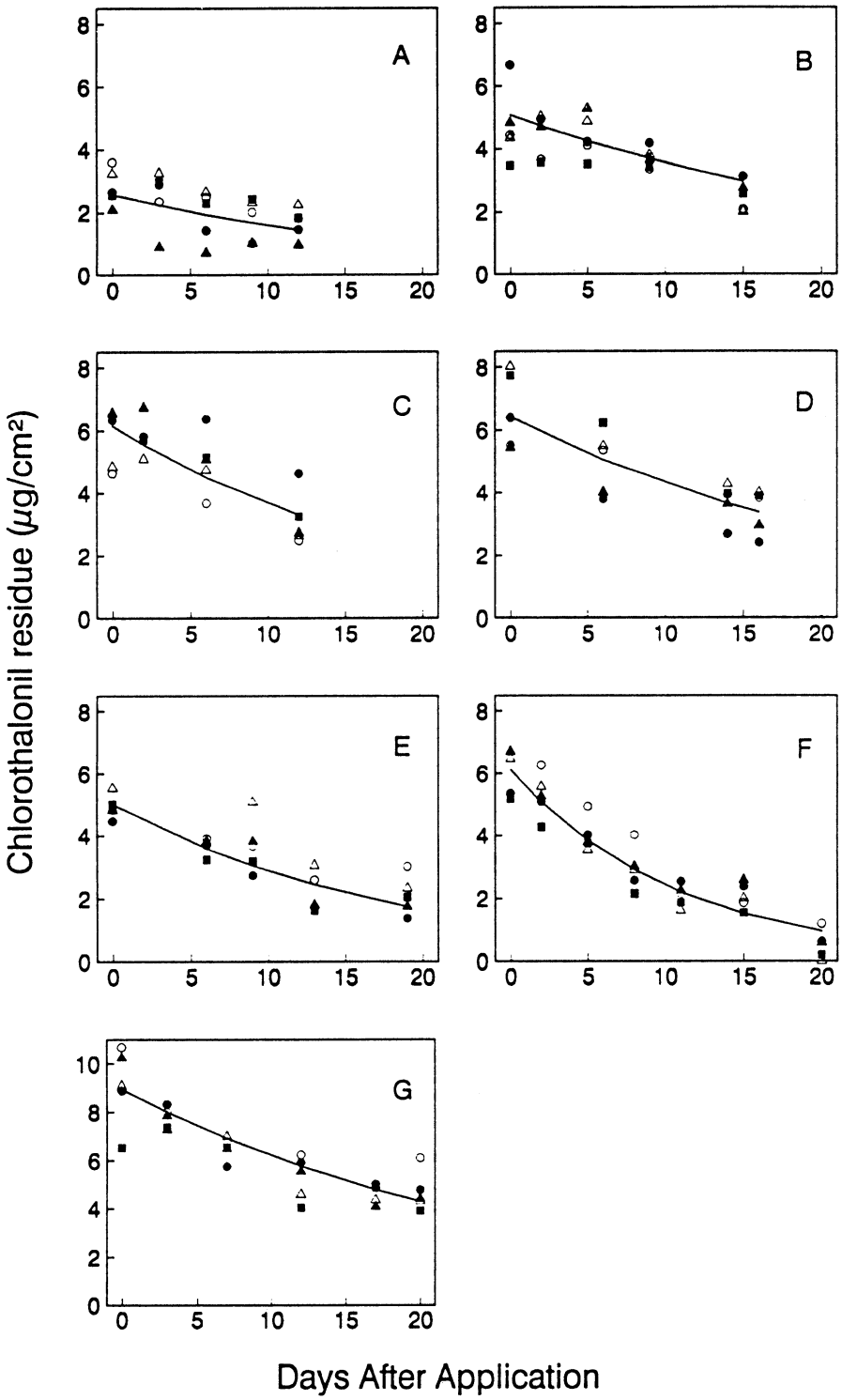

Fig. 1. Chlorothalonil residues levels on Florigiant peanut foliage after a single application of 1.26 kg a.i./ha with a hand-drawn sprayer delivering 375 L/ha. Points represent the actual residue as measured by gas chromatography. Replications are coded by different marker symbols. Lines represent the exponential decay model fitted to the data with regression. **(A–G)** Data from seven trials conducted in 1987, 1988, and 1989; the y-axis in G differs from the others.

