Attenuation of Metalaxyl on Potato Leaves by Simulated Acidic Rain and Residence Time

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ABSTRACT

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Greenhouse-grown rooted potato cuttings (cultivars Norchip and Monona) were sprayed with 200 ppm metalaxyl 78, 30, 6, or 0 hr before exposure to simulated rain at pH 2.8, 3.4, 4.0, or 4.6 at an intensity of 8.8 mm/hr for 0, 10, 20, or 30 min. The experiment was repeated with shorter time intervals between applications of the fungicide and simulated rain (0, 3, 6, 30, and 54 hr) and shorter rainfall durations (0, 3, 6, 10, and 20 min). Metalaxyl content of foliar tissue was determined by a bioassay with *Phytophthora boehmeriae* after chemical extraction. At the end of each experiment, plants treated with metalaxyl and simulated rain were inoculated with *P. infestans* to determine residual activity of the fungicide *in situ*. The concentration of metalaxyl declined exponentially with time after application and with rainfall duration, until asymptotes were reached about 30 hr after spraying or after 10 min of simulated rain (1.47 mm of rain). Fungicide wash-off was not affected by the acidity of rain or cultivar. Attenuation of metalaxyl over time and by rain was predicted accurately by an exponential decay model with an asymptote. Despite a rapid initial decrease in metalaxyl concentration, residual concentrations (5–10% of the original deposit) were still sufficient to control late blight.

Additional key words: acid rain, retention, *Solanum tuberosum*.

In industrialized areas, the pH of precipitation has dropped steadily during the past 15 yr. The average pH of rain is now 4.0 in parts of the northeastern United States (15). Visible injury to crop plants has been observed only at pH levels of simulated rain below 3.0, and direct effects of acidic rain on crop yield have not been demonstrated unequivocally (9,13). However, indirect effects via enhanced disease development or accelerated fungicide removal may be important (17,24).

Weathering of pesticides from plant foliage has been studied intensively to schedule pesticide applications (3,6,10,12,14,19–22). Loss of pesticides from leaf surfaces is determined by physical and chemical conditions of those surfaces and of the pesticides and by environmental factors, of which rainfall has been considered most important (6). In experiments on weathering of fungicides by simulated rainfall, deionized or tap water has commonly been employed (3,20). Results obtained from such experiments may not reflect effects of ambient rainfall on wash-off of certain fungicides, because removal of fungicides can be affected by chemical components of rain (and consequently, its acidity). An increase in fungicide loss by simulated rain at low pH levels was demonstrated recently for two protectant fungicides (24,26).

Systemic fungicides may be affected differently by acidic rain than protectant fungicides. However, effects of acidity of rain have not been reported as yet for retention of those fungicides. Acidity of rain could possibly accelerate wash-off of initial deposits of systemic fungicides on plant surfaces, but the time interval between fungicide application and subsequent rain may be a decisive factor in determining the amount of fungicide wash-off. Even with protectant fungicides, this interval was an important factor determining retention of fungicides on leaves after rain (3,20,22). It is probably even more important for a systemic fungicide, which is presumably not directly affected by rain once it has entered plant tissues.

Metalaxyl is a systemic fungicide that has become increasingly important for control of late blight on potatoes in New York State. Nevertheless, not much is known about weathering of metalaxyl on potato foliage over time or by rainfall, let alone acidic rainfall.

The objectives of this study were 1) to determine attenuation of metalaxyl on potato leaves over time both without and with exposure to simulated rainfall, 2) to investigate whether the pH of rain affects the wash-off rate of metalaxyl, 3) to develop a mathematical model that describes the attenuation of metalaxyl over time and by rain, and 4) to assess the effects of attenuation of metalaxyl on control of late blight on potato. A preliminary report of this research was published (25).

MATERIALS AND METHODS

Plant material. Single-leaf cuttings were taken from mature potato plants (*Solanum tuberosum* L.). Cultivars Norchip and Monona were selected because of their common occurrence in upstate New York. Petioles of the leaf cuttings were dipped in a mixture of auxin and thiram (Rootone F, Union Carbide Agricultural Products, Ambler, PA) and allowed to form roots in moist perlite (Terra-lite, W. R. Grace & Co., Cambridge, MA) on a mist bench in a greenhouse. After 1 wk, rooted cuttings were transplanted into 7-cm-diameter pots containing Cornell peat-lite mix (2) and placed in a greenhouse with a 16-hr photoperiod and day/night temperatures of about 25/18 C and relative humidity of at least 50%. Supplementary lighting was provided by multivapor lamps (MV400/U, General Electric, Bridgeport, CT). Before application of metalaxyl, the potting mix was covered with plastic to prevent dripping of metalaxyl onto the soil and uptake by the roots.

