Removal of Fentin Hydroxide from Pecan Seedlings by Simulated Rain

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ABSTRACT

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A rainfall simulator was used to examine the influence of a synthetic latex spray adjuvant and pecan cultivar on removal of fentin hydroxide (TPTH) from pecan foliage. Six-week-old pecan seedlings were sprayed with TPTH with or without adjuvant, allowed to dry, and exposed to 0, 0.25, 1.27, 2.54, or 5.08 cm of simulated rain. The initial concentration of tin on sprayed leaves was normally distributed, with greater variation on leaves sprayed with TPTH without adjuvant. In most cases the fungicide was removed at a constant rate with increasing rainfall. Addition of the spray adjuvant resulted in significantly greater fungicide tenacity after relatively light rains of 2.54 cm or less, although after an additional 2.54 cm, there was no significant difference between fungicide residues on leaves treated with or without adjuvant. Removal of fungicide by rain was examined on seedlings of 13 pecan cultivars. The percentage of tin removed after 5.08 cm of rain did not differ significantly among cultivars in the first run of the experiment. In the second run, significantly less tin was removed from leaves of seedlings of cultivars Moneymaker and Moore than the other cultivars. Differences in leaf surface characteristics among pecan cultivars have been reported and may be responsible for observed differences in fungicide tenacity.

Control of pecan scab, caused by the fungus *Cladosporium caryigenum* (Ellis & Langl.) Gottwald, is essential to pecan (*Carya illinoensis* (F.A. Wagenheim) K. Koch) production in the southeastern United States. In Georgia, recommended control practices consist of fungicides applied every 2 wk beginning at budbreak (about 1 April) and every 3 wk from pollination (about 1 May) through August (7). Because pecan growers often are not able to cover all their trees within 2 wk, there is considerable interest in extending the spray interval without increasing the risk of infection, particularly early in the season. The length of the effective interval depends upon the concentration of the initial fungicide deposit; the fungicide's retention, weathering characteristics, and efficacy; and dilution of the fungicide by plant growth (6). Adjuvants can alter the effects of a foliar fungicide spray in relation to delivery efficiency, deposition on the target plant, retention on or in the target plant, and toxicity to the target pest, host, and other organisms (9).

This study was undertaken to examine the effects of rainfall, addition of a spray adjuvant, and cultivar characteristics on retention of fentin hydroxide (TPTH), the most widely used fungicide for control of pecan scab in the southeastern United States.

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MATERIALS AND METHODS

Adjuvant experiment. Six-week-old greenhouse-grown Curtis pecan seedlings with three or four fully expanded leaves were sprayed to runoff with TPTH (Super Tin 4L) at a rate of 0.359 g a.i. L^{-1} or the same rate of TPTH amended with a synthetic latex agricultural sticker (Bond) at 0.16 ml L^{-1}. Plants were sprayed so that both upper and lower leaf surfaces were thoroughly wetted. An additional set of seedlings was left unsprayed and exposed to simulated rain to serve as controls and provide estimates of background foliar tin concentrations. The seedlings were allowed to dry overnight before exposure to simulated rain.

Plants were placed on turntables to provide uniform rain treatments. Rain solutions consisted of distilled water amended with background ions and adjusted to a pH of 4.5 (13). The solutions were pumped to each station where raindrops were created by hypodermic needles arranged in the plastic tubing above each turntable (5). Rain was collected in a graduated cylinder on each turntable, and when the desired amount had fallen, the plants were removed from the tables and allowed to dry.

