A Two-Compartment Model for the Dissipation of Deltamethrin on Soil

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The dissipation of deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] on soil was studied in one indoor and three field experiments. When deltamethrin was pipet applied, dissipation was first order if degree-days above 0 °C (deg-day$_0$) rather than days were used as the independent variable. The half-life was 724 deg-day$_0$ indoors and 758 deg-day$_0$ in the field. When deltamethrin was boom sprayed, a biphasic first-order plot was observed. A two-compartment model that predicts an initial fast loss of residue followed by a slower first-order degradation gave a good fit to the data. This model predicted DT_{50} values of 463 and 192 deg-day$_0$ from ground and aerial boom applications, respectively. An outdoor petri dish experiment confirmed that the 0–7 day dissipation was faster when deltamethrin was boom sprayed and a surface loss process was indicated. It is postulated that the high water volumes with pipet application washed the deltamethrin into the soil and, with less surface loss, dissipation was slowed.

INTRODUCTION

There is extensive literature documenting the persistence of insecticide residues in soil. In the statistical analysis of such residue data, a mathematical model is usually applied after the data are obtained, in a retrospective approach to characterizing residue behavior. The use of the zero-order, half-order, first-order, hyperbolic (Michaelis–Menten), and power–rate models, linear and curvilinear regression with various transformations of dependent and independent variables, and multiple linear regression with soil and climatic variables has been reviewed (Edwards, 1972; Hamaker, 1972; Goring et al., 1975; Hurle and Walker, 1980).

Another approach to characterizing residue behavior is to use laboratory measured and estimated chemical properties together with theoretical equations to predict residue persistence in the field. This predictive approach has evolved from the benchmark method (Hamaker, 1972; Goring et al., 1975), through the concepts of model ecosystems (Metcalf et al., 1971) and environmental chemodynamics (Hague and Freed, 1975), to very complex environmental and simulation modeling (Walker, 1974; Walker and Barnes, 1981; Gunther, 1983; Swann and Eschenroeder, 1983). An inherent danger in an exclusively predictive approach is that laboratory measured chemical properties may not truly represent residue behavior in the field (Frehse and Anderson, 1983).

Ideally, the statistical analysis and modeling of residue data should provide (1) meaningful statistics, such as half-life or DT_{50} (disappearance time for initial 50% of residue), to summarize residue dissipation and for comparison with other studies, (2) an appropriate mathematical model that can be used for predictive purposes, and (3) information about the mechanism of the dissipation process. When a residue dissipation can be adequately described by the first-order model (FOM), all three of the above criteria are met. Often however, the FOM does not fit the data because it is too great an oversimplification of the complex soil system. Very few of the models that have been proposed for non-first-order situations meet all three of the above criteria.

In this paper, we propose a simple two-compartment model (2CM) that meets our three criteria and applies to situations where residue dissipation deviates from first-order because of a rapid initial loss. A rapid initial loss of pesticide residues from soil, and thus a biphasic first-order plot, is often observed (Edwards, 1972; Zimdahl and Gwynn, 1977; Williams and Eagle, 1979; Savage and Jordan, 1980; Brewer et al., 1981 Felsot et al., 1982). Gunther and Blinn (1955) were the first to report a two-phase disappearance for insecticides on and in plants, and they predicted such would occur "doubtless also in soils". Our 2CM is complementary to one proposed by Hamaker and Goring (1976). Their model also meets our three criteria, and is applicable to situations where residue dissipation is initially first order but then the rate slows due to adsorptive binding of the residues to the soil.

Deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] is a synthetic pyrethroid insecticide active against several crop pests. Its agricultural use will inevitably produce soil residues. Previous reports have indicated that deltamethrin has a half-life of 3–8 weeks in mineral soils (Chapman et al., 1981; Miyamoto and Mikami, 1983; Hill, 1983). In our previous study (Hill, 1983), where deltamethrin was pipet applied to the soil, the FOM gave a reasonable fit to the dissipation data. These results are summarized in this paper for comparison with our current studies. We are now reporting on field dissipation experiments where the deltamethrin was applied via ground and aerial boom sprayers. When our 2CM was applied to these field experiments, the fit was superior to that of the FOM. It appears that the best-fit model for deltamethrin dissipation depends on the method of application. To confirm and explain this observation, we also conducted an outdoor petri dish experiment by using both methods of application.