Production of simulated rain. Simulated rain was produced at an intensity of 8.8 ± 1.5 mm/hr by plastic hydraulic nozzles (RA2,

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Delevan Corp., West Des Moines, IA) 3 m above rotating turntables, as described previously (26). Simulated rain solutions were acidified to pH 2.8, 3.4, 4.0, and 4.6 with a mixture of sulfuric and nitric acids in a 2:1 mass ratio. Background ions were added to all solutions in concentrations similar to those found in ambient rain of the eastern United States. A more detailed description of the composition of the simulated rain has been given (26).

Fungicide and rain treatments. Plants were sprayed to runoff with 200 ppm (w/w) a.i. metalaxyl (Apron 25WP) with a paint spray gun (T6A series 502, DeVilbiss Co., Toledo, OH). This concentration is comparable to the recommended field rate (4,27). Although this product is not registered for use on potato foliage, its formulation is very similar to that of the registered product, viz., Ridomil MZ 58, but without mancozeb. Between applications of the fungicide and simulated rain, the plants were placed in a greenhouse with the same environmental conditions as mentioned before. The fungicide was applied at varying times and the simulated rain at one time for all treatments, resulting in different time intervals between application of metalaxyl and simulated rain. Even when this interval was 0 hr, the fungicide on the leaf surface had dried before exposure to simulated rain.

Experimental design. For the first series of experiments (in February 1985) the time intervals between metalaxyl treatment and application of simulated rain were 0, 6, 30, and 78 hr. Leaf samples were taken after 0, 10, 20, and 30 min of rain. Because most of the metalaxyl appeared to be washed off within 10 min of simulated rain, the experiments were repeated (in September 1985) with shorter rainfall durations (0, 3, 6, 10, and 20 min) and shorter time intervals between applications of the fungicide and simulated rain (0, 3, 6, 30, and 54 hr). In this last series of experiments, only one cultivar (Norchip) and two pH levels (2.8 and 4.6) were included. Because only four simulated rain exposure tables were available, it was necessary to use a split-split-plot design, with pH of rain as the main plot (with a rain table as experimental unit), cultivar and time interval between spray and rain as the subplot (one plant as experimental unit), and rainfall duration as the sub-sub-plot (one lateral leaflet as experimental unit). Three to five plants were used for each treatment, and the experiments were repeated twice in the first series and four times in the second series (considered as blocks in the statistical analysis).

Sampling procedure. Each sample consisted of one leaf disk (0.33 cm^2, about 1 mg dry weight) per treatment, obtained with a paper punch from the center of a lateral leaflet halfway between the margin and midvein. In one experiment of the second series, 1.5-cm^2 disks were cut out with a cork borer. Because metalaxyl might accumulate in the leaf margins (18,27), paired samples from the tip and center of each leaflet were taken in one of the experiments. This was only done with leaves of Norchip before application of simulated rain and after 10 min of simulated rain at pH 2.8 and 4.6. The difference between concentrations at the tip and in the center was only affected by duration of simulated rain (higher concentrations at the tip) and not by pH of rain or time interval between spraying and raining (Table 1).

Fungicide residue analysis. Residues of metalaxyl were determined with a bioassay method in which *Phytophthora boehmeriae* Sawada (isolate P1257) was used as test organism (1,11). Metalaxyl was extracted from each leaf disk in 2 ml of methanol for 24 hr, with a reported efficiency of about 90% (11). The methanol was evaporated in a water bath at 70–80 C, and the residue was dissolved in 1 ml of cornmeal agar (Difco), autoclaved, and poured into 35-mm-diameter plastic petri dishes. A 4-mm-diameter plug of a 5-day-old colony of *P. boehmeriae* on V-8 agar was placed on the edge of each plate, and after 4 days at 24 C, the largest colony radius was measured to assess the metalaxyl content per leaf disk. Standard series with known metalaxyl concentrations (0, 1, 5, 10, 50, 100, 200, and 500 ppb, w/w) and untreated leaf disks were analyzed simultaneously. Linear regression of colony radius on the logarithm of metalaxyl concentration gave coefficients of determination (R^2) ranging from 90 to 96%. Initially, standard curves were obtained with disks of each potato cultivar at each pH level of simulated rain, but slopes and intercepts of the regression equations were not significantly different, and the data from each experiment were combined to form one regression equation per experiment.