In the first run of this experiment, plants sprayed with TPTH, with or without the adjuvant, were exposed to 0, 0.25, 2.54, or 5.08 cm of continuous rain or were exposed to 2.54 cm of rain, allowed to dry, and then exposed to an additional 2.54 cm. Rain treatments were slightly modified in the second run of the experiment. Plants were exposed to 0, 0.25, 1.27, 2.54, or 5.08 cm of continuous rain. In each run of the experiment, 10 seedlings were used for each adjuvant/rain combination. When the foliage was dry, three leaves were removed from each plant, the leaf surface areas were measured, and fresh weights were determined. The leaves were then dried completely in a drying oven (70 C), weighed, and analyzed for tin content using a plasma emission spectrometer (SpectraSpan V System, Beckman Instruments, Fullerton, CA). Tin residue was expressed as micrograms per square centimeter of upper leaf surface area and was adjusted on the basis of the background levels of foliar tin in unsprayed control plants.

The Shapiro-Wilk statistic, W, available through the SAS univariate procedure (11), was used to test whether the initial tin residue deposited on leaf surfaces was normally distributed. An analysis of variance was performed to determine the effect of the adjuvant on removal of tin from foliage at each level of rainfall. Linear regression of tin residue on rainfall was used to model the removal of tin from foliage in response to cumulative rainfall (4,11).

Cultivar experiment. Seven greenhouse-grown seedlings of each of 13 different cultivars were sprayed to runoff with TPTH, at a rate of 0.359 g a.i. L^{-1}, using a handsprayer. The foliage was allowed to dry overnight, and on the following day plants were subjected to 5.08 cm of continuous simulated rain. When foliage was dry, three leaves from each plant were removed and the leaf area was measured. The leaves were then dried completely, weighed, and analyzed for tin as previously described. The experiment was repeated several weeks later after emergence of new foliage on the plants. For each run of the experiment, tin residue before and after exposure to 5.08 cm of rain was analyzed by ANOVA, using cultivar as the main factor. Where a significant cultivar effect was indicated by the F test ($\alpha = 0.05$), cultivars were separated into distinct nonoverlapping groups based on the Scott-Knott clustering procedure (8,12).

RESULTS

Adjuvant experiment. For all treatments in both runs of the experiment, the initial deposit of tin per square centimeter of leaf surface before exposure to simulated rain was normally distributed (Fig. 1). The initial deposit of tin was significantly higher in run 1 than in run 2 for plants treated with TPTH alone or TPTH plus adjuvant. In run 1, the mean initial deposit of tin on plants sprayed with TPTH alone was significantly lower than that on plants sprayed with TPTH plus adjuvant (1.88 and 2.26 μg Sn cm^{-2}, respectively). There was no significant difference in the initial deposit of tin among treatments in the second run of the experiment.

Rainfall intensity, determined by the pumping rate and size of the hypodermic needles, remained a relatively constant 1.8 cm hr^{-1} during the experiment. In both runs of the experiment, the foliar tin residue decreased linearly with increasing rain up to 5.08 cm. A linear response to rain was observed in both fungicide treatments of the first run and the amended TPTH treatment of the second run. However, the tin residue on plants receiving the unamended TPTH treatment in the second run declined exponentially with increasing rain.

After exposure to 2.54 cm simulated rain or less, leaves treated with TPTH plus adjuvant retained a significantly higher percentage of the initial tin residue than leaves treated with TPTH alone (Fig. 2). However, after a total of 5.08 cm rain, over 60% of the initial tin deposit remained on the leaves and there was no significant difference between the two fungicide treatments.

Fungicide was initially applied to both upper and lower leaf surfaces. Therefore, the measured tin residue represents an average residue for upper and lower leaf surfaces. However, leaves on the seedlings were nearly horizontal so that the action of the simulated rainfall applied from above undoubtedly removed a greater proportion of fungicide from the upper leaf surface than from the lower one. Because leaves on each seedling were few and generally nonoverlapping and seedlings were well separated from each other on the turntables, redistribution of fungicide from one leaf to another was unlikely. If one assumes that the initial fungicide deposit was distributed equally between the upper and lower surfaces of the leaf and that fungicide was removed only from the upper leaf surface and not the lower leaf surface when exposed to simulated rain, the proportion of remaining fungicide on the entire leaf would not be expected to fall below 50%. Results from these experiments are consistent with this hypothesis, since tin residues were not observed to fall below the 50% level. It follows that the actual fungicide residue on the upper leaf surface may have been considerably lower than the measured residue. Based on these assumptions, the percentage of tin residue on the upper leaf surface only, y, was estimated by $y = 2x - 100$, where x is the measured percentage of tin residue on the entire leaf. Estimates of tin residues on upper leaf surfaces only compared with those on both leaf surfaces are shown in Table 1.