Brenneman et al (1) recently reported that chlorothalonil residues on peanut foliage had an average half-life of 4.4 days when the fungicide was applied by a high-volume chemigation method. It is not known whether the half-life values reported for peanut foliage under a sprinkler irrigation application (chemigation) are applicable to a conventional spray boom application because the active ingredient as well as the formulating agents are highly diluted during application.

None of the previous studies addressed the influence of new foliage. Moreover, some of the studies indicated that foliage growth may have influenced the estimates of chlorothalonil persistence, particularly in the upper canopy (1,7).

This research was conducted to provide information on the temporal dynamics of chlorothalonil on peanut foliage. The influence of host growth relative to the dynamics of chlorothalonil residues in the canopy was evaluated using simulation modeling. A preliminary report of part of this study was published (4).

MATERIALS AND METHODS

Chlorothalonil field trials. All tests were conducted at Oxford, North Carolina, in fields of the peanut cultivar Florigiant. Plots were planted in early May and maintained according to practices recommended by the North Carolina Agricultural Extension Service. Seven trials were conducted over a period of 3 yr, from October 1987 through September 1989, at times ranging from 80 to 140 days after planting.

Chlorothalonil (Bravo 720, formulated at 720 g a.i/L) was applied at the rate of 1.26 kg a.i./ha in a volume of 375 L/ha of water. Sprays were applied with a hand-drawn fixed boom sprayer fitted with three D3-25 nozzles per row and operating at 276 kPa. Spray deposits were allowed to dry for several hours before the first sample was taken. Each trial was separated by a minimum of 25 m to avoid interference from drift during fungicide application. Unsprayed areas of the field were periodically monitored, and no residues were detected.

Sampling and residue analysis. Samples were periodically collected at each of five replicate plots (two rows × 3 m) for the duration of each spray trial. Because initial fungicide deposition is sharply

reduced in the lower canopy levels (1,2), sampling was confined to leaves that were exposed in the upper, outer position of the row canopy during application. This sampling plan avoided some of the variation in deposition that might interfere with the measurement of fungicide persistence. Canopy development was evaluated by marking eight to 10 individual shoot terminals in each treated area. The growth of these terminals was monitored to ensure that leaves emerging after fungicide application were not included in the sample. Each sample consisted of 10 leaf disks cut with a 1.1-cm-diameter cork borer honed to a very sharp edge. Cutting was done on a backing of Whatman No. 1 filter paper to standardize any mechanical loss of residue and to eliminate cross contamination. Leaf disks were washed with 5.0 ml of toluene for 30 min with occasional, gentle agitation to remove chlorothalonil residues.

Chlorothalonil residues were analyzed with an HP 5890A gas chromatograph equipped with an HP-1 5.0 m × 0.53 mm capillary column and a ^{63}Ni electron capture detector. A column temperature of 140 C, an injection port temperature of 260 C, and a detector temperature of 300 C were used. A chlorothalonil analytical standard (99.7% purity) was used for calibration. Chlorothalonil residue values obtained by gas chromatography analysis were converted from micrograms per milliliter of solvent to micrograms per square centimeter of leaf area, with the area calculated to include both sides of the sampled leaf disks. The decline in chlorothalonil residues over time was modeled as an exponential decay function (equation 1): $\text{residue}_t = \text{residue}_{t0}{*}\exp^{kt}$, where k is the decay rate in micrograms per square centimeter per day and t is the time since application in days. Parameters were estimated with regression of the $\ln(\text{residue}_t)$ against time, where the slope parameter is the least squares estimate of k. To account for the small differences in the initial amount of fungicide applied to each replicate of a given trial, a separate intercept term was included for each replication. The REG procedure of SAS for personal computers, release 6.04 (11), was used for this analysis. The half-life in days was calculated as (equation 2): $\text{half-life} = [\ln(0.5)]/k$.

Weather data. Rainfall and temperature data were examined to help explain the variation in decay rates between the trials. A weighted rainfall total was calculated to test the possibility that rainfall near the time of application had a greater effect in removing fungicide residues than rainfall occurring later. Rainfall was multiplied by a weight factor calculated as $1/(w + t)$, where t is the time since application and w is a weight coefficient. Small values of w will strongly weight rainfall near the time of application, and larger values for w result in less pronounced weighting. A second rainfall weighting equation (equation 3) was derived from a relationship reported by Bruhn and Fry (3): $wo = 1-\{\exp[-1.091(p_t)^{1/3} + 0.313[p_t(t-1)]^{1/3}]\}$, where wo is the wash-off effect of the rainfall, t is time since application, and p_t is rainfall. The term in braces is equivalent to g in Bruhn and Fry's report (3). They defined g as the proportion of the fungicide deposit remaining after rainfall. Decay rates were examined for correlations with total rainfall, total weighted rainfall, and mean temperature.