Inoculation with *P. infestans*. After samples had been taken from plants that had been treated with metalaxyl and exposed to simulated rain for 30 min, the terminal leaflets (from which no samples had been taken) were inoculated with a 50-μl sporangial suspension of *P. infestans* (Mont.) de Bary and incubated in a mist chamber at 18 C. The mist was generated from a simulated precipitation solution at pH 4.0, produced by a humidifier (DeVilbiss Co., Somerset, PA) as described previously. Sporangial suspensions of *P. infestans* were prepared in the same solutions as used for the mist from 11- to 16-day-old cultures on V-8 agar, resulting in concentrations of 5.4 ($\pm$1.9) $\times$ 10^4 sporangia per milliliter. Control plants were treated with simulated acidic rain and not with metalaxyl, then inoculated with *P. infestans*.

Data analysis. The effects of pH, interval between application of fungicide and rain, duration of rainfall, and their interactions on metalaxyl concentration were analyzed in a regression analysis with a split-split-plot design. Sums of squares with more than two levels of a treatment were partitioned into single degree-of-freedom terms of a polynomial function and tested against their respective error sum of squares. The metalaxyl concentrations were expressed as proportions remaining of the concentration deposited originally, and these were transformed logarithmically so that residual values became normally distributed.

To estimate wash-off rates of metalaxyl from potato leaves, the metalaxyl concentrations were regressed on rainfall duration for each combination of treatments (block, pH, cultivar, and time-interval between spraying and raining), using a nonlinear model. Because of its systemic nature, metalaxyl is probably not washed off completely. Therefore, we selected an exponential decay model with an asymptote, similar to the model used by Pree et al (14) for attenuation of a systemic insecticide over time:

$$C_t = A + (M - A)e^{-Rt} + E_t,$$

in which C = metalaxyl content (ng/cm^2), A = asymptote (ng/cm^2), M = initial metalaxyl content (ng/cm^2), R = wash-off rate (min^{-1}), t = rainfall duration (min), and E_t = error term. The iterative method used was the multivariate secant (or DUD) method in the nonlinear procedure of the Statistical Analysis System (16). The parameter estimates for A, M, and R were analyzed using multivariate regression with a split-plot design (pH in the main plot and cultivar and time interval in subplots).

RESULTS

Metalaxyl retention. The results of both series of experiments were very similar. The proportion of metalaxyl remaining was initially regressed on pH, time interval, cultivar, rainfall duration, and all possible interactions (full regression model). Subsequently the nonsignificant interactions were omitted from the model so that their degrees of freedom were included in the error terms (reduced model). There were significant main effects of time interval and rainfall duration but not of pH and cultivar (Table 2). Metalaxyl was washed off rapidly in the first few minutes of rainfall and reached an asymptote between 10 and 20 min of rainfall (1.5 and 2.9 mm of rain, respectively) (Fig. 1A,B). When simulated rain was applied to leaves within 1 hr after they had been sprayed with metalaxyl, there was a steep decline in the proportion

TABLE 1. Effects of duration of simulated rain on metalaxyl concentration (ng/cm^2) at the tips and centers of potato leaflets (pooled data for different time intervals since spraying)

Min of rain	Metalaxyl conc. from Tip	Metalaxyl conc. from Center	Mean paired difference	t Value	$P > (t)$
0	480 ± 60[a]	500 ± 72	−20 ± 43	−0.5	0.60
10	93 ± 21	42 ± 8	51 ± 18	2.8	0.01

[a]Standard error of the mean.

of metalaxyl remaining on/in the foliage. Eighty percent of the fungicide was washed off by 1.5 mm of rain within 10 min and 90% by 4.4 mm of rain within 30 min. The decline was not as rapid after longer time intervals between applications of fungicide and rain. Before application of simulated rain, the metalaxyl concentrations on/in the leaves also decreased rapidly (Fig. 1A,B). In the first series of experiments (in February), the metalaxyl concentration dropped to 70% of the initial deposit within 6 hr after spraying, and in the second series (in September), the concentration dropped to 40% within 3 hr after spraying. After 30 or 6 hr (in the first and second series, respectively), the concentrations were down to 25% of the original deposit. Subsequent declines were much slower.

There were significant interactions (Table 2) between time interval and rainfall duration, between time interval and cultivar (only in the first series of experiments), and between pH of rain and rainfall duration (in both series). The first interaction, between time interval and rainfall duration, was due to the larger difference in metalaxyl concentration between the different time intervals before rain than after rain (Fig. 1A,B). Plots of proportion of metalaxyl remaining versus time interval or rainfall duration, for different cultivars or pH levels, indicated that the last two interactions occurred when there was only a little fungicide left (Fig. 2A,B). These interactions seemed to be due to sampling error at low concentrations and are probably not biologically meaningful.

