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RITTER, William Frederick, 1942-  
ENVIRONMENTAL FACTORS AFFECTING THE MOVEMENT  
OF ATRAZINE, PROPACHLOR, AND DIAZINON IN IDA  
SILT LOAM.

Iowa State University, Ph.D., 1971  
Engineering, agricultural

University Microfilms, A XEROX Company, Ann Arbor, Michigan

**Environmental factors affecting the movement of atrazine,  
propachlor, and diazinon in Ida silt loam**

**by**

**William Frederick Ritter**

**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Major Subjects: Agricultural Engineering  
Sanitary Engineering (Civil Engineering)**

**Approved:**

Signature was redacted for privacy.

**In Charge of Major Work**

Signature was redacted for privacy.

**For the Major Departments**

Signature was redacted for privacy.

**For the Graduate College**

**Iowa State University  
Ames, Iowa**

**1971**

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## I. INTRODUCTION

In recent years, pesticides have been added to the list of environmental pollutants that have aroused national interest in both scientific and lay communities. Today, the public is demanding legislation against the use of some pesticides. In March, 1969, a shipment of 28,000 pounds of Coho salmon was halted by the U. S. Food and Drug Administration because of high concentrations of DDT. DDT has also been responsible for significant losses of lake trout fry in a New York fish hatchery. In 1964, 50 four-pound bags of over-age 15 percent parathion dust was dumped into the Peace River in Florida by a hired farm laborer. Parathion residues were found in the river water for 2 weeks after the parathion bags were discovered (Nicholson, 1970). The effect of pesticides on human health and on our ecosystem is not completely known.

Pesticides have helped protect our food and fiber from insects and other pests, and have reduced the number of man-hours required to produce a given quantity of crop. Without the use of agricultural chemicals, billions of dollars worth of food would be lost because of weeds, insects, and disease. Since the discovery and use of DDT in 1939, sales of pesticides have been increasing every year. Surveys and reports of industrial and government economists indicate that synthetic organic pesticide production is increasing at an annual rate of 15 percent with indicated sales of \$3 billion by 1975. Since 1963 sales of herbicides have increased 271 percent with a total sales in 1969 of \$800 million in the United States (Iowa Department of Agriculture, 1970).

With the need for increased food production and the concern for en-

vironmental pollution, it is the responsibility of scientists and engineers to develop pesticides and application techniques that will do an effective job of controlling weeds, insects, and disease, without polluting the environment. There is a lack of knowledge concerning the environmental hazards of many pesticides. Also, the processes by which pesticides move in the soil are not clearly understood. If scientists and engineers are to develop new application techniques and design equipment that will help provide more effective weed, insect, and disease control, and reduce the environmental pollution potential of pesticides, they need to gain a better understanding of the factors that affect pesticide movement in soils. This study was initiated to measure the losses of selected pesticides in runoff and sediment under field conditions and to gain a better understanding of the factors that affect pesticide movement in soils.



## II. OBJECTIVES

The main objectives of the research were:

1. To determine the losses of selected pesticides in runoff water and sediment from small agricultural watersheds planted to corn.
2. To determine the extent of vertical movement in the soil profile and the degradation of selected pesticides on small agricultural watersheds planted to corn under two tillage systems.
3. To gain a better understanding of the factors affecting movement of pesticides in soils and to describe the effect of soil moisture content, soil temperature, and bulk density on movement of selected pesticides in soil by molecular diffusion.

### III. LITERATURE REVIEW

Since 1965, a vast amount of literature has appeared on pesticides. Only selected articles directly related to the author's research were reviewed. Several books and symposium proceedings on pesticides have been published (American Chemical Society, 1966; Soil Science Society of America, 1966; Brady, 1967; Kearney and Kaufman, 1969; Gunther, 1970).

Most of the articles in symposium proceedings reviewed recent research findings and were very helpful in reviewing the pesticide literature.

The fate of pesticides in the soil-air-plant environment involves many complex processes. Figure 1 shows the major processes involved.

These are:

1. adsorption,
2. movement in soil,
3. photodecomposition,
4. microbial degradation,
5. chemical degradation,
6. plant uptake and translocation,
7. volatilization.

Articles related to each one of these processes were reviewed.

Lambert et al. (1965) classify the factors that affect the fate of any chemical applied to the soil into five major categories:

1. Type of soil:
  - a. makeup; clay, silt, sand, organic matter.
  - b. structure; bulk density, surface area, heterogeneity.