Cultivar experiment. Tin residue on sprayed leaves not exposed to simulated rain was not significantly different among cultivars in the first run of the

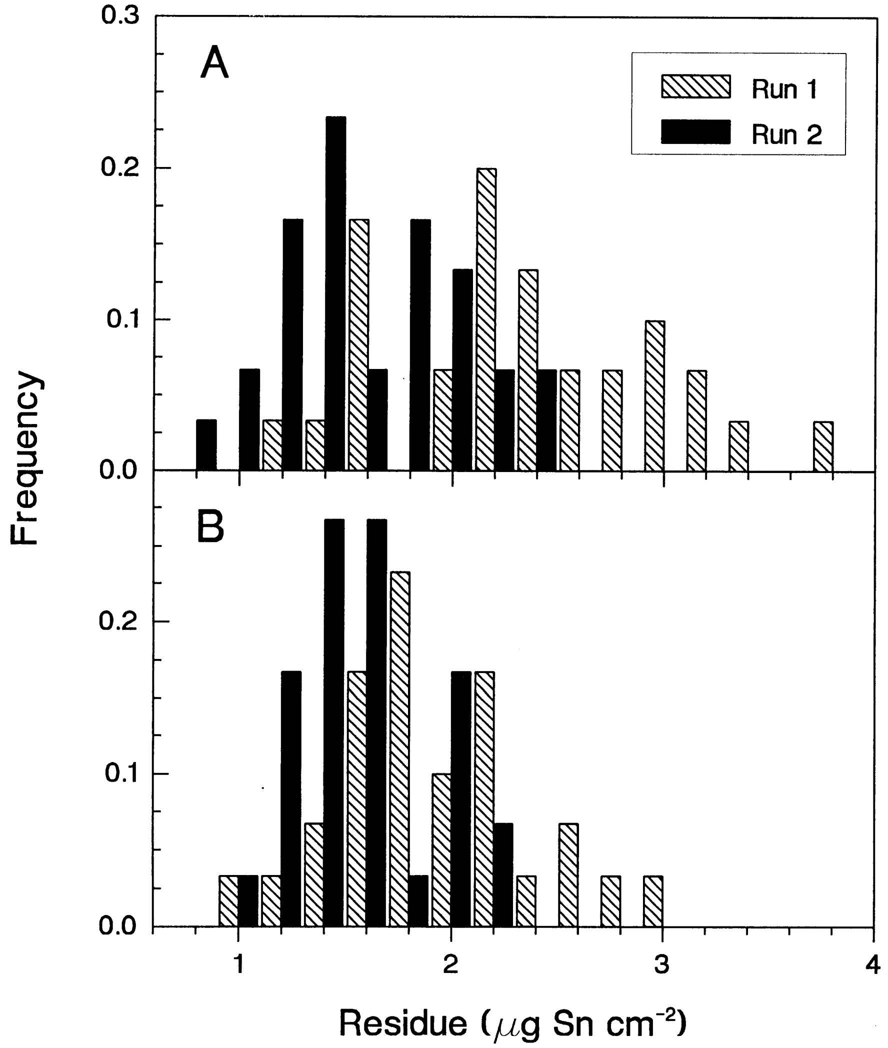

Fig. 1. Initial deposit of tin on the surface of pecan seedlings sprayed with **(A)** fentin hydroxide (TPTH) alone or **(B)** TPTH amended with a synthetic latex spray adjuvant (Bond).

experiment. In the second run, however, there was a significant difference in the initial deposit of tin among the 13 cultivars. The amount of tin removed from the leaves after 5.08 cm of rain was estimated by the difference in foliar tin residue between plants that were exposed and plants that were not exposed to the rain treatment. The amount of tin removed by rain differed significantly with cultivar in both runs of the experiment. However, when removal of tin was expressed as a percentage of the initial deposit per cultivar, no significant differences in the percentage of tin removed were detected among cultivars in the first run of the experiment. In the second run, the proportion of tin removed from the foliage of Moneymaker and Moore seedlings was significantly less than that from seedlings of the other cultivars (Table 2).

