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ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN APPLE ORCHARD ECOSYSTEM

Michigan State University PH.D. 1981

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ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN APPLE ORCHARD ECOSYSTEM

By

Jeffrey James Jenkins

A DISSERTATION

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ABSTRACT

ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN APPLE ORCHARD ECOSYSTEM

By

Jeffrey James Jenkins

The environmental behavior of azinphosmethyl was studied in a Michigan apple orchard watershed to gather data on initial distribution within the orchard, vertical movement of the pesticide under the influence of rainfall, and loss from the orchard with runoff. The estimated proportion of a low-volume application initially distributed within the orchard averaged .624 (standard deviation of .149) over three seasons (1976-1978). Examination of residues reaching each layer showed the majority of the dislodgeable residues were distributed to the trees and grass-broadleaves. The litter-moss and soil contained residue levels roughly ten times lower than tree leaf residues. Runoff studies indicated loss, via this route, of less than 1% of azinphosmethyl residues present in the orchard. The residue data were used to parameterize a model for azinphosmethyl attenuation and movement in an orchard ecosystem. Rates of attenuation within, and movement between, specified orchard compartments were determined under various rainfall regimes. The output of this model was structured to allow the estimation of the time course of azinphosmethyl exposure to ground-dwelling invertebrates. Mean squared errors for the comparison of the model predictions with an independent set of residue data indicated good prediction of azinphosmethyl fate within the tree and grass-broadleaves layers. Prediction of pesticide dynamics within the litter-moss and soil layers was much more difficult. Model predictions estimate that under dry conditions 25% of the daily loss of azinphosmethyl from the orchard trees is due to movement to other parts of the orchard. Greater movement is predicted under rainfall conditions. Estimates of daily airborne loss determined from deposit residues and direct sampling of airborne residues suggest that airborne loss is largely responsible for the early loss of residues, accounting for 40% of the daily loss rate on day 3 of the first spray period, 1978 season. A multi-component kinetic model is presented for estimating simultaneously the early airborne loss of foliar deposits and the often slower dissipation of the remaining residues. Further model development to include the effect of selected environmental parameters on azinphosmethyl degradation is also discussed.

ACKNOWLEDGMENTS

This research comprises a major portion of a project to study and model the fate and effects of azinphosmethyl in an apple orchard ecosystem. Funding was provided by the Environmental Protection Agency. The multidisciplinary nature of this project required cooperation among many researchers and support personnel. I would especially like to express my appreciation to Lester Geissel for his consultation and invaluable asistance in much of the field operations. I also acknowledge Dr. Robert Kon for his contribution in the administration of sample analysis. In addition, I am indebted to Dr. Erik Goodman for his guidance in this research.

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INTRODUCTION

Since the discontinued use of many organochlorine insecticides in the early seventies, use of the generally more toxic and less persistent organophosphate insecticides has increased (Brown, 1978). Because of the greater mammalian toxicity of these compounds (Matsumura, 1975), research of their fate in orchards has been primarily concerned with worker reentry hazard associated with foliar dislodgeable residues, soil, and soil dust residues. Most of this work has been done for citrus (Gunther et al., 1977; Nigg et al., 1977; Thompson and Brooks, 1976; Spear et al., 1975), but studies have also been conducted for peach (Winterlin et al., 1975; Hansen et al., 1978) and apple orchards (Staiff et al., 1975; Hansen et al., 1978). Little work has been done in the area of attenuation and movement of the organophosphates between trees, ground cover, and soil, or loss with runoff from deciduous fruit orchards.

The lack of cultivation, which is the practice in many deciduous fruit growing areas (Haynes, 1980), preserves greater species diversity than is found in many other agroecosystems (Brown, 1978). This diversity can result in a relatively stable deciduous tree fruit ecosystem if undisturbed by pesticides or other management practices (Hoyt and Burts, 1974). Under these conditions, natural control of many arthropod pests through disease, predation, and parasitism is achieved (Croft, 1975). However, to produce marketable fruit, pesticides must be used to control a few key pests (Glass and Lienk, 1971). Control of these key pests with pesticides may reduce natural enemy populations, promoting secondary pests to a major pest status, often requiring additional chemical control (Hoyt and Burts, 1974; Croft, 1978; Ware, 1980). In addition, the increased use of pesticides in orchards, and on all crops, has resulted in an increased number of resistant pest species (Smith, 1976; Brown, 1977, 1978; Croft, 1978). These and other problems associated with the use of pesticides as a sole means of control have resulted in a greater emphasis being placed on integrated pest management as a long-term strategy for the economic control of crop pests (NAS, 1969; Smith, 1976). Such programs are designed to use a broad spectrum of control measures including biological, cultural and chemical methods. This approach to pest management requires a great deal more knowledge not only of the ecobiology of both beneficial and harmful species, but also of pesticide fate and effects. The success of orchard IPM programs may depend largely on the judicious use of pesticides allowing maximum benefit to be gained from biological control measures (Croft and Brown, 1975; Smith, 1976). This will require a better understanding of pesticide fate throughout the entire orchard ecosystem.

Additional consideration must be given to species other than those of benefit to pest control. Because of their relative permanence, deciduous orchards are often a habitat for wildlife indigenous to natural ecosystems (Croft, 1978). Detailed studies of pesticide fate and effects, which would be impractical or undesirable in a natural setting, can be done in an orchard, to give some insight into the ecological hazards associated with pesticide exposure to the fauna of these environments. Such information may be valuable in the development of environmental fate and ecological effects testing guidelines as proposed under the Toxic Substance Control Act and the recently amended Federal Insecticide, Fungicide and Rodenticide Act.

The Toxic Substances Control Act authorizes the Environmental Protection Agency (EPA) to obtain from industry data on the production, use and effects on human health and the environment of chemical substances and mixtures. Testing standards under Section 4 are directed at specific chemical characteristics and effects, including oncogenicity, teratogenicity, mutagenicity, and other health effects, as well as environemntal fate, persistence and ecological effects. All tests are substantially similar to methods proposed by EPA for its pesticide registration program and represent a "base set" of tests from which to select specific tests for specific chemicals in test rules. To date no test standards have been proposed for environmental fate or ecological effects.

In addition to the Section 4 standards which are designed to test specific chemicals or chemical groups, the EPA also plans to issue testing guidelines consistent with these testing standards, but more general in nature, encompassing a wider range of chemical substances and effects of concern to EPA. These guidelines will also be used under Section 5 which allows the agency to limit manufacturing, processing, distribution, use or disposal of new chemical substances (or new uses of existing substances), pending development of information. The administrator is given this authority if he has reason to believe (1) that the chemical substance may present an unreasonable risk or may result in substantial human exposure or environmental release, (2) there are insufficient data or experience for determining or predicting health or environmental effects, and (3) testing is necessary to develop such data. TSCA does not require EPA to provide testing guidance, except when specifically requested under Section 5 (g). Nevertheless, testing guidelines are presently being developed in an effort to streamline the monumental task of TSCA compliance and to encourage more appropriate and cost-efficient information gathering.

So far the EPA has proposed general standards for a number of human health effects. Such standards for environemntal fate and ecological effects are presently at the interagency review stage. To develop generic standards for human health involves only one species, man. Types of exposure (dermal, inhalation, ingestion, etc.), metabolism, and pharmacodynamics are fairly uniform. Generic test standards may need only be modified based on the properties of the chemical or chemical category. Generic standards for environmental fate and ecological effects involves all species of flora and fauna. In addition, all biotic-abiotic relationships must be considered from ocean food chains to soil microbial communities. This diversity of species (and species interaction) and environments makes the development of generic standards to assess the possible hazards of chemical substances to the environment a formidable task. The first problem would seem to be how many different species must be tested to adequately assess ecosystem effect; secondly, what chemical properties are important, and, thirdly, what and how do environmental properties influence exposure and possible ecotoxicity. Due to the enormous complexity, there has been much controversy over the rationale for adopting standards in these areas where scientific methods are less developed and where no validated techniques are available for certain effects.

There may be unreasonable risk to an ecosystem when a component or components are exposed to a concentration of a chemical substance which causes harm. Environmental fate studies are used to predict and estimate the presence of potentially harmful chemical residues in man-made and natural environments. Upon release into the environment a chemical may be metabolized by living organisms, be transformed by chemical or photochemical reaction, or persist unaltered. In some instances degradation or transformation results in toxic products (Menzie, 1972; Crosby, 1973; Goring et al., 1975). The goal of environment test standards should be to identify the dominant pathways of chemical transformation and transport, and then relate this behavior to properties of the chemical and environmental conditions. This knowledge can then be used to infer what biota may be exposed to the chemical, the degree, frequency, and route of exposure. Thus, both the population at risk and the effect of the chemical are determined partly by the detailed fate of the chemical substance. Just as in health effects testing, where in vitro studies and lab animals are used to estimate chemical effects on man, ecosystem effects and chemical fate are estimated primarily from laboratory studies. The foundation for use of laboratory data for environmental fate assessment is based on the assumption that the rate at which a chemical degrades, dissipates, or accumulates in the environment is the sum of the rates of known individual chemical, physical, and biological processes, independently measurable in the laboratory. In addition, it is assumed that the laboratory data for individual processes can be integrated and extrapolated to the appropriate set of "real world" conditions. It is yet to be seen if any set of laboratory tests alone can be used to predict the environmental fate of a chemical substance to the extent that the EPA may adequately assess the possible risk to an ecosystem. The fact is that few of the processes which determine the environmental fate of a chemical substance have been studied in enough detail to predict dominant pathways or rates of change in the "real world." Each possible transformation or transport pathway can be studied in the laboratory and rates may be determined under a given set of "environmental conditions" but how actual environmental conditions influence rates is largely unknown.

A few years ago it was thought that microcosms, controlled laboratory systems that attempt to simulate some selected portion of the real world, might be used to fill this information gap. In a terrestrial microcosm environmental parameters such as temperature, light level, water content, and organism diversity can be controlled and varied by the investigator. A common approach to microcosm development has been to organize some elements of a selected ecosystem in a container so as to resemble some aspects of the ecosystem of interest and then systematically to change the complexity by adding new trophic levels of organisms. Parameters of the system as they affect chemical fate are monitored (Gillette and Witt, 1979). Unfortunately, development of the physical models of these microcosms has not always kept pace with conceptual development. More importantly, complete understanding of the discrete chemical, physical, biological, and climatological processes that control chemical fate in a terrestrial system is not yet directly obtainable from these studies.

Another approach has been to use mathematical models. The development and use of mathematical models usually involves a systems approach; the formalized analysis of any system or of the general properties of systems. The analysis of complex systems as systems, and the modeling of these systems, is contrary to reductionist trends in science. Laboratory experiments which isolate and control very small components of nature have up to the present been the most powerful investigative tools aiding man in understanding nature, but this "science by isolation" has its drawbacks as the larger environment may influence the components of interest to such an extent that an isolated laboratory experiment may exclude some critical components, or the behavior of a system may not be simply the sum of the behaviors of its parts in isolation (Hall and Day, 1977). Mathematical modeling of environmental fate should be based on both reductionist laboratory experiments and key observations of the fate of chemicals in the environment to include the rates of transport and transformation as a function of climatic and other environmental variables. Only a handful of models have been developed which describe chemical environmental fate in general. The present "state of the art" model is EXAMS, a model of fate of toxic organic chemicals in aquatic ecosystems, developed by the

EPA's Athens, Georgia Research Laboratory (Lassiter et al., 1978). This model was used to develop environmental assessments for eleven chemicals in aquatic systems based on laboratory measurements. The model has since been modified to include a library of canonical environments and is now in use on a trial basis in several laboratories and EPA offices.

The work presented here is one portion of an effort to characterize the dynamics and effects of an example compound in the terrestrial environment, utilizing primarily field measurements and the methodology of systems modeling and simulation. Data collection, model refinement, and revised experimental design were done iteratively, yielding a model which is parameterizable and data which are relevant to the problem being attacked.

The study of pesticide dynamics through in situ field studies is difficult due to the lack of natural or planned experiments (inability to control much of the variance, i.e., climatic conditions) and the relatively high levels of error associated with field data. Modeling techniques were employed to aid in the understanding of the necessarily large amount of field data needed to construct a "meaningful" picture of the pesticide's fate.

The field experimental program used to investigate the distribution, attenuation and movement of the organophosphate insecticide azinphosmethyl, 0,0-dimethyl-5-(4-oxo-1,2,3, benzotriazin-3(4H)-ylmethyl) phosphorodithioate (Guthion^R), in a Michigan apple orchard is given in Part I. The compound was followed from its spray application through the orchard vegetation/litter/soil environment and into aquatic systems. The form of the model describing azinphosmethyl movement and attenuation, as well as data handling procedures and the derived rates, are presented in Part II. A companion study was conducted concurrently within the same orchard to examine the effects of azinphosmethyl on several ground-dwelling invertebrates, including detailed studies of the isopod _Tracheolipus_ _rathkei_ (Snider, 1979; Snider and Shaddy, 1980). Field and laboratory data collected on _T._ _rathkei_ were used to develop a model describing its ecobiology and temporally distributed mortality (Goodman et al., 1981). The output of the fate model described in Part II was used to determine the time-course of azinphosmethyl exposure.

In Part III the field experimental program used to determine azinphosmethyl airborne residues is presented. A multi-component kinetic model used in the assessment of the contribution of airborne loss to the overall attenuation of deposit residues is also described.

In Part IV degradative losses of azinphosmethyl are examined as a function of environmental conditions.

PART I

ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN ORCHARD ECOSYSTEM: DEVELOPMENT AND PRESENTATION OF THE EXPERIMENTAL DATA BASE

INTRODUCTION

Reported here is the field experimental program used to investigate the distribution, attenuation, and movement of the organophosphate insecticide azinphosmethyl, 0,0-dimethyl-5-(4-oxo-1,2,3, benzotriazin-3(4H)-ylmethyl) phosphorodithioate (Guthion^{R}), in a Michigan apple orchard. Studies were carried out to gather data on both initial distribution of azinphosmethyl within the orchard and vertical movement of the pesticide under the influence of rainfall, as well as the attenuation of the pesticide in various situations. In addition, plots were designed such that each was a separate watershed, allowing runoff collection from them individually. The compound was followed from its spray application through the orchard vegetation/litter/soil environment and into aquatic systems, to determine possible exposure of the orchard ecosystem biota to the compound. The data presented here were used to parameterize a model (presented in Part II) for azinphosmethyl attenuation and movement in an orchard ecosystem.

ANALYTICAL METHODS

Organic solvents were glass-distilled and the water was distilled-deionized. After washing, the glassware was rinsed with acetone and hexane followed by overnight heating at 250°C.

Dislodgeable Residues. Dislodgeable residues were determined by the procedure of Gunther et al. (1973). Leaf discs were extracted with 50 ml portions of water containing two drops of Triton X-100 in water (1:50, v/v). Samples were then agitated on a wrist-action shaker for 15 minutes. Depending on the bulkiness of the grass, litter, or moss, more water was used to insure good contact with the sample during extraction. One drop of Triton-X 100 solution was added for each additional 25 ml of water used. All samples were given a final rinse by hand with a third 50 ml portion of water. The combined washes were partitioned three times against 50 ml portions of hexane which was then concentrated on a rotary evaporator and diluted to a proper volume for analysis. Using the above method, recovery and standard deviation from the Triton-X 100 water solution fortified with azinphosmethyl standard was 95 ± 3%.

Surface-Penetrated Residues. To estimate the magnitude of the remaining residues on or within the cuticular matrix, selected samples collected on the day of application were given an additional extraction in a manner similar to that described by Steffens and Weineke (1976). Three 20 ml volumes of acetone were successively swirled with the samples just after the dislodgeable residue extraction had been completed. The combined acetone-water extracts were concentrated by rotary evaporation to remove the acetone. The water left in the rotary flask was partitioned in the flask against three 30 ml volumes of hexane which were combined and then dried over anhydrous sodium sulfate and concentrated to about one ml. This procedure was selected as Wieneke and Steffens (1974) were able to recover 100.4% of the ^{14}C azinphosmethyl applied to bean leaves as an aqueous formulation, one day following application.

This extract was cleaned up by the silica gel microcolumn described by Kadoum (1967) with our elution system. One and a half grams of unactivated Adsorbosil CAB, 100/140 mesh (Applied Sciences, Inc.) was packed as a hexane slurry into a Pasteur pipet. The sample was added in hexane and the column eluted with 15 ml of 10% benzene in hexane. Ethyl acetate (4%) in benzene then eluted the azinphosmethyl in 15 ml. Recovery and standard deviation of 2 ml of a 5 ppm azinphosmethyl standard solution added to the column was 94 ± 3%.

Soil. Extraction of soil was based on Schulz et al. (1970). Approximately 50 g of soil (largest roots removed) were mixed with 10 ml of water, if dry, and acetone (1.5 ml/g) on a wrist-action shaker for 15 minutes. The solvent was poured into a rotary flask through a funnel lined with Whatman No. 1 filter paper; as much soil as possible was retained in the extraction flask. A second extraction followed and the combined extracts were treated exactly as the surface-penetrated residues of the previous section, including the clean-up column. Recovery and standard deviation from soil fortified with azinphosmethyl standard was 84 ± 9%.

Filter Paper Targets. Targets, consisting of two circles of Whatman No. 1 paper, 18.5 cm in diameter (attached one atop the other, by a single staple to a cardboard backing), were extracted for two hours in a soxhlet extractor using a mixture of hexane:acetone, 100 ml:25 ml. Recovery and standard deviation from targets fortified with azinphosmethyl standard was 104 ± 5%.

Pesticide Runoff Studies. Azinphosmethyl in runoff samples collected during the 1977 season was examined by extracting one liter subsamples following centrifugation to remove sediment. The sediment was soxhlet extracted for four hours with a 1:1 hexane:acetone mixture, air dried and weighed. The supernatant was extracted with hexane and both sediment and supernatant extracts were concentrated by rotary evaporation. Recovery and standard deviation from runoff water fortified with azinphosmethyl standard was 93 ± 4%.

Quantitation of azinphosmethyl was accomplished using a Tracor 560 gas chromatograph having a flame photometric detector in the phosphorus mode. A six-foot glass column (2 mm i.d.) packed with 3% SE-30 on Gas Chrom Q, 60/80 mesh, was operated at 195 C; N_2, 40 ml/min; air, 90 ml/min; H_2, 60 ml/min. This system was interfaced with a digital PDP 8 Pamila PDP 11/40 RSTS computer for integration of the area under the single peak produced.

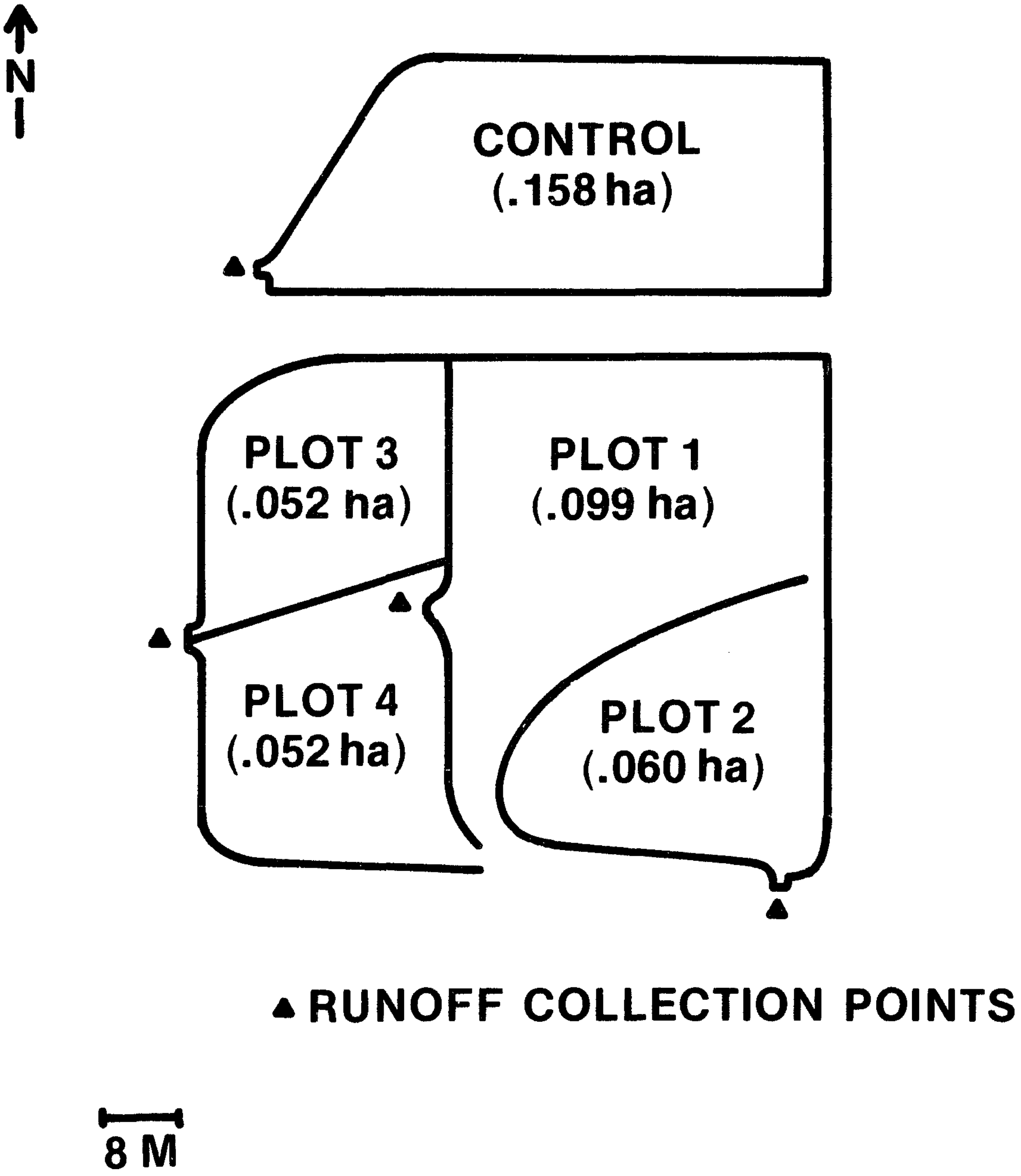
THE EXPERIMENTAL SITE

The experimental apple orchard was located in the vicinity of Grand Rapids, Michigan in Kent County. The twelve-year old trees were a mixture of semi-dwarf duchess and wealthy cultivars. In 1976 the orchard had been left unattended for approximately five years. This was a necessary requirement to assure adequate populations of ground-dwelling invertebrates, unaffected by previous seasons' pesticide applications (Snider, 1979). In the early spring the trees were pruned and understory brush was removed. Just prior to the first spray application the area was mowed to a height of approximately five cm. Due to dry conditions further mowing was not necessary. In 1977 light pruning was repeated and the orchard was mowed just prior to the first, second, and fourth spray applications. A survey of the ground cover by the line-transect method (Cox, 1974) was carried out in 1976; cover type categories were established and their importance values calculated. Above the soil (a marlette sandy clay loam, pH 6.0, 56% sand, 20% silt, 24% clay, and 6.0% o.m. in top 10 cm) was moss intermingled with litter; the most recent litter deposits covered the moss. The herbaceous growth covering the moss and litter was predominantly broad-leaved weeds, with grass being of secondary importance. An examination of the ground cover in the areas sampled for residue analysis yielded similar results. This ground cover composition is not atypical of orchards in the temperate Eastern United States and Canada, although they vary with the level of secondary succession (Whittaker, 1975), climatic, topographic, edaphic conditions, and management practices (Klingman and Ashton, 1975; Teskey and Shoemaker, 1978; Schubert, 1976).

PREPARATION OF ORCHARD FOR RUNOFF COLLECTION

To facilitate the study of azinphosmethyl loss via runoff, four experimental plots and one control plot were established, each a separate watershed (Figure 1). Slopes in plots 1 and 2 and the control were between 6 and 12%, slopes in plots 3 and 4 were between 18 and 25%. All the runoff was collected from a given plot for each event and subsampled for pesticide analysis. A 600-liter galvanized steel livestock tank (61 cm x 61 cm x 183 cm) was placed in an excavation at the natural drainage point for each plot, at a level to collect the runoff. A smaller tank (40 liter capacity) was placed inside the larger tank so that it would fill and any overflow would be contained in the larger tank. Also, an overflow diversion pipe was installed on the collection tank for plot 1; in the event the large tank overflowed, the runoff water would be diverted to a point below plot 4 (see Figure 1). Runoff water was finally channeled into the tanks by galvanized steel collection chutes, 61 cm long with sides 15 cm high, 61 cm wide at the top and 30.5 cm wide at the bottom. A 61 cm by 61 cm area of the tank directly below the chute was covered with a 6.4 mm mesh screen and the rest of the tank was covered with plywood covered with plastic, to keep out rainfall, animals, and debris. The chute and screen were also covered with plastic. Both the tanks and chutes were coated with epoxy paint, as tests showed that after seven days, the residues remaining from a five ppb solution of azinphosmethyl in galvanized steel containers were 30% less than the residues remaining in glass, stainless steel, or epoxy-painted containers. Azinphosmethyl hydrolysis experiments (see Part IV) indicated little degradation over the seven-day period, at solution pH values below 7.0 (first order rate constant of .008 at $25^{\circ}C$). As the pH of the runoff water collected averaged 5.9 ± 0.2, losses by this mechanism prior to sample collection and extraction were thought to be small. Loss via volatilization was also considered to be negligible as azinphosmethyl has

Figure 1 Orchard Plots


N
CONTROL
(.158 ha)
PLOT 3
(.052 ha)
PLOT 1
(.099 ha)
PLOT 4
(.052 ha)
PLOT 2
(.060 ha)
▲ RUNOFF COLLECTION POINTS
8 M

a vapor pressure $< 7.5 \times 10^{-6}$ mm Hg at 20°C (Mobay Chemical Co., personal communication) and the maximum concentration of azinphosmethyl measured in the runoff collected was 22 ppb, well below its water solubility of 33 ppm.

Plots were enclosed and separated from one another by a 30.5 cm, 20 gauge aluminum core fence buried approximately five cm in the ground. This fence was made continuous with the collection chute to aid in the final channeling of runoff at the bottom of the plot slope. Fencing was installed with minimal disturbance of the ground cover and in such a manner that potential runoff would have as little contact as possible with the fencing. This collection scheme was designed and implemented during the 1976 season, but due to dry conditions, no runoff was collected in that year.

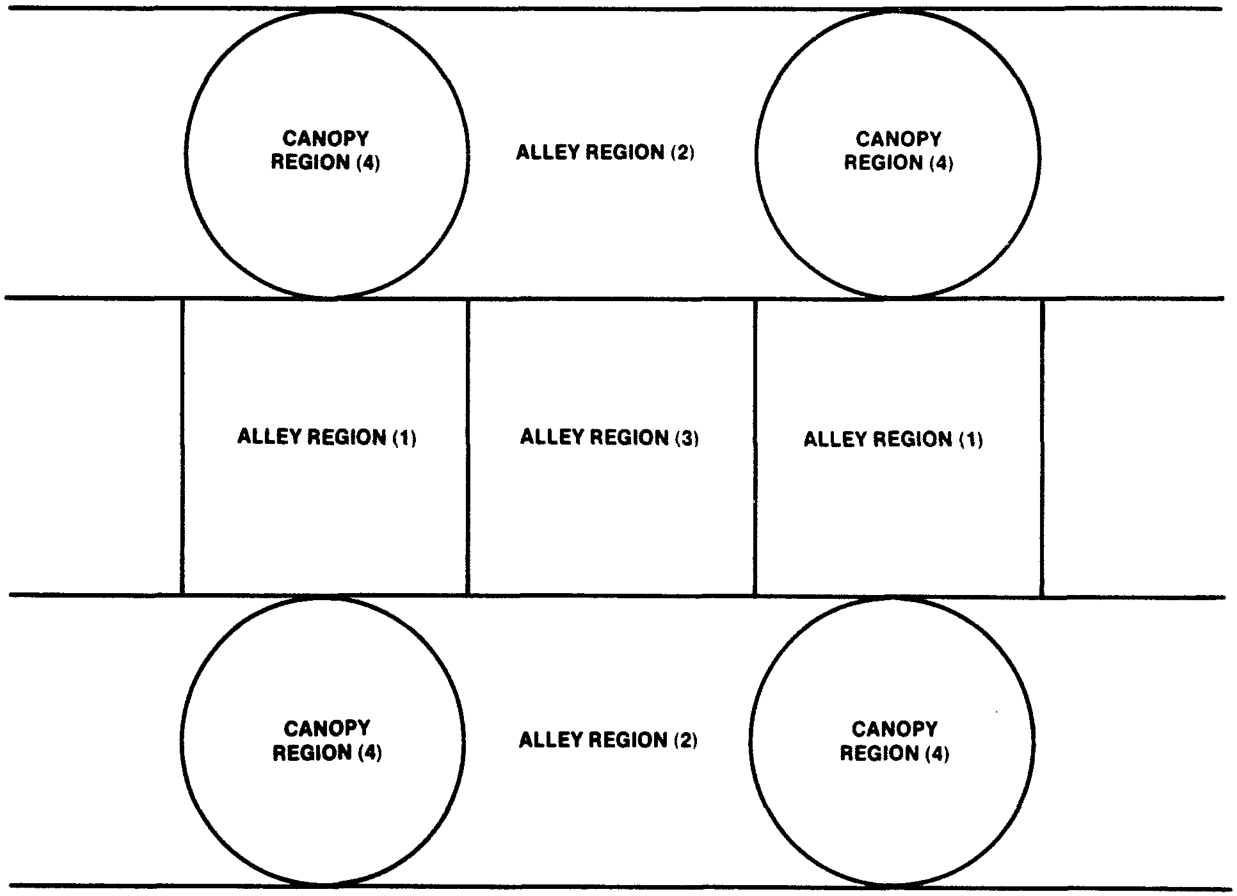
SPATIAL STRUCTURE OF THE ORCHARD PLOTS

The orchard plots (Figure 1) were subdivided both vertically and horizontally in order to represent adequately the variations which affect the behavior and impact of the pesticide in the orchard ecosystem.

Horizontally, each plot was subdivided into four regions potentially different with respect to initial pesticide distribution (see Figure 2). Vertically, each alley region was divided into three compartments: grass-broadleaves, litter-moss, and soil. The canopy regions contained these compartments plus a compartment for the leaves of the tree.

Region 4 (under the canopy) was determined to be 32% of the area in plot 1, 34% in plot 2, 54% in plot 3, and 45% in plot 4. The remainder of the plot area was divided among the three alley regions in a ratio of 2:3:1 for plots 1 and 2, and 1:2:1 for plots 3 and 4. The difference in the ratios was due to the closer spacing of the rows along the North-South axis in plots 3 and 4. The number of trees in each of the plots was as follows: plot 1, 24; plot 2, 15; plot 3, 10; and plot 4, 11. Tree heights averaged 3.0 meters.

Figure 2 Overhead View of Horizontal Regions of Orchard Plots


CANOPY REGION (4)
ALLEY REGION (2)
CANOPY REGION (4)
ALLEY REGION (1)
ALLEY REGION (3)
ALLEY REGION (1)
CANOPY REGION (4)
ALLEY REGION (2)
CANOPY REGION (4)

SPRAYING AND SAMPLING SCHEDULE

The size of the plots and their inaccessibility due to the aluminum fences made the use of commercial spray equipment impossible. What was needed was a plot sprayer that could: 1) be pulled by a small tractor, such as a garden tractor, and 2) match as closely as possible the coverage of a commercial spray unit. To meet these criteria, a low pressure, low volume sprayer similar to one developed by Howitt and Pshea (1965) was constructed. The sprayer was mounted on a trailer and was pulled by a John Deere model 200 garden tractor. Mounted on the trailer was a double inlet, high volume, low velocity blower manufactured by Dayton, model 3C011. The blower was powered by an eight horsepower Briggs and Stratton gasoline engine. Blower output was approximately 10,000 cubic feet per minute (at the highest engine speed setting). The air flow was directed by a fiberglass deflector, constructed for use on Ag-tech crop sprayers. One side of the deflector was widened to accommodate three Beecomist model 350 mini-spin spray heads. The deflector was further modified between 1976 and 1977 seasons to direct more of the spray into the trees. Pesticide was delivered to the spray heads by a Masterflex variable speed tubing pump.

The pesticide application rate was determined by the rate at which the pesticide mixture was delivered to the spray heads, tractor speed, and distance covered to spray each plot. The actual application time was recorded in the field for each plot and the actual amount of pesticide applied was determined by tank residual volume after spraying. In addition, during the first spray period of 1978, samples of spray mixture were taken, at the spray heads, before and after spraying each plot. Results from this method were comparable to those of the residual volume method. The average application rate and standard deviation was 1.62 ± .33 kg ha^{-1} 50% w.p. 100ℓ$^{-1}$ ha^{-1} in 1976 and 1.64 ± .38 kg ha^{-1} 50%

w.p. $100\ell^{-1}$ ha^{-1} in 1977. Plots were sprayed in sequence between 7 a.m. and 9 a.m.

Deposit Residue Samples

To determine initial horizontal distribution of azinphosmethyl, a series of 15 to 20 ground-located filter paper targets was deployed among the four horizontal regions (see Figure 2) in each plot on the date of spraying. Targets were placed in the center of the alley regions, and at the in-row midpoint between the tree trunk and the edge of the canopy region. As soon as a plot had been sprayed, the filter papers were removed from the backing, packaged, and transported in picnic coolers cooled by dry ice. Storage was at -20°C until analysis.

The initial distribution of azinphosmethyl was also determined among the three ground layers: grass-broadleaves, litter-moss, and soil. In each plot, two samples of each layer were taken from the tree and alley regions. A square of sod (15 cm x 15 cm) was cut to a depth of about four cm and the grass-broadleaf plants, litter, and moss were separated into three discrete samples for residue analysis. From the bare sod remaining, three cores (5 cm x 7 cm deep) were taken for analysis, providing a sample of 40 to 60 g.

For analysis of leaf deposits a 2.0 cm diameter disc was taken from the center of each leaf. Three trees were sampled in each plot, taking 30 or more discs per tree. Samples were taken at shoulder height (distributed within the canopy easily reached) around the entire circumference of the tree.

Sampling dates for the 1976 season are shown in Table 1. Infrequent rainfall during this season yielded little information usable to assess movement due to rainfall. In 1977, interspray sampling was optimized for movement data as samples were collected primarily after rainfall events (see Table 2).

Table 1. Summary of Significant Events for the Orchard, 1976 Season

Spray Date	Sample Date	Rainfall Date	Rainfall Amount mm	Rainfall Amount in	Days Since Spray
		Orchard Mowed 28 June			
		30 June	36.3	1.40	
2 July	2 July				0
	6 July				4
	9 July				7
	14 July				12
15 July	15 July				0
	20 July				5
		20 July [a]	22.9	.90	
	22 July				7
		26 July	06.4	0.25	
	27 July				12
28 July		28 July[b]	11.4	0.45	0
	29 July				1
		31 July	04.6	.18	
	2 August				5
	4 August				7
		5 August	10.2	.40	
	10 August				13
		14 August	27.9	1.10	
	16 August				19
17 August	17 August				0
	20 August				3
	24 August				7
		28 August	06.4	0.25	
	30 August				13

[a] Rainfall started immediately after spraying.
[b] Rainfall occurred after sampling.

Table 2. Summary of Significant Events for the Orchard, 1977 Season

Spray Date	Sample Date	Rainfall Date	Rainfall Amount		Days Since Spray
			mm	in	
		Orchard Mowed 23 May			
		25 May	5.1	0.20	
26 May	26 May				0
		30 May	20.3	0.80	4
	1 June				6
		4 June	25.4	1.00	10
	6 June				11
		11 June and 12 June	12.7	0.50	17
	13 June				18
		Orchard Mowed 15 June			
16 June	16 June				0
		17 June and 18 June	6.4	0.25	2
	20 June				4
		27 June	5.1	0.20	11
	28 June				12
		30 June	25.4	1.00	14
	1 July				15
		4 July	12.7	0.50	20
		7 July[a]	5.1	0.20	22
7 July	7 July				0
		18 July	22.9	0.90	11
	19 July				12
		Orchard Mowed 20 July			
22 July	22 July				0
		24 July	2.5	0.10	2
	25 July				3
		29 July	2.5	-.10	6
	1 August				10
		3 August	2.8	0.11	11
		4 August	13.7	0.54	13
		6 August	3.8	0.15	15
	7 August				16
		8 August	2.5	0.10	17
		10 August	22.9	.90	
12 August	12 August				0
		13 August	12.7	0.50	1
	15 August				3
	18 August				6

[a] Rainfall occurred just prior to spraying.

Residues in Runoff

Azinphosmethyl movement out of the orchard with runoff was also determined. Runoff water was removed from the orchard in four-liter, dark glass bottles and stored at 5°C until analysis. Excess runoff was measured volumetrically in the field and discarded.

Rainfall was measured with static rain gauges and this information was correlated with data from recording rain gauges maintained 3/4 mile from the orchard by the Michigan State University Institute of Water Research. Temperature and humidity data shown in Figures 5, 6, 7 and 8 were obtained from the Michigan Weather Service, Grand Rapids, Michigan.

RESULTS AND DISCUSSION

Initial Horizontal Distribution

Tables 3 and 4 show the results of the analysis of the filter paper targets for the first spray day of the 1976 and 1977 seasons. The average amount and standard error (SE) of pesticide are expressed in $\mu g/cm^2$ ground area and proportions shown are proportions of dose applied. The grand average across plots 1 through 4 for both seasons shows that alley region 2 and the canopy region receive the majority of the residues reaching the ground; alley regions 1 and 3 received less. Pesticide distribution was more uniform in the 1977 season, and residue levels were proportionally lower across all regions. The author believes this was due to modification of the sprayer between seasons, after which more of the spray was directed into the atmosphere and away from the ground.