Nonlinear model. The parameter estimates for maximum (initial) concentration (M), wash-off rate (R), and asymptotic concentration (A) of the nonlinear model, in which metalaxyl concentration was regressed on rainfall duration for each combination of treatments, were affected by time interval between applications of the fungicide and simulated rain and by cultivar (first series of experiments). The estimates were not affected by acidity of rain, and there were no significant interactions between any of the independent variables. Therefore, the parameter estimates were regressed on time interval and cultivar only, in a multivariate analysis (Table 3). Estimates of A and M were significantly affected by time interval between spraying and raining in the first series of experiments (Table 3). In the second series, the variability was higher, and the time interval effect was only significant for M (Table 3). Estimates for the wash-off rate were not affected by time interval between spraying and raining but were dependent on cultivar (Table 3). However, multivariate tests showed that only the overall effect of time interval was significant

TABLE 2. Analysis of variance table for metalaxyl retention (expressed as proportion remaining) on potato leaves, as affected by pH of simulated rain, time interval between applications of metalaxyl and simulated rain, potato cultivars, and rainfall duration in two series of experiments, the first with cultivars Norchip and Monona, and the second with Norchip only

	First series		Second series	
Source	df[a]	SS[b]	df	SS
Block (B)	1	1.1	3	19.7
pH[c]	3	12.3	1	13.3
B × pH (error a)	3	8.9	3	9.4
Interval[d] (I)	3	77.1**[e]	4	29.0**
Cultivar (C) × I	4	19.3**	...	...
B × pH × I (× C) (error b)	49	36.6	28	15.1
Duration[f] (D)	3	285.6**	4	55.5**
pH × D	9	15.0**	4	5.0**
I × D	9	14.2**	16	5.9
Residual	170	68.1	127	48.7
R^2 (%)		87.3		73.0
C.V. (%)		21.7		30.9

[a] Degrees of freedom.
[b] Sequential sums of squares.
[c] pH: 2.8, 3.4, 4.0, and 4.6 in the first series; 2.8 and 4.6 in the second series.
[d] Time interval between application of metalaxyl and simulated acid rain: 0, 6, 30, and 78 hr in the first series; 0, 3, 6, 30, and 54 hr in the second series.
[e] Significance level of F-test (** = $P \leq 0.01$).
[f] Rainfall duration: 0, 10, 20, and 30 min in the first series; 0, 3, 6, 10, and 20 min in the second series.

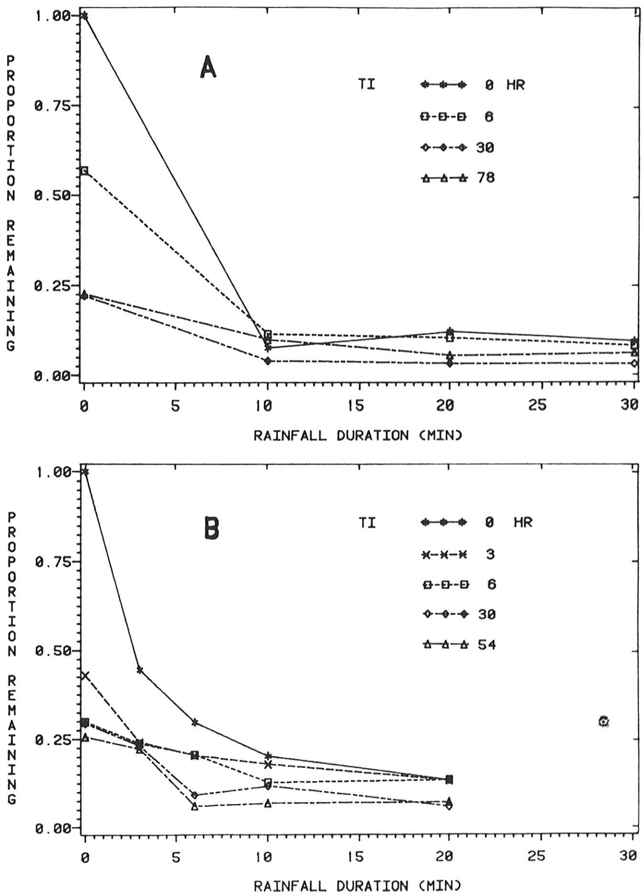


Fig. 1. Decline in metalaxyl concentration on potato leaves (expressed as proportion metalaxyl remaining of the original deposit), attributed to simulated rain, after time intervals (TI) of **A,** 0, 6, 30, and 78 hr since spraying in the first series of experiments and **B,** 0, 3, 6, 30, and 54 hr since spraying in the second series.