Leaf emergence. Leaf production rates on Florigiant peanut were monitored in plots at Lewiston, North Carolina, in 1991 and in plots at Oxford and Lewiston in 1992, resulting in three independent sets of data. Terminal leaves that were still tightly folded but protruding 2–3 cm from the bud were marked by clipping a small notch in the edge. At 7- and 14-day intervals, leaf development for each position at and above the marked leaf was scored for the degree of emergence and expansion. A new set of 10 leaves was marked each week until harvest. The relationship between leaf development rate and days after planting was examined by means of regression.

Simulation modeling. A spreadsheet simulation model was developed to examine the consequences of new leaf emergence on chlorothalonil residue dynamics in the upper canopy. The model allows an examination of the bias that can be introduced if new leaf production is not considered when decay rates are determined. Specifically, the model examines the effects of new leaf growth on the apparent chlorothalonil decay rates compared with the true decay rates. The apparent decay rate is calculated by assuming that with random sampling of the upper canopy foliage, an increasing proportion of new, unsprayed leaves will be included in the successive samples used to estimate the decay rate. The model can also be used to estimate the amount of new leaf tissue that develops between fungicide applications. This foliage remains unprotected until the next fungicide application.

The initiation of the leaf emergence cycle was staggered around the application time. Chlorothalonil residues for leaves that were fully expanded at the time of application were calculated on the basis of an exponential decay rate of -0.05 $\mu g/cm^2$ per day. Leaves that emerged after the application were assumed to have no chlorothalonil residue. The apparent chlorothalonil residue was calculated by averaging the residue on sprayed leaves with the zero level on leaves that emerged after fungicide application. The apparent residue reflects the level that would be measured if a random sample of leaves was collected from a population including the newly developed leaves. We assumed that the upper canopy consisted of the top three fully expanded leaves on each shoot at the time of application plus the new leaves that subsequently developed.

RESULTS

Persistence of chlorothalonil. Chlorothalonil levels measured several hours after application averaged 5.8 $\mu g/cm^2$ (Fig. 1). Residues declined to an average of 2.8 $\mu g/cm^2$ by 15 days. The level of chlorothalonil declined in a similar fashion in each of the seven trials. In general, the exponential decay model

Table 1. Exponential decay model parameters for seven field trials with chlorothalonil on foliage of peanut cv. Florigiant

Trial	Date	Initial residue[a] ($\mu g/cm^2$)	SE of initial residue	k[b] ($\mu g/cm^2$/day)	SE of k	R^2	Half-life[c] (days)
1	2 Oct. 1987	2.94	1.11	−0.040	0.010	0.85	17
2	10 Aug. 1988	5.07	1.05	−0.036	0.005	0.80	19
3	25 Aug. 1988	6.16	1.07	−0.052	0.006	0.87	13
4	7 Sept. 1988	6.42	1.08	−0.040	0.003	0.97	17
5	21 Sept. 1988	5.01	1.06	−0.056	0.005	0.84	12
6	13 Sept. 1989	6.13	1.07	−0.093	0.006	0.89	7
7	21 Sept. 1989	8.95	1.03	−0.037	0.003	0.88	19

[a] Average for all replications within a given trial. Value is back-transformed estimate of the intercept of the regression of ln chlorothalonil residue against days after application.
[b] k = Decay rate, slope of regression of ln chlorothalonil residue against days after application.
[c] Calculated as $[\ln(0.5)]/k$.

Table 2. Correlations of decay rate of chlorothalonil on peanut foliage with rainfall and temperature data collected during each of seven trials

Factor	Pearson's correlation coefficient	Significance probability
Total rainfall		
Unweighted	−0.68	0.09
Weighted[a]		
$w = 0.05$	−0.31	0.49
$w = 1$	−0.35	0.43
$w = 5$	−0.43	0.33
$w = 10$	−0.49	0.26
Weighted, wo[b]	−0.70	0.08
Mean temperature	−0.02	0.95

[a] Calculated by $1/(w + t)$, where t is the days after application and w is a variable used to adjust weighting.
[b] Calculated by $wo = 1-\{\exp[-1.091(p_t)^{1/3} + 0.313[p_t(t-1)]^{1/3}]\}$.