Initial Vertical Distribution

Azinphosmethyl initial vertical distribution for the 1976 and 1977 seasons is given in Table 5. Each plot is represented by only two regions; alley and canopy. In 1976 the alley was randomly sampled. In 1977 the average amounts for the alley represent weighted averages of alley regions 1, 2, and 3, weighted

Table 3. Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, 1976 Season

Plot		Alley (1)	Alley (2)	Alley (3)	Canopy (4)
1	Average Amount ($\mu g/cm^2 \pm$ SE)[b]	2.48 ± 0.22	3.35 ± 0.45	2.76 ± 0.34	2.89 ± 0.51
	Sample size	10	14	7	13
	Proportion[a]	.071	.131	.026	.093
2	Average Amount ($\mu g/cm^2 \pm$ SE)	1.36 ± 0.31	2.46 ± 0.44	1.65 ± 0.39	3.20 ± 0.37
	Sample Size	9	6	9	11
	Proportion[a]	.050	.079	.026	.136
3	Average Amount ($\mu g/cm^2 \pm$ SE)	.75 ± 0.20	3.81 ± 1.00	1.36 ± 0.50	5.10 ± 0.77
	Sample Size	5	5	5	7
	Proportion[a]	.009	.076	.023	.226
4	Average Amount ($\mu g/cm^2 \pm$ SE)	2.51 ± 0.95	3.06 ± 1.28	2.14 ± 0.65	2.90 ± 1.10
	Sample Size	9	4	3	10
	Proportion[a]	.042	.111	.065	.175
Grand Average Amount ($\mu g/cm^2 \pm$ SE)		1.78 ± 0.44	3.17 ± 0.28	1.98 ± 0.31	3.52 ± 0.53

[a] Proportion of amount applied
[b] Standard error

Table 4. Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, 1977 Season

Plot		Alley (1)	Alley (2)	Alley (3)	Canopy (4)
1	Average Amount ($\mu g/cm^2 \pm$ SE)[b]	2.75 ± 0.63	3.12 ± 0.77	2.63 ± 0.50	3.55 ± 1.14
	Sample size	7	7	13	6
	Proportion[a]	.070	.114	.023	.095
2	Average Amount ($\mu g/cm^2 \pm$ SE)	1.34 ± 0.24	1.96 ± 0.12	1.24 ± 0.26	1.83 ± 0.44
	Sample Size	9	3	6	4
	Proportion[a]	.047	.109	.026	.103
3	Average Amount ($\mu g/cm^2 \pm$ SE)	1.03 ± 0.22	2.51 ± 0.13	1.34 ± 0.28	1.39 ± 0.45
	Sample Size	7	5	8	6
	Proportion[a]	.105	.064	.020	.088
4	Average Amount ($\mu g/cm^2 \pm$ SE)	.91 ± 0.43	2.27 ± 0.43	.978 ± 0.28	1.43 ± 0.09
	Sample Size	3	5	8	3
	Proportion[a]	.017	.079	.024	.093
Grand Average Amount ($\mu g/cm^2 \pm$ SE)		1.51 ± 0.42	2.47 ± 0.25	1.55 ± 0.37	2.05 ± 0.51

[a] Proportion of amount applied

[b] Standard error

Table 5. Initial Vertical Distribution of Azinphosmethyl Dislodgeable Residues (μg/cm^2 ± SE)

Year		Tree	Grass-Broadleaves	Litter-Moss	Soil
1976	Canopy				
	Average Amount	2.92 ± .41	1.49 ± .40	.18 ± .04	.20 ± .05
	Sample Size	11	9	9	8
	Alley				
	Average Amount		1.72 ± .33	.15 ± .08	.19 ± .02
	Sample Size		8	5	8
1977	Canopy				
	Average Amount	2.88 ± .42	.55 ± .04	.29 ± .04	.29
	Sample Size	12	6	8	1
	Alley				
	Average Amount		1.15 ± .23	.27 ± .05	
	Sample Size		8	8	

[a] Soil residues were determined on a whole basis, value represents μg/cm^2 in the top 10 cm.

by percent of plot area. These data indicate that for both years the majority of the dislodgeable pesticide residues deposited in the orchard was initially distributed vertically to the tree and the grass-broadleaf layer. Azinphosmethyl residues distributed to the litter-moss layer and soil were roughly ten times lower than leaf residues.

Using the vertical distribution of the dislodgeable residue data along with the pesticide application rates and the plot characteristics, the proportion of the applied pesticide reaching each of the vertical regions was calculated on a plot basis and then averaged across plots (see Table 6). To determine the amount of pesticide distributed to the tree leaves, the tree leaf surface area was estimated by removing all the leaves from two trees, one in plot 2 and one in plot 4, following the 1978 sampling season (an exhaustive search for other methods of determining tree leaf surface was unsuccessful). The leaves from each tree were contained in six 50 l bags. Each bag was weighed and sub samples of ten leaves were randomly selected for each 500 g of leaves. Weights and areas were determined for each sub sample. Total leaf area was determined from these measurements and the total leaf weight. The average for these two trees was approximately 400,000 cm^2 (one side of leaf only). This is a crude estimate due to sampling limitations and is specific for the tree size and vigor found in this orchard. As the pesticide was not evenly distributed vertically in the tree, estimates based on leaf residue data taken from the lower half of the tree in the 1976 and 1977 seasons would tend to overestimate the proportion distributed to the entire tree. In 1978, the upper half of the tree was sampled separately. From these data, a ratio was determined by dividing the average amount of dislodgeable residue found in the entire tree (upper and lower) by the average amount of dislodgeable residue found in the lower half of the tree. This ratio was determined using an across-plot average for each of the sample dates for the

Table 6. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (± SE), from the Analysis of Samples[a]

	1976				
	Alley		Canopy		
	Dislodgeable	Surface-Penetrated	Dislodgeable	Surface-Penetrated	Total
Tree[b]			.376 ± .082	.027	
Grass	.112 ± .015	.021	.060 ± .014	.011	.661 ± .093
Litter-Moss	.014 ± .005	.006	.013 ± .004	.003	
Soil[c]	.015 ± .002		.010 ± .006		
	1977				
Tree			.337 ± .020	.022	
Grass	.070 ± .016	.013	.033 ± .009	.005	.556 ± .011
Litter-Moss	.018 ± .002	.007	.014 ± .004	.005	
Soil[c]	.015[d]		.015		

[a] Data averaged across plots for the first application of the season.
[b] The proportion distributed to the tree includes both leaves and bark.
[c] Soils residues were determined on a whole sample basis.
[d] 1976 value used as there are insufficient data for 1977.

first spray period of the 1978 season. A least squares linear regression of these ratios with time gave an intercept of .7027 and a slope of -.0063T, T being the time since spray in days ($r^2 = .836$). The value for the intercept was then multiplied by the average lower leaf values for the 1976 and 1977 seasons to arrive at an estimate of the average leaf residue level for the entire tree (data in Table 6 and Figures 3 and 4 have been adjusted accordingly). Due to pre-1977 sprayer design the 1976 data are probably still slightly overestimated. This estimate was then multiplied by 400,000 cm^2/tree and by the number of trees per plot. The result was divided by the dose applied to determine the proportion of pesticide distributed to the leaves. The proportion of pesticide distributed to the tree included residues deposited on both leaves and bark. The proportion distributed to the bark was estimated at 15% of that going to leaves, based on the work of Steiner (1969).

The proportion of the pesticide applied that is distributed as surface-penetrated residues was estimated from matched samples from the first spray of the 1978 season. The surface-penetrated to dislodgeable residue ratios and standard errors were as follows; leaves, .081 ± .015; grass, .190 ± .002; litter, .421 ± .018; moss, .272 (one sample). These ratios were multiplied by the appropriate dislodgeable residue proportions to estimate the surface-penetrated residue proportion. All soil residues were determined on a whole sample basis. To estimate the amount of pesticide deposited in the orchard during spray application, all the dislodgeable, surface-penetrated and soil residue proportions were summed across both the alley and canopy regions. In 1976, 66.8% (SE .093) of the pesticide applied was estimated to be initially deposited to the various orchard layers. Confidence in this conservative estimate is subject to the following sources of error; accuracy of amount applied, homogeneity of application, representative sampling of residue distribution, and the tree surface area estimate. The 33.2% not accounted for is assumed to be due to airborne loss, primarily as drift at application, but also as volatilization and wind erosion in the four hours between application and sampling. Another possible pathway of residues not accounted for is foliar penetration and subsequent unavailability to surface strip extraction. Numerous studies have compared dislodgeable to whole-leaf tissue residues (Winterlin et al., 1975; Elliot et al., 1977; Gunther et al., 1977). Their applicability to the present study is uncertain, as the degree of pesticide leaf uptake may vary with pesticide, formulation, mode of application, amount applied, leaf type, and environmental conditions (Hull, 1970). The efficiency of the solvent strip procedure used here, as compared to whole-leaf extraction procedures, in removing freshly deposited azinphosmethyl residues is not known. Use of the solvent strip procedure was based on the results of a detailed study conducted by Weineke and Steffens (1974). These researchers found that 100.4% of the ^{14}C azinphosmethyl applied to bean leaves in an aqueous formulation could be recovered with a water followed by a benzene strip, for samples taken one day following application. In 1977 only 55.4% (SE .001) was estimated to be deposited in the orchard with 45.6% as airborne loss. A similar pesticide mass balance shown in Table 7 uses the target data to estimate the proportion of the pesticide applied that reaches the orchard floor. Tree proportions were estimated in the same manner as for Table 6. This treatment of the data shows that 74.1% (SE .099) of pesticide applied in 1976 was deposited in the orchard, on the average, with 25.9% as airborne loss. In 1977 61.0% (SE .034) was estimated to be deposited in the orchard with 39.0% as airborne loss. Analysis of the plot totals (Table 7) using targets to estimate the proportion of the applied dose distributed to the orchard floor suggests that the amount remaining in the orchard following application is greater in 1976 than in 1977 (paired t-test of plot total proportions gave a $P < .15$). A similar analysis

Table 7. Estimation of Initial Vertical Pesticide Distribution, as a Proportion of the Amount Applied, using Target Data to Calculate Proportion Reaching the Orchard Floor

	1976				
	Orchard Floor		Tree		
Plot	Alley	Canopy	Dislodgeable	Surface-Penetrated	Total
1	.228	.093	.428	.030	.780
2	.155	.138	.374	.026	.694
3	.156	.181	.155	.011	.506
4	.218	.178	.547	.039	.985
					.741 ± .099
	1977				
1	.207	.096	.291	.021	.615
2	.182	.105	.387	.028	.702
3	.088	.101	.337	.024	.550
4	.120	.094	.334	.024	.572
					.610 ± .034

indicated that this difference was not due to amounts distributed to the trees but rather that proportion distributed to the orchard floor. The author believes that this difference may be due to the between-season sprayer modification that directed more of the spray upward into the atmosphere and away from the ground. Wind speed and atmospheric stabiity during application may also have contributed to this difference. There is also some evidence that target residues as a proportion of dose applied were greater than the combined residues distributed to the various orchard floor layers (paired t-test of plot averages across both years gave a $P < .15$). As these data were normalized for extraction efficiency, this result would indicate a substantial loss in residues during the approximately four hours between spray application and sampling. The most likely sources of this loss are thought to be volatilization and/or wind erosion (Gunther and Blinn, 1955; Taylor et al., 1977).

Losses in Runoff

Azinphosmethyl levels found in runoff collected during the 1977 season are given in Table 8. No runoff was found in the orchard plots as a result of the rainfall events that occurred on June 27, July 5, 7, 24, 28, and August 2, 4 (Table 2). These rainfall events averaged 5.8 ± 3.5 mm (intensity, 2.6 ± 1.2 mm/hr) which is considerably lower than the average runoff-producing rainfall event of 21.2 ± 4.7 mm (intensity, 6.5 ± 1.8 mm/hr) shown in Table 8. Rainfall events that occurred on June 11-12 and 17-18 produced small amounts of runoff in some of the plots, but samples were not analyzed. Rainfall intensity for these two events was similar to those that produced no runoff, but the duration of rainfall was slightly longer. The 25.4 mm (intensity, 8.4 mm/hr) rainfall that occurred on August 8-10 produced runoff in all but plot 4, but no analysis was undertaken as samples were not collected until after the spray application on August 12. No runoff-producing events occurred during the 1976 season. The concentration of

Table 8. Azinphosmethyl in Runoff, 1977 Season

Date	Days Since Spray	Rainfall		Runoff	Plot				
		mm	mm/Hr.		1	2	3	4	Control
30 May	4	20.3	5.1	mm x 10^{-2}	0.80	5.00	0.60	1.00	a
				Liters	6.0	20.0	3.5	4.0	
				PPb[c]	10.50	0.70	21.70	18.80	
4,5 June	10	25.4	9.8	mm x 10^{-2}	2.00	2.50	6.70	10.00	1.00
				Liters	14.0	9.8	40.0	40.0	20.4
				PPb	0.74	0.08	0.26	0.25	0.03
30 June	14	25.4	5.4	mm x 10^{-2}	1.00	5.60	1.70	0.10	a
				Liters	8.0	22.5	10.0	0.5	
				PPb	0.40	0.03	0.24	0.73	
18 July	11	22.9	7.1	mm x 10^{-2}	1.30	5.50	2.20	1.00	0.70
				Liters	10.7	22.0	13.0	4.0	10.0
				PPb	3.90	0.15	4.10	2.25	0.20
3,4,6 August	13	20.3	5.1	mm x 10^{-2}	0.06	2.60	0.50	3.10	a
				Liters	0.5	10.5	3.0	12.5	
				PPb	b	1.30	3.40	b	
13 August	1	12.7	6.4	mm x 10^{-2}	0.50	0.80	a	a	a
				Liters	4.0	3.0			
				PPb	14.35	b			

[a] No runoff collected.
[b] Runoff not analyzed.
[c] PPb of Azinphosmethyl in runoff water.

azinphosmethyl in the sediment (sediment amounts were less than 0.5 grams per liter of runoff) was very small compared to levels in the water, and these data are not reported here. The lack of sediment is to be expected as the dense ground cover on the orchard floor allows little soil erosion (Asmussen et al., 1977; Harrold et al., 1970). The amount of runoff is also expected to be less than might be found from tilled fields of similar slope characteristics. This may be attributed to effect of ground cover, which increases infiltration and slows overland flow, thus decreasing total runoff and loss of pesticide. Many researchers have reported that concentrations of pesticides in runoff are highest for rainfall events occurring soon after application (Hall et al., 1972; Baur et al., 1972; Glass et al., 1974; Ritter et al., 1974; Caro et al., 1974). This is indeed what was observed for the pesticide levels in runoff for the orchard studied. The levels of azinphosmethyl in runoff collected on June 6, 10 days after application, were 10 to 100 times less than the levels found in runoff collected on June 1, just 4 days after application. Time since spray has an effect on the amount of pesticide in runoff only as it is related to the amounts of pesticide residue available to runoff. The amount of rainfall preceding the rainfall event that produces runoff also influences the amount of pesticide that is lost to runoff. A comparison of azinphosmethyl concentrations in runoff collected from plots 1, 3, and 4 on June 6 (10 days following application) with azinphosmethyl concentrations in runoff from the same plots collected July 19 (11 days following application) shows much higher levels in the July 19 runoff. This may be explained by the fact that although both events occurred approximately the same number of days following aplication, no rainfall occurred between application and the event producing runoff on July 19, whereas 20.3 mm of rainfall occurred just 4 days prior to the June 6 event. The intervening rainfall event not only produced runoff, removing pesticide residues from the orchard, but also redistributed those residues remaining such that they would be less likely to be removed with successive runoff. The fact that tree leaf residues for June 6 averaged .399, 1.267, and 1.225 $\mu g/cm^2$ for plots 1, 3, and 4, respectively, and leaf residues found on July 19 averaged 1.942, 2,286, and 2,374 $\mu g/cm^2$ for plots 1, 3, and 4, respectively, supports this hypothesis. In general, increased runoff caused increased pesticide loss so that the concentration of pesticide in varying amounts of runoff on a given day remained relatively constant. The data, for the most part, reflected this relationship, except for plot 2. Plot 2 was characterized by consistently high runoff compared to the other plots, but upon analysis, azinphosmethyl levels detected were considerably lower than those in the other plots. I have not yet arrived at a satisfactory explanation for this. One might hypothesize that collected runoff was coming from outside the plot or possibly was interflow from upslope that surfaced just prior to the collection point.

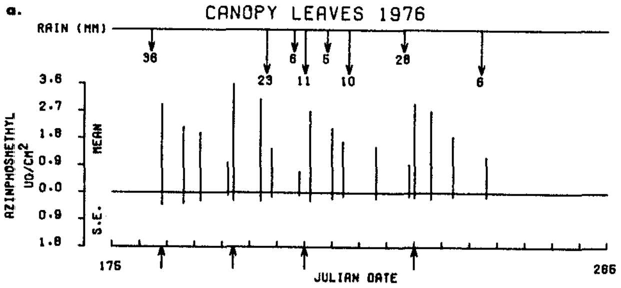
Overall it appears that the contribution of runoff to the azinphosmethyl loss from the orchard was quite small. For example, the 20.3 mm of rain on May 30 produced only .01 mm of runoff from plot 4, which contained 75 mg of azinphosmethyl, whereas 44 g were applied just four days prior to the event. This loss was well under 1% of the residues present at the time of the rainfall.

Residue Data

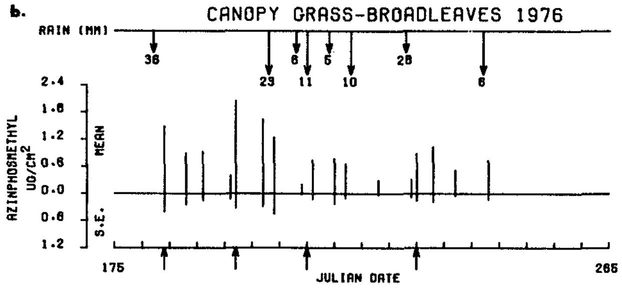
Figures 3 and 4 represent azinphosmethyl dislodgeable residues for the various above ground layers and soil residues, for alley and canopy regions. Leaf residues are shown as entire tree estimates using the method described for Table 6. Prior to averaging across plots, statistical outliers were determined and eliminated using the test proposed by Grubbs (1969). A total of 954 samples for 1976 and 637 samples for 1977 are represented, with the average number of samples per sampling date as follows: leaves, 11, grass-broadleaves, 14; litter-

Figure 3 (a-d) Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1976 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

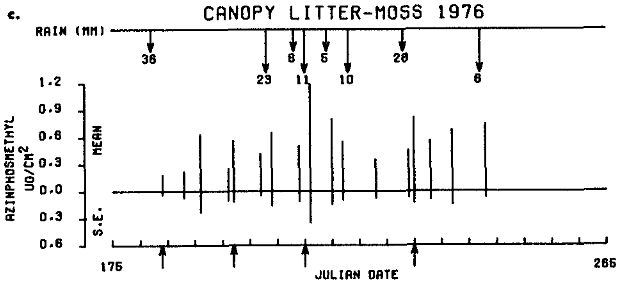
a.


CANOPY LEAVES 1976
RAIN (MM)
36
23
6
11
5
10
28
6
3.6
2.7
1.8
0.9
0.0
0.9
1.8
AZINPHOSMETHYL
UG/CM2
MEAN
S.E.
176
JULIAN DATE
266

b.


CANOPY GRASS-BROADLEAVES 1976
RAIN (MM)
36
23
6
11
5
10
28
6
2.4
1.8
1.2
0.6
0.0
0.6
1.2
AZINPHOSMETHYL
UG/CM2
MEAN
S.E.
176
JULIAN DATE
266

c.


CANOPY LITTER-MOSS 1976
RAIN (MM)
36
23
6
11
5
10
28
6
1.2
0.9
0.6
0.3
0.0
0.3
0.6
AZINPHOSMETHYL
UG/CM2
MEAN
S.E.
176
JULIAN DATE
266

d.

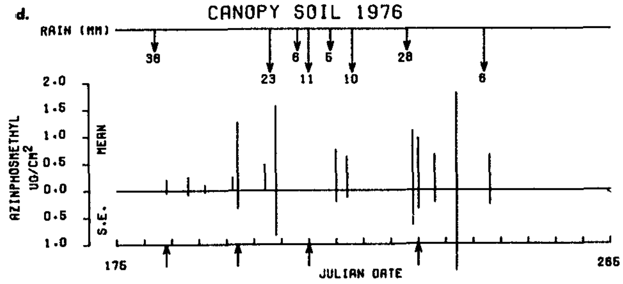
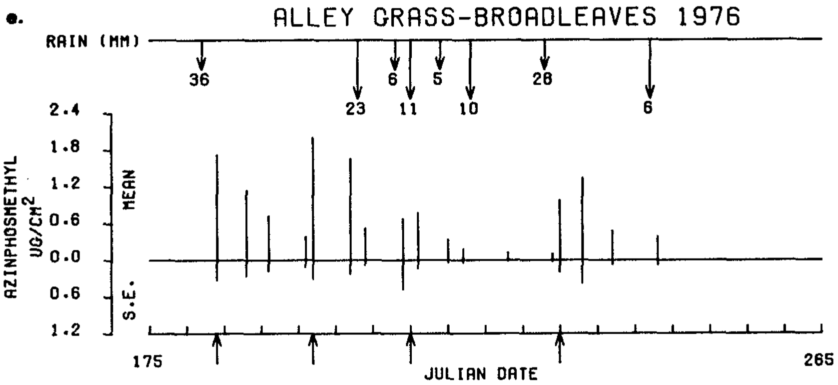
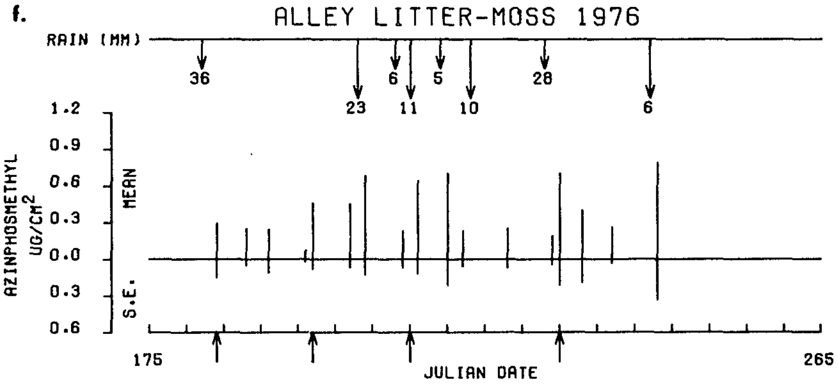

CANOPY SOIL 1976
RAIN (MM)
36
23
6
11
5
10
28
6
2.0
1.5
1.0
0.5
0.0
0.5
1.0
AZINPHOSMETHYL
UG/CM2
MEAN
S.E.
176
JULIAN DATE
266

Figure 3 (e-g) Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1976 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2) is above the line and its corresponding standard error (S.E.) below the line.

e.


ALLEY GRASS-BROADLEAVES 1976
RAIN (MM)
36
23
6
11
5
10
28
6
2.4
1.8
1.2
0.6
0.0
0.6
1.2
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
175
JULIAN DATE
265

f.


ALLEY LITTER-MOSS 1976
RAIN (MM)
36
23
6
11
5
10
28
6
1.2
0.9
0.6
0.3
0.0
0.3
0.6
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
175
JULIAN DATE
265

g.

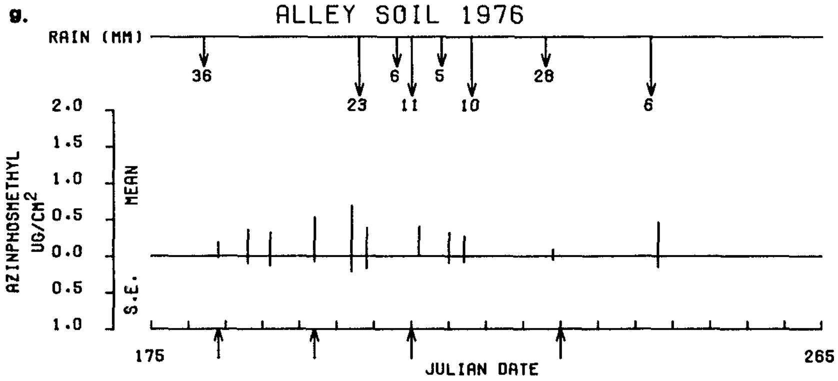
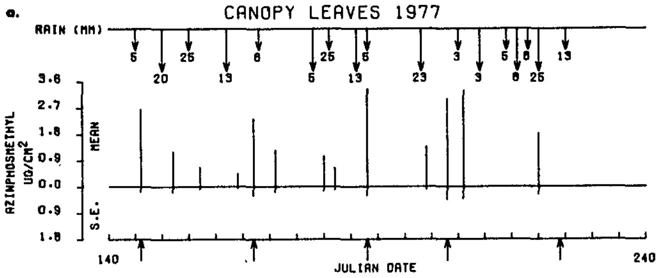
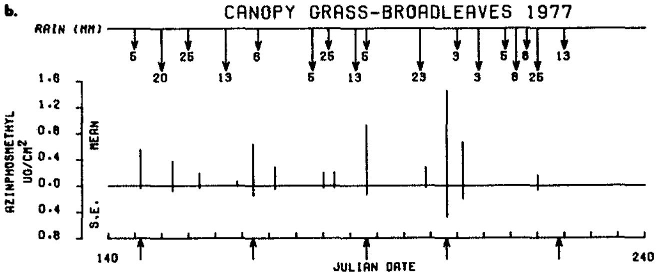
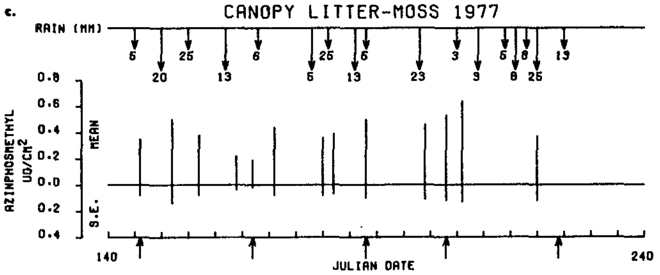

ALLEY SOIL 1976
RAIN (MM)
36
23
6
11
5
10
28
6
2.0
1.5
1.0
0.5
0.0
0.5
1.0
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
175
JULIAN DATE
265

Figure 4 (a-d) Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1977 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.


a.
CANOPY LEAVES 1977
RAIN (MM)
5
20
25
13
8
5
25
13
5
23
3
3
5
8
8
25
13
AZINPHOSMETHYL UG/CM2
3.6
2.7
1.8
0.9
0.0
0.9
1.8
MEAN
S.E.
140
240
JULIAN DATE


b.
CANOPY GRASS-BROADLEAVES 1977
RAIN (MM)
5
20
25
13
8
5
25
13
5
23
3
3
5
8
8
25
13
AZINPHOSMETHYL UG/CM2
1.6
1.2
0.8
0.4
0.0
0.4
0.8
MEAN
S.E.
140
240
JULIAN DATE


c.
CANOPY LITTER-MOSS 1977
RAIN (MM)
5
20
25
13
8
5
25
13
5
23
3
3
5
8
8
25
13
AZINPHOSMETHYL UG/CM2
0.8
0.6
0.4
0.2
0.0
0.2
0.4
MEAN
S.E.
140
240
JULIAN DATE

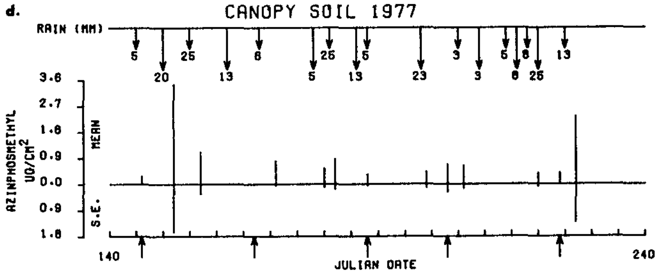
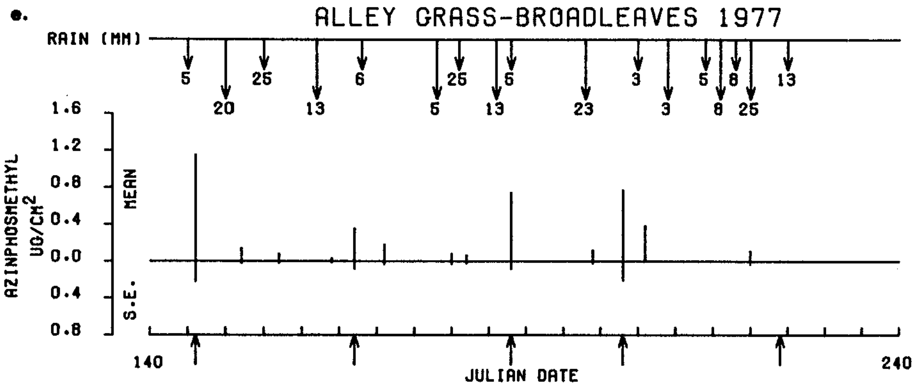
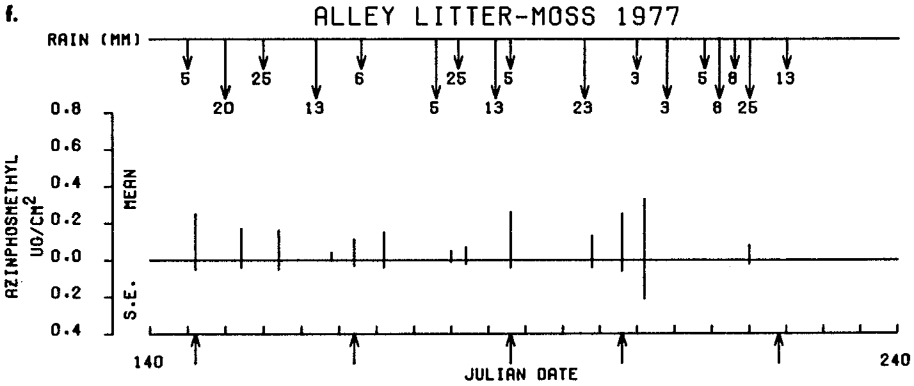

d.
CANOPY SOIL 1977
RAIN (MM)
5
20
25
13
8
5
25
13
5
23
3
3
5
8
8
25
13
AZINPHOSMETHYL UG/CM2
3.6
2.7
1.8
0.9
0.0
0.9
1.8
MEAN
S.E.
140
240
JULIAN DATE

Figure 4 (e-g) Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1977 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

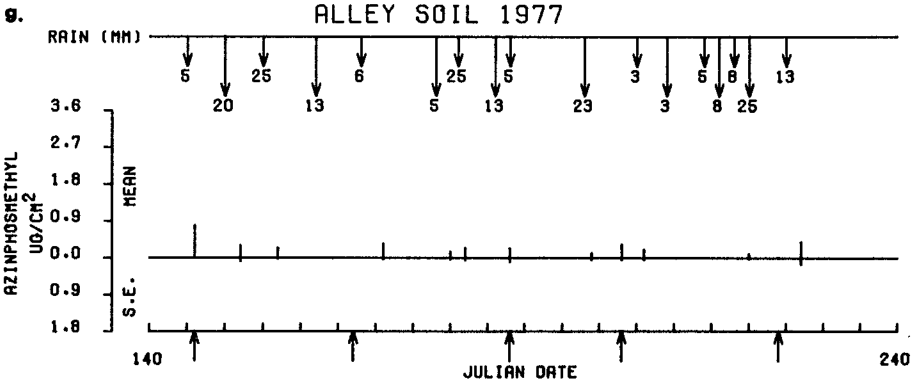
e.


ALLEY GRASS-BROADLEAVES 1977
RAIN (MM)
5 20 25 13 6 5 25 13 5 23 3 3 5 8 8 25 13
AZINPHOSMETHYL UG/CM^2
1.6
1.2
0.8
0.4
0.0
0.4
0.8
MEAN
S.E.
140
240
JULIAN DATE

f.


ALLEY LITTER-MOSS 1977
RAIN (MM)
5 20 25 13 6 5 25 13 5 23 3 3 5 8 8 25 13
AZINPHOSMETHYL UG/CM^2
0.8
0.6
0.4
0.2
0.0
0.2
0.4
MEAN
S.E.
140
240
JULIAN DATE

g.


ALLEY SOIL 1977
RAIN (MM)
5 20 25 13 6 5 25 13 5 23 3 3 5 8 8 25 13
AZINPHOSMETHYL UG/CM^2
3.6
2.7
1.8
0.9
0.0
0.9
1.8
MEAN
S.E.
140
240
JULIAN DATE

moss, 14; and soil, 4. Each bar is divided into two parts. The mean is above the line and its corresponding standard error below the line. Time is represented by the Julian date with upward directed arrows indicating spray application dates. Downward directed arrows above the bars indicate dates and amounts of rainfall in millimeters. (These data are also given in Tables 1 and 2.) The concentration scale is designed so that the highest bar for a given layer, over both canopy and alley regions, is nearly full scale.

The concentration of dislodgeable pesticide residue found in a given layer at any point in time throughout the season is a function of two processes; movement and attenuation. Attenuation is thought to include all degradative processes (chemical, photochemical, and microbial), airborne loss, penetration into plant subsurfaces, and irreversible soil binding (Ebling, 1963; Hull, 1970; Katan et al., 1976). Movement mainly redistributes the pesticide within the orchard. This redistribution, primarily by rainfall, is confounded with the attenuation processes, making determination of attenuation rates in the field difficult. A treatment of this problem using mathematical modeling techniques is described in Part II. An "eyeball" examination of these data indicates contrasting rates of both movement and attenuation among the various vertical strata and horizontal regions of the orchard. Comparison of leaf pesticide residues for the first spray period in 1976 (Figure 3a) with leaf pesticide residues for the first spray period in 1977 (Figure 4a) shows that the residues remaining after eleven days in 1977 are roughly two thirds the value of those pesticide residues remaining after 12 days in the 1976. This difference is possibly due to the 20 mm and 25 mm rainfall events occurring in the interval between pesticide application and the sampling eleven days later in 1977, while no rain fell during the first spray period of the 1976 season. That rainfall is responsible for the reduction of foliar residue deposits has been suggested by a number of researchers, many of the earlier studies are summarized by Ebling (1963). In more recent studies, McMechan et al. (1972) reported that azinphosmethyl applied as a wettable powder formulation to apples was lost at a much more rapid rate from foliage during wet weather as opposed to dry. Similar results were reported by Williams (1961) for azinphosmethyl and carbaryl applied to apples, and by Thompson and Brooks (1976) for dislodgeable residues of azinphosmethyl and four other organophosphate insecticides applied as emulsifiable concentrates to oranges in Florida. Gunther et al. (1977) also noted the influence of rainfall on the decline of parathion dislodgeable residues applied as a wettable powder formulation to oranges in California. Nigg et al. (1977) used multiple linear regression to examine the relationship between residue decline of ethion dislodgeable residues (applied as E.C.) and the variables: degree-days, cumulative leaf wetness, and ordinary time. They found, for the experiment where rainfall occurred, that residue decay was most highly correlated with cumulative rainfall ($r^2 = .963$). In the present study, the leaf residue data also show that rainfall had a significant effect on pesticide residues in the tree. This is indicated by the results of a 23 mm rain occurring six days after the second spray application, which reduced the residue levels to less than half their former value. Similar results were reported by McMechan et al. (1972) for rainfall events occurring much closer to application. In their study, a 17.5 mm rainfall (1.8 mm/hr) that started six hours after a 50 % w.p. azinphosmethyl application (.23 kg a.i. ha^{-1}) to semi-dwarf apple trees, removed 41% of the initial deposit. A much lighter rainfall of 3.0 mm (0.9 mm hr^{-1}) that started five hours after a similar application, removed 12% of the initial deposit. Van Dyk (1976) examined the effect of artificial rainfall on parathion residues applied as both wettable powder and emulsifiable concentrate to orange, lemon, and grapefruit leaves and fruit. Rainfall was applied at 33 mm hr^{-1}. Factorial analysis of variance showed significant interaction ($P < 0.01$) between parathion residues and the simulated rainfall. The type of formulation was not significant. This is not surprising considering the high rate of rainfall applied. By contrast, a 28 mm rain occurring 17 days following the third spray of the 1976 season (present study) had little effect on the apparent residue decline, suggesting that rainfall events occurring close to application have a greater influence on leaf pesticide dislodgeable residue levels. This phenomenon has also been suggested by Ebling (1963), McMechan et al. (1972) for azinphosmethyl applied to apple foliage, and by Steffens and Weineke (1975) for ^{14}C azinphosmethyl applied to bean foliage. One theory that might explain this occurrence was first proposed by Gunther and Blinn (1955), also by Ebling (1963), and most recently by Elliott et al. (1977). These researchers suggest that pesticide deposits on foliar surfaces are lost at different rates due to the degree at which they adhere or penetrate the leaf surface. Initial rapid loss is a result of erosion of loosely bound deposits, possibly adsorbed to the formulations or dust on the plant. More tightly bound residues are lost primarily through volatilization, decomposition, and penetration into subsurface tissues. According to this theory, the percentage of the deposit that is loosely bound decreases rapidly following application. It is this fraction of the deposit that is most susceptible to erosion processes, including rainfall. As the loosely bound residues are lost, those more tightly bound residues that remain are less susceptible to loss with rainfall.