EXPERIMENTAL SECTION

Chemicals. Deltamethrin analytical standard (99.0% purity) was obtained from Roussel Uclaf (Romainville, France) and the formulated products, 25 g/L and 50 g/L emulsifiable concentrates (EC), were supplied by Hoechst Canada Inc. (Regina, Saskatchewan).

Soils. The soil at the Lethbridge, Alberta, site was a Lethbridge sandy clay loam (Typic Haploboroll, fine loamy, mixed, mesic) containing 24.2% clay, 20.5% silt, and 55.3% sand with a cation exchange capacity of 20.1 mequiv/100 g. The organic matter content was 2.2%, the pH was 7.9 as a 1:1 soil–water slurry, and the moisture holding capacity was 18.8% at 30 kPa.

The soil at the Taber, Alberta, site was a Cavendish sandy clay loam (Aridic Haploboroll, fine loamy, mixed, mesic). It contained 23.0% clay, 18.9% silt, and 58.1%

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Table I. Methods for Experiments on the Long-Term Dissipation of Deltamethrin Soil Residues

experiment	location	date of field application	rate of application, g/ha	method of application	water vol, L/ha
1980 indoor incubation[a]			17.5	dropwise via 5-mL pipet[b]	3950
1980 outdoor microplot	Lethbridge	June 19	17.5	dropwise via 5-mL pipet[b]	1250
1981 small field plot	Lethbridge	June 25	17.5	tractor-mounted boom sprayer	110
1982 large field plot	Taber	June 2	10.7	aircraft[c] boom sprayer	9.35

[a] Incubation of treated Lethbridge soil in darkness, with daily regime of 25 °C for 16 h/10 °C for 8 h. [b] Surface application, not incorporated. [c] Pawnee PA 25-235.

sand with a cation exchange capacity of 17.2 mequiv/100 g. The organic matter content was 1.3%, the pH was 6.9 as a 1:1 soil–water slurry, and the moisture holding capacity was 16.4% at 30 kPa.

Long-Term Dissipation Experiments. One indoor incubation (1980) and three field (1980, 1981, 1982) experiments were conducted on weed-free fallow (Table I). In the 1980 indoor incubation experiment, the soil was sampled eight times between 0 and 16 weeks after application. Duplicate pots, 12.7-cm diameter, were sampled at each time by removing all the soil in layers. Similarly, in the 1980 outdoor microplot experiment, the soil was sampled eight times between 0 and 16 weeks, and at 40 and 52 weeks after application. Three different 20 × 20 cm microplots were sampled at each date by again removing all the soil in layers. Extensive method details for the 1980 experiments have been published elsewhere (Hill, 1983). In the 1981 small field plot experiment, four replicate plots, 3 × 9 m each, were sampled seven times between 0 and 16 weeks and at 43 and 52 weeks after application. On each sampling date, 36 soil cores, 2.38-cm i.d., taken from 18 sites (two cores per site) in a stratified random design, were combined to give one composite sample per plot. In the 1982 large field plot experiment, four replicate plots, 20 × 20 m each, were sampled six times between 0 and 5.14 weeks after application. This experiment had to be terminated at 5.14 weeks because of cultivation. Within each replicate, 32 soil cores (as above), taken from 16 sites (two cores per site) in a stratified random design, were combined to give one composite sample. To check on the sampling variation at each date, a second set of 32 soil cores, from 16 different sites, was taken to give a second composite sample. Over the six sampling dates, there was good agreement between the duplicate composite samples (CV = 13.7%), and thus the mean composite residues are reported for this experiment.

For all experiments, the residue results reported pertain to the 0–2.5-cm soil layer. In the 1980 experiments, 2.5–5.0-cm samples showed little, if any (<1% of applied), deltamethrin present (Hill, 1983).