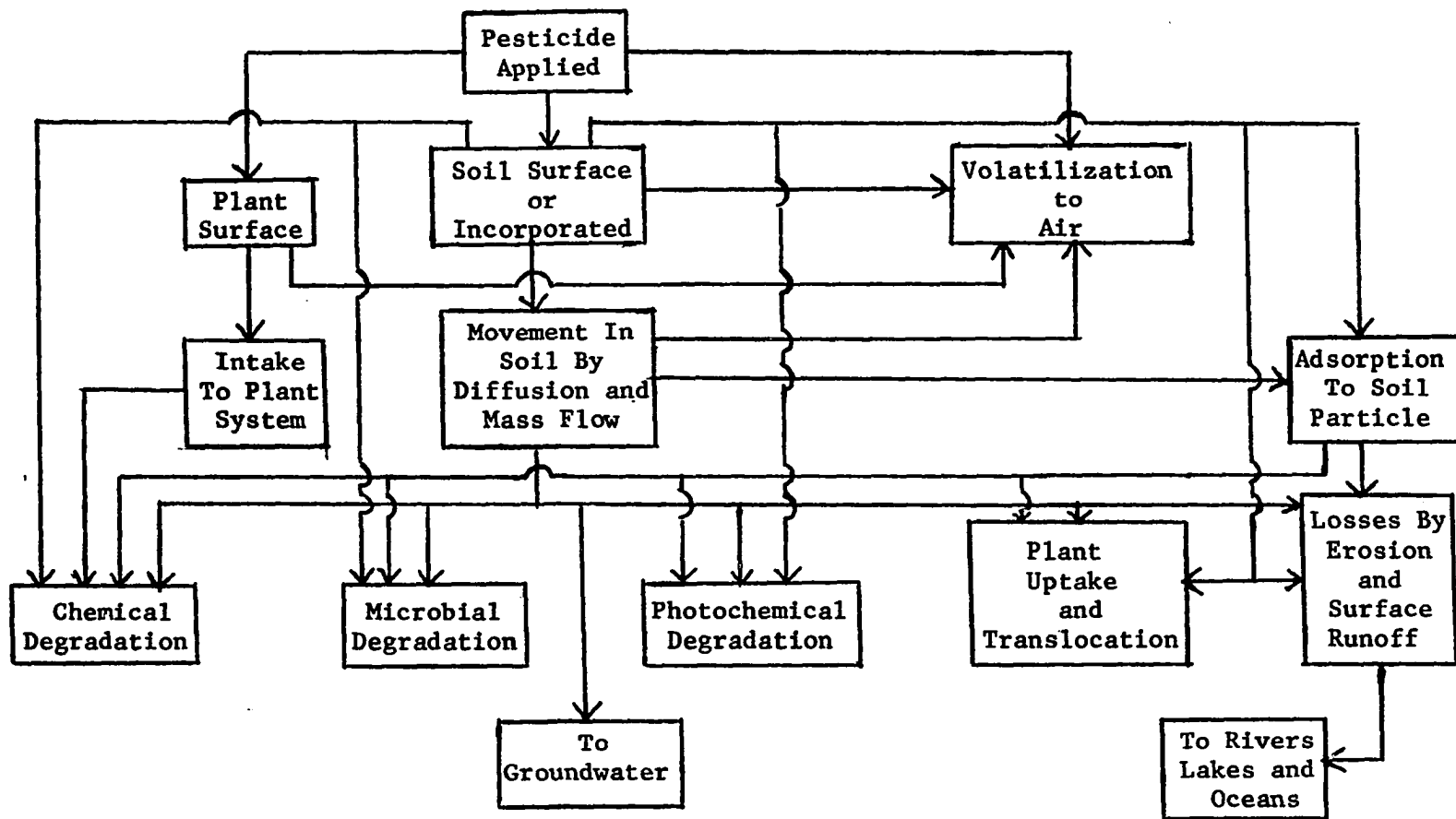


Figure 1. Flow diagram of processes that a pesticide may undergo in soil-air-plant environment

c. prior treatment; chemical, agricultural practices.

2. Type of chemical:

Physical properties, solubility, vapor pressure, stability, volatility.

3. Climatic conditions:

Rainfall, relative humidity, pressure, temperature, solar radiation.

4. Biological population:

Types, nutrient requirement, adaptations, life cycles.

5. Form of chemical:

Granular, wettable powder, solvent, emulsion.

#### A. Adsorption of Pesticides

Sorption, directly or indirectly, influences the other processes a pesticide may undergo. Adsorption appears to be one of the major factors affecting the interactions occurring between pesticides and soil colloids.