Comparison of 1976 canopy leaf residue data (Figure 3a) with canopy grass-broadleaves residue data (Figure 3b) shows little difference in residue decline, under the no-rainfall conditions of the first spray period. The effect of the 23 mm rain in the second spray period of the 1976 season on residue decline in the grass-broadleaves was much less than was seen in the canopy leaves (Figure 3a). This might indicate that in addition to pesticide moving downward out of the grass-broadleaves with rainfall, pesticide is moving in from the tree above. Comparison of canopy litter-moss pesticide residues during the first spray period of 1976 (Figure 3c) with those residues found in the grass-broadleaves (Figure 3b) shows a marked difference in residue decline, as pesticide levels remain at a rather constant level throughout the spray period. This would suggest that under no-rainfall conditions, pesticide is moving into this layer at the same rate that pesticide is moving out and/or being attenuated. An alternative hypothesis would be no movement and no or very slow attenuation, which seems highly unlikely. Residue levels in the canopy litter-moss layer increased following the 23 mm rainfall event occurring during the second spray period of the 1976 season, again suggesting movement of pesticide into the litter-moss from layers above, in amounts greater than movement out and/or attenuation losses. In general, canopy litter-moss residue values remained fairly constant throughout both the 1976 and 1977 seasons. Under no-rainfall conditions (first spray period, 1976 season, Figure 3d), canopy soil residues did not increase with time following application as did the litter-moss residues. As azinphosmethyl has been shown to degrade faster in non-sterile soils as compared to sterile soils (Yaron et al., 1974), microbial degradation may play an important role in losses from this layer. In addition, root uptake and translocation (Al-Adil et al., 1973) may have been partially responsible for the observed soil residue pattern. Pesticide movement into the canopy soil with rainfall is again pronounced, as indicated by the 23 mm rainfall event during the second spray period of the 1976 season (Figure 3d). The first spray period of the 1977 season shows canopy soil residue levels increasing with each rainfall event (Figure 4d).

Alley grass-broadleaves pesticide residues show a systematic decline over the first spray period of the 1976 season (Figure 3e). The decline is slightly steeper than the decline shown for canopy grass residues during the same no-rainfall period (Figure 3b). This difference is probably due to less pesticide movement from the trees into the alley grass-broadleaves. Increased attenuation losses in the alley regions due in part to greater exposure to wind and solar radiation must also be considered. Taylor et al. (1977) in discussing factors influencing dieldrin volatilization from orchard grass, cited solar radiation as the most significant. Associated surface temperatures may also influence rates of chemical and microbial degradation and foliar uptake (Ebling, 1963; Hull, 1970). Azinphosmethyl applied to plant surfaces has been shown in one study (Liang and Lichtenstein, 1976) to be susceptible to photodegradation by sunlight. This degradative pathway is directly related to solar radiation. Rainfall effects are clearly shown when comparing alley grass residue to decline for the first spray period in 1976 (Figure 3a) with the first spray period of the 1977 season (Figure 4e). The difference in rainfall effects between canopy grass-broadleaves and alley grass-broadleaves is shown in the second spray period of the 1976 season (Figures 3b and 3e) which indicates that the pesticide movement, following the 23 mm rainfall event, out of the alley grass-broadleaves is probably greater due to direct exposure to rainfall, and also that there is little or no pesticide movement in from the trees. Again, differential attenuation due to shading cannot be disregarded. Alley litter-moss pesticide residues show a definite decline during the first and last spray periods of the 1976 season (Figure 3c). While canopy litter-moss residue values increased with rainfall during the first spray period of the 1977 season (Figure 4c), the alley litter-moss residue values show a decline, indicating that residue movement out and/or atenuation is greater than residue movement into this alley layer. Alley soil residues for the first spray period of the 1976 season (Figure 3g) are similar to canopy soil residues for the same period (Figure 3d, note the difference in scaling). There appears to be a decrease in alley soil residue levels following the

23 mm rain during the second spray period of the 1976 season (Figure 3c) whereas the canopy soil residues (Figure 3d) increase following this rainfall event. The high variability of these data discourages speculation as to the processes taking place. The general pattern of these residue levels over the season, characterized by a buildup of residues toward mid-season, is surprisingly similar to the azinphosmethyl orchard soil residue pattern reported by Kuhr et al. (1974). A general observation of the data presented in Figure 3 indicates that, as the season progressed, the interrelationship between pesticide movement and attenuation became more difficult to follow. This complexity is possibly a function of changes in weather patterns in addition to rainfall (temperature, humidity and wind). Gunther et al. (1977) attempted to relate temperature data to the decline of azinphosmethyl residues applied to citrus in southern California. They found it difficult to make any meaningful interpretation of the data, but stated that azinphosmethyl dissipation was slightly more rapid during warmer weather. No correlations between residue data and temperature or humidity were attempted in the present study, but weather data was provided for possible future use (Figures 5, 6, 7, and 8). Changes in plant physiology and soil microbial activity or a buildup of tightly bound or penetrated residues, may also have an effect on pesticide residue dynamics throughout the season.

However, from the limited analysis of the data, there is some indication that azinphosmethyl is redistributed throughout the orchard with time following application. Redistribution is indicated during periods without rainfall, but is more pronounced following rainfall events. Little more information can be gained without the aid of a more sophisticated technique of analysis. Such an analysis of the data is presented in Part II. Using mathematical modeling techniques, the change in observed residue levels in each layer and region is etimated as a function of both movement and attenuation.

Figure 5 Daily Temperature Range, 1976 Season

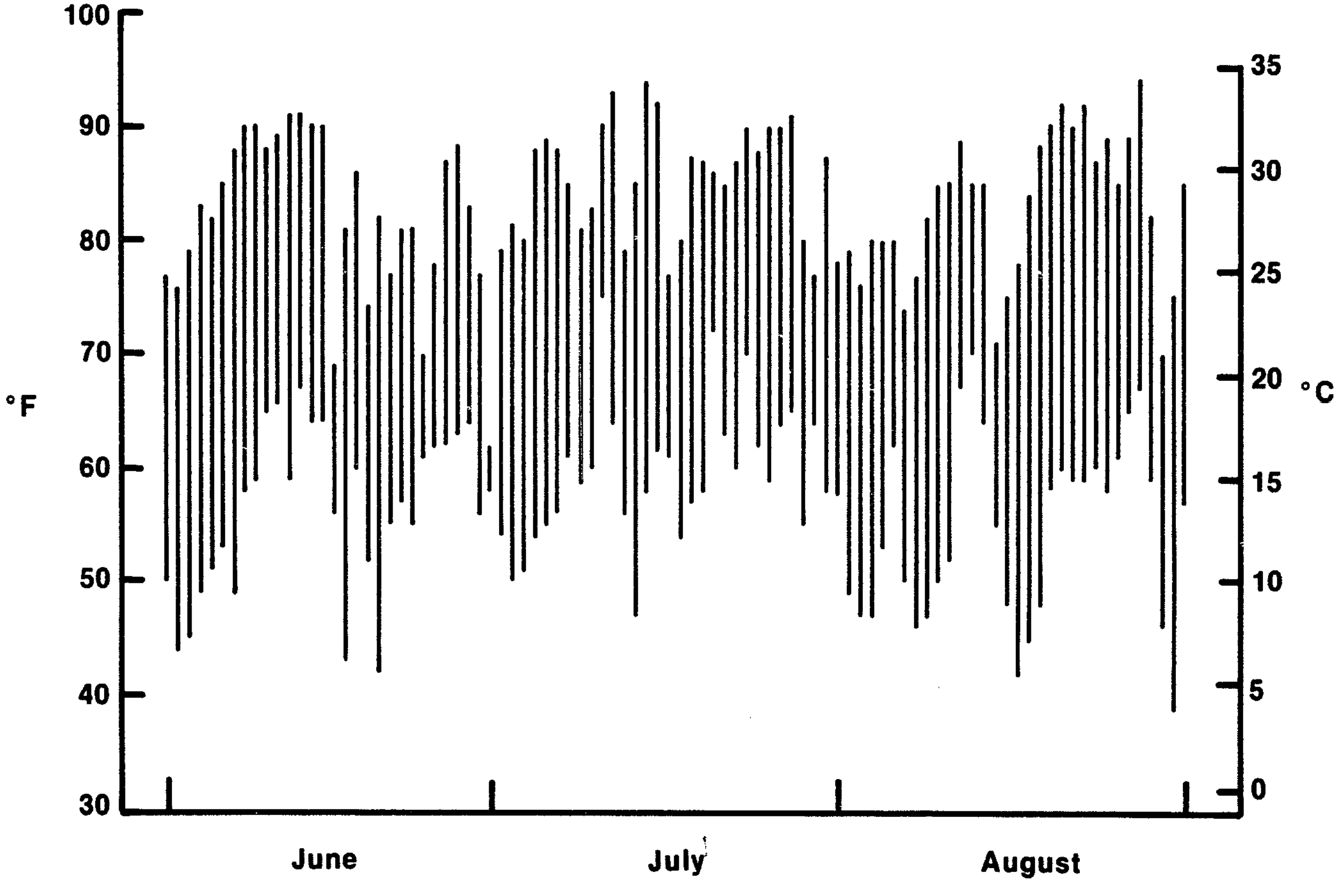

100
90
80
70
60
50
40
30
°F
35
30
25
20
15
10
5
0
°C
June
July
August

Figure 6 Daily Minimum and Maximum Relative Humidity, 1976 Season

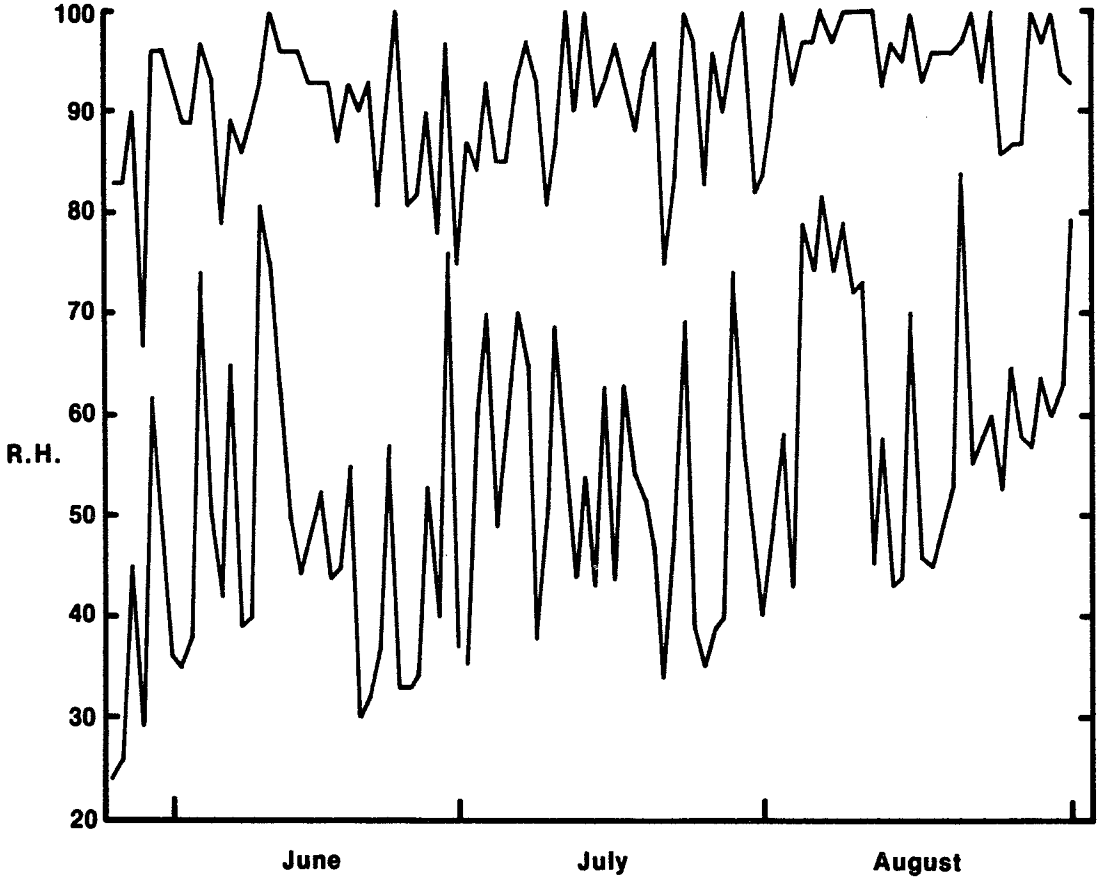

100
90
80
70
60
50
40
30
20
R.H.
June
July
August

Figure 7 Daily Temperature Range, 1977 Season

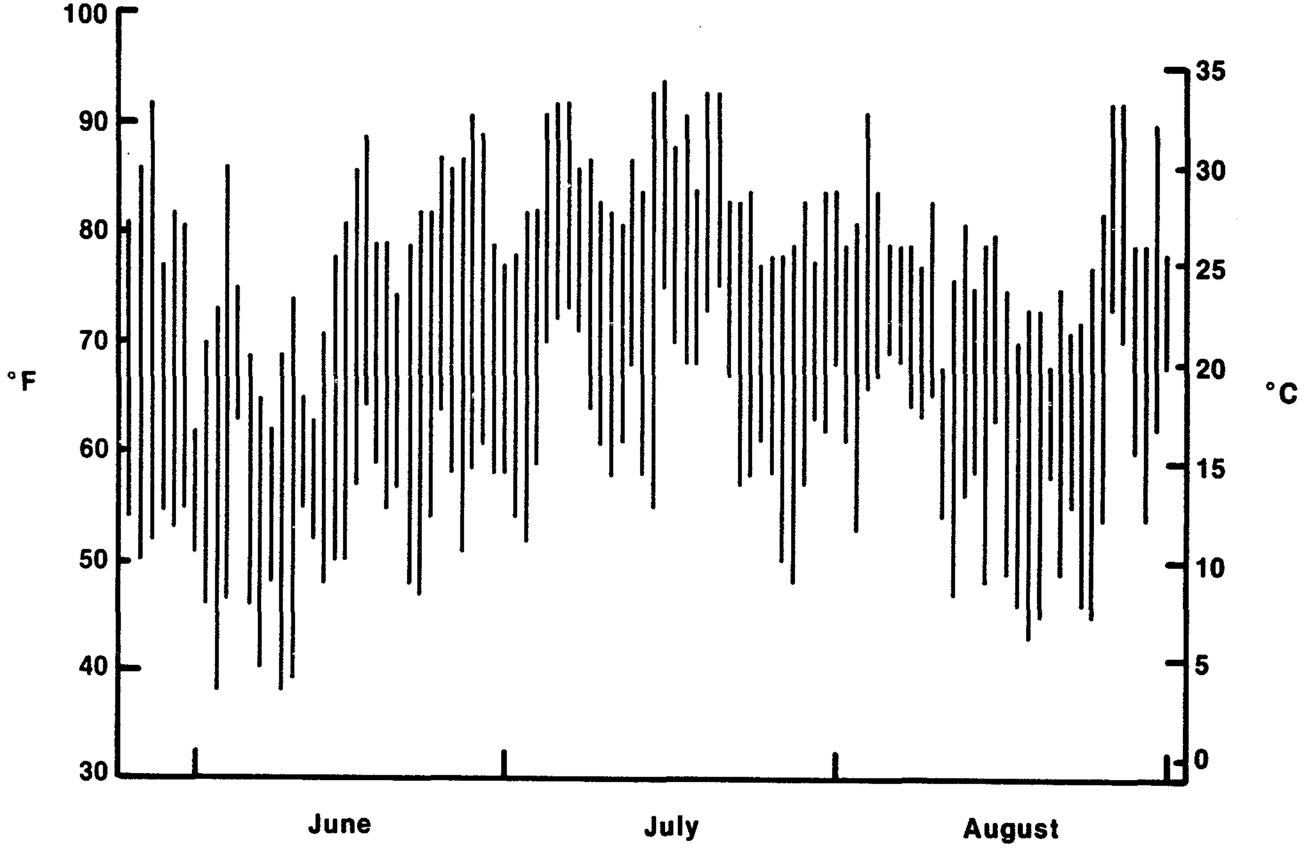
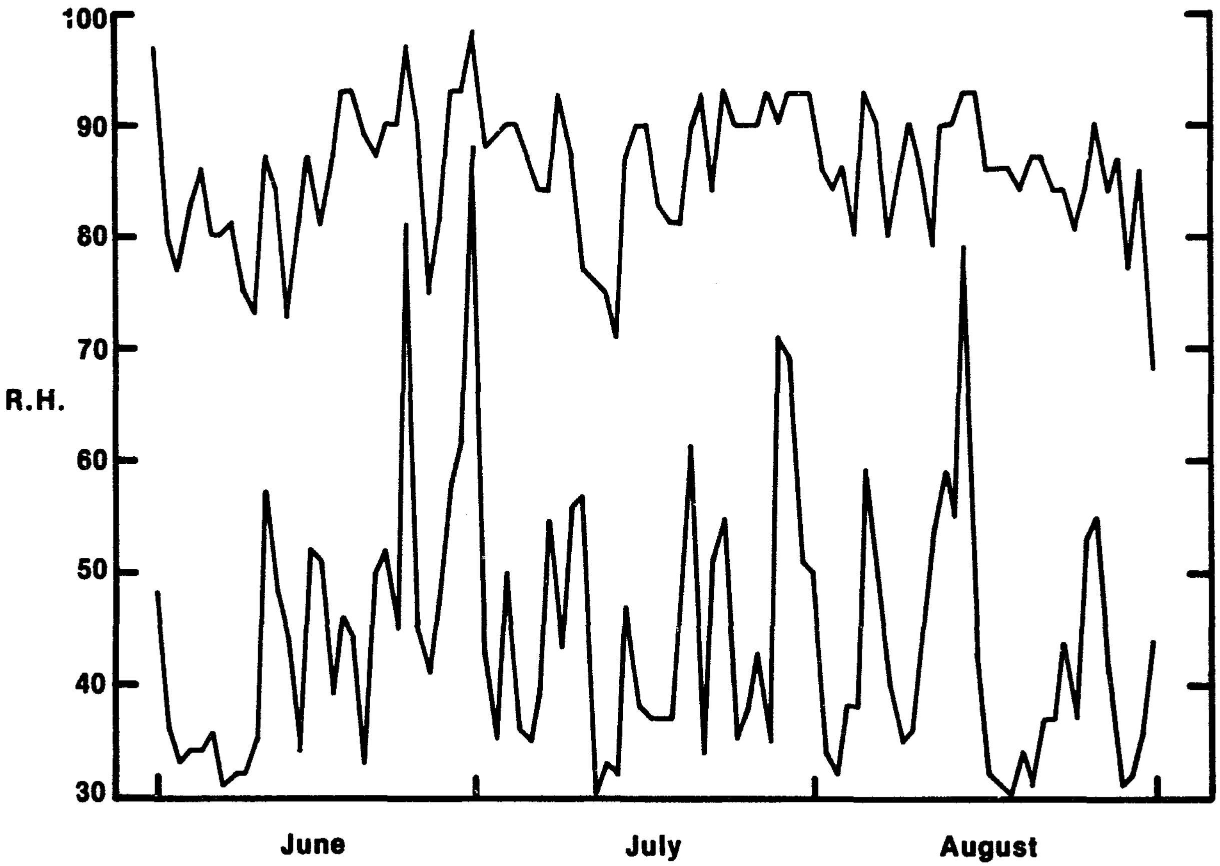

100
90
80
70
60
50
40
30
°F
35
30
25
20
15
10
5
0
°C
June
July
August

Figure 8 Daily Minimum And Maximum Relative Humidity, 1977 Season


100
90
80
70
R.H.
60
50
40
30
June
July
August

Information on pesticide concentrations as a function of movement and attenuation is essential to the estimation of possible exposure to the biota of this agroecosystem. If pesticides are to be used in an effective manner in conjunction with biological control techniques, possible exposure to beneficial populations, as well as the target species, must be better understood under a variety of climatic conditions.

PART II

ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN ORCHARD ECOSYSTEM: PARAMETERIZATION OF A FIELD-BASED MODEL

INTRODUCTION

In Part I a description of the field data collected on the distribution, movement, and attenuation of azinphosmethyl in an experimental apple orchard was given. These data were gathered specifically in order to allow development, refinement, and parameterization of a model describing the spatial and temporal distribution of azinphosmethyl in the orchard in response to rainfall. While the time series of concentrations observed were reported in the earlier part, the model and the parameterization process, together with the parameter values generated, are described in this part. Validation of this model using a third season's data is presented.

The form of this model was chosen to allow: (1) use of model output to provide pesticide exposures for models of organisms dwelling in the orchard floor (Goodman, 1980) and (2) future development to represent the dynamics of other pesticides and the effects of additional environmental factors.

THE MODEL

In order to structure the experimental program and the data analysis, a conceptual model for the distribution, movement, and fate of the pesticide in the orchard was formulated. Information gathered has resulted in continual refinements of the model structure. The conceptual model utilizes a spatial subdivision of the orchard into a canopy region and three alley regions (Figure 2 of Part I).

Vertically, four strata (not necessarily all present at a given sampling location) are identified. These are called tree, grass-broadleaves, litter-moss, and soil.

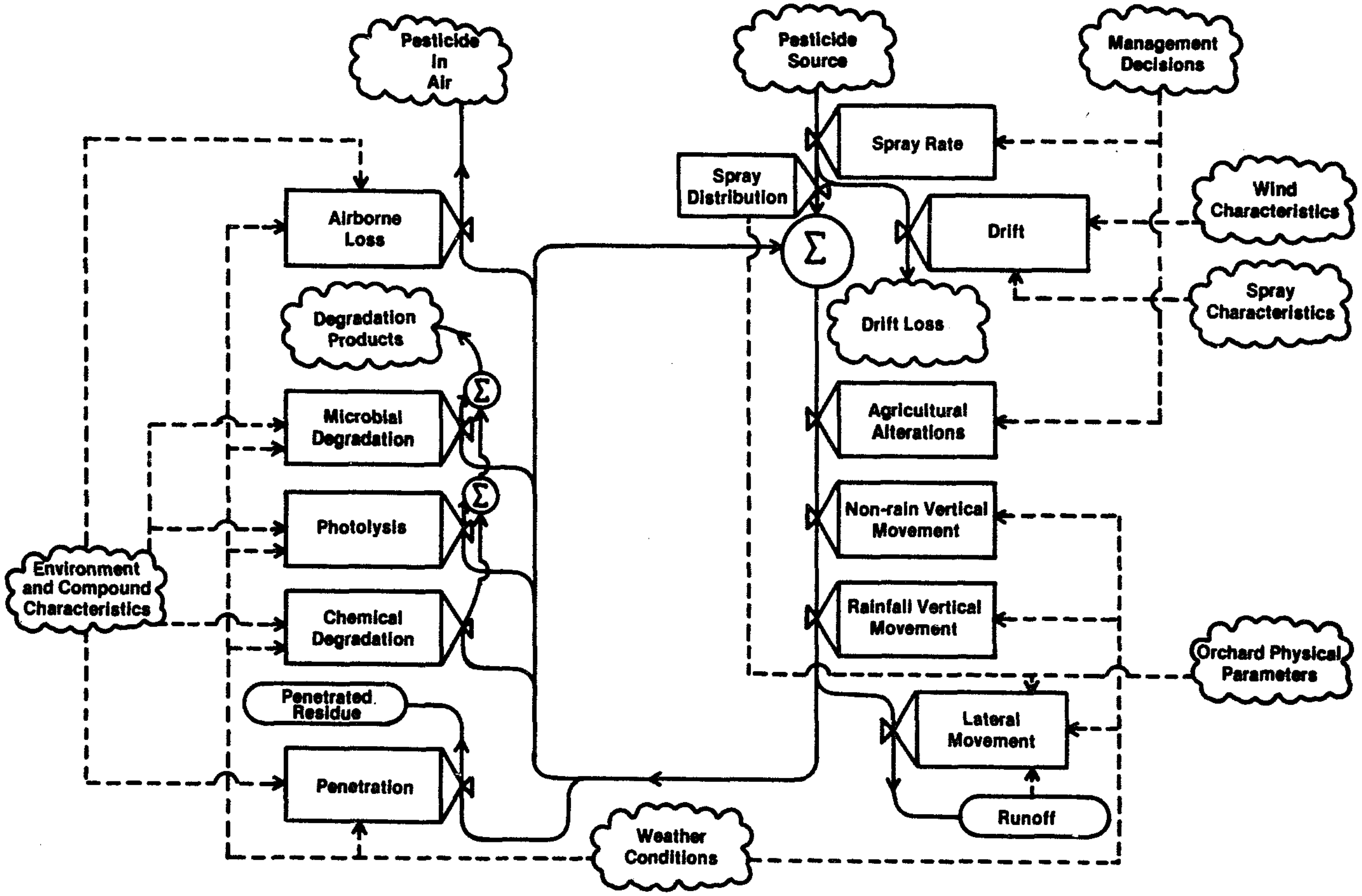
The conceptual model (see Figure 1) describes the dynamics of the pesticide from its spray application to its ultimate disappearance from the orchard via drift, attenuation (including airborne loss, photolysis, chemical degradation, microbial degradation, and penetration of surface residues) and runoff. Each day, a vector C of concentrations of pesticide in each of seven regions (two horizontal by four vertical, minus one for non-existent alley trees) is calculated, based on management actions (spraying, mowing) and rainfall. Figure 1 describes the processes affecting the pesticide concentration in only one of the seven regions.

For analysis of the field data, the processes in Figure 1 are lumped into three categories: initial distribution, movement, and attenuation. Movement is further subdivided according to rainfall intensity (none, light, and heavy). The mathematical forms of the various components of this model are described below:

(1) Initial Distribution

The spray rate (in Kg/ha) is supplied as an input. Drift, including losses from the orchard during spraying and up to the time of post-spray sampling, was estimated using mass conservation, based upon the known application rate, estimated pre-spray residue levels, and measured residues following application (see Part I). The proportion drift averaged .376 ± .149 over the three seasons. Because

Figure 1 Conceptual Model for the Distribution, Movement, and Attenuation of Azinphosmethyl in an Apple Orchard



Pesticide In Air
Pesticide Source
Management Decisions
Spray Rate
Spray Distribution
Σ
Airborne Loss
Drift
Wind Characteristics
Drift Loss
Spray Characteristics
Degradation Products
Σ
Microbial Degradation
Agricultural Alterations
Σ
Photolysis
Non-rain Vertical Movement
Environment and Compound Characteristics
Chemical Degradation
Rainfall Vertical Movement
Orchard Physical Parameters
Penetrated Residue
Lateral Movement
Penetration
Runoff
Weather Conditions

the standard deviation observed among the data was higher than anticipated, an attempt was made to relate the drift loss to wind speed at the time of application from the available data. Mean wind speeds during application were estimated from data of the Michigan Weather Service, Grand Rapids, Michigan. The following relationship was determined:

$$D = .021\ WS + .091 \qquad (r = .475)$$

where D is proportion drift and WS is wind speed in km/hr.

The residue deposited in the orchard is apportioned into the seven regions according to a spray distribution vector, in which each entry specifies the proportion of the spray that is captured by the corresponding region, and added to any remaining residue from earlier sprays in the pesticide concentration vector C. All units are expressed as μg pesticide/cm^2 ground area.

(2) Attenuation

Attenuation is treated in the model as a set of daily proportion losses—a single proportion for each layer. Thus it is conveniently representable as a diagonal matrix A which pre-multiplies the pesticide distribution vector C, a seven-element column vector containing the concentration of pesticide (μg/cm^2) in each region at a particular time. Each day, attenuation is extracted via equation (1):

$$C(\text{after}) = (I-A)C(\text{before}) \tag{1}$$

where I is the 7 x 7 identity matrix.

C_4 and C_7, the pesticide concentrations in canopy and alley soils, respectively, represent total soil residues, while C_1, C_2, C_3, C_5, and C_6 represent only dislodgeable residues. Thus the attenuation for non-soil layers includes surface penetration of residues.

(3) Movement

Daily redistribution of the pesticide within the orchard is modeled using three matrices to pre-multiply the pesticide distribution column vector C. Daily movement not attributed to rainfall is modeled by equation (2):

$$C(\text{after}) = PC(\text{before}) \qquad (2)$$

where P is a 7 x 7 column-stochastic lower triangular matrix known as the non-rainfall pure movement matrix. The matrix P is restricted to containing at most 19 non-zero entries, as the tree layer is the only canopy layer from which movement to alley layers is modeled, so $P_{ij} = 0$, for $i = 5, 6, 7$ and $j = 2, 3, 4$.

Several parameters are necessary to adequately describe a rainfall event; for example, duration, average intensity, peak intensity, etc. Unfortunately the small number of rainfall events during a spray season precluded using so fine a description. Rainfall events were classified on a daily basis into only two categories (heavy and light) in order to obtain enough instances of each category to parameterize the model. Heavy rain was defined as any event of more than 10 mm rainfall or more than 5 mm/hour in a day, with other measurable rain classified as light. Equations (3) and (4) show the pesticide redistributions caused by heavy and light rainfall, respectively:

$$C(\text{after}) = HC(\text{before}) \qquad (3)$$

$$C(\text{after}) = LC(\text{before}) \qquad (4)$$

where H and L are 7 x 7 column-stochastic lower triangular matrices.

As in equation (1), H and L do not model movement between alley and canopy ground layers; thus pesticide movement with overland runoff is not included in these equations.

Attenuation and non-rainfall movement were modeled (and parameterized) as daily phenomena. Thus, to represent the natural changes in pesticide distribution from one day to the next, (C(k) to C(K+1)), exactly one of the following relationships is used:

$$C(k+1) = P(I-A)C(k) \qquad \text{(no rain)} \tag{5}$$

$$C(k+1) = L\ P(I-A)C(k) \qquad \text{(light rain)} \tag{6}$$

$$C(k+1) = H\ P(I-A)C(k) \qquad \text{(heavy rain)} \tag{7}$$

METHODS FOR PARAMETER ESTIMATION

This section describes the techniques used to estimate the model parameters from the data base of field determinations. The routines described are designed to be used repeatedly, i.e., as entries are added to the data base, new parameters including their effects can be quickly generated. This capability for dynamic reparameterization of the model gives it the flexibility to begin with relatively few crude data, producing preliminary outputs, and to produce more accurate results as the data base grows.

Data Base

The data base consists of a large number of sequential disk files, which are updated and utilized by various programs. Rainfall data, orchard plot physical chracteristics, and records of samples analyzed for pesticide are stored in these files. Figure 2 shows how sample and target data, entered as "raw" outputs from gas chromatograph measurements, are transformed into new files of "processed" sample and target data. In this stage, appropriate corrections for analytical technique, sample weight, averages across samples, etc. are made, yielding files suitable for use in calculating the model parameters. Figure 3 is a flowchart of

Figure 2 Flow Chart Showing Data Processing to Yield Files Suitable for Use in Model Parameterization

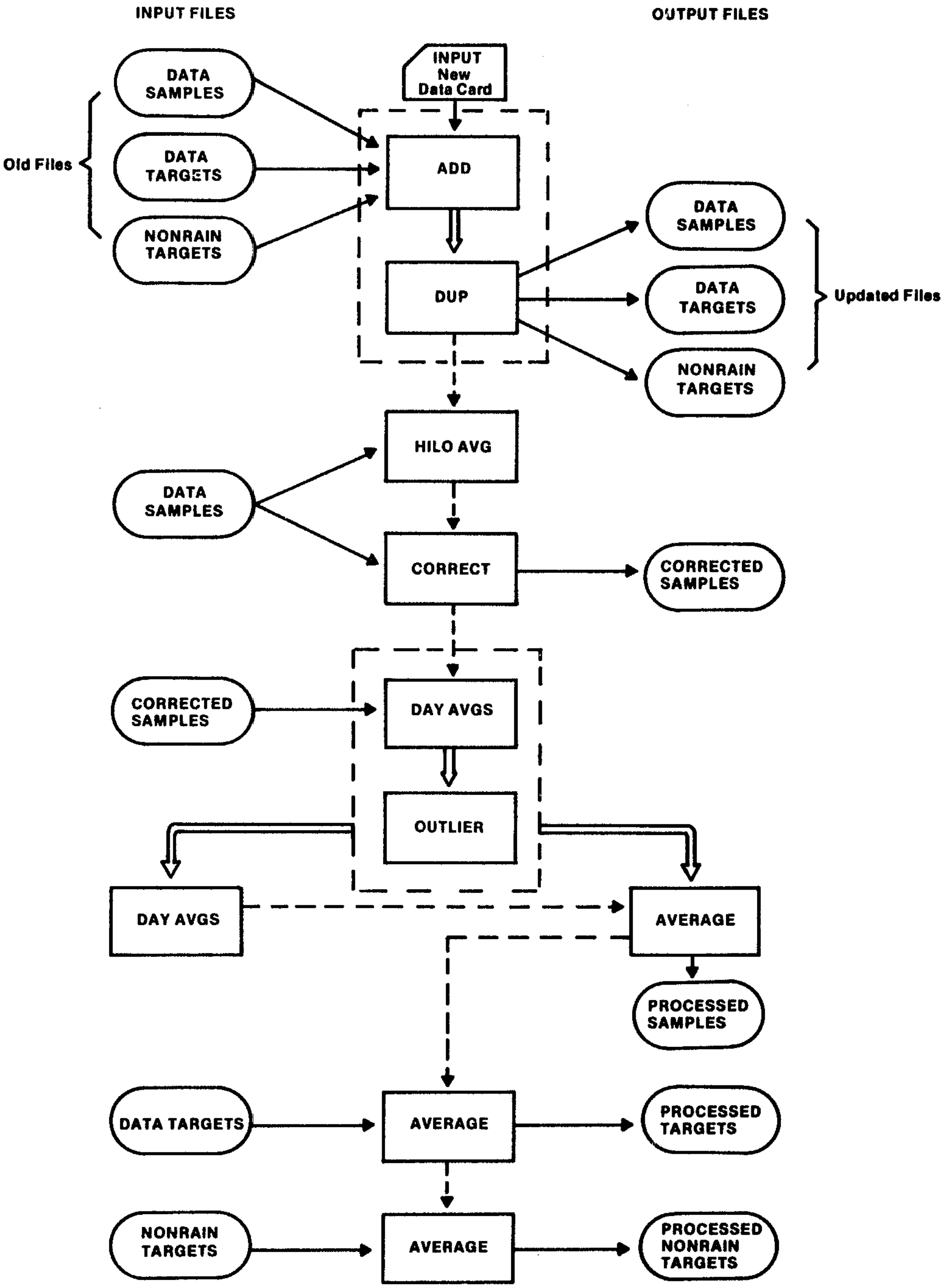
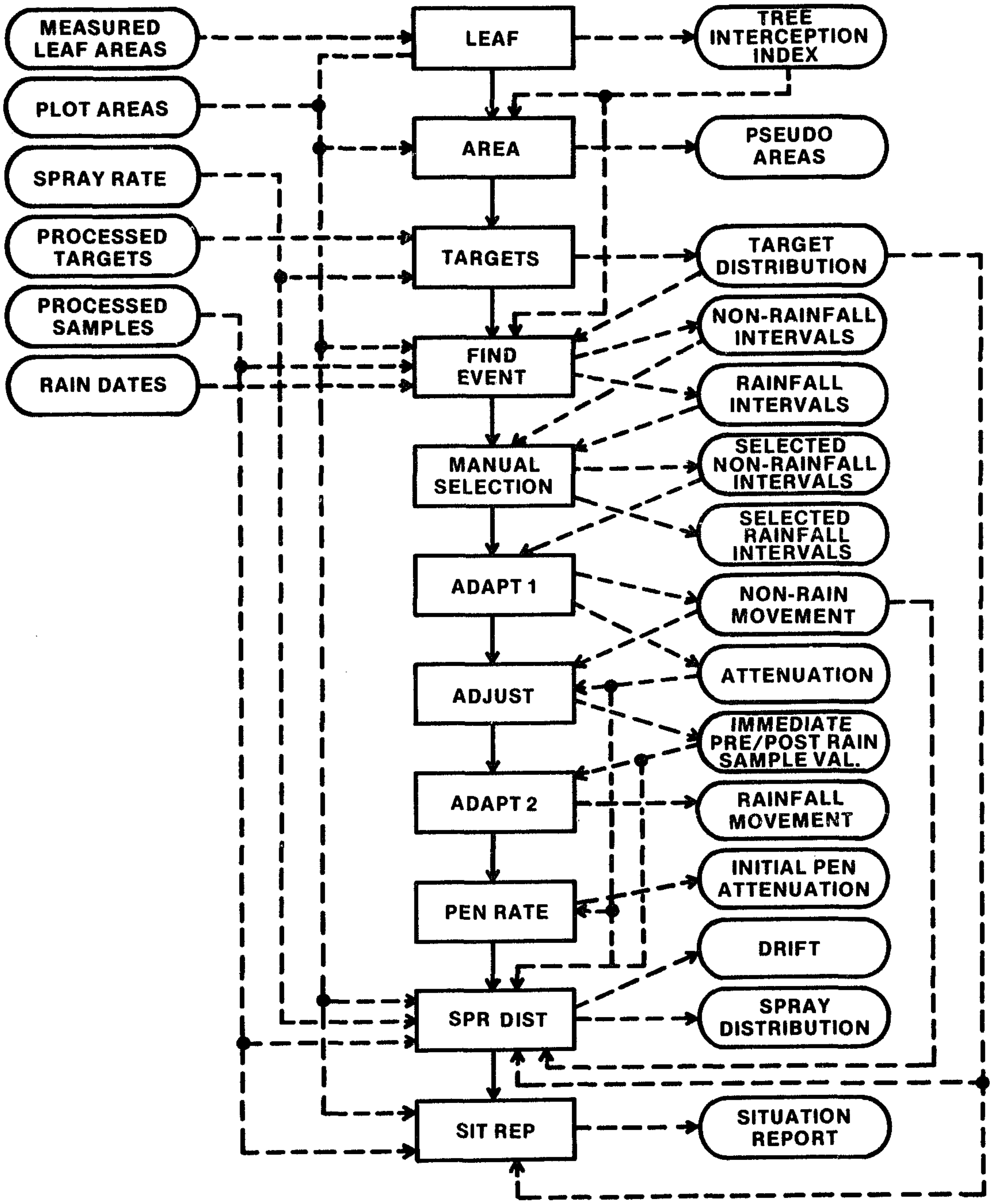

INPUT FILES
OUTPUT FILES
Old Files
DATA SAMPLES
DATA TARGETS
NONRAIN TARGETS
INPUT New Data Card
ADD
DUP
Updated Files
DATA SAMPLES
DATA TARGETS
NONRAIN TARGETS
HILO AVG
DATA SAMPLES
CORRECT
CORRECTED SAMPLES
CORRECTED SAMPLES
DAY AVGS
OUTLIER
DAY AVGS
AVERAGE
PROCESSED SAMPLES
DATA TARGETS
AVERAGE
PROCESSED TARGETS
NONRAIN TARGETS
AVERAGE
PROCESSED NONRAIN TARGETS

Figure 3 Flow Chart of the Process of Calculating the Parameters using the "Processed Files"


MEASURED LEAF AREAS
PLOT AREAS
SPRAY RATE
PROCESSED TARGETS
PROCESSED SAMPLES
RAIN DATES
LEAF
AREA
TARGETS
FIND EVENT
MANUAL SELECTION
ADAPT 1
ADJUST
ADAPT 2
PEN RATE
SPR DIST
SIT REP
TREE INTERCEPTION INDEX
PSEUDO AREAS
TARGET DISTRIBUTION
NON-RAINFALL INTERVALS
RAINFALL INTERVALS
SELECTED NON-RAINFALL INTERVALS
SELECTED RAINFALL INTERVALS
NON-RAIN MOVEMENT
ATTENUATION
IMMEDIATE PRE/POST RAIN SAMPLE VAL.
RAINFALL MOVEMENT
INITIAL PEN ATTENUATION
DRIFT
SPRAY DISTRIBUTION
SITUATION REPORT

the process of calculating the parameters using the "processed" files. Files used by a given routine are shown with a dashed arrow into the routine, and files produced are shown with a dashed arrow to the files. Flow of the program is via the solid arrows.