Outdoor Petri Dish Experiment. In July, 1984, treated samples of Lethbridge soil, 50.0-g each and contained in open glass petri dishes (9.0-cm diameter), were placed outdoors for 7 days to investigate the short-term dissipation of deltamethrin. To simulate the two methods of application used in the previous long-term dissipation experiments, the deltamethrin (50 g/L EC) was either pipet applied or nozzle sprayed onto the soil. In the pipet application, deltamethrin at 18.9 g/ha was added dropwise from a 3-mL pipet yielding an effective water volume of 4720 L/ha. In the nozzle application, deltamethrin was applied at 13.6 g/ha in 56.7 L/ha water volume by using a laboratory sprayer (McDonald and Hall, 1965) equipped with a Delavan LF-.67 (65°) nozzle. These rates and water volumes approximated those in the previous pipet applied and boom sprayed experiments (Table I).

The experiment consisted of four replications of the following seven treatments, each composed of a method of application, a postapplication treatment, and a time of sampling: (1) pipet applied, the soil left undisturbed, 2 h; (2) as per 1, 7 days; (3) nozzle sprayed, the soil left undisturbed, 2 h; (4) as per 3, 7 days; (5) nozzle sprayed, 3 mL of water pipetted on immediately before spraying, 7 days; (6) nozzle sprayed, 3 mL of water pipetted on immediately after spraying, 7 days; (7) nozzle sprayed, a 25.0-g layer of sand (pH, neutral) placed on top of the soil surface 2 h after spraying, 7 days. The amount of deltamethrin remaining in each treatment was determined by residue analysis. Analysis of variance with a completely randomized model was applied to the residue data and specific comparisons between treatments were tested with single degree of freedom contrasts (Steel and Torrie, 1980). These contrasts compared the amount of deltamethrin dissipated between 2 h and 7 days.

The 0–7 day weather was sunny (5 of 7 days), warm (mean maximum 27.4 °C, mean minimum 11.9 °C), and only a trace of rain fell on the treated soil. The soil moisture was 7.6% on day 0 but quickly dried down to 1.1% moisture by day 1. To provide adequate moisture for microbial activity, 1.3 mm of water was added to each soil sample on day 2 and 1.6 mm on day 3. The soil moisture by day 6 had dried down to 4.5%, and on day 7 it was 2.1%.

Residue Analysis. All soil samples were analyzed with a previously reported ^{63}Ni electron-capture GC method (Hill, 1983). The average method recovery ± standard deviation was 92.5 ± 2.4% over fortification levels of 1, 10, and 100 ppb. Residue results were not corrected for method losses.

Data Analysis. For all long-term dissipation experiments, a nonlinear parameter estimation program was used to relate residues (total μg/sample) to either weeks or degree-days above 0 °C (deg-day$_0$) after application of the chemical. The use of degree-days, as previously reported for fenvalerate dissipation on alfalfa (Hill et al., 1982), adjusted for the effect of varying temperatures. Deg-day$_0$ were calculated according to the modified sine wave method of Allen (1976). Two models for the relationship between residues and time (weeks or deg-day$_0$) were fitted to the data:

(1) First-order degradation model (Gunther and Blinn, 1955; Gunther, 1969; Hamaker, 1972; Goring et al., 1975), where the rate of degradation is proportional to the residue remaining, i.e.,

$$\frac{dC}{dt} = -k_d C$$

$$\text{or } C = C_0 e^{-k_d t}$$

where C = residue after time, t, C_0 = initial residue, and k_d = degradation rate constant.

(2) Two-compartment dissipation model (Figure 1), where the overall rate of dissipation depends on the relative contribution of two competing processes, a "fast" surface loss from a deposited residue compartment vs. a "slower" degradation loss from a retained residue compartment. Assuming the two loss processes and the transfer process between compartments are first order, the

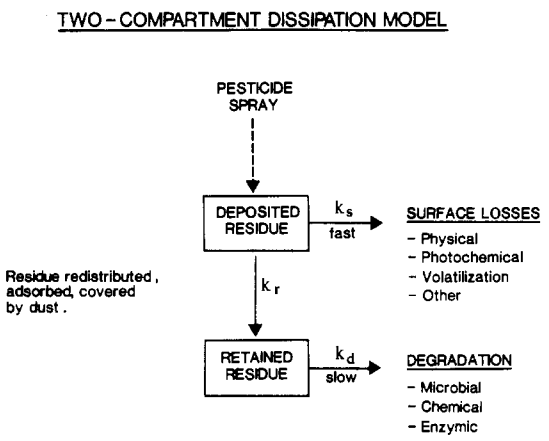

Figure 1. Two-compartment model for the dissipation of deltamethrin on soil.