Several extensive literature reviews on adsorption have appeared in recent years. Bailey and White (1964) published a comprehensive review of research on adsorption and desorption of organic pesticides by soil colloids. They found such factors as soil type, physicochemical nature of the pesticide, soil reaction, nature of the saturating cation on the colloid exchange site, soil moisture content, form of chemical, and temperature all directly influence the adsorption of pesticides by soil systems, whereas the physical properties of the soil and climate exert only an indirect influence. Bailey and White (1970) published a second article

on adsorption in which the literature was reviewed through December, 1969. They briefly treated the adsorption theories of Freundlich, Langmuir, Gibbs, and Brunauer, Emmett, and Teller (BET).

Bailey, White, and Rothberg (1968) studied the adsorption of different classes of herbicides by montmorillonite. They found within a chemical group, basic in chemical character, the magnitude of adsorption was related to and governed by the degree of water solubility. The adsorption of basic compounds by montmorillonite clay systems was principally dependent upon the surface acidity and not the pH of the bulk solution, while the converse was true for the adsorption of acid type compounds. Most of the herbicides conformed to the Freundlich adsorption equation.

Several investigators have studied the adsorption of s-triazine herbicides. Weber (1970) discussed the mechanisms of adsorption of s-triazine herbicides by clay colloids. He found that s-triazines were adsorbed by montmorillonite, illite, and kaolinite clay minerals. Reduction in phytotoxicity of soil applied s-triazine was related to the amount of organic matter and the types and amounts of clay minerals in the soils. At the same symposium on s-triazine herbicides, Hayes (1970) discussed the role of soil organic matter in adsorption of s-triazines. He reviewed articles related to the effects of soil organic matter on triazine adsorption, phytotoxicity, and movement in soils. His discussion presented considerable evidence to demonstrate the importance of soil organic matter in adsorbing triazines, in reducing their phytotoxicity, and in affecting triazine movement in soils.

Nearpass (1967) found that adsorption of simazine and atrazine from

aqueous solutions by a Bayboro clay soil was dependent upon the exchange acidity of the soil. Simazine was adsorbed in greater amounts than atrazine. The degree of adsorption was similar when Ca, Mg, K, and Na were the saturating cations. Turner and Adams (1968) studied the adsorption of atrazine and atratone by anion- and cation-exchange resins. They found the amount of herbicide adsorbed varied with the type of herbicide and with the ion present at the exchange site.

Hance (1969) found adsorption of two urea herbicides, monuron and diuron, by montmorillonite, was insensitive to pH and exchange cation present. Adsorption of atrazine, atratone, simetryne, ametryne, and prometryne, was sensitive to pH and the exchange cation. These results indicate that adsorption of urea herbicides was physical, while adsorption of triazines was chemical in nature.

Weber and Weed (1968) found that paraquat and diaquat were adsorbed by kaolinitic and montmorillonite clay minerals to approximately the cation exchange capacity of the clays. In competitive ion studies paraquat was preferentially adsorbed over diaquat by both types of clay. In the same study, they found prometone was adsorbed in very small amounts by kaolinite clay and in large amounts on montmorillonite clay.

Huang and Liao (1970) studied the adsorption of the organochlorine insecticides; DDT, dieldrin, and heptachlor by illite, kaolinite, and montmorillonite. DDT and heptachlor adsorption was relatively irreversible, while some dieldrin desorption occurred. Adsorption on the nonexpandible clays illite and kaolinite was almost instantaneous, while adsorption of DDT and heptachlor on an expansible montmorillonite clay was gradual. Of the three pesticides studied, DDT was adsorbed in the largest quantity,

heptachlor was next, and dieldrin least.

#### B. Pesticide Movement in Soils

Pesticides can move in porous media by diffusion or mass flow in the liquid or vapor phases (Elrich et al., 1966a). Variables affecting pesticide movement include adsorption, solubility, flow rate and amount, rates of pesticide application, degradation, and formulation (Helling, 1970). In recent years several investigators have studied the movement of certain pesticides by molecular diffusion. Ehlers et al. (1969a, 1969b) studied lindane diffusion in soils and developed a model to describe the diffusion process. According to the model developed by Ehlers et al. (1969b), diffusion is a function of: (a) chemical properties of the pesticide, (b) soil moisture content, (c) soil temperature, and (d) soil structure.

Ehlers et al. (1969a) found that diffusion of lindane in Gila silt loam was strongly influenced by soil water content, bulk density, and soil temperature. In a similar study, using the same techniques, Farmer and Jensen (1970) found no correlation between soil texture and the diffusion coefficient of dieldrin. The diffusion coefficient in three soils varied between 0.40 and 0.64 mm<sup>2</sup>/week at 75 percent relative humidity and between 3.8 and 9.7 mm<sup>2</sup>/week at 95 percent relative humidity. At the high humidity, the diffusion coefficient increased with increasing clay content.