DISCUSSION

The distribution of fungicide on foliage following a spray application is influenced by a number of factors, including droplet size (as determined by delivery pressure and by nozzle size and arrangement) and density of foliage (6). The use of small, individually potted seedlings (five or fewer fully expanded leaves) in these experiments allowed very thorough coverage of foliar surfaces. The result was a more symmetric distribution of initial fungicide residue with lower variation than previously reported for initial fungicide deposits on field-grown plants. For example, asymmetric distributions such as gamma and lognormal have been employed to describe the initial deposit of chlorothalonil and metalaxyl, respectively, on potato foliage in the field (2,3,10). Mature pecan trees may reach heights of 25 m or more and may be quite densely foliated. Thus one might expect the initial fungicide residue on orchard-grown pecan trees to be considerably more variable than on seedlings, reflecting differences in canopy density and distance between the sprayer and the target foliage.

A study by van Bruggen et al (18) also included evaluation of washoff of TPTH (Du-Ter F30) from potato leaves. Plants were exposed to simulated rain 2 days after fungicide was applied to the upper leaf surfaces only. After exposure to 0.37 cm of rain (1.12 cm hr^{-1} for 20 min), 38% of the original fungicide deposit remained on the upper leaf surface (for the flowable formulation of TPTH). No attempt was made by the authors to model the loss of fungicide residue with increasing rainfall, since only one level of rainfall was tested. Differences in leaf surface characteristics of pecans and potatoes may account for the difference in tenacity observed in the two studies. It should also be noted that the flowable formulation of TPTH used in the study by van Bruggen et al (18) was an older version of the fungicide used in the present study and may be responsible for the divergent results.

Removal of TPTH from foliage by precipitation has been studied by other researchers, particularly with respect to the influence of the acidity of rainwater on fungicide retention. Results differ somewhat among these earlier studies

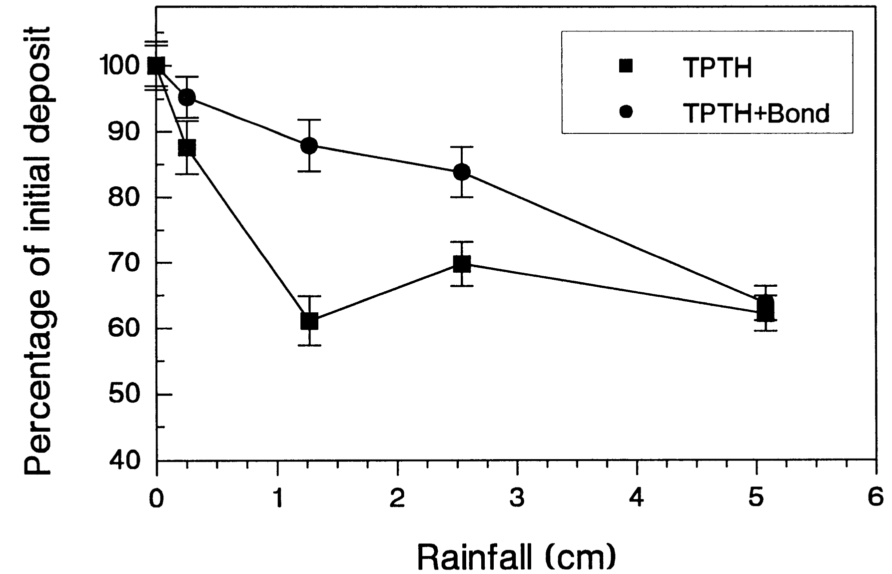

Fig. 2. Effects of a synthetic latex spray adjuvant (Bond) on removal of tin from foliage of pecan seedlings sprayed with fentin hydroxide (TPTH) and exposed to simulated rain. Points represent treatment means of combined data from two runs of the experiment, with standard errors shown as vertical bars. The 1.27-cm rainfall treatment was included in experiment 1 only.