loss of residue from the two-compartment system can be described by

$$\frac{dC_1}{dt} = -(k_s + k_r)C_1$$

and

$$\frac{dC_2}{dt} = k_rC_1 - k_dC_2$$

and, since $C = C_1 + C_2$, the following expression can be derived:

$$C = C_0e^{-(k_s+k_r)t} + C_0\frac{k_r}{k_s + k_r - k_d}e^{-k_dt} - e^{-(k_s+k_r)t}$$

where C = total residue after time t, C_1 = deposited residue after time t, C_2 = retained residue after time t, C_0 = initial residue deposited, k_s = surface loss rate constant, k_t = retention rate constant, and k_d = degradation rate constant.

The decision as to whether to use deg-day$_0$ rather than weeks as the independent variable was based on a visual assessment of "goodness of fit" as well as comparisons of the residual sums of squares. Choice of model, FOM or 2CM, was made by using a significance test of the following statistic:

$$F = \frac{(SSR_1 - SSR_2)/(df_1 - df_2)}{SSR_2/df_2}$$

where SSR_1, SSR_2 = residual sum of squares for the FOM and 2CM, respectively, and df_1, df_2 = residual degrees of freedom for the FOM and 2CM. Since the FOM is actually a special case of the 2CM, this statistic has an approximate F distribution under the null hypothesis. Similar test statistics (Hill et al., 1982) were used in the 1980, 1981, and 1982 field experiments to test for differences between replicates with respect to initial depositions and rate constants.

RESULTS

In the 1980 indoor incubation experiment, deltamethrin dissipated according to the FOM with a half-life of 4.9 weeks (Figure 2).

In the 1980 outdoor microplot experiment, the FOM gave a good fit to the dissipation data for the 0–12 week period only (Figure 3). The rate of dissipation slowed between 12 and 16 weeks (Sept/Oct), remained slow over the winter, then appeared to increase between 40 and 52 weeks (March/June). This seasonal effect on the rate of dissipation was caused by changes in temperature. When residue amounts were plotted against deg-day$_0$, the dissipation of deltamethrin was first order over the entire experiment (Figure 4).

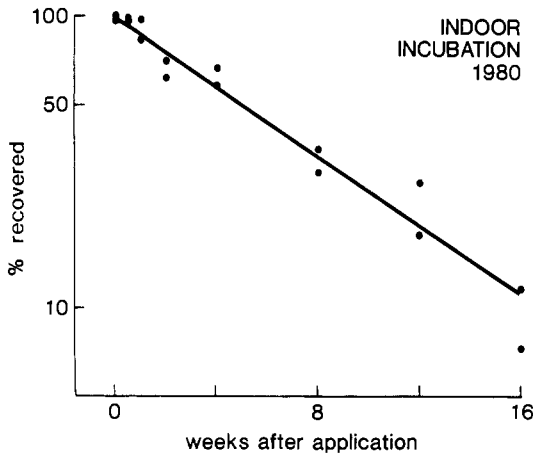

Figure 2. Dissipation of deltamethrin in the 1980 indoor incubation experiment. Deltamethrin was pipet applied at 17.5 g/ha; 100% recovery at week 0 was 13.5 g/ha.

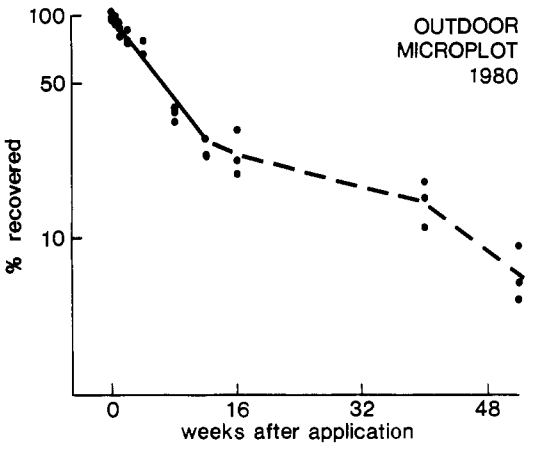

Figure 3. Dissipation of deltamethrin in the 1980 outdoor microplot experiment. Solid line is fitted by regression analysis, dashed line is drawn through mean values. Deltamethrin was pipet applied on June 19 at 17.5 g/ha; 100% recovery at week 0 was 14.0 g/ha.