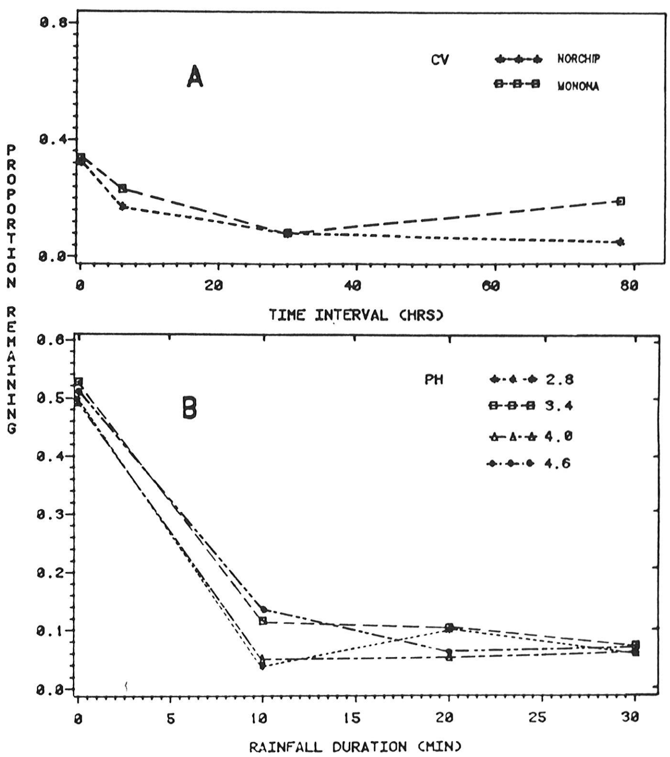


Fig. 2. Interactions **A,** between time interval after spraying of metalaxyl and potato cultivar and **B,** between rainfall duration and pH of simulated rain for effects on proportion of metalaxyl remaining on potato leaves after application of simulated rain.

for the combined parameter estimates and not the overall cultivar effect. Thus, the three parameters for the nonlinear model were estimated anew for the different time intervals, regardless of any of the other independent variables (Table 4). The predicted values from nonlinear regression (using the parameter estimates from Table 4) described the observed trends very well (Fig. 3A,B). Both M and A decreased when simulated rain was applied at longer time intervals after the fungicide spray (Table 4). Parameter estimates for M and A for the different blocks (replicates) were regressed on time interval. In the first series of experiments, both linear and quadratic trends were significant for M and A. In the second series, linear, quadratic, and cubic trends were significant for M. These trends were again described by an exponential decay model with an asymptote (Fig. 4A,B).

Infection by *P. infestans*. In the first series of experiments, the control plants of both cultivars became severely infected. Plants sprayed with metalaxyl and subjected to 4.4 mm of rain within 30 min had very few lesions on cultivar Monona only (Table 5). In the second series, only 40% of the control plants became infected, but none of the plants treated with metalaxyl and simulated rain became infected. Yet, at the time of inoculation, the metalaxyl concentrations had decreased to 5–10% of the original deposit, equivalent to 20–60 ng/cm^2 of leaf area (or 6–18 μg/g dry weight). Regression analysis for the percentage of plants infected and the logarithm of the number of lesions per plant indicated that there were no significant effects of pH of rain, and there were no significant interactions between pH and any of the other factors. The differences in late blight infection between metalaxyl and control treatments were highly significant ($P < 0.01$) in the first series of experiments but significant at only the $P = 0.06$ in the second. In the first series, there was a significant interaction between metalaxyl and cultivar in their effects on number of lesions per plant: late blight control by the residual metalaxyl was better on Norchip than on Monona.

TABLE 3. Analysis of variance for regression of parameter estimates of the asymptotic concentration (ng/cm^2), rate of wash-off by rain (min^{-1}), and initial concentration (ng/cm^2) of metalaxyl on block, potato cultivar, and time interval between applications of metalaxyl and simulated rain in two series of experiments