Table 1. Mean percentage of initial tin deposit remaining on leaf surfaces of pecan seedlings sprayed with fentin hydroxide (TPTH), with or without a synthetic latex spray adjuvant (Bond), after exposure to simulated rain[y]

Rainfall (cm)	Upper and lower leaf surfaces		Upper leaf surface only[z]	
	TPTH	TPTH + Bond	TPTH	TPTH + Bond
0	100.0	100.0	100.0	100.0
0.25	87.6	95.3	75.2	90.6
1.27	61.1	87.9	22.2	75.8
2.54	69.8	83.8	39.6	67.6
5.08	62.2	63.8	24.4	27.6

[y] Treatment means of pooled data from two runs of the experiment.

[z] Estimated from measured tin residues on both upper and lower leaf surfaces based on following equation: $y = 2x - 100$, where y = percentage of tin on upper leaf surface and x = percentage of tin on both leaf surfaces.

Table 2. Removal of tin from the leaf surfaces of 13 pecan cultivars sprayed with fentin hydroxide (TPTH), allowed to dry, and exposed to 5.08 cm of simulated rain[y]

Run 1		Run 2	
Cultivar	Tin removed (%)	Cultivar	Tin removed (%)
Moore	83.8 a[z]	Desirable	63.6 a
Cherokee	78.2 a	Mahan	57.9 a
Schley	76.9 a	Stuart	54.1 a
Stuart	76.5 a	Curtis	53.2 a
Cheyenne	75.7 a	Elliot	51.5 a
Moneymaker	75.6 a	Cheyenne	49.8 a
Desirable	75.4 a	Sumner	48.2 a
Sumner	74.7 a	Success	48.2 a
Cape Fear	74.2 a	Cherokee	45.4 a
Mahan	73.0 a	Schley	43.4 a
Success	71.6 a	Cape Fear	42.7 a
Curtis	69.3 a	Moneymake	34.1 b
Elliot	63.9 a	Moore	20.6 b

[y] Values are means of seven seedlings per cultivar.

[z] Values within each run followed by the same letter are not significantly different based on the Scott-Knott cluster analysis ($\alpha = 0.05$).

because of differences in the amount and intensity of simulated rain, foliar surface characteristics of the particular plant species, and fungicide formulations and application techniques used in each study. Troiano and Butterfield (17) observed a constant rate of removal of fungicide from leaves of snap beans with the duration of simulated rain (pH 4.6) up to 2 hr (2.0 cm of rain total), following application of a wettable powder formulation of TPTH (Du-Ter 50WP) to the upper leaf surfaces only. In their studies, TPTH concentrations on leaf surfaces decreased from 15 $\mu g\ cm^{-2}$ to 2.8 $\mu g\ cm^{-2}$ (19% of the initial deposit). However, in another study (15) using the same rainfall simulator, TPTH (Super Tin 4F) was applied to the upper surface of greenhouse-grown potato leaves and exposed to 1 cm of rain the following day. Loss of fungicide residue from the leaf surface as a function of rain was modeled by a modified negative exponential function (15). Although actual data on fungicide residue were not provided, prediction equations indicated approximately 40% of the initial fungicide deposit remaining after 1 cm of rain. This level is similar to the fungicide residue remaining on upper leaf surfaces of pecan seedlings as estimated in the present study (Table 1). Based on the available data, it appears that TPTH may decrease exponentially with the first few millimeters of rain but that the rate of fungicide loss appears to stabilize (i.e., decrease at a constant rate) as rainfall increases from 1 to 5 cm.