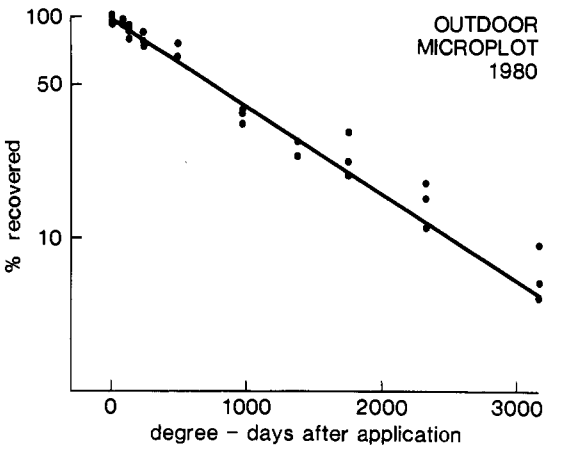

Figure 4. Dissipation of deltamethrin in the 1980 outdoor microplot experiment as a function of cumulative degree-days above zero after application.

Because there was also a seasonal effect (not shown) on the rate of dissipation in the 1981 small field plot experiment, percentage residue recovered was again plotted against deg-day$_0$ (Figure 5). The dissipation of deltamethrin was then first order except for a rapid initial loss between 0 and 113 deg-day$_0$ (0–1 week). Applying the

Table II. Dissipation of Deltamethrin Soil Residues in Long-Term Experiments

experiment	best-fit dissipation model[a]	rate constants $10^4(k_s \pm SE)$	rate constants $10^4(k_r \pm SE)$	rate constants $10^4(k_d \pm SE)$	DT_{50}, deg-day_0	mean deg-day_0/day[b]
1980 indoor incubation	FOM			9.6 ± 0.8	724	20.3[c]
1980 outdoor microplot	FOM			9.1 ± 0.4	758	15.6
1981 small field plot	2CM	177 ± 1870	426 ± 4730	7.7 ± 0.4	463	15.5
1982 large field plot	2CM	97 ± 23	111 ± 42	5.6 ± 2.6	192	16.8

[a] FOM = first-order model, 2CM = two-compartment model. [b] For the 0–16 week period of 1980, 1981 experiments; 0–5.14 week period of 1982 experiment. The DT_{50} (deg-day_0) divided by the mean deg-day_0/day will yield an approximate DT_{50} (days). [c] In darkness, no additional radiant heating.

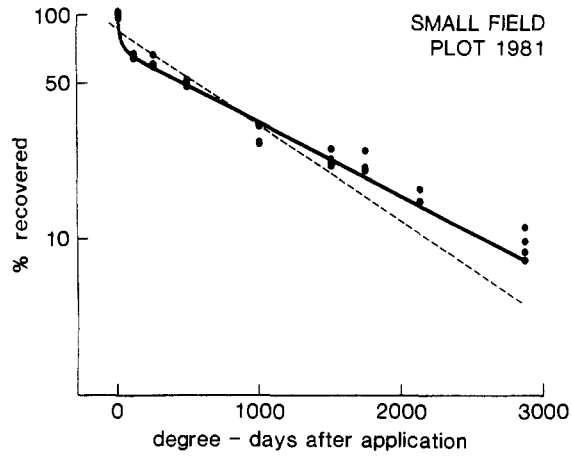

Figure 5. Dissipation of deltamethrin in the 1981 small field plot experiment. Solid line is predicted by the 2CM; dashed line is predicted by the FOM. Deltamethrin was boom sprayed (ground application) on June 25 at 17.5 g/ha; 100% recovery at week 0 was 11.8 g/ha.