Subroutines LEAF and AREA perform needed conversions of some residue measurements (for example, from μg pesticide/cm^2 leaf area to μg pesticide/cm^2 ground area). TARGETS uses "processed" target values to determine a proportion of pesticide reaching each plot and region.

The process of parameterizing this model continues with FINDEV, a subroutine which searches the data files for sets of samples useful for calculating redistribution and losses of the pesticide. For estimating loss and movement in the absence of rain, it prepares a file of sample sets each of which consists of a vector of concentrations (in each region and layer) at the beginning of a non-rainfall interval and a similar vector at the end of the interval. Of course, either rain or a spray intervening will exclude a pair of sequential sample vectors from being used for this purpose. FINDEV also prepares similar files of vectors representing samples before and after rainfall events of various intensities to allow estimation of the effects of these rains on the pesticide distribution. As shown in the diagram, manual selection is utilized to determine rain events to be classified as similar, and to exclude sample dates which are unacceptable for the task to be performed (when numerous data are missing for a given sample date). The matrices A and P (equations (5), (6) and (7)) are determined from a matrix Q = P(I-A). After Q is found (see equation (9) below), the entries A_{ij} are calculated as:

$$A_{ij} = \sum_{k=1}^{7} Q_{ik},\ i = j;\ A_{ij} = 0,\ i \neq j,\ i = 1,\ldots,7;\ j = 1,\ldots,7$$

$$\text{Then } P = Q(I-A)^{-1}. \qquad (8)$$

From equation (8), Q should relate the pesticide vector C(k) to C(k+1) for each day k_i on which no rainfall occurred. Thus, given matrices B = $[C(k_1)\ C(k_2)...C(k_n)]$ and A = $[C(k_1 + 1)\ C(k_2 + 1)...C(k_n + 1)]$, $k_i\ \Sigma$ [days without rainfall], the following relationship should hold:

$$A = QB. \tag{9}$$

So long as at least seven sets of before/after concentrations are available, Q should be uniquely determinable using Gaussian elimination. However, owing to both random and systematic variations in the data sets, such a procedure did produce a feasible solution. It is necessary to introduce additional constraints that a "best fit" must satisfy. Entries in Q must be restricted to the range [0, 1], so that pesticide removed from a region is limited to what is available for movement. Also, because too few soil samples were analyzed to allow for a reliable solution for the pesticide attenuation rate in soils, a rate determined from the incubation of the orchard soil in the lab was introduced into the solution matrix before the remainder of the 19 were determined. Solution for the entries in Q to optimize the fit to all available data for non-rainfall intervals was carried out in program ADAPT1, using the adaptive optimization technique of Holland (1975), also described in DeJong (1980).

The optimization was done on a broadened version of equation (9) allowing varying intervals between sampling days, since:

$C(k_i+m) = Q^m C(k_i)$, $m \geq 1$, so long as no rain falls on days $k_i, ..., k_{m-1}$.

Once Q was determined, it was used, together with Equation (6) and data surrounding light rainfall events, to calculate L, the light rain movement matrix. Because samples were typically collected at intervals of three to five days, the effects of degradation and non-rainfall movement were removed from the data surrounding each rainfall before the rain effect could be determined. Using equations (5) and (6), we obtained:

$C(k_i+p+q) = Q^q\ L\ Q^p\ C(k_i)$, where C was known at days k_i and k_{i+p+q} and light rain occurred on day k_i+p. Thus $(Q^{-1})^q\ C(k_i+p+q) = L\ Q^p\ C(k_i)$, and matrices of before- and after-rainfall estimated concentration vectors were assembled as

$$A_L = [(Q^{-1})^{q_1} C(k_1+p_1+q_1) \ldots (Q^{-1})^{q_n} C(k_n+P_n+q_n)]$$

$$B_L = [(Q^{p_1} C(k_1) \ldots (Q^{p_n} C(k_n)]$$

and the matrix L in $A_L = L\ B_L$ was optimized by ADAPT2, a program similar to ADAPT1. It also solves, in an analogous fashion, for the heavy rainfall movement matrix H of equation (8).

Once the movement matrices are parameterized by the adaptive routines, the initial pesticide distribution for spray applications subsequent to the first application of the season are estimated. The attenuation and movement matrices are used, along with the residue distribution on the last sampling day of the preceding spray period, to estimate the dislodgeable residues present just prior to application. Pen rate (Figure 3) calculates the estimate of the amount of surface-penetrated residues present at the time of application based upon its estimate of the dislodgeable residue and a ratio of surface-penetrated to dislodgeable residues. This ratio was determined from matched samples taken the last sampling day for selected spray periods over the 1976, 1977 and 1978 seasons. The surface-penetrated to dislodgeable residues and standard errors were as follows: leaves, 0.110 ± .003; grass, 1.075 ± .195; litter, 2.367 ± .263; moss, 1.701 ± .184. These ratios were multiplied by the appropriate dislodgeable residues to estimate the surface penetrated residues present just prior to application. To estimate the initial pesticide distributon, the estimates of dislodgeable and surface-penetrated residues present at the time of application were subtracted from the total residues measured the afternoon following application. Assuming these estimates are conservative (see Part I), drift is determined as the difference between the estimate of the amount deposited in the orchard at application and the amount applied. Using the method described above, the average proportion and standard deviation of the dose initially distributed to the orchard, for all spray applications over the three seasons (except two applications for which there was rainfall following the last sampling day of the preceding spray period) was .624 ± .149, giving an average drift estimate as reported earlier.

The final routine, situation report, produces a daily record of both measured and predicted residue values. The data is output in both tabular and graphical form, as shown in Figures 8a-g.

RESULTS AND DISCUSSION

Parameterization of the Attenuation and Movement Matrices

The model was parameterized with azinphosmethyl residue data, collected over two seasons (1976, 1977) as previously described in Part I, plus a third season (1978). The matrices generated (for equations (1) to (4)) are shown in Figures 4, 5, 6, and 7. The matrices describe the daily attenuation and movement of pesticide under three specified rainfall conditions; none, light, and heavy. The no-rainfall movement matrix (P) shows some pesticide movement from the tree, possibly due to wind erosion, dew or guttation, with the majority of the residue being trapped in the litter-moss layer. Also of interest is the fact that the model estimates that equal amounts of residues (approximately 0.9%) move from the tree to the canopy litter-moss and alley litter-moss layers. Gunther et al. (1977) estimated the movement of parathion from orange trees to the ground over a five-day dry period to be less than 1% of the applied dose. In order to directly detect this movement in the orchard used in this study, filter paper targets were placed on the orchard floor (as described in Part I) for periods without rainfall of up to four days. Recovery of approximately 0.5% of initial tree residues confirmed the existence of some pesticide movement. The

Figure 4 Azinphosmethyl Attenuation Matrix

ATTENUATION

CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
.049						
	.041					
		.167				
			.079			
				.067		
					.223	
						.079

Figure 5 Azinphosmethyl Non-Rainfall Movement Matrix

NON-RAINFALL MOVEMENT MATRIX

		FROM						
		CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
TO	CANOPY LEAVES	.983						
	CANOPY GRASS-BROADLEAVES	0.0	.935					
	CANOPY LITTER-MOSS	.008	.065	.907				
	CANOPY SOIL	0.0	0.0	.093	1.0			
	ALLEY GRASS-BROADLEAVES	0.0				.973		
	ALLEY LITTER-MOSS	.009				.027	.996	
	ALLEY SOIL	0.0				0.0	.004	1.0

Figure 6 Azinphosmethyl Light Rainfall Movement Matrix

FROM

LIGHT RAINFALL		CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
	CANOPY LEAVES	.932						
	CANOPY GRASS-BROADLEAVES	.030	.747					
	CANOPY LITTER-MOSS	.002	.071	1.0				
TO	CANOPY SOIL	.036	.182	0.0	1.0			
	ALLEY GRASS-BROADLEAVES	0.0				.869		
	ALLEY LITTER-MOSS	0.0				0.0	1.0	
	ALLEY SOIL	0.0				.131	0.0	1.0

Figure 7 Azinphosmethyl Heavy Rainfall Movement Matrix

FROM

	HEAVY RAINFALL	CANOPY LEAVES	CANOPY GRASS-BROADLEAVES	CANOPY LITTER-MOSS	CANOPY SOIL	ALLEY GRASS-BROADLEAVES	ALLEY LITTER-MOSS	ALLEY SOIL
	CANOPY LEAVES	.822						
	CANOPY GRASS-BROADLEAVES	.020	.613					
	CANOPY LITTER-MOSS	.096	0.0	1.0				
TO	CANOPY SOIL	.008	.387	0.0	1.0			
	ALLEY GRASS-BROADLEAVES	.027				.280		
	ALLEY LITTER-MOSS	0.0				.447	1.0	
	ALLEY SOIL	.027				.273	0.0	1.0

unknown rate of loss from the targets precludes a direct assessment of the movement rate based only on these data.

Figure 4 shows an attenuation rate for azinphosmethyl dislodgeable residues in the tree of 4.9% day^{-1}. Hall et al. (1975) examined the loss of azinphosmethyl dislodgeable residues applied to apples using two types of air blast sprayers. Trees were sprayed on one side only and each tree was divided into nine sites for sampling. The average residues remaining for sites one to five (which most closely correspond to the tree area sampled in the present study) over a 14-day period were used to determine the loss rate. Rates determined were 7.6% day^{-1} ($r^2 = .914$) for the high flow-rate application and 5.5% day^{-1} ($r^2 = .887$) for the low air flow-rate application. These loss rates are higher than the attenuation rate alone as determined in the present study, but are in excellent agreement with the overall loss rate of azinphosmethyl dislodgeable residues from the tree of 6.7% day^{-1} (obtained by summing attenuation and movement from the tree under dry conditions). These results suggest that approximately 25% of the daily loss of azinphosmethyl dislodgeable residues from the tree is redistributed within the orchard, under dry conditions.

Figure 5 shows that less movement occurred from the grass-broadleaf to litter-moss layer in the alley region than in the canopy, suggesting that conditions under the tree canopy may be more favorable to movement, in the absence of rainfall. The attenuation rate for the canopy grass-broadleaves is similar to that observed in the tree. However the attenuation rate for the alley grass-broadleaf layer is considerably higher. Increased exposure to solar radiation resulting in higher surface temperatures, which in turn influence losses by volatilization, degradation, and plant uptake (Ebling, 1963; Hull, 1970; Bukovac, 1970) may be responsible for the observed difference. Movement out of the canopy litter-moss layer in the absence of rainfall was similar to that from the grass-broadleaves, with virtually no movement from the alley litter-moss. Attenuation rates observed in the litter-moss layer are higher than might be expected, but little is known about pesticide attenuation on these surfaces. Again the rate observed in the alley was greater than that in the canopy. The reason for this difference is thought to be the same as for the grass-broadleaf layer. The laboratory-determined rate for azinphosmethyl attenuation in soil (7.9% day^{-1}) is only an approximation of the field rate. However this rate is in rough agreement with the rate of 6.3% day^{-1} determined from the field data of Kuhr et al. (1974), in which samples were taken from beneath apple trees in an upstate New York orchard (ignoring any movement of azinphosmethyl into the soil). A loss rate of 5.8% day^{-1} was determined from the field data of Schulz et al. (1970), in which azinphosmethyl was applied as an emulsifiable concentrate to the soil surface. The experiment was run in the early spring in Wisconsin (soil temperature 5-15^{o}C). Only a general comparison can be made with these field studies, as soil type, pH, available moisture, ground cover, and temperature, as well as amount and mode of application, may influence azinphosmethyl loss from soil (Hamaker, 1972; Schulz et al., 1970).

Rainfall-induced losses of azinphosmethyl and other deposit residues in orchards have been indicated by a number of researchers (McMechan et al., 1972; Williams, 1961; Thompson and Brooks, 1976; Gunther et al., 1977; Nigg et al., 1977). The influence of rainfall on the removal of azinphosmethyl from apple foliage is discussed in Part I. The present treatment of the data calculates azinphosmethyl loss as a function of heavy or light rainfall (as defined above). No attempt was made to relate susceptibility to rainfall removal with the age of the residue deposit. Figures 6 and 7 show that approximately 7% and 12% of the residues are moved out of the tree by light and heavy rainfall, respectively. The light rain moves all these residues into the canopy region, while the heavy rainfall moves two-thirds to the canopy and one-third to the alley region. Values for proportions moved to the individual layers are probably not as reliable, but generally light rain moves the residues to the canopy grass-broadleaf and soil layers while the heavy rain moves the largest proportion ot the canopy litter-moss layer. Canopy and alley grass-broadleaves and alley soil receive lesser amounts. Eighteen and 38% of the residues deposited on the canopy grass-broadleaf layer are moved to the soil following light and heavy rainfalls, respectively. Thirteen percent is moved from the alley grass-broadleaves to the soil as a result of light rainfall, whereas 27% is moved as a result of heavy rainfall. The largest proportion of alley grass-broadleaf residue (45%) is moved to the litter-moss following a heavy rainfall. No movement is indicated from the litter-moss layer as a result of either light or heavy rainfall.

Certain types of movement are difficult to distinguish based on the available data. For example, a large amount of movement from the canopy grass-broadleaves to the soil, accompanied by a similar amount of movement from the tree to the canopy grass-broadleaves, can produce the same result as a direct movement from the tree to the soil. Only a widely varying set of initial pesticide distributions would enable the parameterization routes to distinguish these two processes definitively. However, in the operation of the model, the net resulting distribution will be similar in either case, so long as the initial distribution is similar to the one used to parameterize the model. More credibility should be attached to the model-generated distributions than to the individual matrix entries.

Comparison of the Model Outputs with the Field Data

Figures 8a-8g show a test of the model's predictions as compared to the field data obtained during the 1978 season. The continuous lines (solid or dashed) represent the model's daily prediction of azinphosmethyl dislodgeable foliar and

Figure 8 (a-d) Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$ ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the change in residues using 1976 and 1977 data only, while the dashed line shows the predicted change in residues based on all three years data.

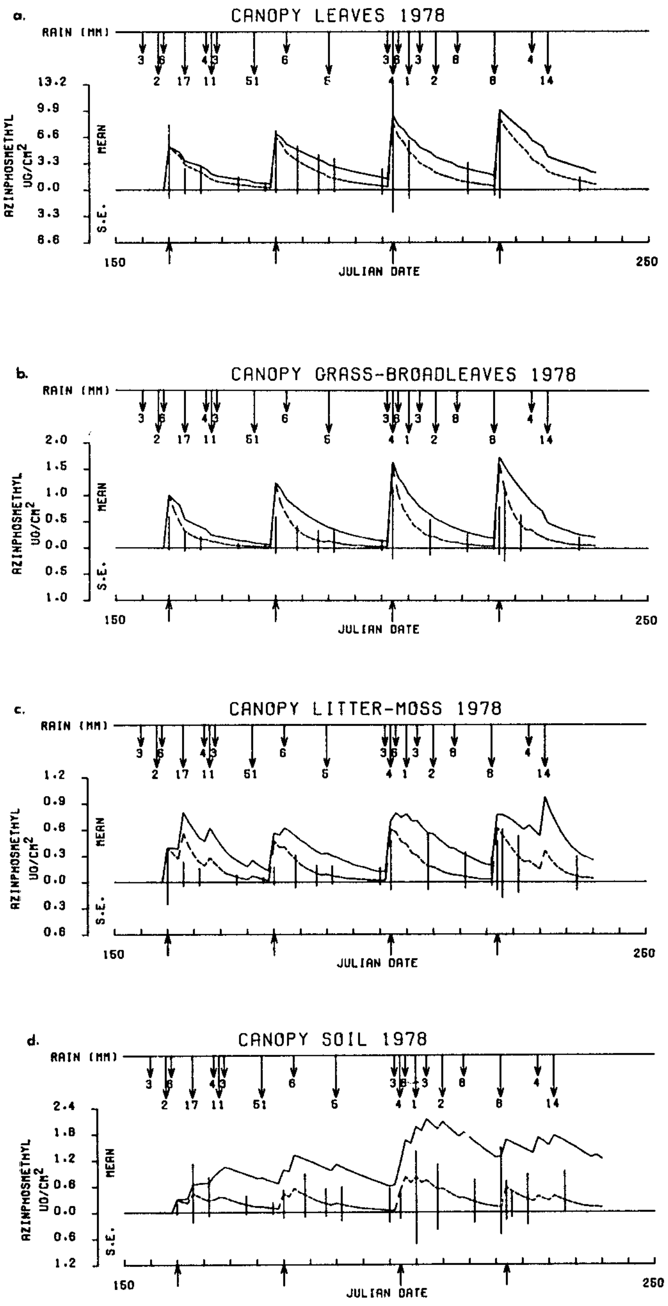
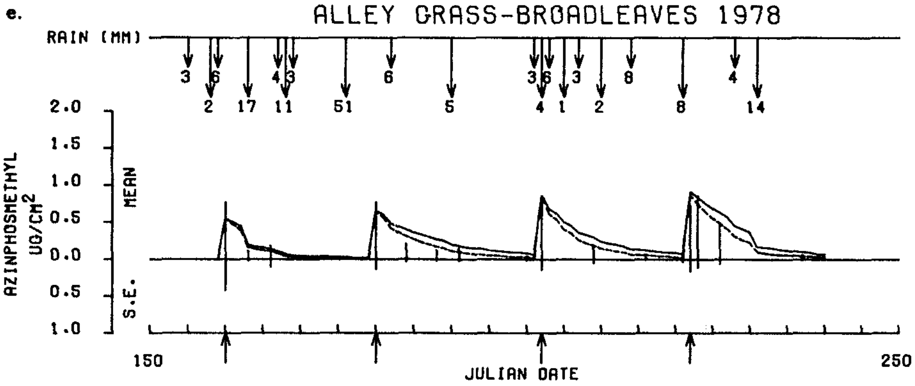
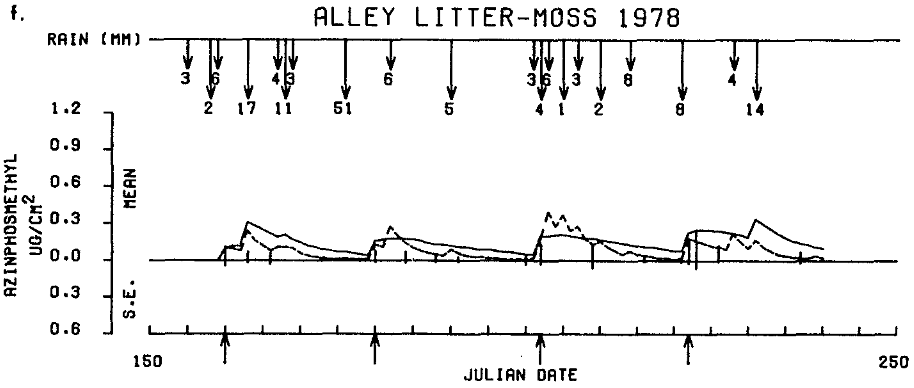

a.
CANOPY LEAVES 1978
RAIN (MM)
3 6 2 17 4 3 11 51 6 5 3 6 4 1 3 2 8 8 4 14
13.2
9.9
6.6
3.3
0.0
3.3
6.6
AZINPHOSMETHYL UG/CM^2
MEAN
S.E.
150
250
JULIAN DATE
b.
CANOPY GRASS-BROADLEAVES 1978
RAIN (MM)
3 6 2 17 4 3 11 51 6 5 3 6 4 1 3 2 8 8 4 14
2.0
1.5
1.0
0.5
0.0
0.5
1.0
AZINPHOSMETHYL UG/CM^2
MEAN
S.E.
150
250
JULIAN DATE
c.
CANOPY LITTER-MOSS 1978
RAIN (MM)
3 6 2 17 4 3 11 51 6 5 3 6 4 1 3 2 8 8 4 14
1.2
0.9
0.6
0.3
0.0
0.3
0.6
AZINPHOSMETHYL UG/CM^2
MEAN
S.E.
150
250
JULIAN DATE
d.
CANOPY SOIL 1978
RAIN (MM)
3 6 2 17 4 3 11 51 6 5 3 6 4 1 3 2 8 8 4 14
2.4
1.8
1.2
0.6
0.0
0.6
1.2
AZINPHOSMETHYL UG/CM^2
MEAN
S.E.
150
250
JULIAN DATE

Figure 8 (e-g) Actual and Predicted Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean (μg/cm^2 ground area) is above the line and its corresponding standard error (S.E.) below the line. The solid line running through the bars represents the model's prediction of the change in residues using 1976 and 1977 data only, while the dashed line shows the predicted change in residues based on all three years data.

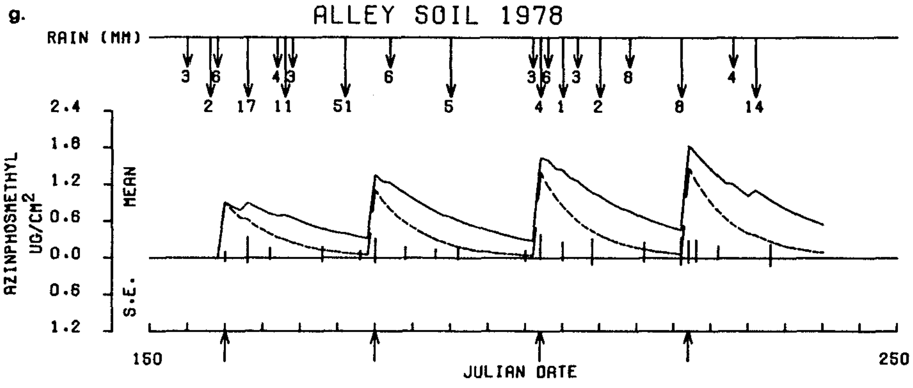
e.


ALLEY GRASS-BROADLEAVES 1978

f.


ALLEY LITTER-MOSS 1978

g.


ALLEY SOIL 1978

soil residues in each region for the 1978 season and are directly comparable with the vertical lines showing measured residue levels (and standard errors) in 1978. All residues are expressed as $\mu g/cm^2$ ground area, including the tree residues, to maintain a material balance in the transfer of pesticide between layers and regions of the orchard. The models were driven by 1978 rainfall data (shown as descending arrows in the figures) and the 1978 spray application rates (shown as ascending arrows). The matrices used to generate the solid line in Figures 8a-8g were calculated using 1976 and 1977 data only, while the dashed line was generated from the matrices (Figures 4, 5, 6, and 7) calculated using data from all three years. The 1978 sample data therefore represents an independent set of field data, collected from the same orchard plots, by which to judge the predictive capability of the model parameterized using data from the 1976 and 1977 seasons (continuous solid line).

In the tree leaves and grass-broadleaf layers, to which over 80% of the residues are initially deposited, the trends in the data are predicted quite well. Lower residue levels and the high variability in the amount and composition of the litter-moss layer are most likely responsible for the difficulty in predicting attenuation and movement in and out of this layer. Trends in the soil data were also difficult to predict; this may have been due in part to the relatively small number of soil samples analyzed as compared to the other layers. In addition, the overall predictive capability of the model should improve with a better estimate of drift loss.

Mean squared errors (MSE) for the comparison of model predictions with the azinphosmethyl residue data for the 1978 season are shown in Table 1. Column 1 shows the MSE values for a comparison of the model, parameterized with data from the 1976-1977, with the 1978 sample data. Column 2 shows the 1978 sample data versus the model parameterized with all three years data.

Table 1. Comparison of the Model Predictions with Azinphosmethyl Residue Data for the 1978 Season

Region	Mean Squared Error[a]		
	1	2	3
Canopy Leaves	2.079	1.613	4.419
Grass-broadleaves	.129	.154	.075
Litter-moss	.071	.067	.057
Soil	.152	.557	.681
Alley grass-broadleaves	.017	.015	.054
Litter-moss	.033	.021	.005
Soil	.207	.229	.055

[a] Mean squared errors for the relationship between the predicted and sample values shown in figures 8a-8g. Column 1 shows the relationship of the 1978 data to the model parameterized with data from 1976-1977, while column 2 shows the 1978 data versus the model parameterized with 1976-1978 data. Column 3 shows the mean squared error determined for the individual 1978 samples versus the mean.

Column 3 shows the MSE determined for the individual 1978 samples versus the mean. This statistic suggests that, except for the alley litter-moss and soil layers, the error associated with the model predictions is comparable to the error about the mean.

The effects of rainfall on the model predictions are quite striking. In some layers a net movement out is seen while in others more pesticide is carried in. Of major importance is the fact that throughout the season the residues in the tree are continually redistributed to the orchard floor. This movement counteracts the attenuation mechanisms, resulting in a slower net loss rate of pesticide and, in some situations, a net increase in residue deposits to layers of the orchard floor. Such information on pesticide dynamics within the orchard ecosystem has in the past been given little consideration in assessing crop protection. Future pest management strategies, involving the integration of chemical control techniques with biological, cultural, and other control measures, must consider pesticide fate throughout the entire orchard ecosystem.

Although the estimation of pesticide fate is an end in itself, the overall goal of this research was to model the effect of azinphosmethyl on ground-dwelling invertebrates which inhabit the orchard. Field studies conducted concurrently within the same orchard, along with laboratory data, collected on the isopod Trachelipus rathkei (Snider, 1979; Snider and Shaddy, 1980) were used to develop a model describing its ecobiology and temporally distributed mortality (Goodman et al., 1981). A form of the fate model presented here was used to determine the time-course of azinphosmethyl exposure.

The model in the form reported here predicts azinphosmethyl redisribution and attenuation as a function of time and rainfall data only. In order to account for the effects of other environmental factors on pesticide dynamics, a more sophisticated model is required. Further model development should involve the decomposition of both the movement and attenuation matrices to represent their component physical, chemical, and biological processes, each a function of the relevant environmental variables (see Parts III and IV). This decomposition requires controlled experiments, many of which can only be performed in a laboratory setting. However, the data reported here remain as a set of field measurements against which such lab studies may be compared or calibrated.

PART III

ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN ORCHARD ECOSYSTEM:
ASSESSMENT OF AIRBORNE LOSS

INTRODUCTION

Recent field studies have indicated that airborne loss plays a major role in the attenuation of field-applied pesticide residues (Taylor et al., 1976; Taylor et al., 1977; White et al., 1977; Woodrow et al., 1977; Claith et al., 1980). Taylor et al. (1977) report that attenuation of dieldrin applied to orchard grass was due solely to volatilization. In-depth reviews of both laboratory and field studies have been prepared by Spencer et al. (1973) and Spencer and Claith (1975, 1977). Volatilization of pesticides under field conditions is discussed by Taylor (1978). Techniques for measuring volatilization rates in the field are described by Caro et al. (1971) and Parmele et al. (1972). Orchard sampling of airborne pesticides has been for the most part limited to studies of worker re-entry inhalation or dermal contact with airborne residues (Westlake et al., (1977; Iwata et al., 1977; Gunther et al., 1977).

Airborne loss consists of spray droplet drift, evaporation and volatilization at application, and post-application losses by volatilization and wind erosion (Ebling, 1963; Leonard et al., 1976). The work described here was designed to assess the contribution of airborne loss to the overall attenuation of the organophosphate insecticide azinphosmethyl, 0,0 dimethyl-S-(4-oxo-1, 2,3, benzotriazin-3(4h)-ylmethyl) phosphorodithioate (Guthion^R), in a Michigan apple orchard ecosystem. Previous field work (Part I) designed to estimate the distribution, attenuation, and movement of azinphosmethyl in a deciduous orchard environment suggested that airborne loss was the major pathway of pesticide attenuation soon after application. In the present study airborne residues of azinphosmethyl were measured directly, accompanied by meteorological data, over a season of periodic low-volume spray applications. These measurements along with orchard deposit residue data were used to estimate pesticide airborne flux from the orchard as a part of the total attenuation of pesticides over the season.

ANALYTICAL METHODS

Procedures for the residue analysis of all sample types are described in Part I. Briefly, dislodgeable residues were determined by the procedure of Gunther et al. (1973), surface-penetrated residues procedure of Steffens and Wieneke (1976), and soil residues by the procedure of Schulz et al. (1970). Targets, consisting of two circles of Whatman No. 1 paper, 18.5 cm diameter (attached one atop the other by a single staple to a cardboard backing), were extracted for two hours in a soxhlet extractor using a mixture of hexane:acetone, 100 ml:25 ml.

Airborne Residues. The porous polyurethane foam (PPF) plugs (ester form), five cm long and 4.5 cm in diameter, were used as the trapping medium for sampling azinphosmethyl airborne residues. The PPF plugs were rinsed with distilled, deionized water in a Nalgene pipet washer for six hours followed by soxhlet extraction with 500 ml acetone for six hours and then 500 ml hexane for six hours prior to use. This method is similar to that used by Turner and Glotfelty (1977). After sampling, the PPF plugs were soxhlet extracted for four hours with

500 ml of a 4:1 hexane-acetone solution. Extracts were further concentrated by rotary evaporation followed by air evaporation prior to analysis by GLC.

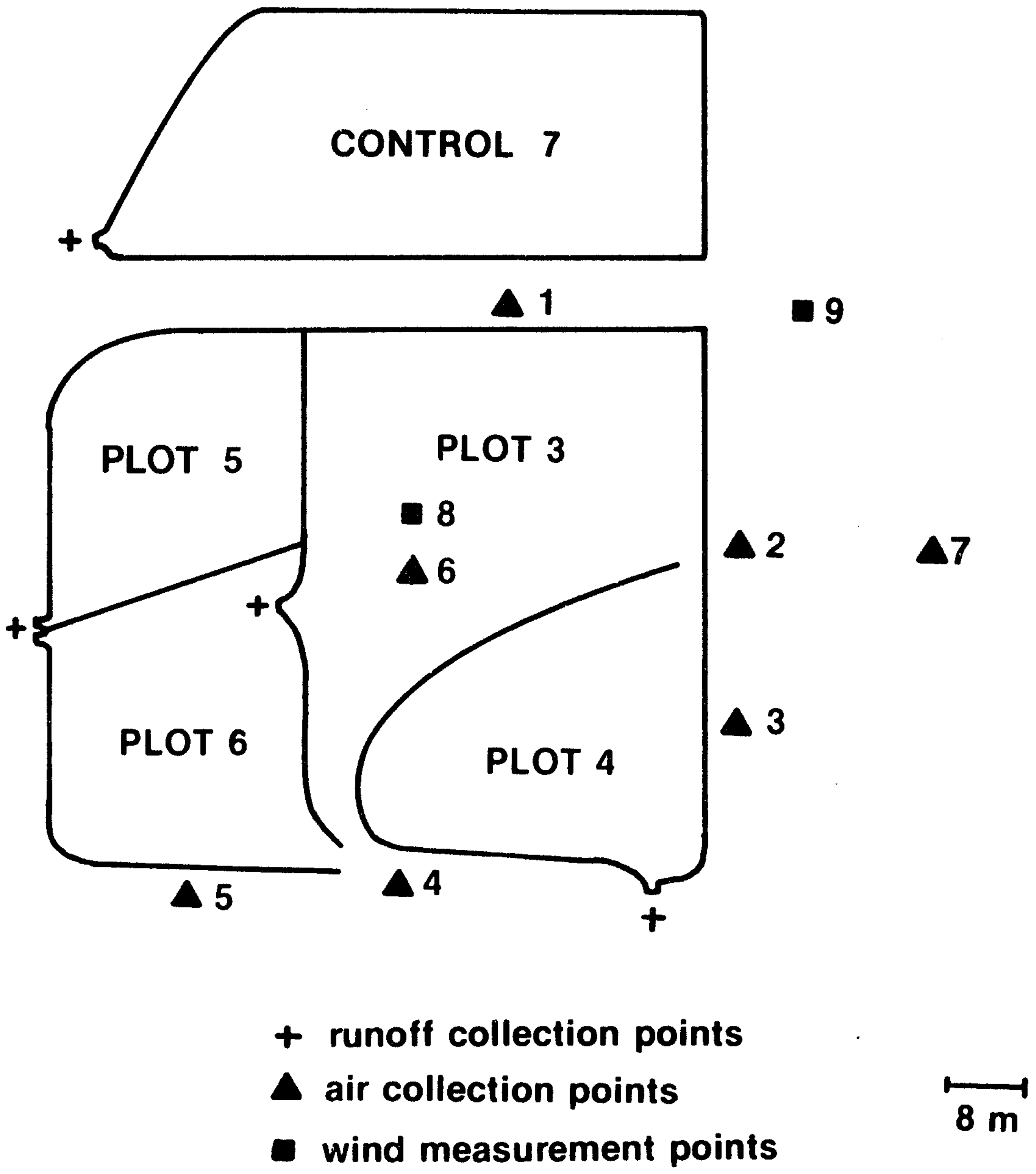
Trapping ability and extraction procedures were tested in the laboratory. A closed glass system consisting of a volatilizing chamber (U-tube) followed by two plugs in series, followed by a cold trap (dry ice in acetone) was used. Air flow was drawn at 1.0 m^3/hr for 60 minutes. At this flow no pressure drop could be measured with a mercury barometer. No azinphosmethyl was found in the second plug or the cold trap (limit of detection was 1.0 ng). Recovery and standard deviation was 91.7 ± 1.6% from the volatilization of 42.8 ± 13 μg (three repetitions). The detection limit for azinphosmethyl in air was approximately .01 μg/m^3.

Quantitation of azinphosmethyl was accomplished using a Tracor 560 gas chromatograph having a flame photometric detector in the phosphorus mode. A six-foot glass column (2 mm i.d.) packed with 3% SE-30 on Gas Chrom Q, 60/80 mesh, was operated at 195 C; N_2, 40 ml/min; air, 90 ml/min; H_2, 60 ml/min. This system was interfaced with a digital PDP 11/20 RSTS computer for integration of the area under the single peak produced.

EXPERIMENTAL SITE AND PESTICIDE APPLICATION

The apple orchard was located in the vicinity of Grand Rapids, Michigan in Kent County. The 12 one-year old trees were a mixture of semi-dwarf duchess and wealthy cultivars. In the spring of 1976, the orchard received a moderate pruning and cleaning to counter several years of disuse. The orchard plan was mowed to a height of approximately 5 cm prior to the first, second, and third spray applications. Four experimental plots and one control plot (Figure 1) were established by a method designed to facilitate the study of azinphosmethyl loss via surface runoff. Results of the runoff study conducted in 1977 are reported in Part I.

Figure 1 Orchard Plots Showing Air Sampling Locations


CONTROL 7
PLOT 5
PLOT 3
PLOT 6
PLOT 4
+
▲ 1
■ 9
■ 8
▲ 6
▲ 2
▲7
▲ 3
▲ 4
▲ 5
+ runoff collection points
▲ air collection points
■ wind measurement points
8 m

Azinphosmethyl (Guthion^{R}, 50% W.P., Mobay Chemical Company) was applied with a custom-built, low pressure, low volume sprayer similar to one developed by Howitt and Pshea (1965). The across plot average application rates and standard deviations (kg ha^{-1}, 50 % w.p. 100ℓ$^{-1}$ ha^{-1}) were 1.3 ± 0.2 on June 9, 1.6 ± 0.6 on June 29, 1.0 ± 0.1 on July 21, and 1.6 ± 0.2 on August 10. A more detailed description of the experimental site, sprayer design, and application techniques can be found in Part I.