			Sequential sums of squares		
Series	Source	df[a]	Asymptotic conc.	Wash-off rate	Initial conc.
1	Block	1	1,335	1.73*[b]	881,513**[b]
	Cultivar[c]	1	891	1.53*	1,187
	Time interval[d]	3	7,797**	0.65	3,746,684**
	Residual	58	35,138	16.93	1,467,184
	R^2 (%)		22	19	76
	C.V. (%)		90	99	40
	MANOVA test			HLT[e]	F
	Overall interval effect			2.78	16.9**
	Overall cultivar effect			0.10	1.9
2	Block	3	9,573*[b]	0.42	624,369**[b]
	Time interval	4	2,003	0.44	148,359*
	Residual	27	35,887	3.40	354,018
	R^2 (%)		24	20	69
	C.V. (%)		130	109	61
	MANOVA test			HLT	F
	Overall interval effect			0.68	1.3

[a]Degrees of freedom.
[b]Significance level of F-test (** = $P < 0.01$, * = $P < 0.05$).
[c]Norchip and Monona.
[d]Time interval between spraying and raining: 0, 6, 30, and 78 hr in first series; 0, 3, 6, 30, and 54 hr in second series.
[e]Hotteling-Lawley test criterion for MANOVA (multivariate analysis of variance).

TABLE 4. Estimates of the parameters in the model $C(t) = A + (M - A)e^{-Rt}$: asymptotic concentration (A in ng/cm^2), rate of wash-off by rain (R in min^{-1}), and initial concentration (M in ng/cm^2) of metalaxyl on/in potato leaves in two series of experiments

		Parameters in model						
	Time interval	A		R		M		
Series	(hr)	Est.[a]	SE[b]	Est.	SE	Est.	SE	R^2
1	0	48.91	20.91	0.265	0.068	776.10	26.53	81.6
	6	50.32	23.01	0.198	0.051	565.26	26.46	70.8
	30	17.66	7.94	0.269	0.246	170.58	9.82	61.9
	78	27.74	17.96	0.171	0.089	198.27	18.72	40.6
2	0	68.30	37.64	0.268	0.100	423.06	45.72	56.9
	3	49.72	29.03	0.253	0.137	221.55	28.11	51.0
	6	49.43	20.92	0.236	0.171	144.14	21.55	48.0
	30	14.07	34.58	0.161	0.109	134.82	19.46	37.7
	54	25.47	16.36	0.250	0.127	133.82	17.11	48.3

[a]Parameter estimate.
[b]Asymptotic standard error.

DISCUSSION

Attenuation by acidic rain. In this study, we showed that attenuation of metalaxyl was not affected by pH of simulated rain. So far, only wash-off of hydroxyl compounds has been found to be accelerated by acidic rain (24,26). Metalaxyl has a relatively high solubility in pure water (7,100 ppm), and its hydrolysis is little affected by pH levels lower than 7 (4). Regardless of acidity of rain, metalaxyl was washed off rapidly from potato foliage, which could be explained by its high solubility in water. After 20 min of rain (2.9 mm), only 5–15% of the metalaxyl was left. The remaining metalaxyl might have been inside the leaf tissues, because part of the metalaxyl applied can be taken up within 15 min after foliar