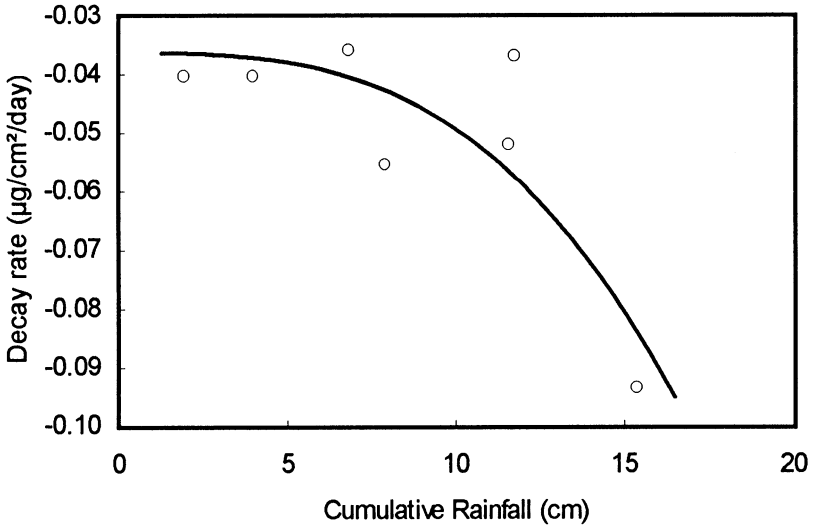

Fig. 2. Relationship between the decay rate of chlorothalonil on Florigiant peanut foliage and the cumulative rainfall during each trial. Points represent the actual data for each of the seven trials, and the line represents the cubic regression model.

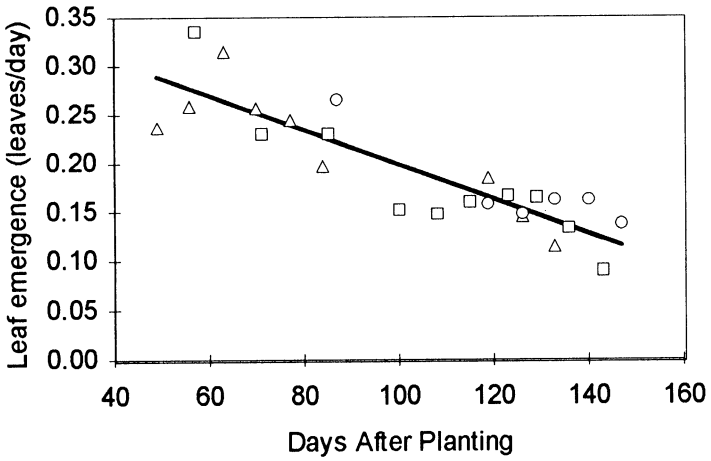

Fig. 3. Leaf emergence rates for Florigiant peanut as a function of the number of days after planting. Data for 1991 Lewiston, North Carolina, are shown as triangles, for 1992 Lewiston as squares, and for 1992 Oxford, North Carolina, as circles. The line represents the regression model using combined data.

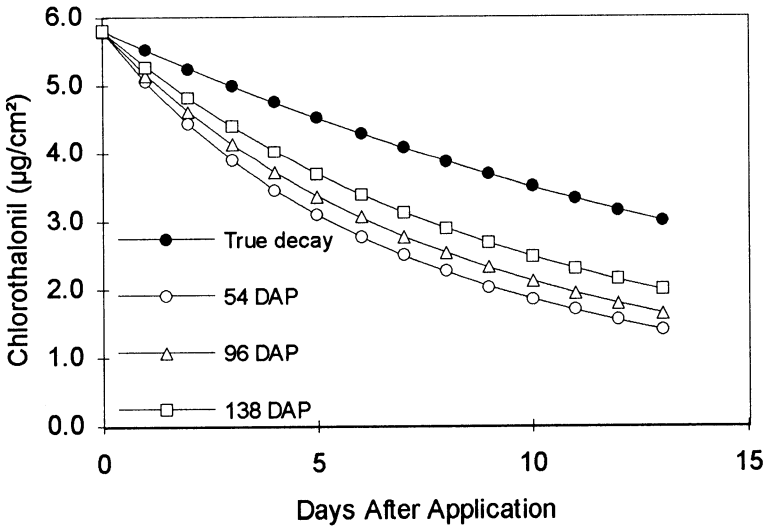

Fig. 4. Simulation of true chlorothalonil decay compared with apparent decay for applications 54, 96, and 138 days after planting. The true residue curve is based on an exponential decay of an initial deposit of 5.8 $\mu g/cm^2$ at the rate of -0.05 $\mu g/cm^2$ per day. The apparent decay curve is calculated by assuming that under random sampling of the upper canopy foliage, an increasing proportion of new, unsprayed leaves will be included in the successive samples used to estimate the residue level.