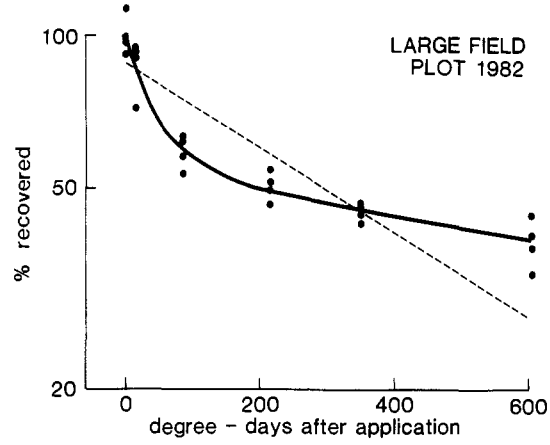

Figure 6. Dissipation of deltamethrin in the 1982 large field plot experiment. Solid line is predicted by the 2CM; dashed line is predicted by the FOM. Deltamethrin was boom sprayed (aerial application) on June 2 at 10.7 g/ha; 100% recovery at week 0 was 5.1 g/ha.

FOM to all the data gave an average fit which overestimated the short-term residues and badly underestimated the long-term residues (Figure 5). The 2CM gave a better fit to the data although it also slightly underestimated the long-term residues. There was a severe drought between 996 and 1739 deg-day_0 which may have slowed subsequent degradation. The 2CM would not take this effect into account.

A rapid initial loss of deltamethrin was also observed in the 1982 large field plot experiment (Figure 6). The 2CM fitted the data much better than did the FOM.

The best-fit models, parameter estimates, and DT_{50} values for the long-term dissipation experiments are summarized in Table II. The very large standard errors for k_s and k_r in the 1981 experiment should not be taken to indicate that the 2CM was inappropriate for these data. The significance test indicated a much better fit ($p < 0.001$) for the 2CM than for the FOM, but there were not enough observations early in this experiment to estimate both k_s and k_r with much precision. However, the average discrepancy between predicted and observed residue values (Figure 5) was small ($\simeq 3\%$) indicating that predictions based on the 2CM were insensitive to the uncertainty in k_s and k_r.

In the 1984 outdoor petri dish experiment, the 0–1 week dissipation of deltamethrin in the undisturbed treatments was significantly faster after nozzle spraying compared with pipet application (Table III). Within the nozzle-sprayed treatments, both covering the soil surface with sand or pipetting water on the soil after spraying slowed the dissipation of residues compared with the samples left undisturbed.

DISCUSSION

The dissipation of deltamethrin varied between experiments and the best-fit dissipation model correlated to the method of application (Table II). The FOM fitted the two pipet-applied 1980 experiments, while the 2CM better described the boom-sprayed 1981 and 1982 experiments. The biphasic dissipation of deltamethrin in our boom-sprayed field experiments is consistent with the pattern of dissipation reported for other synthetic pyrethroids on soil (Chapman and Harris, 1981). These authors consistently found that the 0–1 month rate of residue decline was faster than the 1–3 month rate. They also suggested that, since the dissipation of fenvalerate on the surface of a mineral soil was faster than when incorporated, the method of application was influencing persistence.

The overall rate of deltamethrin dissipation, indicated by the DT_{50} values (Table II), was much faster in the boom-sprayed 1981 and 1982 experiments than in the pipet-applied 1980 experiments. If the 2CM is correct, the 1981 and 1982 dissipation was faster only because of the additional surface losses with a boom-sprayed application. In support of this reasoning, the estimated k_d values (Table II), which represent the degradation rates without surface

Table III. Dissipation of Deltamethrin Soil Residues in the Outdoor Petri Dish Experiment

method of application	postapplication treatment	% deltamethrin remaining[a]
3-mL pipet	left undisturbed	84.3a
nozzle sprayer	left undisturbed	56.8c
	3 mL water pipetted on before spraying	53.5c
	3 mL water pipetted on after spraying	66.8b
	covered with sand after spraying	77.7a

[a] Deltamethrin remaining at day 7 compared with amount present 2 h after application. Amounts at 2 h were 18.0 g/ha for pipet application, 9.8 g/ha for nozzle sprayed. Means ($N = 4$) followed by different letters are significantly different ($p < 0.01$).

losses (Figure 1), were very similar between experiments.