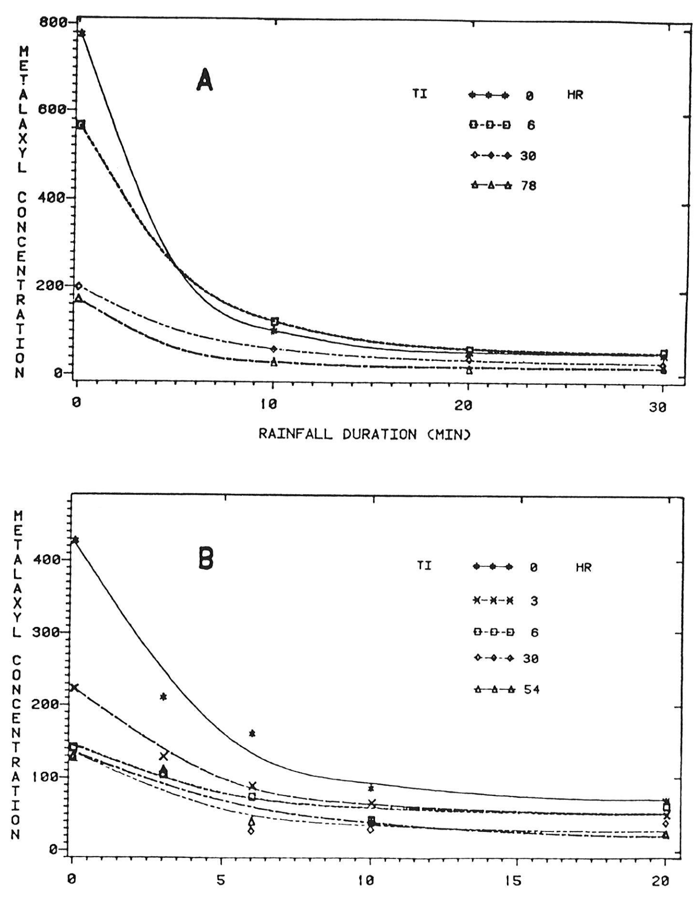


Fig. 3. Decline in metalaxyl concentration on potato leaves (ng/cm^2), attributed to simulated rain, after time intervals (TI) of **A,** 0, 6, 30, and 78 hr since spraying in the first series of experiments and **B,** 0, 3, 6, 30, and 54 hr since spraying in the second series of experiments. Predicted values from nonlinear regression are indicated by lines, and mean values of observed concentrations by stars, crosses, squares, diamonds, and triangles after 0, 3, 6, 30, and 54 or 78 hr since spraying, respectively.

application (18). Besides rainfall duration and chemical composition of rain, several other factors could influence wash-off of pesticides from leaf surfaces, such as intensity and distribution of rain and relative humidity (24). These factors would need to be investigated to improve the predictive ability of pesticide wash-off models.

Attenuation over time. Metalaxyl concentrations declined rapidly even without rainfall, so only 25% of the original concentration was left 30 hr after spraying. Wynn and Crute (27) reported a similar loss of metalaxyl from leaf disks. Because the leaves did not grow, and the distribution in the lamina was probably uniform, the most likely explanations for the decrease in metalaxyl content would be translocation to the root system, metabolic decomposition inside the plant tissues, and volatilization at the leaf surface (27). Basipetal translocation of metalaxyl into the roots was only minimal (less than 1% after 2 wk) in tomato (28) and somewhat higher (7% after 24 hr) in pea (18). Metabolic decomposition in lettuce was only 6% within 1 wk (27). Thus, the main factor contributing to attenuation over time is probably volatilization. Indeed, vapor activity of metalaxyl has been demonstrated (27). Attenuation of metalaxyl over time was faster in September than in February, which might be explained by higher temperatures (27), despite the fact that the greenhouse temperature was controlled at 25 C during the day and 18 C at night during both series of experiments. Photodegradation could be another explanation, but we have not found any report on photodegradation of metalaxyl.

Distribution in the lamina. Although leaf disks were always taken from the center of a leaflet, metalaxyl concentrations were probably representative for the whole leaflet (before application of rain), because we did not observe significant differences in concentration between disks taken from the tip and those taken from the center of a leaflet. Metalaxyl has been found to accumulate in the leaf margins of certain plants (18,27), but it is uniformly distributed in the lamina of others (18,28). Potato may belong to the latter group, as does tomato (28). Only after application of simulated rain were the concentrations higher at the tip than in the center, probably because of redistribution on the leaf surface. This is common with pesticides in general (7).

Modeling of attenuation. The metalaxyl concentration decreased curvilinearly with rainfall duration and time interval between spraying and application of simulated rain. Similar curvilinear decays have been found for other protectant and systemic pesticides (6,14). The most common model used to describe pesticide weathering has been the exponential decay model, based on first-order kinetics (6,21,22). This simple model, in which a constant rate of decay was assumed, often did not fit the data very well (6). It was improved by fitting two curves (8) or by logarithmic (21) or cubic root (3,20) transformation of the weathering factor. The results of these manipulations were that the initial part of the decay curves was steeper and the final part shallower than those of the simple exponential decay model. A similar effect has been obtained by incorporating an asymptote into the exponential decay model (14). This model seems especially appropriate to describe weathering of a systemic fungicide during the first few days after spraying, until surface residues have disappeared and further decay (caused by redistribution and metabolic decomposition) is relatively slow. The asymptotic exponential decay model accurately described our data on attenuation of metalaxyl over time and by simulated rain. Incorporation of both factors simultaneously into the model failed to describe the observed data properly (*unpublished*). A combined model could probably be improved by including parameters for two asymptotes, one for attenuation over time and one for loss by simulated rain.