SPATIAL STRUCTURE OF THE ORCHARD

The orchard plots were subdivided both vertically and horizontally. Hortizontally, each plot was subdivided into four regions potentially different with respect to initial pesticide distribution (see Figure 2 of Part I). Region 4 (under the canopy) was determined to be 32% of the area in plot 1, 34% in plot 2, 54% in plot 3, and 45% in plot 4. The remainder of the plot was divided among the three alley regions in a ratio of 2:3:1 for plots 1 and 2, and 1:2:1 for plots 3 and 4. The difference in the ratios was due to the closer spacing of the rows along the North-South axis in plots 3 and 4. The number of trees was 24 in plot 1, 15 in plot 2, 10 in plot 3, and 11 in plot 4. Tree heights averaged 3.0 meters. Vertically, each alley region was divided into three compartments; grass-broadleaves, litter-moss, and soil. The canopy regions contained these compartments pluts two compartments for the leaves of the tree.

ORCHARD SAMPLING PROCEDURES

Deposit residue sampling was carried out in a manner similar to the two previous seasons, as described in Part I. An abbreviated description of sampling procedures is given here. To determine azinphosmethyl initial horizontal distribution, a series of 15 to 20 ground-located, filter paper targets was deployed among the four regions (Figure 2 of Part I) in each plot prior to application. Targets were placed in the center of the alley regions and at the in-row mid point between the tree trunk and the edge of the canopy region. The distribution of azinphosmethyl residues was also determined for the trees and among the three ground layers (grass-broadleaves, liter-moss, soil). In each plot, three trees were sampled and four samples of each ground layer were taken, two from the canopy and two from the alley regions. Trees were subdivided for sampling into lower (1-2 m) and upper (2-3 m) regions. Tree heights averaged 3 m. Thirty to 35 leaf discs were taken per sample. Block sampling was employed for both ground samples and trees. One-half m^2 ground area sites and trees were selected randomly for consecutive sampling in the first and second spray periods; areas at the end of rows and close to adjacent plots were avoided. Similarly, new sites were chosen for consecutive sampling during the third and fourth spray periods. Plots were sampled in sequence, between 1300 and 1500 hr at various times following application, as shown in Table 1.

AIRBORNE RESIDUE SAMPLES

Two air sampling masts were employed, one located at the center of the sprayed plots and one at the downwind edge (Figure 1). The PPF plugs were positioned in glass cylinders, tapered at one end, and located at heights of 0.5, 1.0, 3.0 and 6.0 meters above the orchard floor. Air was drawn through each plug at a rate of 8.33 ℓ/minute giving a combined flow rate of 33.33 ℓ/minute measured by a flowmeter, controlled by an adjustable needle valve. Flow rate was maintained with an electric vacuum pump powered by a gas generator. On June 9 the orchard air was sampled during application at the downwind edge (Location 2, Figure 1) and also at Location 1, as the wind direction had a slight northern component. Samples were taken from 0700 to 1000. During the June 29 application samples were taken at the downwind edge (Location 2) and 20 meters from the downwind edge (Location 7). The two remaining spray applications (July 21, August 10) were sampled at the downwind edge only. The

Table 1. Summary of Significant Events for the Orchard, 1978 Season

Spray Date	Sample Date	Days Since Spray	Rainfall Date	Rainfall Amount (mm)	Windspeeds[a] (m s^{-1}) during Air Sampling	
					3 m	6 m
			Orchard Mowed 1 June			
			7 June	2.0		
			8 June	6.1		
9 June	9 June	0			2.4[c], 2.2[d]	4.4
	12 June	3	12 June[b]	17.3	2.7	4.5
	15 June	6			1.6	3.9
			16 June	3.6		
			17 June	11.2		
			18 June	3.0		
	22 June	13			1.3	2.2
			25 June	51.3		
	27 June	18			1.6	2.1
			Orchard Mowed 28 June			
29 June	29 June	0			e	e
			1 July	5.6		
	3 July	4			1.3	2.0
	7 July	8				
	10 July	11	9 July	5.1	2.1	3.6
	19 July	20			0.9	2.2

Table 1 continued

Spray Date	Sample Date	Days Since Spray	Rainfall Date	Rainfall Amount (mm)	Windspeeds[a] ($m\ s^{-1}$) during Air Sampling	
			Orchard Mowed 20 July			
			20 July	3.0		
21 July	21 July	0	21 July[b]	4.3	[f]N.D.,1.1[f]	N.D.[c]
			22 July	5.6		
	24 July	3	24 July[g]	0.8	0.5[d]	0.9
			26 July	3.0	N.D.[f]	N.D.[f]
	28 July	7				
			29 July	1.5		
			2 Aug	7.6		
	4 Aug	15			1.6	3.0
	9 Aug	20	9 Aug[b]	8.1	1.8	3.1[d]
10 Aug	10 Aug	0			0.7	1.3
	11 Aug	1			0.91	.3
	14 Aug	4			0.9	1.5
			16 Aug	3.6		
			19 Aug	14.2		
	21 Aug	11			0.7	0.9
	25 Aug	15			0.5	1.5

[a] Two hr mean, measured at 3 m and 6 m above the orchard floor (Figure 1, Location 6) between 1300 and 1500 hours.

[b] Rainfall occurred before sampling.

[c] Six hr mean, measured at 3 m above the orchard floor (Location 9) between 0600 and 1200 hours.

[d] Estimated value determined from the average ratio of wind speeds at 3.0 m and 6.0 m for the entire season and the wind speed measured for this date.

[e] Recorder malfunction

[f] None detected, limit of detection 0.5/ms.

[g] Rainfall occurred after sampling.

orchard air was sampled in the afternoon following each application and on successive dates for two hours, between 1300 and 1500 (see Table 1). Wind speed was measured at three meters (Location 12) during application and at three and six meters (Location 13) during afternoon sampling periods. Wind direction was continuously recorded from a wind vane mounted on the same mast. Additional measurements of temperature, humidity, solar radiation, and rainfall were continuously recorded throughout the season (Location 9). Rainfall amounts and wind speed data are included in the summary of significant events for the 1978 season shown in Table 1. Temperature and humidity data are shown in Figures 7 and 8.

RESULTS AND DISCUSSION

Table 2 shows the results of the analysis of targets for the first spray day of the 1978 season. The average amount is expressed in $\mu g/cm^2$ ground area and proportions shown are proportions of the dose applied to each plot. The grand average across plots shows that alley region 2 and the canopy region receive the majority of the residues reaching the ground. This agrees with the pesticide horizontal distribution data for the 1976 and 1977 seasons (Part I).

Vertical pesticide distribution for the first spray period of the 1978 season is given in Table 3. The across plot average is represented by only two regions; alley and canopy. The average amounts for the alley represent weighted averages of alley regions 1, 2 and 3, weighted by % plot area. These data agree with the results of the 1976 and 1977 field studies in that the majority of the residues are initially distributed vertically to the tree leaves and the grass-broadleaves layer. Orchard soil received approximately 1.5% of the dose applied.

The vertical distribution of pesticide residues as proportion of dose applied is shown in Table 4. Proportions were determined from the dose applied to each

Table 2. Azinphosmethyl Initial Horizontal Distribution from the Analysis of Targets, First Spray Period of the 1978 Season

Plot		Alley (1)	Alley (2)	Alley (3)	Canopy (4)
1	Average Amount (μg/cm^2 ± SE)	1.40 ± .15	1.16 ± .33	0.86 ± .27	1.04 ± .15
	Sample size	3.	3.	4.	4.
	Proportion	.052	.052	.010	.044
2	Average Amount (μg/cm^2 ± SE)	0.62 ± .16	1.37 ± .34	1.52 ± .25	1.09 ± .30
	Sample Size	3.	5.	4.	5.
	Proportion	.021	.096	.030	.081
3	Average Amount (μg/cm^2 ± SE)	1.09 ± .35	1.94 ± .28	0.95 ± .14	1.05 ± .35
	Sample Size	5.	4.	5.	3.
	Proportion	.018	.053	.014	.062
4	Average Amount (μg/cm^2 ± SE)	0.18	1.24 ± .27	0.57 ± .15	1.07 ± .22
	Sample Size	1.	3.	6.	3.
	Proportion	.004	.059	.016	.094
Grand Average Amount (μg/cm^2 ± SE)		0.2 ± .27	1.431 ± .18	0.98 ± .20	1.06 ± .01

Table 3. Initial Vertical Distribution of Azinphosmethyl Dislodgeable Residues,[a] First Spray Period of the 1978 Season[b]

	Leaves				
	Upper	Lower	Grass-Broadleaves	Litter-Moss	Soil
Canopy					
Average Amount (μg/cm^2 ± SE)	1.69 ± .17	4.64 ± .71	0.59 ± .03	0.11 ± .05	0.21 ± .04
Sample Size	11	12	4	6	8
Alley					
Average Amount (μg/cm^2 ± SE)			1.00 ± .56	0.12 ± .04	0.09 ± .05
Sample Size			4	7	5

[a] Except soil residues which were determined on a whole sample basis.

[b] Across plot average and standard errors expressed as μg/cm^2 ground area, except tree leaves which are μg/cm^2 leaf area. Lower (1-2m) and upper (2-3m) regions of the tree were sampled separately.

Table 4. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied (± S.E.) from the Analysis of Samples for the First Spray Period of the 1978 Season

	Alley		Canopy		
	Dislodgeable	Surface-Penetrated	Dislodgeable	Surface-Penetrated	Total
Tree			.513 ± .093	.036	
Grass-Broadleaves	.077 ± .036	.015	.028 ± .002	.005	.721 ± .100
Litter-Moss	.009 ± .002	.004	.008 ± .003		
Soil	.009 ± .005		.014 ± .004		

plot and then averaged. Tree surface area was estimated as 460,000 cm^2/tree (Part I). The proportion of the pesticide applied that was distributed as surface penetrated residues was estimated from matched samples from the first spray day of the 1978 season. The surface-penetrated to total dislodgeable residue ratios and standard errors were determined as follows: leaves, .081 ± .015; grass-broadleaves, .190 ± .002; litter, .421 ± .078; moss, .272. These ratios were multipled by the appropriate dislodgeable residue proportions to estimate the surface-penetrated proportion. Soil residues were determined on a whole sample basis. Summing all dislodgeable, surface-penetrated and soil residue proportions for the first spray day of 1978, across both alley and canopy regions, yielded the estimate that 72.1% of the pesticide applied was initially deposited in the various orchard strata. This estimate is considerably higher than the 1977 estimate of 55.6%. The 1976 estimate was 66.1% (Part I). These are only crude estimates which, after accounting for extraction efficiency, assume that all residues in the samples analyzed were accounted for (a more detailed discussion of the point can be found in Part I). The most likely sources of error are: (1) underestimation of the amount applied and (2) uneven application (due to steep slope in plot 4) and sampling not representative of residue levels present. The estimated proportion of pesticide applied initially distributed to the trees in plot 4 for the first spray of the 1976 season was also greater than the estimates for the other plots, resulting in a total deposit estimate of 84.6% of the dose applied for that plot. The 1977 data shows no great variation in tree proportion (31.5%, S.D.-6.2%) among plots.

On the premise that all the residues deposited in the orchard were accounted for, the 27.9% of the dose applied to the orchard in the first spray period of the 1978 season is assumed to be due to airborne loss, primarily as drift at application, but also as volatilization and wind erosion in the four hours

Table 5. Estimation of Initial Vertical Pesticide Distribution as a Proportion of the Amount Applied, Using Target Data to Calculate the Proportion Reaching the Orchard Floor, for the First Spray Period of the 1978 Season

Plot	Orchard Floor		Tree		Total
	Alley	Canopy	Dislodgeable	Surface-Penetrated	
1	.114	.044	.391	.028	.607
2	.147	.081	.483	.029	.670
3	.085	.061	.459	.032	.637
4	.079	.094	.789	.056	1.018
					.733 ±.096

between application and sampling. Table 5 shows estimates by plot of airborne loss using target data to determine proportion distributed to the orchard floor. The across plot average airborne loss estimate of 26.7% is in close agreement with the estimate made using the orchard floor deposit residue samples.

Azinphosmethyl concentrations in the air measured during application at sampling heights betwen 0.5 meters and 6.0 meters above the orchard floor are given in Table 6. For those samples taken at the downwind edge, concentrations measured are roughly uniform from 0.5 to 6.0 meters. Differences in mean amounts sampled between the four spray dates is thought to be primarily a function of wind speed. Temperature and relative humidity (R. H.) also determine the amount of pesticide reaching the downwind edge sampling sites. Conditions favoring rapid evaporation tend to reduce the droplet spectrum towards smaller droplets which travel farther before being deposited out. Temperature, through its effect on atmospheric conditions, also influences spray drift. Inversion conditions favor a smaller drift cloud by discouraging vertical diffusion. Turbulent atmospheric conditions accelerate both vertical and lateral dissipation of spray droplets (Yates and Akesson, 1973; Maybank and Yoshida, 1977). The mean pesticide concentration measured during application on June 9 was 22.9 $\mu g/m^3$. The mean wind speed at 3.0 meters was 2.2 m/s. The temperature ranged from 3.9^oC (0600) to 11.9^oCC (1200) and the R. H. ranged from 92% (0600) to 35% (1200). On July 21 the mean pesticide concentration measured during application was 15.4 $\mu g/m^3$. The mean wind speed measured at 3.0 meters during sampling was 1.1 m/s. The temperature ranged from 17.2^oC (0600) to 18.4^oC (1200) and the R. H. ranged from 89% (0600) to 78% (1200). Comparison of wind speeds between these two dates suggests that the higher wind speed during application on June 9 was responsible for the higher concentrations measured at the downwind edge. If the airborne pesticide

Table 6. Azinphosmethyl Concentrations (µg/m^3) at Sampling Heights between 0.5 and 6.0 Meters over Orchard

Date		Center				Location[a]	Downwind Edge				Location[a]
	Days Since Spray					Height Above Orchard Floor					
		0.5	1	3	6		0.5	1	3	6	
9 June[b]							17.70	27.70	29.30	22.80	2
9 June[b]							12.70	3.40	15.80	15.10	1
9 June	0	6.90	5.20	4.80	4.40	6	5.70	4.60	4.40	5.30	2
12 June	3	1.58	0.23	2.10	1.00	6	0.35	0.92	2.40	1.13	4
15 June	6	0.36	0.17	0.78	0.59	6	0.13	0.09	1.47	0.80	1
22 June	13	0.17	0.44	0.37	0.93	6	0.07	0.13	0.27	0.31	1
27 June	18	0.07	0.07	0.23	0.17	6	0.05	N.D.[c]	0.29		2
29 June[b]							26.40	25.00	24.10	27.60	2
29 June[b]							6.67	7.69	27.70	9.54	7
29 June	0	1.00	1.92	2.88	1.38	6	1.94	2.53	0.91	0.64	2
3 July	4	1.55	1.26	0.35	0.67	6	1.77	.96	0.59	2.30	5
10 July	11	0.09	0.62			6	0.32	0.24	1.00	0.05	3
19 July	20	0.17	0.11	0.11	0.22	6	0.25	1.14	0.11	0.16	2
21 July[b]							11.82	18.18	18.18	13.33	1
21 July	0	1.02	0.19	0.57	0.82	6	1.30	1.51	0.87	1.15	1
24 July	3	0.63	0.35	0.91	0.38	6	0.36	0.38	0.35	0.53	1
28 July	7	0.23	0.09	0.22	0.16	6	0.13			0.25	2
4 Aug	15	0.09	0.05	0.05	0.09	6	0.16	0.32	0.28	0.25	3
9 Aug	20	0.06	0.21	0.14	0.22	6	0.57	0.09	0.07	0.10	1

Table 6 continued

Date	Days Since Spray	Center 0.5	Center 1	Center 3	Center 6	Location[a]	Downwind Edge 0.5	Downwind Edge 1	Downwind Edge 3	Downwind Edge 6	Location[a]
		Height Above Orchard Floor									
10 Aug[b]							14.06	15.22	18.33	16.67	4
10 Aug	0	0.86	1.29	3.13	0.95	6	0.57	0.27	0.43	0.25	3
11 Aug	1						0.73	0.40	0.61		2
14 Aug	4						0.34	0.70	0.77		2
21 Aug	11						0.32		0.67		2
25 Aug	15	0.22				6					

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[a] Location of sites shown in Figure 1.

[b] Azinphosmethyl concentrations measured during application, all others are 2 hr mean sample concentrations taken between 1300 and 1500 hours.

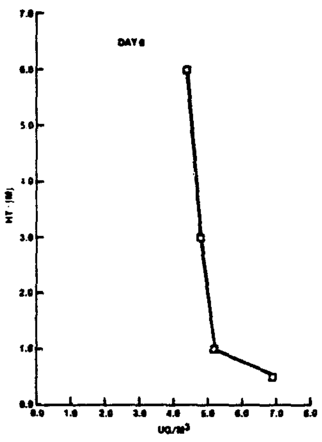
[c] None detected, limit of detection .01 μg/m^3.

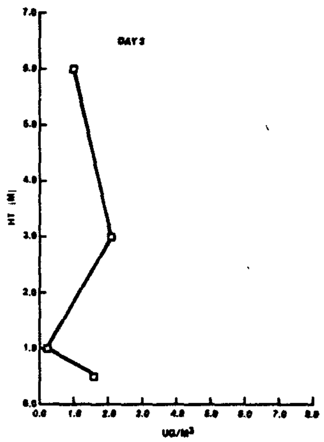
concentrations measured during application on these two dates are scaled by the average amount of pesticide applied the difference is more pronounced.

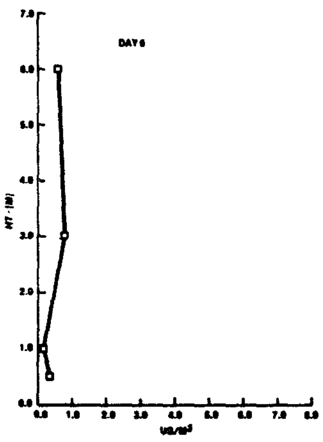
On June 29 a second mast was located 20 meters from the downwind edge. Air samples taken during application indicated that there was rapid dissipation of airborne residues between the two masts at all heights except 3.0 meters. This persistence at 3.0 meters may be the result of pesticide moving through the air as a plume generated by the closer passes of the sprayer.

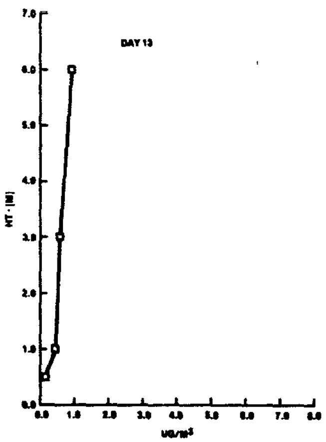
Table 6 also shows azinphosmethyl concentrations in air at sampling heights between 0.5 meters and 6.0 meters over the orchard at two locations; the center of the sprayed plots (Figure 1, Location 6) and at the downwind edge. Samples were taken between 1300 and 1500 hr on the day of application and on selected days following application (Table 1). Mean wind velocities at 3.0 and 6.0 meters for the two-hour sampling period are also given in Table 1. Graphical representation of airborne pesticide residues for the first spray period is shown in Figures 2 and 3. These figures show a systematic decline in airborne pesticide residues at all heights above the orchard floor over the 18-day sample period. Data for the remaining spray periods (Table 6) also show this trend. As might be expected, the decline in airborne pesticide residues agrees fairly closely with the decline in orchard deposit pesticide residues (Figure 4). Variation in airborne pesticide residues between the heights sampled is the greatest on the early sample days following application, with the highest airborne pesticide residue levels at 0.5 meters the day of application (day 0) and at 3.0 meters 3 and 6 days following application. Lower levels of azinphosmethyl airborne residues were measured in the afternoon of the second, third, and fourth application dates as compared to the first. In discussing reasons for observed diurnal variations in vertical vapor flux of dieldrin and heptachlor applied to pasture, Taylor et al. (1977) concluded the phenomenon was directly related to diurnal variation in

Figure 2 Diurnal Azinphosmethyl Airborne Residues at Sampling Heights Between 0.5 and 6.0 Meters above the Orchard, Measured at the Center Location During the First Spray Period of the 1978 Season


DAY 8
HT - (M)
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


DAY 3
HT - (M)
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


DAY 6
HT - (M)
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


DAY 13
HT - (M)
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

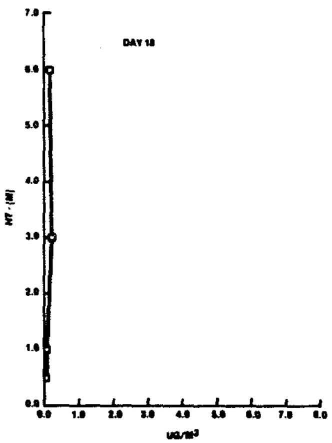
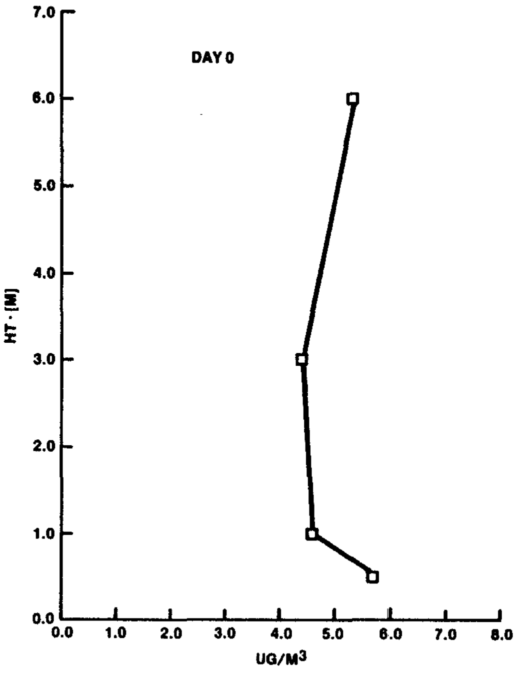
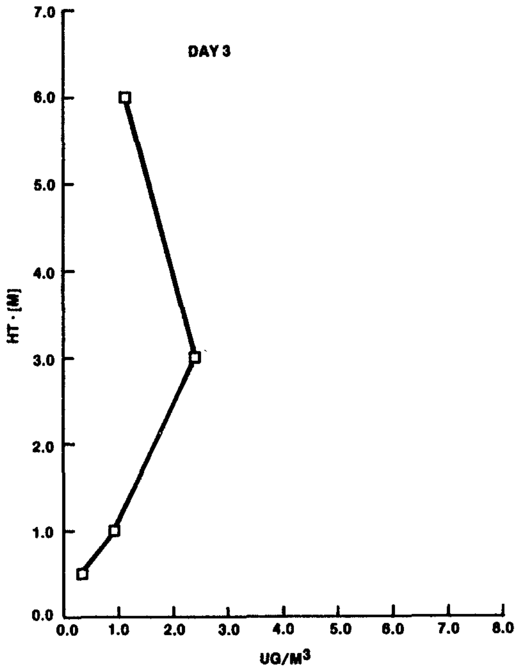
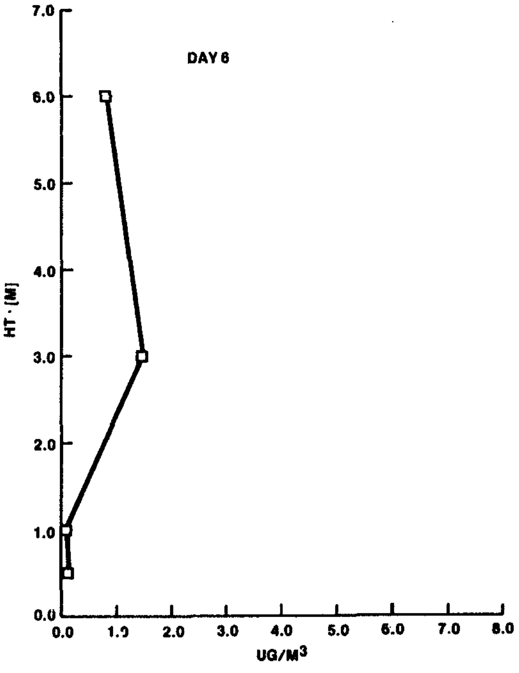

DAY 18
HT - (M)
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 3 Diurnal Azinphosmethyl Airborne Residues at Sampling Heights Between 0.5 and 6.0 Meters Above the Orchard, Measured at the Downwind Locations During the First Spray Period of the 1978 Season


DAY 0
HT - [M]
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


DAY 3
HT - [M]
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0


DAY 6
HT - [M]
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

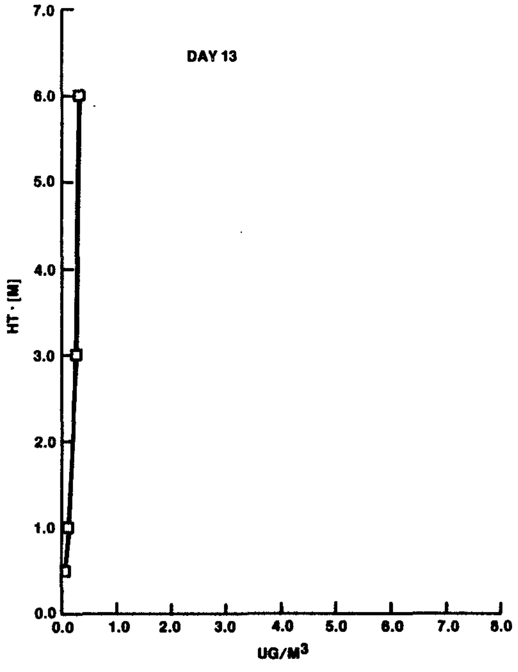

DAY 13
HT - [M]
UG/M3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 4 (a-d) Azinphosmethyl Dislodgeable and Soil Residues for the Canopy Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

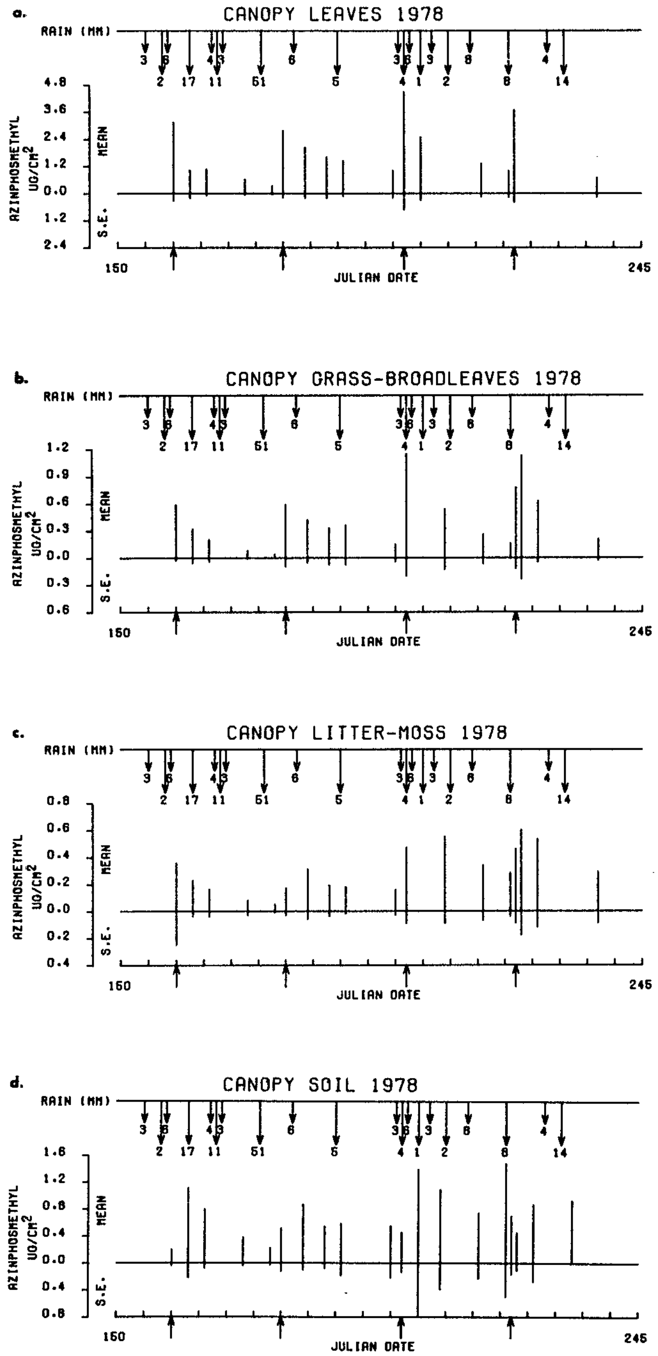
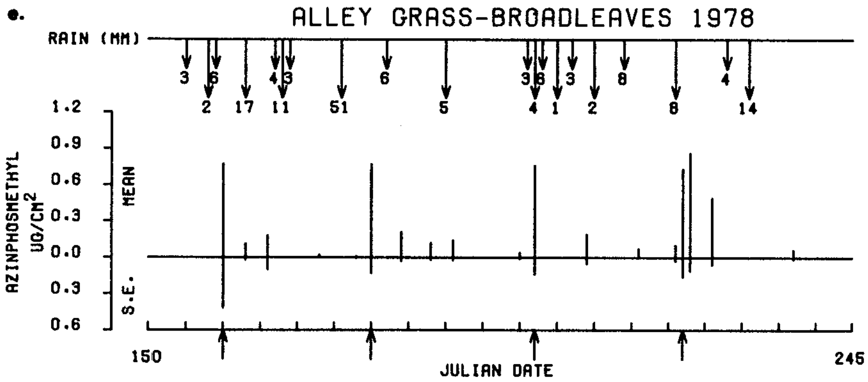

a.
CANOPY LEAVES 1978
RAIN (MM)
3 2 6 17 4 11 3 51 6 5 3 4 6 1 3 2 8 8 4 14
4.8
3.6
2.4
1.2
0.0
1.2
2.4
AZINPHOSMETHYL UG/CM2
MEAN
S.E.
150
JULIAN DATE
245
b.
CANOPY GRASS-BROADLEAVES 1978
RAIN (MM)
3 2 6 17 4 11 3 51 6 5 3 4 6 1 3 2 8 8 4 14
1.2
0.9
0.6
0.3
0.0
0.3
0.6
AZINPHOSMETHYL UG/CM2
MEAN
S.E.
150
JULIAN DATE
245
c.
CANOPY LITTER-MOSS 1978
RAIN (MM)
3 2 6 17 4 11 3 51 6 5 3 4 6 1 3 2 8 8 4 14
0.8
0.6
0.4
0.2
0.0
0.2
0.4
AZINPHOSMETHYL UG/CM2
MEAN
S.E.
150
JULIAN DATE
245
d.
CANOPY SOIL 1978
RAIN (MM)
3 2 6 17 4 11 3 51 6 5 3 4 6 1 3 2 8 8 4 14
1.6
1.2
0.8
0.4
0.0
0.4
0.8
AZINPHOSMETHYL UG/CM2
MEAN
S.E.
150
JULIAN DATE
245

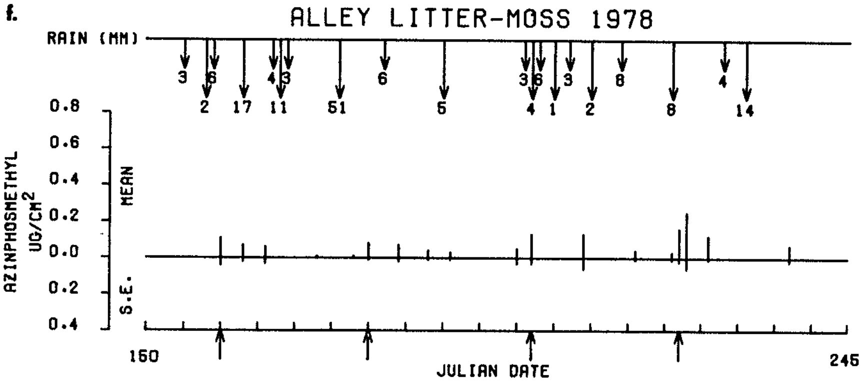
Figure 4 (e-g) Azinphosmethyl Dislodgeable and Soil Residues for the Alley Region, 1978 Season. Upward directed arrows show dates of spray application, and downward directed arrows indicate dates and amounts of rainfall in mm. Each bar is divided into two parts; the mean ($\mu g/cm^2$) is above the line and its corresponding standard error (S.E.) below the line.

e.



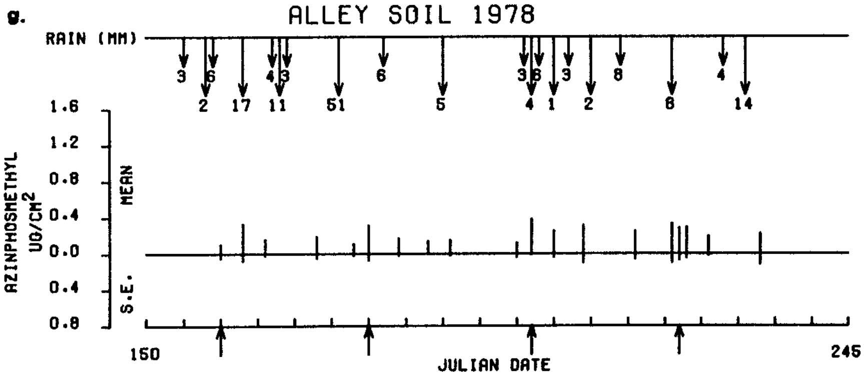
ALLEY GRASS-BROADLEAVES 1978
RAIN (MM)
3 6 4 3 6 3 6 3 8 4
2 17 11 51 5 4 1 2 8 14
1.2
0.9
0.6
0.3
0.0
0.3
0.6
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
150
245
JULIAN DATE

f.



ALLEY LITTER-MOSS 1978
RAIN (MM)
3 6 4 3 6 3 6 3 8 4
2 17 11 51 5 4 1 2 8 14
0.8
0.6
0.4
0.2
0.0
0.2
0.4
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
150
245
JULIAN DATE

g.



ALLEY SOIL 1978
RAIN (MM)
3 6 4 3 6 3 6 3 8 4
2 17 11 51 5 4 1 2 8 14
1.6
1.2
0.8
0.4
0.0
0.4
0.8
AZINPHOSMETHYL
UG/CM^2
MEAN
S.E.
150
245
JULIAN DATE

solar radiation input. The authors qualify this statement with the hypothesis that solar radiation is one factor that may be singled out as a source of vapor flux variation, as solar radiation input affects all other parameters of the complex relationship between the crop microclimate and the adjacent atmosphere. One parameter which solar radiation most definitely affects is the temperature at the leaf surface, which has a direct effect on the rate of volatilization. A similar conclusion was reachd by Phillips (1974) from the results of laboratory experiments in which the volatilization rate of dieldrin from glass and cotton leaf surfaces was measured at various temperatures and wind speeds. Phillips stated that "clearly the factor having the most dramatic effect on loss was temperature." These observations would suggest that a possible partial explanation for differences in airborne concentrations measured in the afternoon on successive spray dates may be the differences in solar radiation input. The average solar radiation (cal cm^{-2} min^{-1}) measured during the afternoon sampling periods on each of the four application days was as follows: 1.11 on June 9, 1.06 on June 29, 0.57 on July 21, and 1.00 on August 10. The value of 1.11 cal cm^2 min^{-1} on June 9 was 100% of the available solar radiation (cloudless day). June 29 was also clear, July 21 was cloudy, and August 16 was partly cloudy. Comparison of solar radiation with the average airborne pesticide concentration measured at the center location (Location 6, Figure 1) for these application days (Table 1) shows a nonlinear trend with the highest airborne residues on June 9, which had the highest solar radiation input, and the lowest airborne residues on July 21, which had the lowest solar radiation input. In addition to solar radiation, the influence of wind speed on the airborne pesticide concentrations measured was also examined. In the comparison of the mean wind speed at 6.0 meters (see Table 1) measured during the afternoon sampling period (1300-1500 hr) with the average airborne pesticide concentration measured at the center location for the four application dates (Table 1), a nearly linear relationship was observed. Again the June 9 application date, on which the highest airborne pesticide concentrations were measured, also had the highest mean wind speed. The July 21 application date, on which the lowest airborne pesticide concentrations were measured, had the lowest mean wind speed (none detected, < 0.5 m s^{-1}). Phillips (1971) demonstrated using wind tunnel experiments that there was a marked increase in the rate of loss of dieldrin deposits on glass surfaces at wind speeds of 3.2 km hr^{-1} (.89 m s^{-1}) as compared to still air. Dieldrin was deposited as a thin film in a manner designed to prevent mechanical loss from wind. I feel that increased wind speed is responsible for increased loss in azinphosmethyl deposits in the orchard. Both volatilization and wind erosion are mechanisms thought to be affected by wind speed. What is not clear is whether increased airborne loss of deposits due to increased wind speed should be reflected in the increased airborne pesticide concentrations measured, as increased wind speed, although removing more pesticide, should have a diluting effect on concentrations measured in the air. It is possible that wind erosion of freshly deposited residues is responsible for the marked difference between airborne residues measured the afternoon of June 9 and those measured the afternoon of July 21. The combined effect of wind speed and solar radiation input must also be considered. Further data collection under a variety of environmental conditions (actual and/or simulated) is needed to better describe the processes contributing to pesticide airborne loss.

On sampling dates following the application date, more often than not, airborne pesticide residue levels measured at 6.0 meters exceeded those measured at 0.5 or 1.0 meter. Six meters is twice the average tree height. One wonders how far above the orchard airborne residue levels are measurable. The data recorded did not allow estimation of horizontal airborne residue flux by direct methods. Estimation of either pesticide vertical airborne flux or mass horizontal flow of pesticide vapor by aerodynamic methods requires knowledge of wind speed profiles. Reliable interpretation of these profiles requires minimal fluctuation in atmospheric turbulence. While this criterion may be satisfied by uniform stands of short crops (Parmele et al., 1972; Taylor et al., 1977), the orchard profile does not satisfy it. An indirect estimate utilizing both deposit pesticide residues and airborne residues is presented as an alternative approach.