The comparatively dense foliage of mature pecan trees in the orchard and the redistribution of fungicide from upper to lower canopy levels may also result in much slower removal of fungicide by rain than was observed on seedlings. In their investigation of fungicide washoff from apple foliage, Smith and MacHardy (14) demonstrated that captan residues applied in the laboratory decreased exponentially as the duration of simulated rainfall increased but that in the orchard, captan residues decreased linearly with increasing rainfall.

Use of a spray adjuvant may not necessarily result in better fungicide retention or provide improved disease control. The use of adjuvants that act as spreaders (surfactants) rather than stickers in conjunction with flowable fungicides could conceivably encourage residue washoff from rain because flowables generally contain some spreading agents with the formulation (9). For this reason, use of a spreader adjuvant should be accompanied by a sticker unless rapid residue loss is desired (9). Information available on the product label indicates that Bond can be used as an effective agricultural sticker or extender, and when used at the recommended rates in combination with a pesticide, the adjuvant can reduce the rate of loss of pesticide from foliage. As a sticker, Bond is therefore compatible for use with a flowable fungicide formulation such as Super Tin 4L. Results of the present study indicate that while the addition of Bond may result in improved fungicide retention characteristics under low rainfall conditions, it does not appear to provide any significant improvement in retention characteristics under prolonged periods of rain.

While adjuvants may provide some benefit as the result of improving deposition or retention of pesticides, addition of adjuvants may also have undesirable effects on crop growth, development, or yield. One recently published study (1) included the evaluation of chlorothalonil treatments applied with and without Bond in controlling late leaf spot of peanut, caused by *Cercosporidium personatum*. The author reported that although the addition of Bond resulted in significantly less disease, there was no significant difference in the yield of plants treated with Bond when compared with yields of untreated plants. When one considers the additional cost of materials, use of the adjuvant for improved disease control may not be economically justified.

The variation in leaf surface characteristics among the different cultivars may influence the deposition and retention of TPTH on foliage. Ultrastructural differences in surface anatomy of young pecan leaves have been observed among different cultivars (19). Lower trichome densities have been observed on leaves of cultivars Desirable, Wichita, and Schley than leaves of Elliot and Curtis, but only slight differences in the ultrastructure of the cuticle and epidermis have been observed among cultivars (19). In a more recent study (16), washed surfaces of leaves of cultivars Stuart and Curtis were found to be rougher and contain more numerous granulations than those of cultivars Desirable and Schley (16). However, of the cultivars that have been reported to differ in surface morphology, none were found in the present study to be significantly different in terms of fungicide removal by rain. It should be noted that the present study was conducted on greenhouse-grown seedlings while the earlier ultrastructural studies included only orchard-grown grafted plant material. Seedlings might be expected to exhibit greater variability in foliar surface characteristics than grafted material and may or may not possess characteristics typical of the maternal parent. Furthermore, because the environment in which the plants are grown is likely to have a significant impact on leaf surface characteristics, it may not be possible to directly relate the rates of fungicide washoff on cultivars grown in the greenhouse with ultrastructural differences in leaf surface morphology of orchard-grown plants. Detailed ultrastructural examination of greenhouse-grown leaf material would be necessary to establish a relationship between leaf surface morphology and fungicide washoff characteristics.

Results of this study suggest that incorporation of a synthetic latex spray adjuvant may decrease the loss of TPTH from pecan foliage after a rainfall of 2.5 cm or less. However, the adjuvant does not appear to provide any significant increase in fungicide tenacity after heavier rainfalls of 5 cm. Although significant differences were observed in the removal of fungicide from leaves of seedlings of different cultivars of greenhouse-grown pecans, whether orchard-grown plants exhibit similar differences remains to be determined. The overall importance of spreader-sticker adjuvants becomes less critical when spray intervals are shortened and spray programs are started early in relation to disease severity (9). This would certainly apply to early-season control of pecan scab in Georgia, where recommended control practices consist of fungicides applied every 2 wk prior to pollination.

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