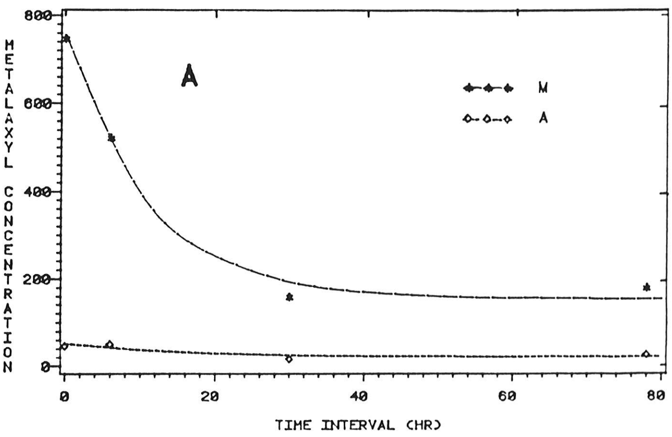
Stanley et al (22) obtained a slightly better fit to their data on loss of an insecticide over time and by rain with a concentration-dependent model than with a first-order model with an asymptote. However, the rate parameter for fungicide loss caused by rain in our model with an asymptote was not dependent on the initial concentration of metalaxyl after different periods since spraying of the fungicide. Therefore, we did not try to fit a concentration-dependent model to our data.

Conclusion. Metalaxyl concentrations on potato leaves declined rapidly over time and with simulated rain, regardless of its acidity (pH 2.8–4.6). Despite attenuation to 5–10% of the original metalaxyl concentration, late blight was almost completely controlled by the remaining metalaxyl when it was applied at a rate comparable to that recommended for the field. The concentrations remaining after 3 days or after 4.4 mm of simulated rain (6–18 $\mu g/g$ of dry leaf tissue) were similar to those obtained for lettuce by Wynn and Crute (27) after 3 days (assuming that lettuce leaves contain 95% water). This amount of metalaxyl was apparently sufficient to control late blight and probably entered potato leaf tissue within 1 hr after spraying. Rain at any pH may be irrelevant

TABLE 5. Percentage of plants infected by *Phytophthora infestans* and number of late blight lesions per potato cutting after treatment with metalaxyl (200 ppm, w/w) and simulated acidic rain (8.8 mm/hr) for 30 min, or with simulated acidic rain only (control), in two series of experiments

		Control		Metalaxyl	
Series	Cultivar	Infection (%)	No. lesions	Infection (%)	No. lesions
1	Norchip	95 (±5)[a]	9 (±3)	0 (±0)	0 (±0)
	Monona	100 (±0)	4 (±1)	5 (±2)	0.05 (±.02)
2	Norchip	40 (±15)	5 (±3)	0 (±0)	0 (±0)

[a]Standard error of the mean.



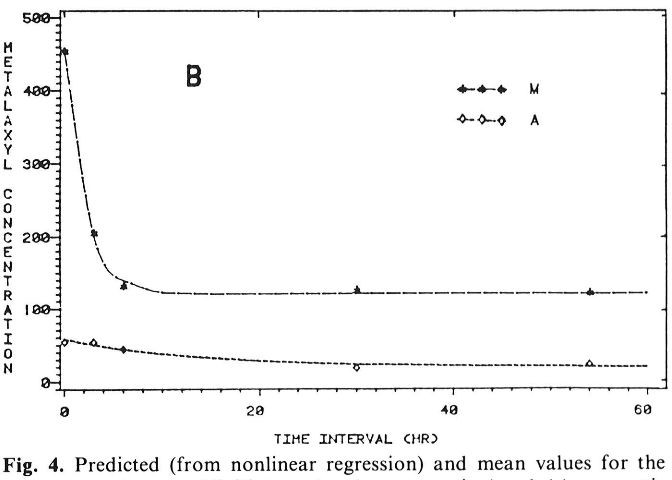


Fig. 4. Predicted (from nonlinear regression) and mean values for the parameter estimates M (initial metalaxyl concentration) and A (asymptotic metalaxyl concentration) for an exponential decay model with asymptote for wash-off of metalaxyl by rain, as affected by time interval (TI) between application of fungicide and simulated rain. Regression equations for predicted values **A**, in the first series of experiments: $M = 154.4 + (755.1 - 154.4)e^{-0.09\mathrm{TI}}$ ($R^2 = 93\%$) and $A = 21.4 + (51.7 - 21.4)e^{-0.06\mathrm{TI}}$ ($R^2 = 94\%$), and **B**, in the second series of experiments: $M = 120.0 + (454.0 - 120.0)e^{-0.47\mathrm{TI}}$ ($R^2 = 75\%$) and $A = 19.1 + (57.5 - 19.1)e^{-0.07\mathrm{TI}}$ ($R^2 = 56\%$).

to control of late blight by metalaxyl if all the metalaxyl that can possibly be taken up by the plant enters almost instantaneously after spraying, because metalaxyl is most effective in controlling growth and development of *P. infestans* after penetration into the plant (5). Weathering of metalaxyl at the surface (over time or by rain) may be important if amounts retained on the surface can contribute to further uptake later, e.g., after rewetting of the foliage by mist or dew (23).

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