provided an adequate fit to the experimental data and accounted for an average of 87% of the variation in chlorothalonil residues over time (Table 1). Decay rate parameter estimates varied from -0.093 to -0.036, with a mean value of -0.051 $\mu g/cm^2$ per day. The experimentally observed decay rates corresponded to half-life values ranging from 7 to 19 days, with a mean value of 13.6 days (Table 1). Initial levels varied from 2.94 to 8.95 $\mu g/cm^2$, and variation was primarily due to differences in application between each trial. No relationship was detected between initial residue levels and decay rates.

Influence of weather on chlorothalonil persistence. Decay rate had the highest correlation with total rainfall weighted with equation 3 or with total (unweighted) rainfall (Table 2). Correlations decreased as more pronounced weightings of rainfall were evaluated. Decay rates showed little correlation to mean temperature.

The nature of the relationship between chlorothalonil decay rates and rainfall was further analyzed by means of regression analysis. A series of models using rainfall and weighted rainfall were evaluated. The most suitable model was (equation 4): $k = -0.036 - 0.000013*(p_t)^3$, where k is the decay rate, p_t is the rainfall in centimeters, and t is the days after application (Fig. 2). This model had an R^2 of 69%. It should be noted that the highest rainfall observation shown on Figure 2 had a strong effect on the parameter estimates, as judged by Cook's D statistic generated with SAS.

Leaf emergence. Leaf emergence rates calculated from field data varied from 0.34 leaves per day at the beginning of the spray season to 0.10 leaves per day near harvest (Fig. 3). Analysis of variance showed no differences between the three sets of data with regard to the parameters being estimated, so data were pooled for regression. The model developed to describe the relationship between leaf development rate and days after planting was (equation 5): $LER = 0.376 - 0.0017*DAP$, where LER is the leaf emergence rate (leaves per day) and DAP is the days after planting. The model had an R^2 of 77%.

Simulation modeling. Simulations were initiated at 54 days after planting to coincide with the time when the fungicide application schedule is usually started. Leaf emergence rates during the season were calculated with equation 5. Half-life estimation errors caused by new leaf emergence was the first problem addressed with the model. Applications at 54, 93, and 138 days after planting were simulated (Fig. 4). The greatest overestimation of decay rate was observed with the application made at 54 days, when the leaf emergence rate averaged 0.27. The decay rate was estimated to be -0.107 $\mu g/cm^2$ per day (half-life of 6.4 days) compared with a true

rate of -0.05 $\mu g/cm^2$ per day (half-life of 13.6 days). The application made at 138 days when the leaf emergence rate was 0.10 leaves per day showed an estimated decay rate of -0.082 $\mu g/cm^2$ per day (half-life of 8.4 days).

The second problem addressed with the simulation model was the development of new unprotected leaves. A typical spray season on a 14-day schedule was simulated (Fig. 5). Between the first and second applications, about 3.4 leaves developed at each shoot apex. After the sixth application, 1.9 leaves developed.

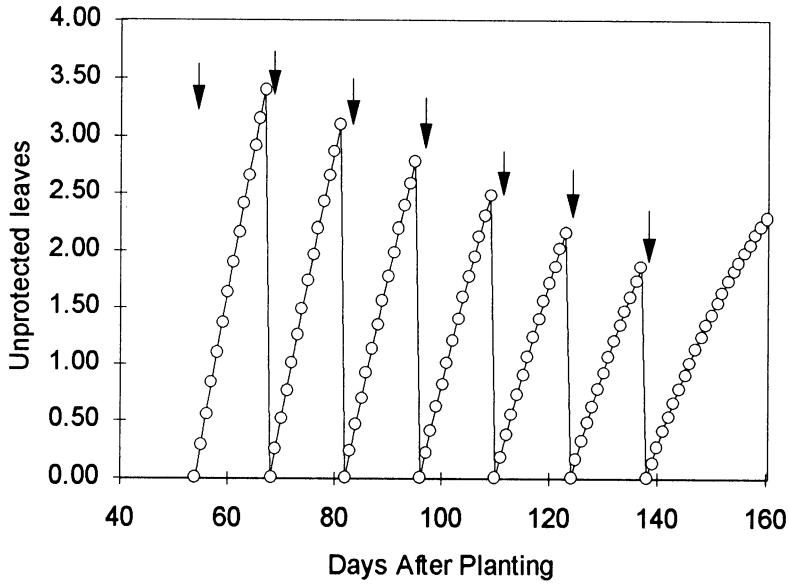

Fig. 5. Simulation of the number of new leaves produced on a shoot between successive fungicide applications (arrows). A 14-day application schedule was simulated. Leaf development rates were calculated using the equation: $LER = 0.376 - 0.0017 * DAP$, where LER is the leaf emergence rate (leaves per day) and DAP is the days after planting.