The 1984 outdoor petri dish experiment was conducted to confirm and help explain the differences in deltamethrin dissipation between previous experiments. The fact that significantly more deltamethrin remained in the "left undisturbed" treatments after pipet application than after nozzle application (Table III) confirmed the trend in the long-term dissipation experiments. It was of concern whether this experiment could simulate "normal" field dissipation; however, the results correlated well with previous field results. The 84.3% deltamethrin remaining after pipet application (Table III) approximates the 90% deltamethrin left after 7 days of the pipet-applied 1980 experiment (Figure 3). Similarly, the 56.8% deltamethrin remaining after nozzle application compares with the 65% deltamethrin left after 7 days of the boom-sprayed 1981 experiment (Figure 5). The warm 0–1 week weather probably caused the dissipation to be slightly faster in the 1984 petri dish experiment.

Our 2CM predicts a surface loss of field residues when deltamethrin is boom sprayed. The outdoor petri dish experiment supports this "surface loss" theory because covering the soil surface with nonadsorptive sand slowed the dissipation of deltamethrin to that observed from pipet application (Table III). The decrease in dissipation when 3 mL of water was pipetted onto the soil immediately after spraying (Table III) probably indicates that some of the freshly deposited residue was washed below the soil surface. Pipetting 3 mL of water onto the soil before spraying also might have been expected to facilitate movement of residue into the soil, however, this subtreatment had no effect on the rate of dissipation. The results of this petri dish experiment suggest that a direct pipet application of an EC–water solution would place much of the deltamethrin below the soil surface. Thus, we attribute the first-order rate of dissipation previously observed in the 1980 experiments to the high water volumes with pipet applications (Table I). Instead of being distributed between two compartments (Figure 1), the high water volumes would have effectively "washed" the deltamethrin directly into the retained residue compartment followed by first-order degradation.

Although the 1981, 1982, and 1984 experiments suggest that a fast initial loss of deltamethrin occurs on the soil surface, further research would be required to specify the exact nature of this surface loss. With a reported vapor pressure of 1.5×10^{-8} mmHg for the technical product at 25 °C (Hoechst Canada Inc., 1983), it is difficult to attribute the surface loss of deltamethrin to volatility. According to the formulae of Nash (1983), deltamethrin deposited on the soil at 5.1 g/ha would have an expected flux of 25.8 mg/ha over the 0–1 week period. The actual loss of deltamethrin during the first week of the 1982 experiment was 2040 mg/ha (Figure 6). It is more plausible that deltamethrin was lost from the soil surface via photodecomposition. The photolabile nature of deltamethrin in solution and in the solid phase on glass or silica gel is well known (Ruzo et al., 1977). Although the importance of pesticide photolysis on soil surfaces is not well understood (Miller and Zepp, 1983), it has been observed for other synthetic pyrethroids. Holmstead et al. (1978) reported that for permethrin spotted at 2 g/ha on soil, there was 20% additional loss after 48 days in the sunlight compared with dark controls. Mikami et al. (1980) found that sunlight significantly accelerated the degradation of fenvalerate on soil thin-layer plates. The half-life of fenvalerate was 2–18 days depending on the soil type. More recently, Quistad and Staiger (1984) reported that fluvalinate had a half-life of about 1 day on sterilized sandy loam soil exposed to sunlight.

The 2CM applied to the boom-sprayed experiments satisfied our three criteria (previously described) for the statistical analysis of residue data. The estimates of k_d were relatively precise because several data points contributed to their estimation. The k_s and k_r estimates were not precise, especially in the 1981 experiment, where more 0–2 week samplings were required. Hamaker and Goring (1976) also noted that often one or more parameters in a nonlinear system will be very poorly determined by the data. The uncertainty in the k_s and k_r values should not detract from the overall usefulness of the 2CM. Our 2CM is designed for situations where a fast initial loss of residues is observed. When a deviation from first order occurs due to the binding of long-term residues, the model of Hamaker and Goring (1976) should apply. Both models provide a reasonable approach to the statistical analysis of biphasic residue dissipation.