Hartley (1969) proposed that the volatilization rate (F_b) of one pesticide, from a non-adsorbing surface, could be predicted from that (F_a) of another pesticide, given the vapor pressures (P) and molecular weights (m) of the two compounds, by the following equation:

$$F_b = \frac{P_b(m_b)^{1/2}}{P_a(m_a)^{1/2}} \cdot F_a \qquad (1)$$

This relationship assumes that vapor flux is solely a function of molecular diffusion through the stagnant air closely surounding the surface. Taylor (1978) points out that when examining vapor flux from plant surfaces, this equation is valid only during the time when there is complete coverage of the plant surface, i.e., when the pesticide vapor pressure is not reduced due to adsorption and is in effect volatilizing from itself. As the deposits become increasingly smaller the vapor flux is no longer strictly a function of molecular diffusion, but also a function of the degree of adsorption to the plant surface. In addition residue may penetrate leaf tissues or accumulate in cracks and fissures in the epicuticular wax superstructure or leaf specialized structures. With these limitations in mind, equation (1) was used to predict the airborne loss of azinphosmethyl from the orchard using dieldrin vapor flux over orchard grass determined by Taylor et al. (1977), along with vapor pressure data found in the literature. Using the aerodynamic model described by Parmele et al. (1972), Taylor et al. (1977) estimated the dieldrin vapor flux to be 80.4 g/ha/hr during the 1300 to 1500 hours sampling period 3.5 hours following application.

The vapor pressure reported dieldrin is 2.6×10^{-6} mm Hg at 20°C (Spencer and Claith, 1969). Only an upper limit for the vapor pressure of azinphosmethyl has been reported; $< 7.5 \times 10^{-6}$ mm Hg (no temperature given, Schrader, 1963). The vapor pressure of the ethoxy analog, azinphos-ethyl is given as 2.2×10^{-7} mm Hg at 20°C by Spencer (1968). To better estimate the vapor pressure of azinphosmethyl from the data available, the relationship between the possible crystal structures of these two analogs was examined. Rohrbaugh et al. (1976) examined, using x-ray diffraction crystallography, the crystal and molecular structure of azinphosmethyl. The unit cell stereograph depicted indicates that crystal structure is dictated, in part, by overlapping of the nearly planar ring systems and by intermolecular repulsion effects of the methoxy groups; the repulsion working against the packing forces of the crystal. The increased size of the ethoxy group of azinphos-ethyl should result in weaker packing forces by increasing the allowed distance between molecules. This effect is in turn reflected in the heat of sublimation, which varies directly with the magnitude of the packing forces, and the observed vapor pressure, which varies inversely with the magnitude of the heat of sublimation (Barrow, 1966). In addition, the melting point of azinphosmethyl (73-74°C) is approximately 18° higher than azinphosmethyl (56°C), indicating stronger packing forces and therefore a lower vapor pressure. Based on these observations, it was estimated that the vapor pressure of azinphosmethyl was slightly less than 2.2×10^{-7} mm Hg at 20°C, the vapor pressure of its ethoxy analog. This value was used in equation (1) as P_b, along with the dieldrin vapor pressure of 2.6×10^{-6} mm Hg at 20°C as P_a, and 80.4 g ha^{-1} hr^{-1}, the field diurnal vapor flux (1300-1500 hr) as F_a, to give an upper limit estimate for azinphosmethyl diurnal airborne flux (1300-1500 hr) of 6.2 g ha^{-1} hr^{-1}. To examine the sensitivity of equation (1) to vapor pressure data, the value of 1.0×10^{-7} mm Hg, reported as the maximum for azinphosmethyl vapor pressure by Schrader (1963), was also used, resulting in an estimated azinphosmethyl diurnal airborne flux of 2.82 g ha^{-1} hr^{-1}. These predicted values for azinphosmethyl diurnal flux (1300-1500 hr) from the orchard are by no means precise estimates, but rather crude approximations, due in part to the general nature of the azinphosmethyl vapor pressure data. Other sources of variation are the differences in application rate (5.6 kg ha^{-1} a.i. for dieldrin vs. .65 kg ha^{-1} a.i. for azinphosmethyl), and the increased influence of wind that tree deposits may receive as compared to grass deposits. In theory, if there was complete coverage in both experiments the application rate should have little effect, as the vapor flux is independent of the amount of pesticide applied. As both pesticides were applied as water base sprays, which are deposited on plant surfaces as droplets, complete coverage is doubtful (Taylor, 1978). Under these "non-ideal" conditions, vapor flux is no longer independent of the amount of pesticide present. As stated earlier, one explanation for the dependency of vapor flux on pesticide deposit residues is the hypothesis that incomplete coverage affects the apparent vapor pressure of the pesticide due to adsorptive effects of the foliar surface. Depending on the degree of coverage, part of the pesticide deposit will be unencumbered by external adsorptive effects and will evaporate at the maximum allowable rate (governed only by molecular diffusion through the stagnant layer); the remaining portion of the pesticide deposit will volatilize at some slower rate, depending on the degree of adsorption. To approximate the effect of foliar adsorption (i.e., incomplete coverage) on the vapor flux predicted in equation (1), it was assumed that the higher the application rate the greater the percentage of the pesticide deposit that is affected by foliar adsorption. This is a necessarily simple approximation of a complex phenomenon, as additional factors including formulation, spray droplet size, climatic conditions during application, and characteristics of the foliar surface may influence the state of the pesticide deposit and the volatilization rate (Ebling, 1963; Hartley, 1969; Hull, 1970). With these limitations in mind, equation (1) was modified in the following manner

$$F_b = \frac{P_b(m_b)^{1/2}}{P_a(m_a)^{1/2}} \cdot F_a \cdot \frac{D_b}{D_a} \tag{2}$$

where D_a is the application rate of pesticide a and D_b is the application rate of pesticide D_b. As 75% of the pesticide deposited in the orchard was applied to the trees, tree surface area must be considered when comparing airborne loss from the orchard with that of a grass field. Therefore the application rate of azinphosmethyl was based not only on the .263 ha of ground area but also the .276 ha of tree surface area. The average application rate for the first spray period of 1978 was 0.65 kg ha^{-1} a.i. Three fourths was applied to .276 ha tree surface area and one fourth to .263 ground surface area. If the tree and ground surface areas are weighted by the proportion of the pesticide they receive and averaged, the adjusted application rate is 0.63 kg ha^{-1} a.i. This value was divided by 5.6 hg ha^{-1} a.i. of dieldrin applied to the grass pasture to give a D_b/D_a ratio in equation (2) of .112. In using this ratio as a crude approximation of foliar adsorptive effects on vapor flux, it must also be assumed that both application rates represent pesticide deposits that are less than or equal to complete coverage. The azinphosmethyl flux estimates determined from equation (2) were 0.697 g ha^{-1} hr, using 2.2 x 10^{-7} mm Hg and 0.317 g ha^{-1} hr^{-1} using 1.0 x 10^{-7} mm Hg for the vapor pressure of azinphosmethyl. Diurnal airborne loss during this sample period, for the remaining dates samples, was estimated by assuming this loss is directly proportional to the measured horizontal flux ($g \cdot m^{-2} \cdot s^{-1}$) at 3.0 meters, determined from airborne pesticide concentrations (Table 6) and wind speed measurements at 3.0 meters taken during sampling (Table 1). Daily airborne loss was estimated on the work of Taylor et al. (1977), who reported a marked diurnal change in volatilization rates of dieldrin and heptachlor, when applied to orchard grass. Similar diurnal variations were reported by Taylor et al. (1976) for soil incorporated dieldrin. These researchers measured a peak flux early in the afternoon with virtually no volatilization measured before 0500 or after 2300 hr. Based on these findings, daily diurnal airborne loss was estimated assuming peak flux occurred during the two-hour sampling period between 1300 and 1500 hr, that no airborne loss occurred before 0500 or after 2300 hr, and that the loss rate varied linearly between the end points and the peak. Integration of the area under the triangle formed gives a daily airbone loss of 9.0 times the peak hourly flux measured between 1300 to 1500 hours. To estimate the loss occurring during the afternoon of the first day (from 1300 to 2300) one-half the daily estimate, or 4.5 times the peak flux, was used. Table 7 shows the estimated daily airborne loss of azinphosmethyl from the orchard for the first spray period of the 1978 season. Loss is shown both as an absolute loss in g/ha and also as a percentage of the total dislodgeable residues and soil residues present on a given sample date. No daily loss estimate on a percentage basis was made for the application date as absolute loss shown is the estimated loss from 1300 to 2300 hr, rather than the entire day. These estimates suggest a marked decline in the daily airborne loss over the 18-day sample period. As a part of the parameterization of the model presented in Part II, first-order rate constants were determined for the disappearance of azinphosmethyl foliar dislodgeable residues and soil residues in each canopy and alley layer (accounting for movement). If these individual rate constants are weighted by the proportion of the total dislodgeable residues and

Table 7. Estimated Azinphosmethyl Daily Airborne Loss from the Orchard, First Spray Period of the 1978 Season

Days After Application	Mean Horizontal Flux at 3.0 m During Sampling (1300-1500) ($\mu g\ m^{-2}\ s^{-1}$)	Estimated Loss[a] During Sampling g ha^{-1} hr^{-1}		Estimated Daily Loss[b] g ha^{-1} da^{-1}		Estimated Daily Loss[b] % day^{-1}	
		Downwind Edge					
0		1	2	1	2	1	2
3	10.6	.697	.317	.313[c]	1.43[c]		
6	2.4	.158	.072	1.42	0.65	0.4	0.34
13	0.4	.026	.012	0.24	0.11	0.24	0.11
18	0.4	.026	.012	0.24	0.11	0.43	0.20
		Center					
0	11.5	.697	.317	3.13[c]	1.43[c]		
3	5.7	.345	.157	3.11	1.41	1.51	0.68
6	1.2	.073	0.33	0.65	0.30	0.34	0.16
13	0.5	.030	.014	0.27	0.12	0.27	0.12
18	0.4	.024	.011	0.22	0.10	0.39	0.18

[a] Based on the estimated airborne loss at peak flux (1300-1500 hr) on day 0, calculated using 2.2×10^{-7} mm Hg at 20°C (column 1 and 1.0×10^{-7} mm Hg (column 2) for the V.P. of azinphosmethyl in equation (2). Diurnal loss for the remaining sample dates was estimated by assuming this loss is directly proportional to the measured horizontal flux at 3m.

[b] Daily diurnal loss was estimated assuming peak flux during the 2 hr sampling period (1300-1500 hr), that no airborne loss occurred before 0500 and after 2300, and that the loss rate varied linearly between the end points and the peak. The daily loss in % da^{-1} was determined by dividing the daily loss in grams by the total g ha^{-1} dislodgeable residues (including soil residues) remaining.

[c] One-half day estimate.

soil residues which they attenuate, the average attenuation rate is 5.1%/day. The estimated air loss rate on day 3, based on measurements made at the downwind edge (Table 7, Column 1), is 1.86% day^{-1}. This loss rate represents approximately 36% of the total attenuation. By day 6 air loss is 15%, day 13 it is 5%, and on day 18 air loss represents 8% of the total attenuation. These observations indicate that initially airborne loss plays a major role in the overall attenuation dislodgeable residues, however, this contribution drops off rapidly between 3 and 6 days following application. The change in the rate of airborne loss is believed to be a function of the state of residue deposits with the loosely bound residues being rapidly lost to the atmosphere soon after application. The remaining more tightly adsorbed and/or protected dislodgeable residue deposits volatilize at a slower rate. The effects of rainfall on the state of the pesticide deposits within the orchard must also be considered (see Part I). Certainly rainfall events that occurred during the first spray period (see Figure 5) had an effect on the pesticide airborne concentrations and deposit residues measured. Again, loosely bound residues should be most susceptible to rainfall effects redistributing these residues to other parts of the orchard or as runoff leaving the orchard. These redistributed residues may no longer be loosely bound, as they may be more evently distribued over a larger foliar surface than at application. By contrast, residues that were initially distributed to protected plant areas could be redistributed with rainfall as to increase their susceptibility to airborne loss. Rainfall may also enhance volatilization if the soil moisture level is low prior to a rainfall event, the increased soil water may displace adsorbed pesticide, increasing its effective vapor pressure at the soil surface (Spencer et al., 1973). Heavy rains on unsaturated soils may also move initially displaced pesticide to lower soil depths (Spencer and Claith, 1977; Helling et al., 1971).

In the model described in Part II, movement is separated from overall attenuation only, and this attenuation process is assumed to be first order. Modeling pesticide disappearance using first-order kinetics assumed that the individual attenuation processes are first order and strictly additive, giving an exponential decay of pesticide residues with time. As early as 1955, Gunther and Blinn proposed that the first-order loss curve was an approximation of a bilinear or trilinear loss curve. This hypothesis was again proposed by Gunther et al. (1969, 1977), by Hill (1971), and Van Dyk (1974, 1976). Taylor et al. (1977) indicated that the disappearance of heptachlor and dieldrin from orchard grass and soil could be attributed solely to airborne loss. They represented pesticide loss as a bilinear process with two regression equations; one for days 1 to 5 and another for days 5 to 107. Stamper et al. (1979) proposed an alternative to first-order kinetics for foliar applied insecticides, showing for a number of foliar applied organophosphate insecticides, that ln concentration versus ln time gave a linear relationship with a better correlation coefficient than the linear relationship established by plotting ln concentration versus time (which indicates first-order kinetics). The author suggests the reason the ln - ln plots give a better linear relationship is that one form of the equation describing the fitted line is in agreement with equations describing molecular diffusion from small volumes. Their solution is interesting, but the use of ln time would not be compatible with the algorithms used in the model presented in Part II.

A third approach to modeling airborne loss was proposed by Phillips (1971). He suggested that a double exponential equation

$$T = A_e^{-kt} + B_e^{-k't} \tag{3}$$

may apply when two volatilization processes are occurring simultaneously at different rates. This model was later proposed by Popendorf and Leffingwell

(1978) to explain the observed bilinear loss of parathion dislodgeable residues on citrus foliage. The approach used here is an extension of the double exponential equation. At the present, residues deposited in the orchard are classified as either dislodgeable, surface-penetrated, or soil. This classification is based on analytical procedures for the recovery of these residues as outlined in the experimental section. Dislodgeable residues are pictured as residing on the foliar surface, whereas surface-penetrated residues are embedded on or in the cuticular matrix. Further penetration, resulting in tissue bound residues, is also thought to occur (Wieneke and Steffens, 1974). To model airborne loss, it was assumed that a portion of the dislodgeable residues are loosely bound. The loss of these residues to the atmosphere therefore being only slightly affected by the adsorptive effects of the leaf surfaces. The remaining dislodgeable residues are more tightly bound and volatilize more slowly. A similar theory for the decrease in the daily airborne loss rate of foliar applied pesticides is presented by Taylor (1978). Volatilization of surface-penetrated and tissue-bound residues is thought to be negligible and the kinetics of the disappearance of these residues is not treated here. Making these assumptions, pesticide airborne loss from foliar surfaces is represented in the differential form as:

$$\frac{dT}{dt} = -a_1 D(t) - a_2 L(t) - a_3 T(t) \tag{4}$$

where t is time in days, D is dislodgeable residues, L is loosely bound residues, T is total residues (dislodgeable plus loosely bound residues, and excluding penetrated residues), a_1 is the air loss rate of the tightly bound dislodgeable residues, a_2 is the air loss rate of loosely bound residues, and a_3 is the attenuation rate of the total residues (other than air loss and assumed to be independent of binding state). The constant a_3 is thought to be primarily a function of degradation at the foliar surface and penetration to subsurface tissues. As T = D + L, equation (4) can be reduced to:

$$\frac{dT}{dt} = -(a_1 + a_3)D(t) - (a_2 + a_3)L(t) \tag{5}$$

and therefore:

$$\frac{dD}{dt} = -(a_1 + a_3)D(t) \tag{6}$$

and

$$\frac{DL}{dt} = -(a_2 + a_3)L(t) \tag{7}$$

As loosely bound residues are what their name implies, these residues are more easily lost to wind erosion and volatilize at a rate governed only by diffusion across the stagnant air layer. Consequently it is assumed that airborne loss of these residues is responsible for the observed early rapid decay of total residues; this loss is represented by Gunther et al. (1958) and more recently by Popendorf and Leffingwell (1978) as the first phase of a bilinear loss pattern. With the disappearance of these residues from the foliar surface the rate of decline of remaining dislodgeable residues is primarily responsible for the observed rate. The loss rate of these more tightly bound residues is determined by the combination of airborne loss (a_1), degradation and penetration (a_3) of the remaining dislodgeable residues. This represents the second phase of an observed bilinear loss pattern. As current sampling or analytical techniques cannot distinguish between loosely bound and more tightly adhered dislodgeable residues, D, L and the rate constants a_1, a_2 and a_3 were determined indirectly. In determining the two rate constants in the double exponential equation, Popendorf and Leffingwell (1978) used dislodgeable residue data and a constrained optimization procedure that compared predicted and observed values. As the hypothesized mechanism for the observed bilinear loss of foliar applied pesticides presented here is based on the assumption that early pesticide disappearance is primarily due to airborne loss, the change in the estimated daily airborne loss rate was used to estimate when the loosely bound residue deposits approached zero. If the daily air loss rates (average of center and downwind edge estimates in Table 7, Column 1) are examined, it is noted that there is a sharp decrease in the rates between day 3 (1.69%) and day 6 (0.54%). The average rate and standard deviation for days 6, 13, and 18 is 0.40% ± 0.18%. It was therefore assumed that the loosely bound residues disappeared between 3 and 6 days following application and that the average daily air loss rate of 0.40% represented the air loss rate (a_1) of tightly bound dislodgeable residues. The total loss rate ($a_1 + a_3$) of the tightly bound dislodgeable residues was determined from a least squares linear regression of log g ha^{-1} total residues versus time since applications, for days 3, 6, and 13 of the first spray period. Total residues included foliar dislodgeable residues and soil residues. Soil was included to give a conservative estimate with respect to movement of residues present in the orchard following rainfall events. Day 18 was omitted from this analysis as it was felt that the 51.3 mm (2.1") of rainfall the orchard received on day 16 redistributed the residues in such a manner as to not allow a conservative estimate of residues present. From this analysis the daily loss rate ($a_1 + a_3$) was determined to be 7.5% ($r^2 = .958$). This rate is considerably faster than the daily attenuation rate of 4.2% ($r^2 = .985$), determined from total residues for days four to 20 of the second spray period of the 1978 season. Only one rainfall event occurred during the second spray period (5.1 mm on day 10), whereas 17.3 mm of rainfall fell just prior to day 3, and 16.8 mm fell between days 3 and 13 of the first spray period (see Table 1 and Figure 4). This would suggest that the disappearance of these residues was influenced by rainfall (although other environmental parameters such as wind speed, solar radiation, humidity, or some combination of the above also may have contributed). The results may have been that the pesticide residues measured during the first spray period were not conservative (i.e., movement of pesticide to unsampled soil depths, pesticide carry-in with moisture uptake by litter and foliar surfaces, increasing the penetrated residue pool). Also, as stated earlier, rainfall may have redistributed foliar residues as to allow increased volatilization. An influx of moisture at the soil surface may have also caused an increase in volatilization. That this may be the case is suggested by the increase in the estimated average daily air loss rate between day 13 (0.26%) and day 18 (0.41%) (Table 7, Column 1). Until the effects of rainfall and other climatic conditions on pesticide disappearance can be adequately differentiated, uniqueness of the daily attenuation rate ($a_1 + a_3$) to this set of environmental conditions must be assumed. Given a_1 to 0.40% and $a_1 + a_3$ to be 7.5%, then a_3 is 7.1%. L and a_2, the amount and rate of airborne loss of the loosely bound residues, were estimated using an optimization routine similar to that employed by Popendorf and Leffingwell (1978). Equation (3) was rearranged to solve for T (total residues) at some sample date L:

$$T(k_i) = D(k_{i-1}) \cdot (1 - (a_1 + a_3))^{(k_i - k_{i-1})} +$$

$$L(k_{i-1}) \cdot (1 - (a_2 + a_3))^{(k_i - k_{i-1})} \qquad (8)$$

As T is known at sample dates $k_i = 0, 3, 6, 13$, and a_1 and a_3 have previously been estimated, values for L and a_2 were tried in equation 8 to give a minimum value for the test statistic:

$$\frac{T_i - (L_i + D_i)^2}{T_i} \qquad (9)$$

Using this statistic, it was estimated that 37.5% of azinphosmethyl dislodgeable residues, initially deposited in the orchard, were loosely bound. The daily air loss rate (a_2) of the loosely bound fraction was estimated to be 90% day^{-1}. This indicates a rapid loss of approximately one third of the residues to the atmosphere, resulting in the disappearance of this fraction in approximately 3 days. It is also suggested that loss of the remaining dislodgeable residues is governed by a much slower air loss rate and attenuation at the foliar surface. Figure 5 shows the solution to equation (5) as a line through the observed residue values (total dislodgeable residues and soil residues) for the first spray period of the 1978 season.

The proportion of azinphosmethyl deposit residues estimated to be loosely bound and the rate of loss of this fraction is thought to be a function of factors associated with application, environmental conditions, and orchard characteristics. This is suggested by the difference in the decline of total dislodgeable and soil residues between the first and second spray periods as shown in Figures 5 and 6. Parameterization of equation (4) using the residue data from the second spray resulted in an estimate of 7.7% for the loosely bound fraction (L) with an estimated daily air loss rate (a_2) of 30% day^{-1} for this fracation. The rate constant $a_1 + a_3$ was determined from linear regression of the total dislodgeable and soil residues for days 4 to 20 to be 4.2% day^{-1} ($r^2 = .985$). The air loss rate (a_2) of the dislodgeable fraction (D) was assumed to be the same as determined for the first spray period, 0.4% day^{-1}. The lack of an initial period of rapid loss during the second spray period may have been due solely to the lesser amount of rainfall received, as compared to the first spray period. That rainfall may affect airborne loss has been discussed earlier. In addition, rewetting of the residue deposit may enhance penetration and plant uptake (Hull, 1970; Bukovac, 1976), resulting in an increase in the observed loss

Figure 5 Decline in Total Azinphosmethyl Dislodgeable and Soil Residues Measured During the First Spray Period of the 1978 Season

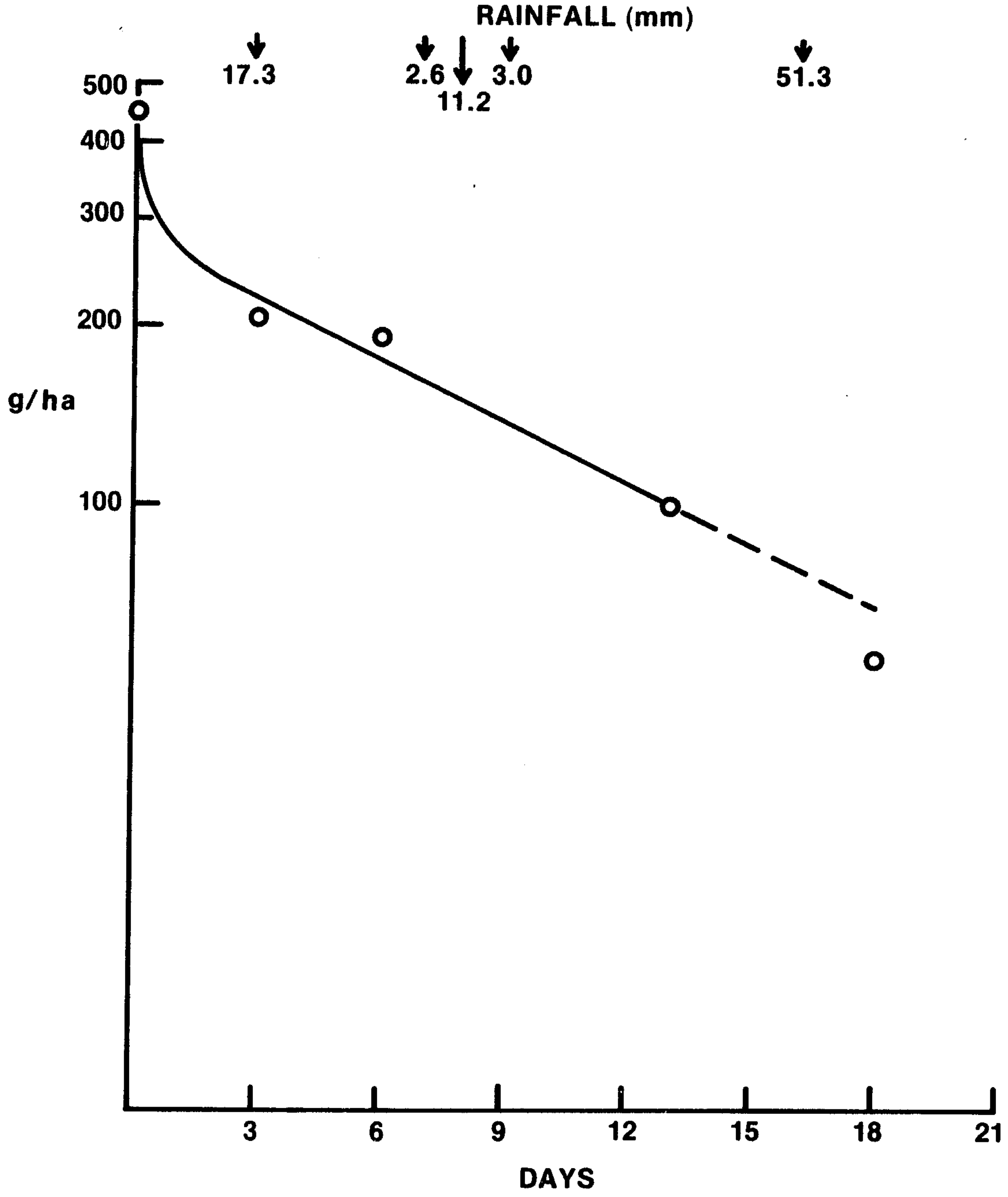
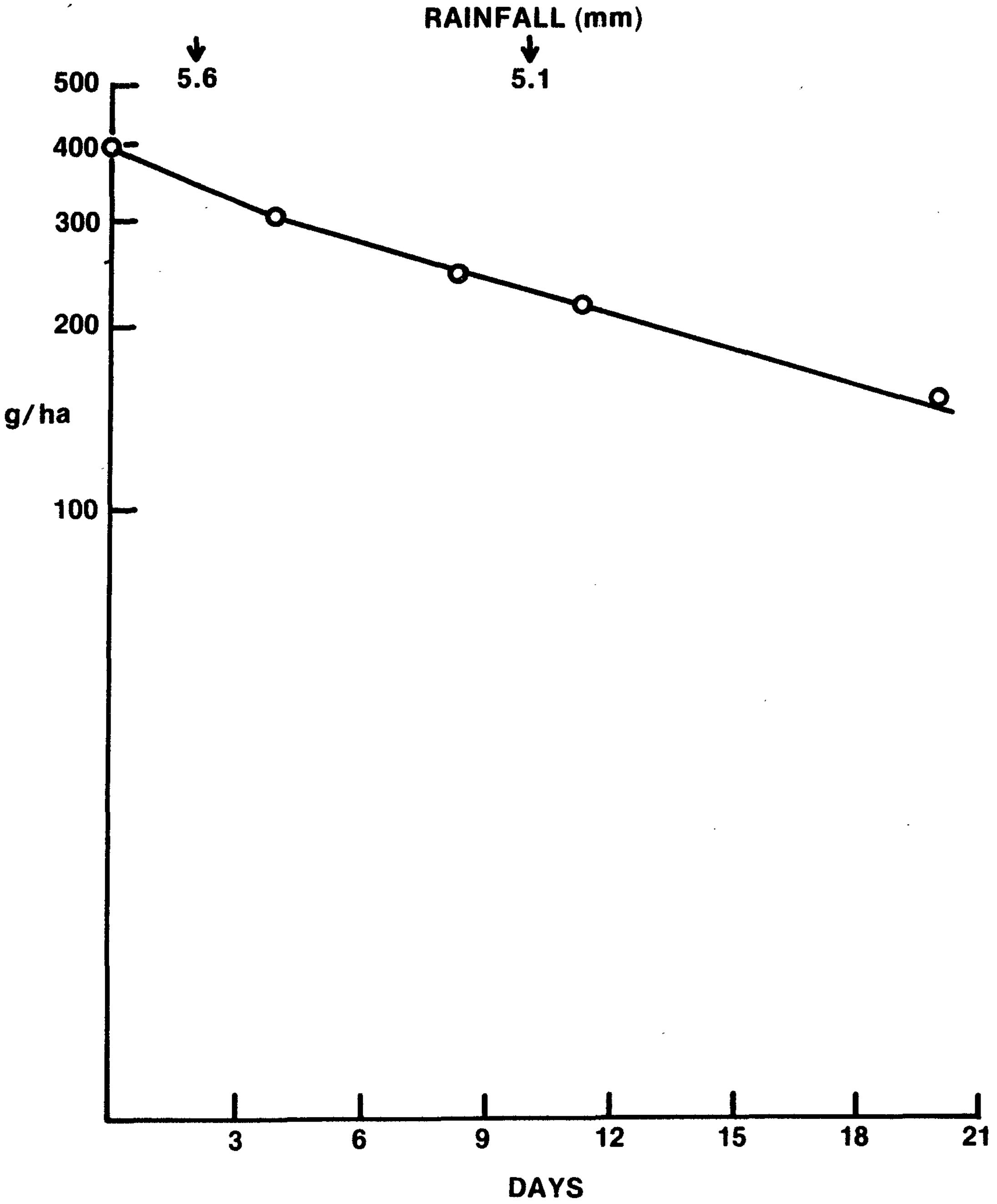

RAINFALL (mm)
17.3
2.6
11.2
3.0
51.3
500
400
300
200
100
g/ha
3
6
9
12
15
18
21
DAYS

Figure 6 Decline in Total Azinphosmethyl Dislodgeable and Soil Residues Measured During the Second Spray Period of the 1978 Season


RAINFALL (mm)
5.6
5.1
500
400
300
200
100
g/ha
3
6
9
12
15
18
21
DAYS

rate of dislodgeable residues. The effects of other environmental parameters (i.e., solar radiation, ambient temperature, relative humidity, wind speed and atmospheric stability) should also be considered.

To better understand the influence of those factors associated with the formulated pesticide, its application, and environmental conditions on the attenuation of residue deposits in orchards, a more thorough sampling program of both airborne and deposit residue is required. The pesticide should be applied and its disappearance monitored under a variety of properly characterized "natural conditions." The multi-component kinetic model presented here provides a tool for investigating those parameters that influence pesticide airborne loss and the overall attenuation of deposit residues.

Figure 7 Daily Temperature Range, 1978 Season

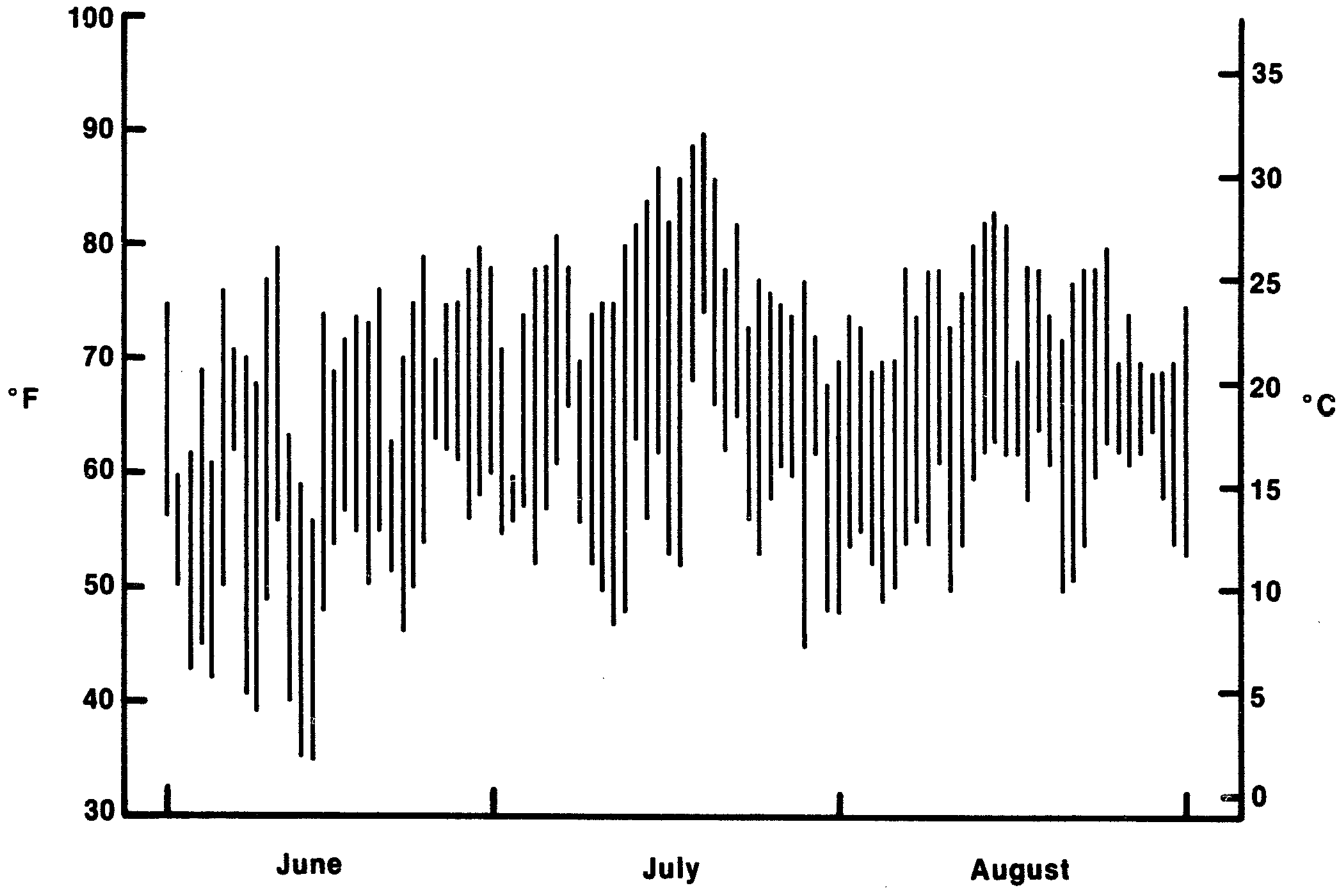
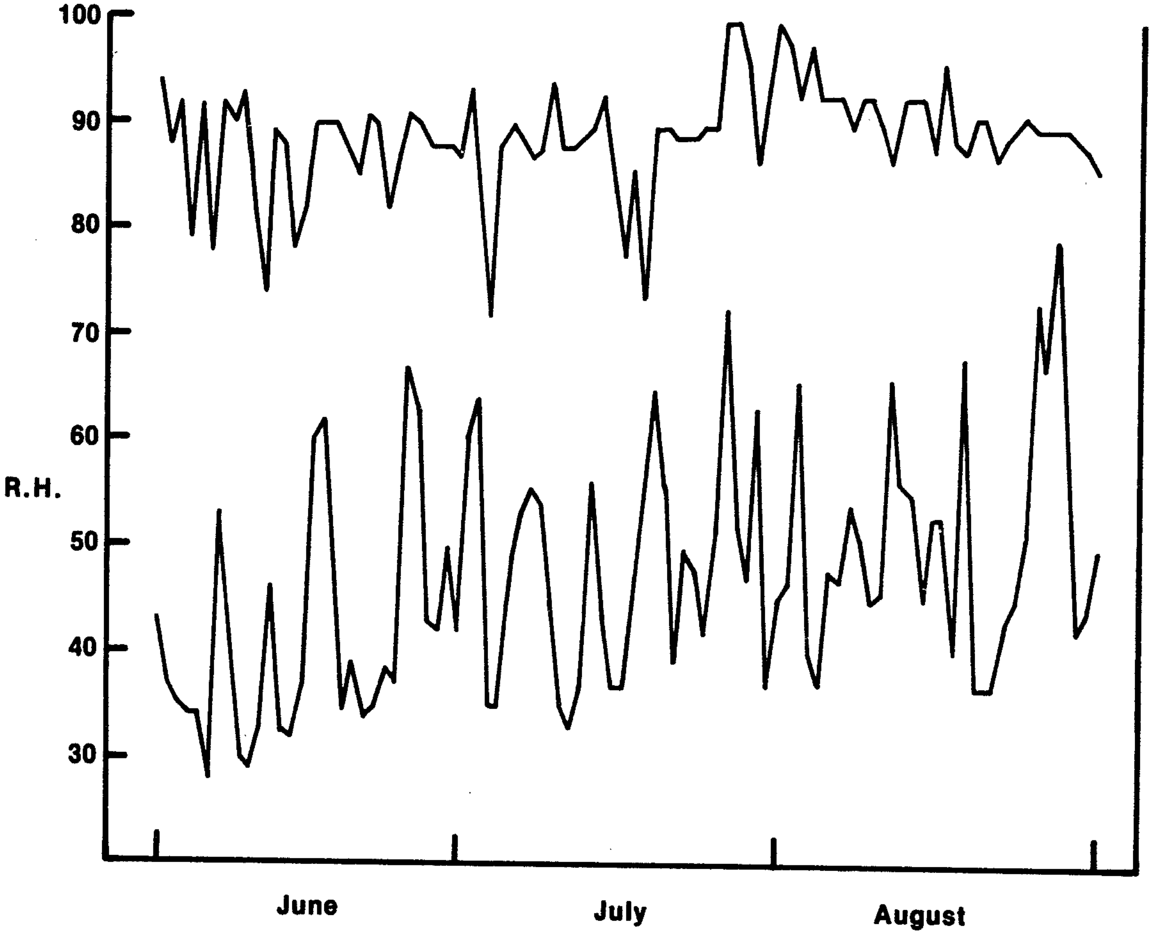

100
90
80
70
60
50
40
30
°F
35
30
25
20
15
10
5
0
°C
June
July
August

Figure 8 Daily Minimum and Maximum Relative Humidity, 1978 Season

Figure 8 Daily Minimum and Maximum Relative Humidity, 1978 Season


100
90
80
70
60
R.H.
50
40
30
June
July
August

PART IV

ASSESSMENT OF THE ATTENUATION AND MOVEMENT OF AZINPHOSMETHYL IN A MICHIGAN APPLE ORCHARD ECOSYSTEM: FURTHER MODEL DEVELOPMENT

INTRODUCTION

It would be unrealistic to believe that a model of pesticide fate in any terrestrial ecosystem, driven by time and rainfall conditions only, would be capable of explaining all the variation observed in the field data. To better explain the variation observed, both movement and attenuation should be decomposed to represent their component physical, chemical, and biological processes, each a function of the relevant environmental parameters (i.e., solar radiation, temperature, humidity, wind speed, atmospheric stability, etc.).