DISCUSSION

The temporal dynamics of chlorothalonil residues on peanut foliage could be explained by an exponential decay model. This general model also explained chlorothalonil persistence on tomato foliage (7), potato foliage (3), and peanut foliage (1). The period over which a protective deposit remains can be calculated if the minimum residue level required to stop infections is known. Although the level of chlorothalonil needed to protect peanut foliage against *Cercospora arachidicola* or *Cercosporidium personatum* is not precisely known, an estimate of the necessary residues can be made. We observed through in vitro testing that 0.1 $\mu g/ml$ of chlorothalonil inhibited growth of *Cercospora arachidicola* on acid potato-dextrose agar. Relating this inhibitory concentration to activity on the leaf surface is complicated by the low aqueous solubility of chlorothalonil (about 0.6 $\mu g/ml$) (13), by the accumulation of chlorothalonil by fungal cells (13), and by the physical nature of the surface deposit (7). Some estimates of minimal inhibitory levels can be taken from the literature. Lukens and Ou (7) reported that a 1.2-$\mu g/cm^2$ deposit of chlorothalonil was needed to protect tomato foliage against *Alternaria solani*. Brenneman et al (1) indirectly estimated that 1–2 $\mu g/cm^2$ was needed to protect peanut foliage against *Cercosporidium personatum*. On the basis of the above information, a minimal inhibitory level in the range of 1.5 $\mu g/cm^2$ is probably a good but conservative estimate. Given this information, the protective period can be estimated. Assuming a minimum protective level of 1.5 $\mu g/cm^2$, an initial deposit of 5.0 $\mu g/cm^2$ decaying at an average rate of -0.05 $\mu g/cm^2$ per day should persist at protective levels for 24 days. This figure should be taken as a theoretical value for the upper canopy. Since fungicide deposition in lower canopy levels may be exponentially lower (2) and since redistribution from upper canopy levels may occur, this 24-day value may not apply to lower canopy levels.

The average decay rate, -0.051 $\mu g/cm^2$ per day, and the corresponding half-life value, 13.6 days, in these experiments indicate that chlorothalonil residue persisted considerably longer than the upper foliage half-life values of 3.8 days reported for tomato (7), 3.6 days for potato (3), and 3.8 days for peanut (1). The differences in chlorothalonil persistence seen in the present study and the previous reports might be explained in part by the dilution effect of canopy growth. Differences in host, formulation, and application method might also account for some of the discrepancies.

Rainfall seemed to account for a substantial amount of the variation in decay rates among the seven trials in this study. Weighting the rainfall data did not seem to improve the relationship between decay rate and rainfall as reported in other studies (3). This may be because no rain fell on the day of application in any of the seven trials and only in trial 7 did rain fall on the day after application. The cubic nature of the relationship between decay rate and rainfall indicates that low levels of rainfall had a small effect, whereas higher levels of rainfall had a disproportionately large effect. This could be related to other factors correlated with periods of high cumulative rainfall such as rain intensity, number of rain events, or extended periods of leaf wetness, but rainfall data in this study did not include these measurements. Detailed analysis of this type of field data can present problems because, as Bruhn and Fry (3) pointed out, weather-related field observations are often confounded by the correlations with time and other measured or unmeasured variables.

The influence of new leaf emergence in relation to the temporal dynamics of chlorothalonil residues on the upper canopy indicated that if leaf growth is not considered, estimates of fungicide persistence can be biased. More important, significant new growth can occur between applications. Although some redistribution may occur to this new tissue, it is thought to be minimal in the upper canopy (3). Hence, this newly emerged tissue is probably unprotected until the next application. The development of new, unprotected tissue may be a more important factor in scheduling a protectant fungicide application than the persistence of the fungicide on the treated foliage.

Chlorothalonil residue dynamics and leaf growth could be incorporated into improved simulation models to study protectant fungicide management on peanuts and other crops.

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