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Polyphenols in Mung Bean (*Vigna radiata* (L.) Wilczek): Determination and Removal

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Ten cultivars of mung bean (*Vigna radiata* (L.) Wilczek) were analyzed for polyphenol content by three methods: modified vanillin, Prussian blue, and protein precipitation. Polyphenols in mung bean had low protein precipitating capacity, relatively high flavanol levels, and were concentrated in the seed coat. Soaking seeds in water reduced assayable polyphenol content from 24 to 50%. Boiling for 30 min and roasting for 10 min resulted in 73% and 17% reduction of polyphenols, respectively. The lowering of polyphenols was significantly positively correlated with the decrease in protein-precipitable phenols (+0.95**). Mung bean sprouts had 36% less polyphenols after 48 h germination than after longer germination in which polyphenol content increased.

INTRODUCTION

Leguminous seeds constitute one of the richest and cheapest sources of proteins and are consequently becoming an important part of the people's diet in many parts of the world. Unfortunately, although the protein content of legume food is high (20–25%), its protein quality is low. This has been attributed to two factors: the deficiency of sulfur-containing amino acids (Elias et al., 1964; Bressani et al., 1973; Elias and Bressani, 1974) and the presence of antiphysiological and toxic factors such as trypsin inhibitors, hemagglutinins, cyanogenic glycosides, saponins, flatulence factors, and phytates (Jaffe, 1968; Liener, 1980; Elkowicz and Sosulski, 1982). Moreover, the presence of tannins (polyphenols) in sorghum and several legumes which could lower their protein digestibility has been reported. These legumes include the common beans *Phaseolus vulgaris* L. (Elias et al., 1979), winged beans *Psophocarpus tetragonolobus* L. (De Lumen and Salamat, 1980), broad and tick beans *Vicia faba* L., and maple beans *Pisum sativum* L. (Griffiths, 1981; Griffiths and Moseley, 1980), chick peas *Cicer arietum* L., green bean or mung bean *Vigna radiata* (L.) Wilczek, soybean *Glycine max* L., hyacinth bean *Dolichos lablab*, pigeon pea *Cajanus cajan* (L.) Millsp. (Narasinga Rao and Prabhavathi, 1982), horse gram *Macrotyloma uniflorum* (Lam.) Verdc., moth bean *Phaseolus aconitifolia* (Jacq.) Marechal (Satwadhar et al., 1981), and cowpea *Vigna unguiculata* (L.) Walp. (Laurena et al., 1984a,b).

In the Philippines, one of the most popular legume foods is mung bean (*Vigna radiata* (L.) Wilczek). Boiled whole mature seeds are utilized in native delicacies such as "hopia", "butse-butse", and "halo-halo"; mung bean flour can be processed to a noodle "sotanghon", or it can be used as a vegetable dish (boiled whole beans or sprouted seeds known as "togue") in combination with shrimp and meat. Because of the increasing importance of mung bean, it is imperative to study the role of protein-precipitable phenols on the nutritional quality of this legume. This paper reports on the determination and localization of polyphenols and the effects of soaking, heating, and germination on polyphenol content of mung bean. Related studies deal with the purification and characterization of condensed tannins from mung bean and their effect on its in vitro protein digestibility (Barroga et al., 1985).

EXPERIMENTAL SECTION

Materials. Mature seeds of ten cultivars of mung bean with yellow and green seed coat color were obtained from the National Plant Genetic Resources Laboratory of the Institute of Plant Breeding, University of the Philippines at Los Baños. The dried seeds were ground in a UDY cyclone mill and passed through a 100-mesh sieve. All chemicals used were of analytical grade.

Analysis of Polyphenol Content. The polyphenol content of 10 mung bean cultivars was determined and compared by using three different assays: modified vanillin (Price et al., 1978), Prussian blue (Price and Butler, 1977), and protein precipitation (Hagerman and Butler, 1978). For the modified vanillin and the Prussian blue assays, 1% HCl in methanol was used as extractant. Plain methanol was used as extractant for the protein precipitation assay, since tannic acid in 1% HCl in methanol failed to precipitate due perhaps to its hydrolysis. Catechin and tannic acid were used as standards.

Localization. Polyphenol distribution in the mung bean was determined by the Prussian blue assay by using both raw and soaked seeds of two cultivars, Pag-asa 1 and

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