The conceptual model shown in Figure 1 of Part II was developed to represent those processes which determine the distribution and fate of a pesticide applied to an orchard ecosystem. The initial mathematical form of the model describes azinphosmethyl fate in terms of attenuation and movement, based only on field data from three seasons. The attenuation rate constants determined represent the combined effects of a number of individual processes as indicated in the conceptual model. These processes are thought to be individually influenced by different combinations of environmental parameters. In addition, because these processes occur simultaneously, the use of field experiments to study their individual contribution to the overall attenuation rate is difficult.

Laboratory experiments, designed to isolate and study individual processes under controlled environmental conditions, are at present the preferred method for studying environmental fate. Such experiments, while giving the researcher much greater control of the variables involved, often do not give results that can be extrapolated to the real world. However, much progress has been made recently in determining rate constants for a number of attenuation processes under various sets of environmental conditions (Zepp et al., 1975; Smith et al., 1977; Freed et al., 1979).

One approach to the development of a more precise model of pesticide fate would employ both in situ field measurements and data from laboratory experiments. Laboratory experiments should be designed to isolate and examine the influence of selected environmental parameters on the individual processes that in combination result in the observed field attenuation rate. In addition, in situ field rate data should be collected under a variety of "natural conditions" to allow the partial isolation of individual environmental effects. Further model development and experimental design should address the following questions:

(1) How are various loss processes influenced by individual environmental parameters, and

(2) What is the contribution of each process to the overall attenuation rate under a given set of environmental conditions.

In Part II, a matrix A of daily attenuation rates of azinphosmethyl in various orchard layers was developed. The orchard is treated as four vertical layers (tree, grass-broadleaves, litter-moss, and soil) by two horizontal areas (canopy, alley). Seven regions (no alley tree region exists) appear in each of the matrices and vectors below, beginning with canopy trees and proceeding to alley soil. Each diagonal element A_{ii} represents the fraction of azinphosmethyl lost from region i in one day, excluding any movement to or from another region (which is accounted for in matrices P, L, and H, the nonrain movement, light rain movement, and heavy rain movement matrices, respectively).

To investigate the influence of rainfall and other environmental parameters of pesticide loss, the attenuation matrix A may be decomposed into the diagonal matrices:

$$A = A_p + A_c + A_v + A_m + A_u$$

where the summand matrices A_p, A_c, A_v, A_m, and A_u represent photolysis, chemical degradation, volatilzation, microbial degradation, and plant uptake, respectively, and are called the attenuation component matrices. Each of these matrices is a 7 x 7 diagonal matrix with one non-zero entry for each region. Each attenuation component matrix is decomposable into a diagonal matrix of constants (the rates under "standard conditions") and a set of functions which modify those rates based on environmental conditions. The "standard" rates for each process should sum to the field-determined values. To examine the feasibility of this approach to further model development, the relationship between azinphosmethyl degradation kinetics and a number of environmental parameters was determined from laboratory data and the results of other laboratory experiments reported in the literature. The volatilization kinetics of azinphosmethyl were discussed in Part III.

Pesticide degradative mechanisms have been reviewed by a number of researchers (Ebling et al., 1963; Crosby, 1973; Leonard et al., 1976). Pesticide degradation has been traditionally divided into three major areas: chemical, photochemical, and biological. Pesticides may undergo a number of chemical transformations in the environment to include: hydrolysis and other nucleophilic reactions, oxidation, isomerization, reduction and free radical reactions (Goring et al., 1975). For the organophosphates, including azinphosmethyl, hydrolysis and oxidation are thought to be the most commonly occurring. Biological degradation includes plant and animal uptake and metabolism. Microbial degradation is a major pathway for the disappearance of many pesticides in the soil (Kearny and Helling, 1969). The diverse microbial populations of most soils are capable of degrading pesticides with little difficulty, either by adaption, or more commonly, by co-metabolism (Matsumura, 1975). Microbial degradation on plant surfaces must not be excluded in assessing possible causes of pesticide disappearance (Wieneke and Steffens, 1975). Photochemical degradation of pesticides has been demonstrated in water and air and on soil and foliar surfaces (Crosby, 1969; Nilles and Zabik, 1975; Liang and Lichtenstein, 1976; Zepp and Cline, 1977).

Chemical Degradation

As with the overall attenuation rate, the rates for the individual processes are assumed to be first-order or pseudo first-order. Chemical degradation of azinphosmethyl is assumed to occur primarily by hydrolysis, but oxidation is also possible (Eto, 1974). Oxidation may occur in all regions. The oxidation rate is represented by

$$\frac{DC}{Dt}\text{(oxidation)} =_{\text{def}}, \quad R_{ox} = K_{ox}C$$

The most likely oxidation pathway is through the reaction with free radicals, assuming an excess of free radicals available for interaction (r generation > K_{ox}) then K_{ox} is rate limiting and the reaction is pseudo first-order (Smith et al., 1977). Photooxidation, as a result of reaction with photochemically formed free radicals, the oxygen triplet diradical, or the more reactive singlet oxygen, may be more responsible for many pesticide non-biological oxidations (Crosby, 1973; Khan, 1976). Soil free radicals may also be important in the oxidation of pesticides in this medium (Plimmer et al., 1967; Armstrong and Konrad, 1974). Spear et al. (1978) indicated that paraoxon production may be related to both ozone and dust levels on citrus in central California. Spencer et al. (1975) also noted paraoxon formation on dust and dry soil beneath citrus trees in southern California. Oxidation of azinphosmethyl dislodgeable residues on southern California citrus foliage has also been indicated (Gunther et al., 1977). However, azinphosmethyl-oxon levels never exceeded 1.0% of the azinphosmethyl present. The oxon formed was more stable, but dissipated rapidly following rainfall. The likelihood that oxidation would contribute significantly to the degradation of azinphosmethyl during the relatively wet and humid summer months normally experienced in the temperate eastern United States is doubtful.

Hydrolysis has been shown to be an important mechanism of organophosphate degradation in both soil and aqueous environments (Freed et al., 1979). Hydrolysis resulting from reaction with moisture on foliar surfaces must also be considered. A discussion of hydrolytic mechanisms for the organophosphates in water can be found in Faust and Gomaa (1972) and Smith et al. (1977). The reaction is a function of pH, and can be either neutral, acid, or base-catalyzed. Again, the reacting species (H_2O, $H+$, OH^-) were assumed to be in excess of the pesticide, and the reaction first order, at a given pH.

Azinphosmethyl aqueous hydrolysis as a function of pH was determined by the procedure of Freed et al. (1979). Buffers used were as follows: pH 1.0, 0.01 m KCl and 0.01 m HCl; pH 3.0 and 5.0, 0.01 m potassium hydrogen phthalate and 0.01 m NaOH; pH 7.0, 7.5, 8.0, 8.5, 9.0, 0.01 m TRIS and 0.01 m HCl. Azinphosmethyl concentration was determined by analysis of residual parent compound by GLC (see Part I). First-order rate constants at 25^oC were determined from linear regression of log concentrations versus time, over a 20-day incubation period. Hydrolysis rate constants at pH 1, 3, 5, and 7 averaged 0.8% day^{-1} (standard deviation, 0.1%). The observed stability under neutral and acid conditions is in agreement with the observations of Liang and Lichtenstein (1972). Faust and Gomaa (1972) report that many organophosphates are stable under acid conditions. (Azinphosmethyl hydrolysis as a function of pH is shown in Figure 1). The relationship between pH and the base-catalyzed reaction rate (pH 7.5-9.0) is represented by the linear regression equation:

$$K_h = 0.095 \text{ pH} - .713 \ (r^2 = .996) \tag{1}$$

where K_H is the aqueous hydrolysis rate constant (time^{-1}).

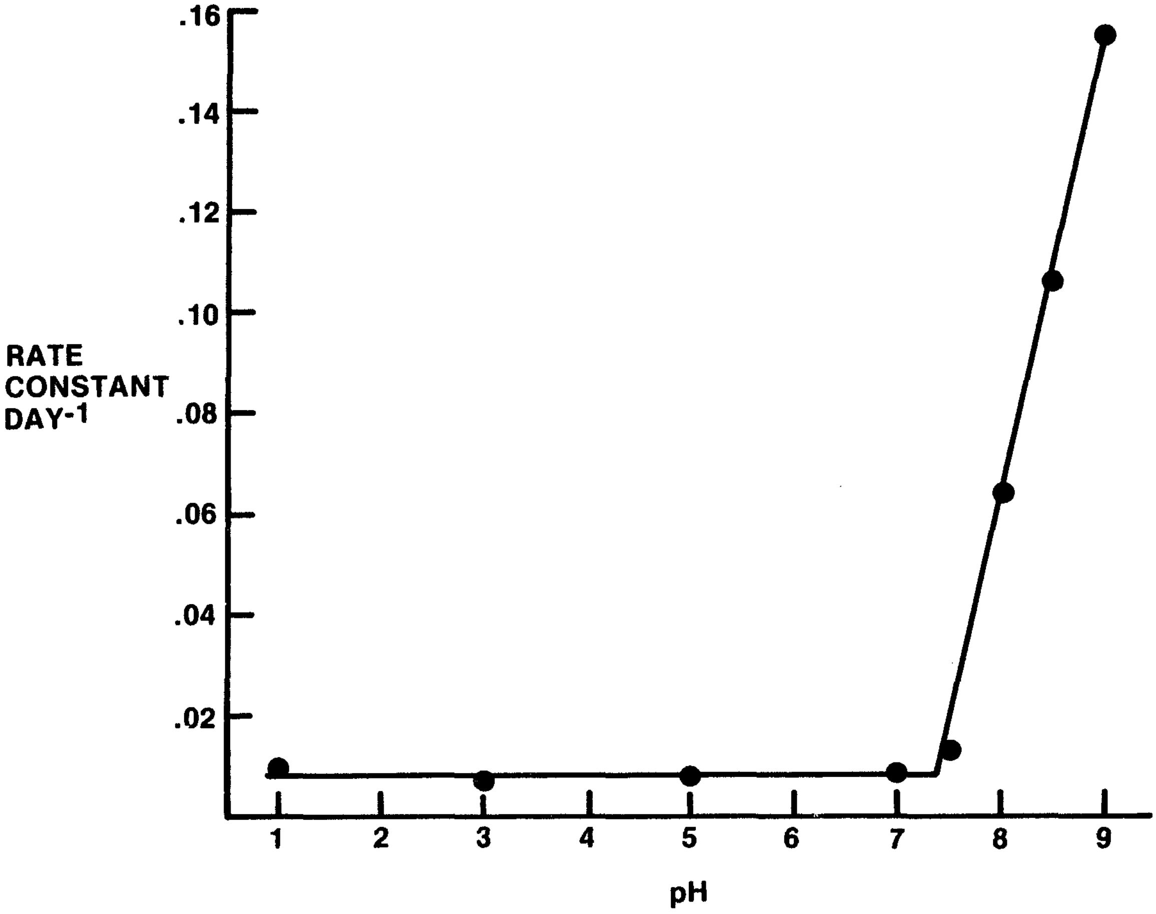
The rate of hydrolysis as a function of temperature was represented using the Arrhenius equation:

$$K_h = Ae^{-Ea/RT} \tag{2}$$

where K_h is the aqueous hydrolysis rate constant (time^{-1}) at temperature T, A is a constant depending on the chemical and other non-thermal factors, R is the gas constant, and Ea is the energy of activation. If K_h is determined over some temperature range, Ea can be calculated from the slope of the line, for a plot of log K_h versus 1/T. To estimate temperature effects on azinphosmethyl hydrolysis the data of Liang and Lichtenstein (1972) was analyzed using equation (2) as shown in Figure 2. The value determined for Ea, over the temperature range 5-50°C, was 12.5 Kcal/mole. This is an approximate value and will vary with pH and the temperature range used. Buffer composition and strength may also influence hydrolysis rates and associated values for Ea (Smith et al., 1977).

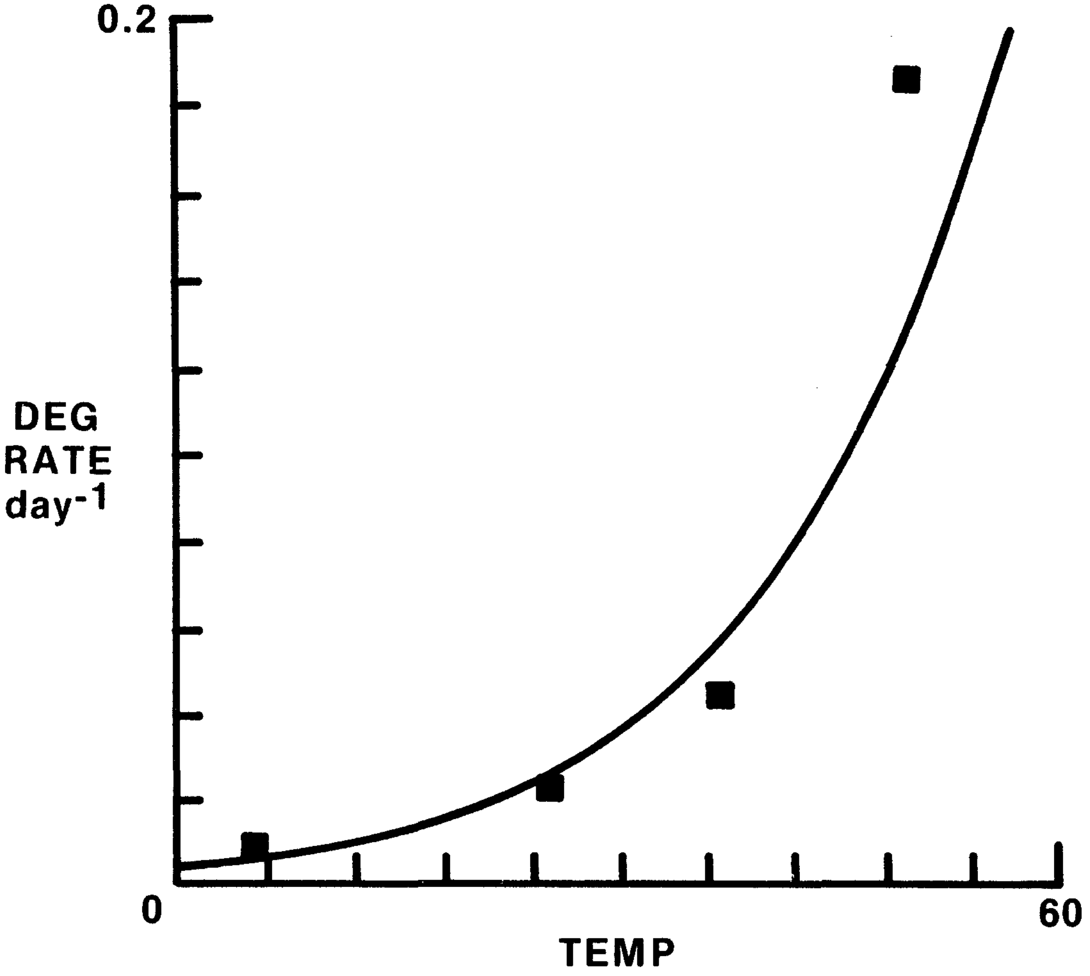
Hydrolysis of azinphosmethyl is assumed to be important in all regions. Although little is known about reactions occurring on foliar surfaces, it is assumed that, due to transpiration, there is an environment with sufficient moisture to allow hydrolysis to occur (Wieneke and Steffens, 1974). A neutral pH is assumed in all but the soil regions. Hydrolysis is treated as a function of air temperature only. This again is an approximation as temperatures at the foliar surface will often exceed the ambient air temperature. In the soil regions hydrolysis is treated as a function of both soil temperature and pH. Properties

Figure 1 Azinphosmethyl Hydrolysis Rate Constant Versus pH


.16
.14
.12
.10
RATE CONSTANT DAY-1
.08
.06
.04
.02
1
2
3
4
5
6
7
8
9
pH

of the soil which influence hydrolysis are discussed by Freed et al. (1979). Adsorption to clay and organic matter is thought to play an important role in degradation, as adsorbed organophosphates may be protected from hydrolysis or, in some cases, may result in increased reaction rates due to surface catalysis (Crosby, 1970). The use of the Arrhenius equation (2) to represent the effects of temperature on hydrolysis and other non-biological degradative mechanisms in the soil environment is discussed in Hamaker (1972). This author suggests that the heterogenous nature of soils as a reaction medium may not allow the use of equation (2) as it has traditionally been applied to reactions in homogenous solutions. This is indicated by the fact that the distribution coefficient, Kd (pesticide adsorbed/pesticide in solution), may change as the pesticide is transformed, and also by the exothermic nature of the adsorption process resulting in an equlibrium shift towards sorption to organic matter with increasing temperature (Felsot and Daum, 1979). Because both these phenomena will influence the concenration of pesticide in the soil solution and, theoretically, the rate of hydrolysis, this suggests that the "A" term in equation (2) is not a constant, but a function of both pesticide concentration and soil temperature. Until the influence of soil properties on hydrolysis is better understood, and for the purposes of this study, "A" is assumed to be a constant. The data of Yaron et al. (1974) were used to determine the relationship between temperature and the azinphosmethyl hydrolysis rate constant in soil. Degradation rates for wet soil (50% of saturation) incubated at 6, 25, and 40 ^{o}C, were used to parameterize equation (2) as shown in Figure 3. The Ea determined from this data was 13.5 Kcal/mole. The soil used in this study was a silty loam, pH 8.4, and < 1% organic matter. Both pH and soil type should be considered when comparing rates determined from the data in this particular study with other research. Soil in the orchard used in the present study was a marlette

Figure 2 Azinphosmethyl Hydrolysis Rate Constant Versus Air Temperature

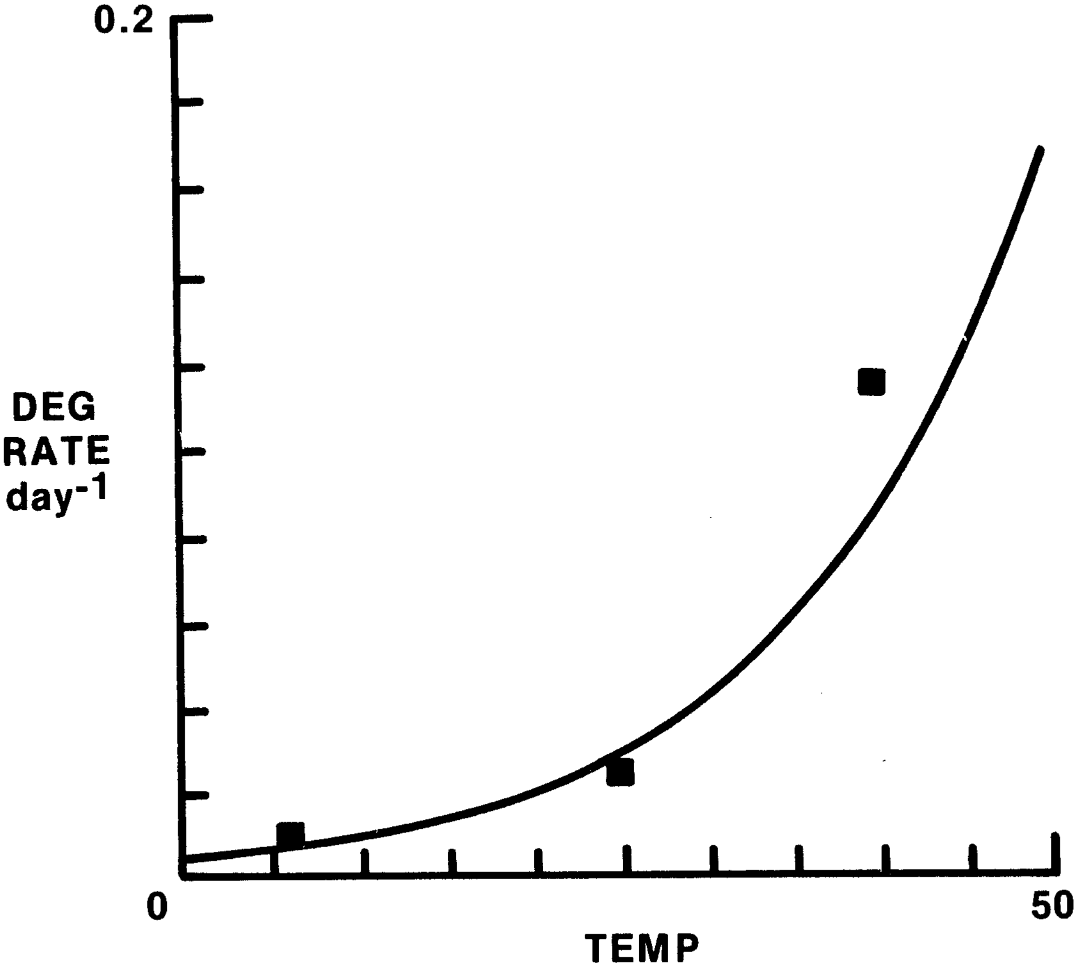

0.2
DEG
RATE
day^{-1}
0
60
TEMP

sandy clay loam, pH 6.0, 56% sand, 20% silt, 24% clay, and 6.0% organic matter in the top 10 cm. The results of degradation studies in the laboratory, using soil from the orchard (moisture content 30% = 48% of saturation) sterilized with sodium azide, fortified with 10 ppm azinphosmethyl, and incubated at 25 ± 1°C for 20 days, showed no degradation. This is not surprising considering the acid pH and the clay and organic matter content of the soil.

Microbial Degradation

Although microbial degradation cannot be ruled out as contributing to the overall attenuation of residues deposited on foliar surfaces, microbial degradation is thought to be a major degradative pathway in the litter-moss and soil layers. In some instances, pesticides can be used as the sole food source of microorganisms, but more often they are co-metabolized with other organics. If the pesticide is used as a primary nutrient by the microorganisms of the soil, then a lag period may be observed following application while the soil microorganisms population adapts to the new food source. This period may become shorter with successive applications (Hamaker, 1972). With co-metabolism, as long as the pesticide represents a small fraction of the total food source, no lag period should occur. This is the situation assumed to be present in the orchard soil and litter, with regard to azinphosmethyl biodegradation. The rate of biological degradation will therefore vary with the total available food source (i.e., organic mater content of the soil), temperature, and moisture (Hamaker, 1972). To determine the microbial degradation rate, a 20-day incubation at 25 ± 1°C, of the non-sterilized orchard soil (moisture content 30% = 48% of saturation) fortified with 10 ppm azinphosmethyl, was performed. The first-order rate constant, determined from linear regression of concentration of azinphosmethyl remaining versus time, was 7.9% day^{-1} ($r^2 = .969$).

Figure 3 Azinphosmethyl Hydrolysis Rate Constant Versus Soil Temperature


0.2
DEG
RATE
day^{-1}
0
50
TEMP

The influence of organic matter content of the soil on microbial degradation of azinphosmethyl was based on the data of Iwata et al. (1975). Soils in this study were passed through a 100 mesh sieve and moisture was added to 40% saturation. The soils were fortified at 450 ppm azinphosmethyl and incubated at 30^{o}C. Characteristics of these soils and the corresponding azinphosmethyl degradation rates over a 20-day period are as follows.

Table 1. Azinphosmethyl Degradation when Incubated with Various Soils[a]

Soil	% Organic Matter	Mechanical Analysis, %			pH	K_m[b]	r^2
		Sand	Silt	Clay			
1	0.8	53.6	31.0	15.4	6.9	-.010	.992
2	1.8	56.0	33.0	11.0	7.6	-.033	.996
3	2.1	12.5	50.7	36.8	7.3	-.050	.991
4	2.3	22.4	34.5	43.1	7.3	-.061	.969
5	6.0[a]	56.0	20.0	24.0	6.0	-.079	.969

[a] Data for soils 1-4 reported in Iwata et al. (1975). Soil 5 was taken from the orchard used in the present study.

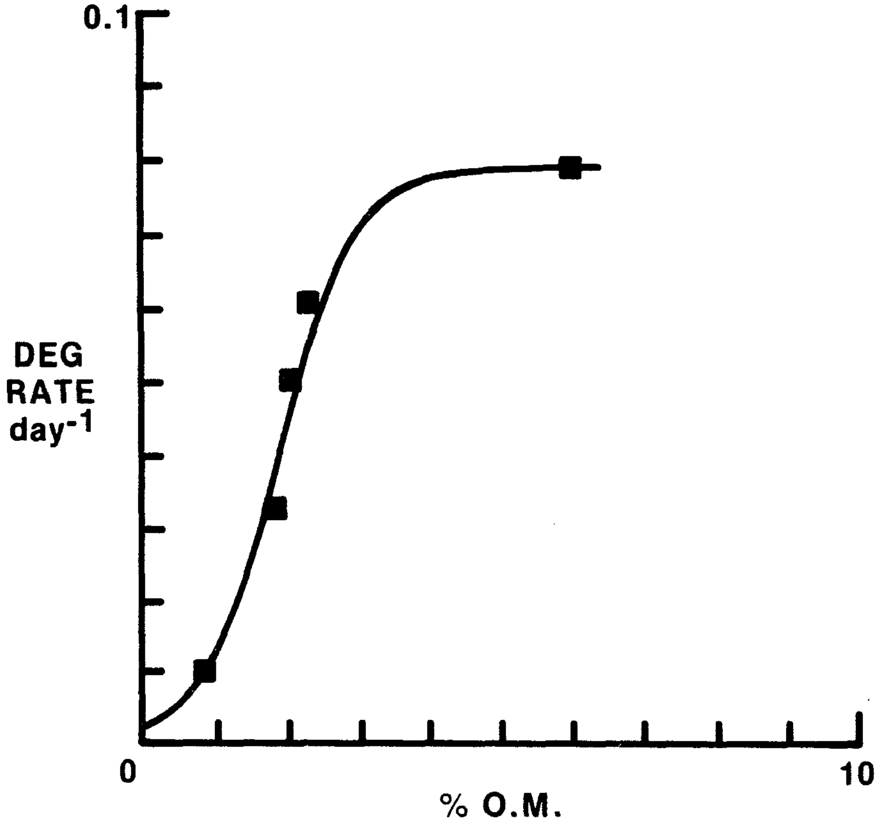
[b] Proportional daily loss determined from the data of Iwata et al. (1975) (Soils 1-4) and the orchard soil used in the present study (soil 5).

Figure 4 shows a plot of percent organic matter versus the azinphosmethyl degradation rate. Degradation is assumed to be primarily microbial, due to the neutral or acidic pH values for these soils. However, hydrolysis and other forms of chemical degradation may also have contributed to the observed rates derived from the data of Iwata et al. (1975) A modified from of the Verhulst-Pearl logistic equation (Pielou, 1969) was fit to the data to give the following relationship:

$$K_m = .079\ [1 + e^{-1.85(\%\ \text{o.m.} - 1.87)}]^{-1}$$

The correlation of azinphosmethyl degradation with a single soil factor (organic matter) must be interpreted with some caution, as the organic matter

Figure 4 Azinphosmethyl Microbial Degradation Versus Soil Percent Organic Matter


0.1
DEG
RATE
day-1
0
10
% O.M.

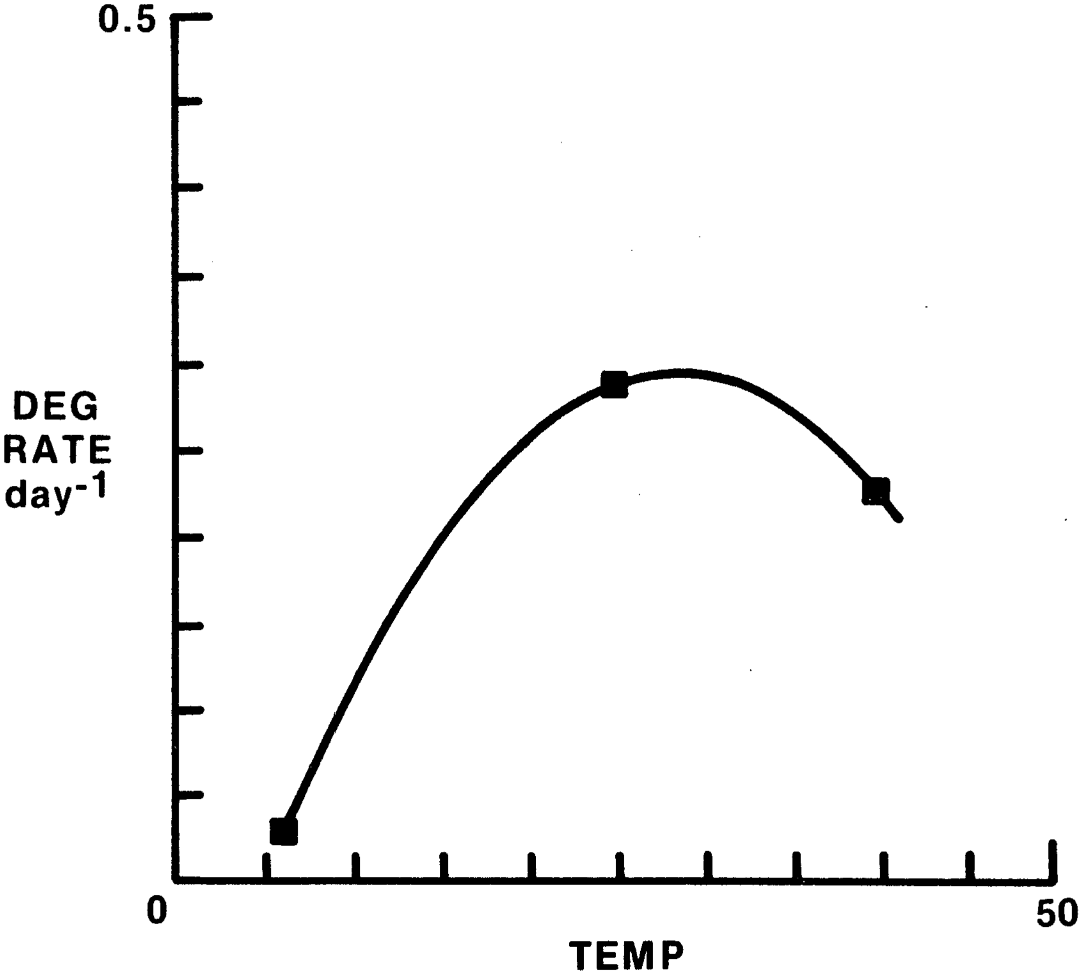
content may be correlated to other soil conditions effecting degradation. High organic matter is usually accomplished by a low soil pH, and adsorption has been shown to be positively related to organic matter content (Saltzman et al., 1972). Even though the data presented here shows a positive correlation of degradation rate to organic matter content, a number of researchers have found that at very high organic matter contents of peat and muck soils, degradation is decreased, presumably due to adsorption (Beynon et al., 1966; Hamaker, 1972; Kaufman, 1964). In addition, the relationship between the data of Iwata et al. (1975) and that of the present study must be viewed in light of the differences in initial concentrations used. Hamaker (1972) cites a number of studies which indicate that the degradation rate, on a percentage basis, increases with decreasing concentration. The azinphosmethyl microbial degradation rate of 7.9% day^{-1} determined using an initial concentration 10 ppm, may have been lower if the initial concentration of 450 ppm, employed by Iwata et al., (1975) was used. Temperature differences between the two studies are not thought to be significant, as indicated by the temperature relationship shown in Figure 5.

The relationship between temperature and soil microbial degradation was determined from the data of Yaron et al. (1974). The difference in degradation rates between sterile and non-sterile wet soil (50% of saturation, incubated at 6^{o}, 25^{o}, and 40^{o}C, was used to determine this relationship. The data was fit to the following polynomial equation:

$$K_m(t) = .00298T - .00005T^2 - .013$$

where K_m is the microbial degradation rate at a given temperature, T. This fit shows the optimum temperature to be approximately 30^{o}C. This is in agreement with the data of Day et al. (1961) for degradation of amitrole in soil. This temperature relationship is thought to refelct a response to temperature by the microorganism population. Changes in population size, distribution, or adaption

Figure 5 Azinphosmethyl Microbial Degradation Versus Soil Temperature


0.5
DEG
RATE
day-1
0
50
TEMP

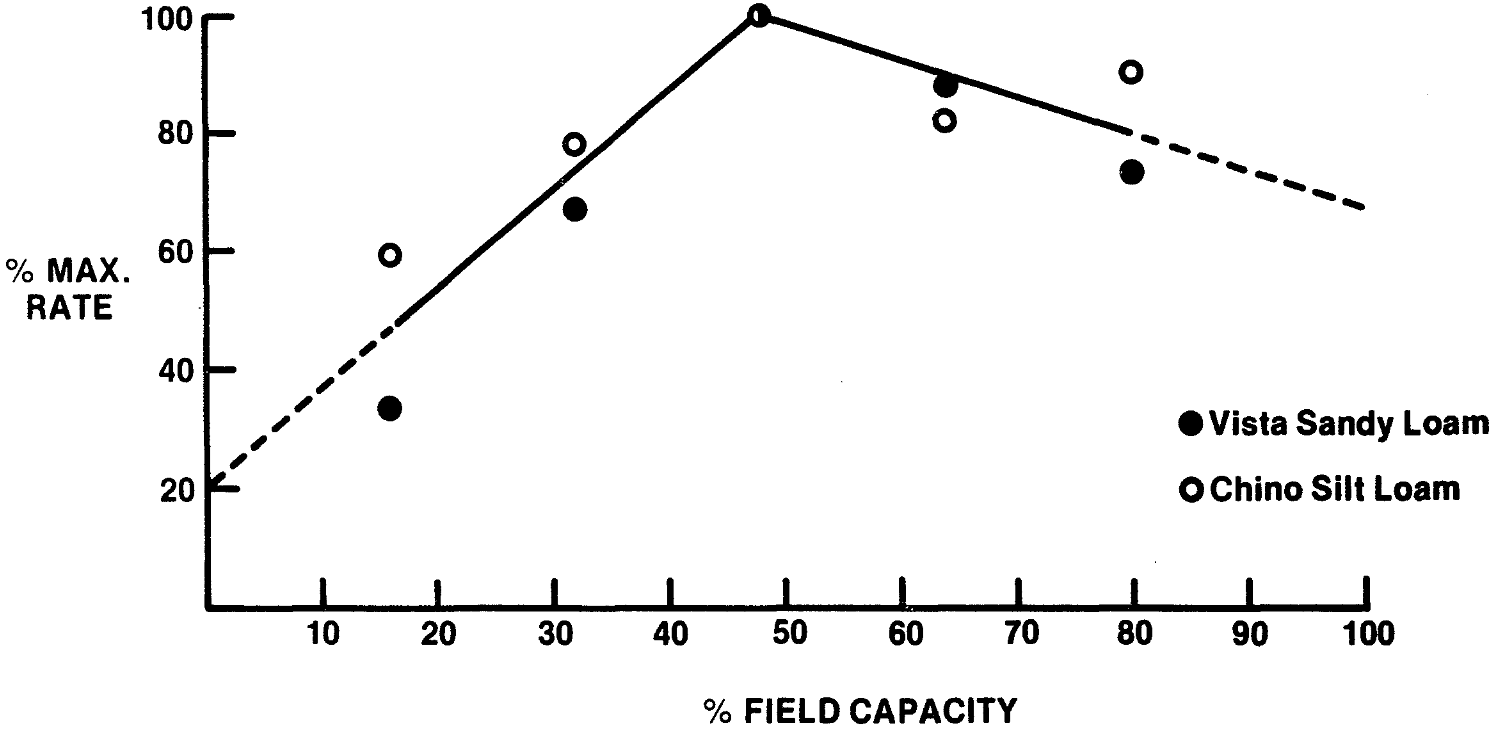
to degradation of the chemical may all be responsible for the observed temperature effect. The response may also be due in part to an Arrhenius type mechanism. At temperatures above the optimum (30°C) the rate no longer shows a positive relationship to temperature, possibly due to the heat lability of the microoganisms.

Soil moisture has also been shown to be an important factor in soil degradation of pesticides. The data assembled by Hamaker (1972) show much slower rates in dry as compared to moist soils and that rates tend to level off at higher moisture levels ($>$ 30% of saturation). At saturation levels rates often drop due to the lack of oxygen necessary for aerobic degradation. Many pesticides are capable of being degraded anaerobically, so this possible mechanism must not be neglected. Soil moisture in the orchard may remain at saturation levels only briefly. Under these conditions the development of an anaerobic microorganism population able to significantly alter pesticide concentration is not likely.

The data of Yaron et al. (1974) shows little or no degradation of azinphosmethyl for both sterile and non-sterile dry soils. Increased adsorption, due to the dry conditions, may be partially responsible for the observed results. At 50% of saturation, the degradation rate for the non-sterile soil at 25°C was twice that of the sterile soil. No other data was found in the literature on the relationship between azinphosmethyl degradation and soil moisture. As microbial degradation has been shown to be the primary pathway of amitrole loss in soils (Kearny and Helling, 1969), the treatment by Hamaker (1972) of the data of Day et al. (1961) for amitrole is presented as a crude estimate of the influence of soil moisture on azinphosmethyl microbial degradation (Figure 6).

The effect of both soil moisture content and temperature on the degradation of a number of herbicides was examined by Walker (1974, 1976a,

Figure 6 Amitrole Degradation Versus Soil Moisture for Two Soil Types


100
80
60
40
20
% MAX. RATE
10
20
30
40
50
60
70
80
90
100
% FIELD CAPACITY
● Vista Sandy Loam
○ Chino Silt Loam

1976b, 1976c), Smith and Walker (1977), and Walker and Smith (1979). In these studies no distinction was made between chemical and biological degradative pathways. In all cases a positive correlation was observed between the degradation rate and both soil moisture content and soil temperature. These data were used to develop and test a model for herbicide persistence. Assuming first-order kinetics, herbicide half-life as a function of soil moisture was represented by the following empirically derived equation (Walker, 1974):

$$H = am^{-b}$$

where H is the herbicide half-life, m is the soil moisture content, and a and b are constants. The Arrhenius equation was used to represent the effect of temperature on the degradation rate. Herbicide persistence in the field was estimated from these two equations using both laboratory determined values and simulated seasonal and diurnal soil temperature and moisture flux (Walker, 1974; Walker and Barnes, 1981). The model was tested against herbicide loss when applied to bare soil, and the model worked best when the herbicide was incorporated. Applicability to cropped fields and particularly perennial crops such as orchards lies in the ability of the model to represent the effects of the crop and/or ground cover on soil temperature and moisture flux. The model in its present state does not have this capability. Further development to represent the effect of soil moisture and temperature on chemical and biological degradative pathways individually would also be desirable.

pH and soil texture may also be important factors influencing microbial degradation. Soils with extremes in pH will most likely have developed microbial populations adapted to these conditions. The influence of pH might be more important, however, if a soil amendment which drastically alters the soil pH is used, thereby requiring adaption by the microbial community. Soil texture describes the soil aggregate size and the pore space of the soil, which may influence the availability of moisture and air to the microbial population. The interrelationship between all soil properties and the microorganism population must be considered in assessing pesticide degradation.

Photodegradation

Solar radiation is known to be important to the attenuation of pesticides in the environment, as it supplies thermal energy which influences pesticide volatilization and the rate of many degradative reactions. The energy of the photons may also be adsorbed by the bond (electronic) energy of the molecule, which may result in transformation. Much research has been done in the laboratory on the photolysis of pesticides and the photoproducts formed (Zabik et al., 1976). Only recently have attempts been made to determine rates of photodegradation under natural conditions. The most promising approach uses computer modeling techniques to extrapolate laboratory findings to field conditions (Zepp and Cline, 1977). These authors have attempted to predict photolysis of a number of compounds in the aquatic environment. The study of photolysis in solution is preferred as the homogeneity of this medium allows the researcher to accurately monitor and vary the chemical environment. Experiments to determine the photochemistry of compounds in the solid or sorbed state, such as pesticides applied to the soil and plant surfaces, are far less manageable (Zabik and Ruzo, 1981). Relatively few studies have attempted to determine the rate of photolysis on plant and soil surfaces under natural conditions. One of the major difficulties associated with this kind of study is differentiation between photodegradation, volatilization, and metabolism. In addition, the presence of sensitizers and quenchers may greatly alter the rate of photolysis determined in the absence of these substances. For example, Liang and Lichtenstein (1976) reported that following an eight-hour exposure to sunlight, 2.8% of the ^{14}C azinphosmethyl applied to bean leaves was determined to be the oxygen analog, whereas no oxygen analog was found for applications to corn leaves or glass plates. No oxygen analog was present in the dark controls. The authors suggest that a component of the bean leaf may have enhanced the formation of azinphosmethyl oxon in the presence of sunlight. Ninety-three, 88, and 94% of the radiocarbon was recovered from the glass, corn, and bean leaf dark controls. In all cases, the radiocarbon recovered was determined to be unaltered azinphosmethyl. Sixty-six, 86, and 72% was recovered from the glass, corn, and bean leaves following the eight-hour sunlight exposure with 5.7, 8.9, and 4.3% of that recovered determined to be photoproducts, based on differential extraction and thin layer chromatography. Substantial loss to volatilization of azinphosmethyl on glass and foliar surfaces as a result of the sunlight exposure is indicated. The greater volatilization of the azinphosmethyl on exposed surfaces, as compared to the control (covered with black cloth), may have been due in part to higher temperature and greater air exchange at the foliar surface. Volatilization of photoproducts must also be considered. If it is assumed that only a small amount of the photoproducts are lost to volatilization, then a crude estimate of the initial rate of photolysis can be made from the percent of photoproducts formed.

As the eight-hour exposure period (0900 to 1700 hr) used by Liang and Lichtenstein (1970) represents only a portion of the daily solar radiation exposure during the summer months in North America, the relationship between the photolysis rate of carbaryl and time of day (July) reported by Zepp and Cline (1977) was used to estimate the initial daily loss rate. Based on the relationship reported by these authors it was assumed that the peak rate of photolysis occurred at approximately 1300 hr, that no photolysis occurred before 0600 hr or after 2000, and that the loss rate varied linearly between the end points and the peak. Integrating the area under the triangle formed yields an estimate that exposure to sunlight between 0900 and 1700 hr is responsible for approximately 82% of the daily loss due to photolysis, during the summer months. The amount of photoproducts formed (estimates of azinphosmethyl loss due to photolysis during the eight-hour exposure), as a percent of dose applied to each surface, was adjusted accordingly to arrive at an estimate of azinphosmethyl initial daily loss due to photolysis. The initial daily loss rates calculated were 6.9, 10.8, and 5.2% day^{-1} for azinphosmethyl on glass, corn, and bean leaves, respectively. The azinphosmethyl degradation rate for dislodgeable residues on apple foliage and the orchard grass determined in Part II was approximately 4.5% day^{-1}. The initial daily losses due to photolysis, as determined above, would indicate that photolysis may contribute significantly to the disappearance of azinphosmethyl foliar deposits.

Factors that must be considered when estimating direct photolysis under natural conditions are discussed by Zepp and Cline (1977) and Smith et al. (1977). These include: the incident light intensity, as a function of season, latitude, time of day, cloud cover, percent of light adsorbed by the pesticide (as compared to its surroundings) and quantum yield (fraction of photons adsorbed that results in transformation). As many pesticides show maximum adsorbance in the ultra violet region, outside the range of wavelengths reaching the surface of the earth, sensitized reactions are often important to pesticide photodegradation. A sensitizer adsorbs, light at a wavelength present, followed by an energy transfer to the pesticide (Khan, 1974). The components of a plant surface which may act as sensitizers are largely unknown.

The data of Liang and Lichtenstein (1976) also indicated that azinphosmethyl on the soil surface undergoes photodegradation. Estimated daily initial rates of photodegradation for the three soil types used (sand, loam, muck) were slightly faster than those estimated for the glass and foliar surfaces. Due to limited data available, no attempt was made to estimate the rate of azinphosmethyl photodegradation on plant or soil surfaces as a function of environmental conditions. Much research needs to be done in this area, before such estimates will be possible.

Plant Uptake

Greenhouse studies on plant uptake and metabolism of ^{14}C azinphosmethyl applied to bean leaves (Steffens and Wieneke, 1976) suggest that this loss mechanism may be an important pathway in the attenuation of foliar deposit residues in an apple orchard. The influence of environmental factors such as solar radiation, temperature, humidity and other conditions influencing leaf wetness on plant uptake of pesticides is discussed by Hull (1970), Steffens and Wieneke (1975) and Bukovac (1976). However, no quantitative relationships are presented. A computer model for foliar uptake of pesticides was reported by Bridges and Farrington (1974). This model represents plant uptake by both diffusion and mass flow through the observable structure of a wheat leaf. The model structure does not allow for the influence of environmental conditions on the rate of foliar uptake. A general lack of data in the literature points to the need for further research to investigate the contribution of plant uptake and metabolism to the overall attenuation of foliar residues as a function of environmental conditions.

CONCLUSIONS

The literature reviewed and the results of the preliminary experiments reported provide a basis for additional work. Further model development, as a method for better understanding of pesticide environmental dynamics, will require the formulation of laboratory and field experiments that are specifically designed to provide data to be used in the numerical analysis of pesticide fate as a function of environmental conditions. The conceptual model presented identifies the key processes in the assessment of pesticide fate in an orchard ecosystem and the working model provides a framework for further investigation.

PART V

SUMMARY AND CONCLUSIONS

SUMMARY

A model for azinphosmethyl attenuation and movement in a Michigan apple orchard ecosystem was developed to assess the fate and exposure of this compound to the orchard flora and fauna. The model was parameterized primarily through the use of field data gathered over a number of seasons. Rates of attenuation within, and movement between, specified orchard compartments were determined under various rainfall regimes. The output of this model was structured to allow the estimation of the time course of azinphosmethyl exposure to ground-dwelling invertebrates. Mean squared errors for the comparison of the model predictions with an independent set of residue data indicated good prediction of azinphosmethyl fate within the tree and grass-broadleaves layers. Prediction of pesticide dynamics within the litter-moss and soil layers was much more difficult. This is thought to be due in part to the lesser amounts of residues distributed to these layers, variability in the composition of the litter-moss layer, and the strong dependence of pesticide dynamics in these layers on environmental factors other than rainfall.

The model in its present form provides a new approach to the analysis of field residue data. To the author's knowledge, this is the first study of its kind to simultaneously determine pesticide attenuation and movement within an agroecosystem through the numerical analysis of field data. In addition, the output of the fate model was specifically designed to be used as input in a model describing the ecobiology and temporally distributed mortality of the ground-dwelling isopod *Trachelipus rathkei* (Goodman et al., 1981). This model was partially parameterized using data from field studies conducted concurrently within the same orchard as the fate studies (Snider, 1979; Snider and Shaddy, 1980). Fate model predictions estimate that under dry conditions 25% of the daily loss of azinphosmethyl from the orchard trees is due to movement to other parts of the orchard. Greater movement is predicted under rainfall conditions. This movement resulted in increased pesticide exposure and additional mortality, especially among the immature age classes represented in the *T. rathkei* model (Goodman, 1980).

The results of the initial distribution studies indicated that airborne loss played a major role in the early attenuation of azinphosmethyl residue deposit residues. Estimates of daily airborne loss determined from deposit residues and direct sampling of airborne residues suggested that airborne loss was in fact largely responsible for the early loss of residues (40% of the daily loss rate on day 3 of the first spray period, 1978 season), under the specific set of environmental conditions that prevailed during and following application. A multi-component kinetic model was presented for estimating simultaneously the early airborne loss of foliar deposits and the often slower dissipation of the remaining residues. Variation in the set of equation parameters determined separately from data gathered during the first two spray periods of the 1978 season suggests that the rate of airborne loss and other attenuation mechanisms (i.e., degradation, plant uptake and metabolism) are dependent, in part, on rainfall and other environmental parameters yet to be characterized.

CONCLUSIONS

Understanding pesticide fate throughout the entire orchard ecosystem is now gaining importance as a result of the interest in integrated pest management as a long-term strategy for pest control. In orchards and many other crops, where chemicals are still heavily relied upon, the success of biological control as a major component of IPM may depend largely on the judicious use of pesticides. The trend in pest management research has been to use modeling techniques to better understand the ecobiology of pest, host, and beneficial species so as to maximize the effectiveness of biological control measures. A comparable effort in modeling pesticide fate and effects on both harmful and beneficial species is essential to the development of effective and efficient orchard integrated pest management programs.

The use of modeling techniques to better understand pesticide fate in orchards may also provide a basis for the development of models describing the fate of organic toxicants in terrestrial ecosystems in general. Ecosystems use energy from the sun to constantly recycle their water, air, mineral, plant and animal resources. Natural mechanisms thought to be essential to these systems include: biogeochemial cycling, host-parasite relations, competititon for food and habitat, predator-prey relationships, food chains, symbioses, community-diversity and succession, and natural selection (Odom, 1971; Pimentel and Goodman, 1974; Southwick, 1976; NSF/RA, 1976). The effect of the introduction of chemical substances into the environment on the above-mentioned natural mechanisms of ecosystems is largely unknown. No tests are currently available which can address ecosystem effects at this level. The EPA admits that proposed tests under FIFRA and TSCA are only screening tests and that there is an urgent need for development of higher level ecosystem tests. The question now arises as to whether these screening tests can adequately select those compounds which will most likely pose no hazard to ecosystems. Does a negative result in an acute toxicity test preclude behavioral effects on a population influencing its ability to compete for food and/or habitat? There is no evidence that even chronic toxicity or life cycle studies can give the answer to this question. It is disturbing that negative results for all of the proposed "ecosystem effects" tests may allow continuous low level exposure of a chemical substance when nothing is known about the effects of this exposure on any of the aforementioned "essential natural mechanisms" of ecosystems. A large effort by the scientific community is needed to better understand ecosystem effects above the species level. This effort seems paramount in light of the apparent inability of present screening tests to preclude higher level effects. Rapid development of ecosystem effects test standards should include the use of mathematical modeling techniques to deal with the complexity of the interactions involved. These ecosystem effects models can then be coupled with chemical exposure models producing a very powerful tool in ecosystem hazard assessment. The development of ecosystem models appears to be much farther off than exposure models. In the near future, much emphasis must be placed on rapid development of exposure models, in screening chemicals for ecosystem effects. Accurate predictions of exposure may offset much of the uncertainty in ecosystem effects screening tests.

LIST OF REFERENCES

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Al-Adil, K. M., White, E. R., Winterlin, W. L. and Kilgore, W. W. (1973) Uptake and translocation of Guthion by beans and barley. J. Agric. Food Chem. 21, 376-379.

Asmussen, L. E., White, A. W., Jr., Hauser, E. U. and Sheridan, J. M. (1977) Reduction of 2,4-D load in surface runoff down a grassed waterway. J. Environ. Qual. 6, 159.

Armstrong, D. E. and Konrad, J. G. (1974) Nonbiological degradation of pesticides. In Pesticides in Soil and Water. (Ed. by Guenzi, W. D.), p. 123-131. SSSA, Madison, Wisconsin.

Barrow, G. M. (1966) Physical Chemistry. McGraw-Hill, Inc., New York, 843 p.

Bauer, J. R., Bovey, R. W. and Merkle, M. G. (1972) Concentration of Picloram in runoff water. Weed Sci. 20, 309-314.

Beynon, K. I., Davies, L., and Elgor, K. (1966) Analysis of crops and soils for residues of diethyl 1-(2,4 dichlorophenyl)-2-chlorovinyl phosphate. J. Sci. Food Agr. 17, 167-174.

Bridges, R. C. and Farrington J. A. (1974) A compartmental computer model of foliar uptake of pesticides. Pestic. Sci. 5, 365-381.

Brown, A. W. A. (1977) How have entomologists dealt with resistance. Proc. 68th Ann. Meet. Am. Phytopathol. Soc. 3, 67-74.

Brown, A. W. A. (1978) Ecology of Pesticides. John Wiley and Sons, New York, 525 p.

Bukovac, M. J. (1976) Herbicide entry into plants. In Herbicides: Physiology, Biochemistry, Ecology. (Ed. by Audus, L. J.), p. 335-364. Academic Press, London.

Caro, J. H., Taylor, A. W. and Lemon, E. R. (1971) Measurement of pesticide concentrations in air overlying a treated field. International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Canada.

Caro, J. W., Freeman, H. P., and Turner, B. C. (1974) Persistence in soil and losses in runoff of soil-incorporated carbaryl in a small watershed. J. Agric. Food Chem. 22, 860.

Claith, M. M., Spencer, W. F., Farmer, W. J., Shoup, T. D., and Grover, R. (1980) Volatilization of S-ethyl n,n-dipropylthiocarbamate from water and wet soil during and after food irrigation of an alfalfa field. J. Agric. Food Chem. 28, 610-613.

Cox, G. W. (1974) Laboratory Manual of General Ecology. Wm. C. Brown Company, Dubuque, Iowa, 196 p.

Croft, B. A. (1975) Tree fruit pest management. In Introduction to Pest Management. (Eds. Metcalf, R. L. and Luckmann, W. H.). Wiley Interscience, New York.

Croft, B. A. (1978) Potentials for research and implementation of integrated pest management on deciduous fruit-trees. In Pest Control Strategies (Eds. Smith, E. H. and Pimentel, David), p. 101-115. Academic Press, New York.

Croft, B. A. and Brown, A. W. A. (1975) Responces of arthropod natural enemies to insecticides. Ann. Rev. Entomol. 20, 285-335.

Crosby, D. G. (1969) Experimental approaches to pesticide photodecomposition. Residue Reviews 25, 1-12.

Crosby, D. G. (1970) The non-biological degradation of pesticides in soils. In Pesticides in the Soil: Ecology, Degradation, and Movement, p. 86-94, Mich. State Univ., East Lansing, MI.

Crosby, D. G. (1973) The fate of pesticides in the environment. Ann. Rev. Plant Physiol. 24, 467.

Day, B. E., Jordon, L. J. and Hendrixson, R. T. (1961) The decomposition of amitrole in California soils. Weeds 9, 443-456.

DeJong, K. (1980) Adaptive system design: a genetic approach. IEEE Trans. Syst. Man Cybern., SMC-10, p. 566-574.

Ebling, W. 1963. Analysis of the basic processes involved in the deposition, degradation, persistence and effectiveness of pesticides. Residue Reviews 3, 35.

Elliot, D. L., Iwata, Y., Carman, G. E., and Gunther, F. A. 1977. Post-application slough-off of pesticide deposits on orange trees. Bull. Environ. Contam. Toxicol. 18, 711-718.

Eto, M. (1974) Organophosphate pesticides: organic and biological chemistry. CRC Press, Cleveland, Ohio. 368 p.

Faust, S. D. and Gomaa, H. M. 1972. Chemical hydrolysis of some organic phosphorus and carbamate pesticides in aquatic environments. Environ. Lett. 3, 171-201.

Felsot, A. and Dahm, P. A. (1979) Sorption of organophosphorus and carbamate insecticides by soil. J. Agric. Food Chem. 27, 557-563.

Freed, V. H., Chiou, C. T. and Schmedding, D. W. 1979. Degradation of selected organophosphate pesticides in water and soil. J. Agric. Food Chem. 27, 706-708.

Gillette, J. W. and Witt, J. M., Eds. (1979) Terrestrial Microcosms Proc. Symp. Workshop on Terrestrial Microcosms, NSF/RA 790034.

Glass, B. L.. and Edwards, W. M. (1974) Picloram in lysimeter runoff and percolation water. Bull. Environ. Contam. Toxicol. 11, 109-112.

Glass, E. H. and Lienk, S. E. (1971) Apple insect and mite populations developing after discontinuance of insecticides: 10 year record. J. Econ. Entomol. 63/23-26.

Goodman, E. D. (1980) Modeling pesticide fate and effects on soil/litter invertebrates in an orchard ecosystem. Abstract. Environmental Risk Assessment - An Integrated Approach. Society of Environmental Toxicology and Chemistry First Annual Meeting, Arlington, Virginia.

Goodman, E. D., J. J. Jenkins, R. M. Snider, R. T. Kon, P. A. Weston, M. J. Zabik, T. Julian and M. Tabatabai. (1981) A study and model of azinphosmethyl fate and effects in a Michigan apple orchard ecosystem. Final Technical Report, EPA Cooperative Agreement R805624. (In preparation).

Goring, C. A. I., Laskowski, D. A., Hamaker, J. W. and Meikle, R. W. (1975) Principles of pesticide degradation in soil. In Environmental Dynamics of Pesticides (Eds. Haque, R. and Freed, V. H.), p. 135-172. Plenum Press, New York.

Grubbs, F. E. (1969) Procedures for detecting outlying observations in samples. Technometrics 11, 1.

Gunther, F. A. 1969. Insecticide residues in California citrus fruit and products. Residue Reviews 28.

Gunther, F. A. and Blinn, R. C. (1955) Analysis of Insecticides and Acaricides. Interscience, New York.

Gunther, F. A., Jeppson, L. R., Barkley, J. H., Elliott, L. M., Blinn, R. C., and Dunn, C. L. (1958) Persistence of residues of 2,3-p-dioxane-dithol S,S-bis(0,0-diethyl phosphorodithioate) as an acaricide on and in mature lemons and oranges. J. Agr. Food Chem. 6, 210.

Gunther, F. A., Westlake, W. E., Barkley, J. H., Winterlin, W. and Langbehn, L. 1973. Establishing dislodgeable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 9, 243-249.

Gunther, F. A., Iwata, Y., Carman, G. E., and Smith, C. A. 1977. The citrus reentry problem: research on its causes and effects, and approaches to its minimization. Residue Reviews 67, 1-139.

Hall, A. S. and Day, J. W., Jr., Eds. (1977) Ecosystem Modeling - In Theory and Practice. Wiley-Interscience, New York. 684 p.

Hall, F. R., Reichard, D. L., and Krueger, H. R. (1975) Dislodgeable azinphosmethyl residues from air blast spraying of apple foliage in Ohio. Arch. Environ. Contam. Toxicol. 3, 352-363.

Hall, J. K., Paulus, M. and Higgins, E. R. (1972) Losses of atrazine in runoff water and soil sediment. J. Environ. Quality 1, 172-176.

Hamaker, J. W. (1972) Decomposition: quantitative aspects. In Organic Chemicals in the Soil Environment. (Eds. Goring, C. A. I. and Hamaker, J. W), p. 253-340. Marcel Dekker, New York.

Hansen, J. D., Schneider, B. A., Olive, B. M., and Bates, J. J. (1978) Personnel safety and foliage residue in an orchard spray program using azinphosmethyl and captan. Arch. Environ. Contam. Toxicol. 7, 63-71.

Harrold, L. L., Triplet, G. B., Jr., and Edwards, W. M. (1970) No-tillage corn-characteristics of the system. Agric. Eng. 51, 128.

Hartley, G. S. (1969) Evaporation of pesticides. In Pesticide Formulations Research. (Ed. Gould, R. F), p. 115-134. Am. Chem. Soc. 'Advances in Chemistry Series,' 86.

Haynes, R. J. (1980) Influence of soil management practice on the soil agro-ecosystem. Agro-Ecosystems 6, 3-32.

Helling, C. S., Kearney, P. C., Alexander, M. (1971) Behavior of pesticides in soils. Adv. Agron. 23, 147-241.

Hill, K. R. (1971) Report of half-life working party. J. Ass. Offic. Anal. Chemists 54, 1316-1317.

Holland, J. H. (1975) Adaptation in natural and artificial systems. The University of Michigan Press, Ann Arbor. 183 p.

Howitt, A. J. and Pshea, A. (1965) The development and use of ultra low volume ground sprayers for pests attacking fruit. Mich. Quart. Bull. 48, 144.

Hoyt, S. C. and Burts, E. C. (1974) Integrated control of fruit pests. Ann. Rev. Entomol. 19, 231-252.

Hull, H. G. (1970) Leaf structure as related to absorption of pesticide and other compounds. Residue Reviews 31, 1-150.

Iwata, Y., Ousch, M. E., Westlake, W. E., and Gunther, F. A. 1975. Behavior of five organophosphorus pesticides in dust derived from several soil types. Bull. Environ. Contam. Toxicol. 14, 49.

Iwata, Y., Westlake, W. E., Barkley, J. H., Carman, G. E., and Gunther, F. A. (1977) Behavior of phenthoate (cidial) deposits and residues on and in grapefruits, lemons and lemon leaves, oranges and orange leaves, and in the soil beneath orange trees. J. Agric. Food Chem. 25, 362-368.

Kadoum, A. M. (1967) A rapid micromethod of sample cleanup for gas chromatographic analysis of insecticidal residues in plant, animal, soil, and surface and ground water extracts. Bull. Environ. Contam. Toxicol. 2, 264.

Katan, J., Fuhrmann, T. W. and Lichtenstein, E. P. (1976) Binding of ^{14}C parathion in soil: a reassessment of pesticide persistence. Science 193, 891-894.

Kaufman, D. D. (1964) Microbial degradation of 2,2-dichloro-propionic acid in five soils. Can. J. Microbiol. 10, 843-852.

Kearney, P. C. and Helling, C. S. (1969) Reactions of pesticides in soils. Residue Reviews 25, 25-44.

Khan, M. A. Q., Khan, H. M., and Southerland, D. J. (1976) Ecological and health effects of the photolysis of insecticides. In Survival in Toxic Environments (Eds. Khan, M. A. Q. and Bederka, J. P., Jr.), p. 333-355. Academic Press, New York.

Klingman, G. C. and Ashton, F. M. (1975) Weed Science: Principles and Practices. Wiley Interscience, New York, p. 32-33.

Kuhr, R. J., Davis, A. C. and Bourke, J. B. (1974) Dissipation of Guthion, Sevin, Polyram, Phygon and Systox from apple orchard soil. Bull. Environ. Contam. Toxicol. 11, 224-230.

Lassiter, R. R., Baughman, G. L. and Burns, L. A. (1978) Fate of toxic organic substances in the aquatic environment. In State-of-the-Art in Ecological Modeling (Ed. Jorgensen, S. E.), 219-245. Inter. Soc. Ecol. Mod., Copenhagen.

Leonard, R. A., Bailey, G. W., Swank, R. R., Jr. (1976) Transport, detoxification, fate and effects of pesticides in soil and water environments. In Land Application of Waste Materials, 49-78. Soil Conservation Society of America, Ankeny, Iowa.

Liang, T. T. and Lichtenstein, E. P. (1972) Effect of light, temperature, and pH on the degradation of azinphosmethyl. J. Econ. Entomol. 65, 315-321.

Liang, T. T. and Lichtenstein, E. P. (1976) Effects of soils and leaf surfaces on the photodecomposition of [^{14}C] azinphosmethyl. J. Agric. Food Chem. 24, 1205-1210.

Matsumura, Fumio. Toxicology of Insecticides. Plenum Press, New York, 503 p.

Maybank, J., Yoshida, K. and Grover, R. (1977) The Magnitude and Importance of Spray Drift from Agricultural Applcations. 70th Ann. Meeting Air Poll. Control Assoc., Toronto, Canada.

McMechan, A. D., Morgan, C. V. G. and Wardle, G. A. (1972) Erosion of azinphosmethyl from apple leaves by rain and overtree irrigation. J. Entomol. Soc. Brit. Columbia, 69, 5-8.

Menzie, C. M. (1972) Fate of pesticides in the environment. Ann. Rev. Ent. 17, 199-221.

National Academy of Sciences. 1969. Insect Pest Management and Control. Publ. 1695. Washington, D. C. 508 pp.

Nigg, H. N., Allen, J. C., King, R. W., Thompson, N. P., Edwards, G. J. and Brooks, R. F. (1977) Dislodgeable residues of ethion in Florida citrus and relationships to weather variables. Arch. Environ. Contam. Toxicol. 6, 257-267.

Nilles, G. P. and Zabik, M. J. (1975) Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran. J. Agric. Food Chem. 23, 410-414.

NSF/RA. (1976) Ecosystem processes and organic contaminants, research needs and an interdisciplinary perspective. NSF/RA 760008.

Odom, E. P. (1971) Fundamentals of Ecology. 3rd Edition, W. B. Saunders Co., Philadelphia. 547 p.

Parmele, L. H., Lemon, E. R. and Taylor, A. W. (1972) Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Poll. 1, 433-451.

Phillips, F. T. (1971) Persistence of organochlorine insecticides on different substrates under different environmental conditions. I. The rates of loss of dieldrin and aldrin by volatilization from glass surfaces. Pestic. Sci. 2, 255-266.

Phillips, F. T. (1974) Some aspects of volatilization of organochlorine insecticides. Chem. Ind. 5, 197-201.

Pielou, F. C. (1969) An Introduction to Mathematical Ecology. Wiley Interscience, New York, p. 19-22.

Pimentel, D. and Goodman, N. (1974) Environmental impact of pesticides. In Survival in Toxic Environments. (Eds. Khan, M. A. Q. and Bederka, J. B., Jr.), 25-52.

Plimmer, J. R., Kearney, P. C., Kaufman, D. D. and Guardia, F. S. (1967) Amitrole decomposition by free radical generating systems and by soils. J. Agric. Food Chem. 15, 996-999.

Popendorf, W. J. and Leffingwell, J. T. (1978) Natural variations in the decay and oxidation of parathion foliar residues. J. Agric. Food Chem. 26, 437-441.

Ritter, W. F., Johnson, H. P., Lovely, W. G. and Molnau, M. (1974) Atrazine, propachlor, and diazinon residues on small agricultural watersheds, runoff losses, persistence and movement. Environ. Sci. Technol. 8, 38-42.

Rohrbaugh, W. J., Meyers, E. K. and Jacobson, R. A. 1976. Crystal and molecular structure of organophosphorus insecticides.

Saltzman, S., L. Kliger and Yaron, B. (1972) Adsorption-desorption of parathion as affected by soil organic matter. J. Agric. Food Chem. 20, 1224-1226.

Schrader, G. (1963) Die entwichlung neuer insecktizider phosphazsaure-ester. Weinhein/Bergstr.: Verlag Chemie GmbH.

Schubert, O. E. (1972) Plant cover changes following herbicide applications in orchards. Weed Sci. 20, 124-127.

Schulz, K. R., Lichtenstein, E. P., Liang, T. T. and Fuhrmann, T. W. (1970) Persistence and degradation of azinphosmethyl in soils, as affected by formulation and mode of application. J. Econ. Entomol. 63, 432-438.

Smith, A. E. and Walker, A. (1977) A quantitative study of asulam persistence in soil. Pestic. Sci. 8, 449-456.

Smith, J. H., Mabey, W. R., Bohonos, N., Holt, B. R., Lee, S. S., Chou, T. W., Bomberger, D. C. and Mill, T. (1977) Environmental Pathways of Selected Chemicals in Freshwater Systems. EPA Report 600/7-77-113.

Smith, R. F. (1976) Insecticides and integrated pest management. In The Future for Insecticides, Needs and Prospects. Wiley Interscience, New York, p. 489-506.

Snider, R. M. (1979) The effects of azinphosmethyl (Guthion^R) on a population of Trachelipus rathkei (Isopoda) in a Michigan orchard. Pedobiol. 19, 99-105.

Snider, R. M. and Shaddy, J. H. (1980) The ecobiology of Trachelipus rathkei (Isopoda). Pedobiol. 20, 394-410.

Southwick, C. H. (1976) Ecology and the Quality of Our Environment. 2nd Ed., D. Van Nostrand, London. 426 p.

Spear, R. C., Popendorf, W. J., Leffingwell, J. T., and Jenkins, D. (1975) Parathion residues on citrus foliage. Decay and composition as related to worker hazard. J. Agric. Food Chem. 23, 808-810.

Spencer, W. F. and Claith, M. M. (1975) Vaporization of chemicals. In Environmental Dynamics of Pesticides. (Eds. Haque, R. and Freed, V. H.), p. 61-78. Plenum Press, New York.

Spencer, W. F. and Claith, M. M. (1977) The solid-air interface: transfer of organic pollutants between the solid-air interface. In Fate of Pollutants in the Air and Water Environments, Part I. (Ed. Suffet, I. H), p. 107-126. John Wiley and Sons, Inc., New York.

Spencer, W. F., Farmer, W. J. and Claith, M. M. (1973) Pesticide Volatilization. Residue Reviews 49, 1-47.

Staiff, D. C., Comer, S. W. and Foster, R. J. (1975) Residues of parathion and conversion products on apple and peach foliage resulting from repeated spray applications. Bull. Environ. Contam. Toxicol. 14, 135-139.

Stamper, J. H., Nigg, H. N. and Allen, J. C. (1979) Organophosphate insecticide disappearance from leaf surfaces: an alternative to first-order kinetics. Environ. Sci. Tech. 13, 1402-1405.

Steffens, W. and Wieneke, J. (1975) Influence of humidity and rain on uptake and metabolism of ^{14}C-azinphosmethyl in bean plants. Arch. Environ. Contam. Toxicol. 3, 364-370.

Steffens, W. and J. Wieneke. (1976) Studies on the uptake, metabolism and degradation of ^{14}C-labelled ^{R}Gusathion in kidney beans. Pflanzenschultz-nachrichten 29, 1-17.

Steiner, P. W. (1969) The distribution of spray material between target and non-target areas of a mature apple orchard by airblast equipment. M.S. Thesis, Cornell Univ.

Taylor, A. W. (1978) Post-application volatilization of pesticides under field conditions. J. Air Poll. Control Assoc. 28, 922-927.

Taylor, A. W., Glotfelty, D. E., Glass, B. L., Freeman, H. P. and Edwards, W. M. (1976) Volatilization of dieldrin and heptachlor from a maize field. J. Agric. Food Chem. 24, 625-631.

Taylor, A. W., Glotfelty, D. E., Turner, B. C., Silver, R. E., Freeman, H. P. and Weiss, A. (1977) Volatilization of dieldrin and heptachlor residues from field vegetation. J. Agric. Food Chem. 25, 542-548.

Teskey, B. J. E. and Shoemaker, J. S. (1978) Tree Fruit Production. AVI Publishing Co., Inc., Westport, Conn., 19-25.

Thompson, N. P. and Brooks, R. F. (1976) Disappearance of dislodgeable residues of five organophosphate pesticides on citrus leaves and fruit during dry and wet weather in Florida. Arch. Environ. Contam. Toxicol. 5, 55-61.

Turner, B. C. and Glotfelty, D. E. (1977) Field air sampling of pesticide vapors with polyurethane foam. Anal. Chem. 49, 7-10.

Van Dyk, L. P. (1974) The persistence of some pesticides on South African citrus. Environ. Qual. Safety, suppl. III, p. 330-335.

Van Dyk, L. P. (1976) Parathion persistence on South African citrus. Arch. Environ. Contam. Toxicol. 4, 289-311.

Walker, A. (1974) A simulation model for the prediction of herbicide persistence. J. Environ. Quality 3, 396-401.

Walker, A. (1976a) Simulation of herbicide persistence in soil. I. Simazine and Prometryne. Pestic. Sci. 7, 41-49.

Walker, A. (1976b) Simulation of herbicide persistence in soil. II. Simazine and Linuron Long-Term Experiments. Pestic. Sci. 7, 50-58.

Walker, A. (1976c) Simulation of herbicide persistence in soil. III. Propyzamide in Different Soil Types. Pestic. Sci. 7, 59-64.

Ware, G. W. (1980) Effects of pesticides on nontarget organisms. Residue Reviews 76, 173-201.

White, A. W., Jr., Harper, L. A., Leonard, R. A. and Turnbull, J. W. (1977) Trifluralin volatilization losses from a soybean field. J. Environ. Qual. 6, 105-110.

Whittaker, R. H. (1975) Communities and Ecosystems. MacMillan Publishing Co., New York.

Wineke, J. and Steffens, W. (1974) Degradation of ^{14}C-azinphos on glass plates as compared to the metabolism on bean leaves. Environ. Qual. Safety, Suppl. III., 544-548.

Williams, K. (1961) Note on the effect of rain, and sprinkler irrigation, on the persistence of spray residues of Guthion and Sevin on apple leaves. Can. J. Plant Sci. 41, 449-451.

Winterlin, W., Bailey, J. B., Langbehn, L. and Mourer, C. (1975) Degradation of parathion applied to peach leaves. Pest. Mont. J. 8, 263-269.

Woodrow, J. E., Seiber, J. N., Crosby, D. G., Moilanen, K. W., Soderquist, C. J. and Mourer, C. (1977) Airborne and surface residues of parathion and its conversion products in a treated plum orchard environment. Arch. Environ. Contam. Toxicol. 6, 175-191.

Yaron, B., Hever, B. and Birk, Y. (1974) Kinetics of azinphosmethyl losses in the soil environment. J. Agric. Food Chem. 22, 439-441.

Yates, W. E. and N. B. Akesson. (1973) Reducing pesticide chemical drift. In Pesticide Formulations. (Ed. Van Valkenburg, W.), p. 275-339. Marcel Dekker, Inc.

Zabik, M. J. and L. O. Ruzo. (1981) Factors Affecting Pesticide Photodecomposition Studies. In Test Protocols for Environmental Fate and Movement of Toxicants, p. 20-27. Proc. Symp. 94th Ann. Meeting Ass. of Offic. Anal. Chemists, Washington, D.C.

Zabik, M. J., Leavitt, R. A. and Su, G. C. (1976) Photochemistry of bioactive compounds: a review of pesticide photochemistry. Ann. Rev. Entomol. 21, 61-79.

Zepp, R. G., Wolfe, N. L., Gordon, J. A., and Baughman, G. L. (1975) Dynamics of 2,4-D esters in surface waters hydrolysis, photolysis, and vaporization. Environ. Sci. Tech. 9, 1144-1150.

Zepp, R. G. and Cline, David M. (1977) Rates of direct photolysis in aquatic environment. Environ. Sci. Tech. 11, 359-366.