Lindstrom et al. (1968) developed a mathematical model for 2,4-D diffusion in saturated soils. They found the diffusion coefficient for 2,4-D under saturated conditions in nine soils was inversely related to the percent clay. Graham-Bryce (1969) reported the diffusion coefficients of

disulfoton and dimethoate, two organophosphate insecticides, in a silt loam soil varied little with the concentration of the two insecticides. The diffusion coefficients for dimethoate increased rapidly with increased soil moisture content. In contrast, diffusion coefficients for disulfoton, which is more volatile, less soluble, and more strongly adsorbed than dimethoate, were smaller and did not change much with soil moisture content.

Lavy (1968) studied the movement of three s-triazine compounds in the vicinity of plant roots growing in soil, by autoradiography. He found for a silty clay loam soil, atrazine and propazine moved by mass flow, while simazine moved by diffusion. For a sandy loam soil, atrazine moved by mass flow, simazine by diffusion, but no movement was observed for propazine. In a later paper Lavy (1970) measured diffusion coefficients for atrazine, simazine, and propazine in light soil types. He found atrazine diffused faster than simazine or propazine and that total surface area and organic matter were the most significant soil properties affecting the diffusion rate. Based on the relatively slow diffusion rates of the three s-triazines, Lavy (1970) concluded that molecular diffusion would not be expected to contribute significantly to the vertical movement of s-triazines in a soil profile.

Walker and Crawford (1970) studied diffusion of propazine and prometryne in six soils. The magnitude of their diffusion coefficients varied from  $1.5 \times 10^{-7} \text{ cm}^2/\text{sec}$  for propazine in a sandy soil to  $3.1 \times 10^{-9} \text{ cm}^2/\text{sec}$  for prometryne in an organic soil. In general, they found the diffusion coefficients for propazine and prometryne decreased in proportion to the extent of adsorption.



Green and Obien (1969) used the concept of herbicide partition into the adsorbed and solution phases in the soil to predict the effect of soil water content on the concentration of atrazine in solution. They concluded that the principal effect of soil water content on herbicide phytotoxicity probably was associated with herbicide transport, which was more sensitive to change in water content than the concentration of herbicide in soil solution.

Oddson, et al. (1970), from a purely mathematical approach, developed equations to describe the movement of organic chemicals through soil by mass flow and evaluated the equations for various soil conditions. Movement due to diffusion was assumed to be negligible. The model assumed the relationship

$$\frac{\partial S}{\partial t} = \alpha (KC - S) \quad (3-1)$$

where S is the adsorbed concentration (mass per total volume), C is the solution concentration (mass per total volume), t is time, and K and  $\alpha$  are constants. In their mathematical development, they also considered the effect of applying various amounts of chemical to the soil surface and allowed for a prior adsorbed concentration in the soil ahead of the wetting front.

The miscible displacement method has been used to study chemical movement in soils (Corey, 1966; Elrick et al., 1966b). Kay and Elrick (1967) studied the movement and adsorption of lindane by miscible displacement techniques. They tried to fit the chromatographic model

$$D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} - (1 + \rho_b P / \theta) \frac{\partial C}{\partial t} = 0 \quad (3-2)$$

to the movement of lindane through three types of soil, where

$D$  = dispersion coefficient  $\text{cm}^2/\text{hr}$ ,

$C$  = tracer concentration in solution  $\mu\text{g/ml}$ ,

$U$  = average pore water flow rate  $\text{cm/hr}$ ,

$\theta$  = average volumetric water content  $\text{cm}^3 \text{water} / \text{cm}^3 \text{bulk volume}$ ,

$\rho_b$  = bulk density  $\text{gm/cm}^3$ ,

$P$  = distribution coefficient between soil and water.

They found the model fit a Honeywood silt loam soil at a flow rate of 1.44  $\text{cm/hr}$ , but gave poor results for the other types of soil. Elrick and MacLean (1966) also used equation 3-2 to describe the movement and adsorption of 2,4-D in miscible displacement studies. They also found the model fit the Honeywood silt loam soil for 2,4-D at a moisture content of 84 percent of saturation, but did not fit several other soil types.

Several other attempts, beside those applied to miscible displacement studies, have been made to use chromatographic theory to describe movement of pesticides in soils. Lambert et al. (1965) developed a slotted tube technique to test the applicability of chromatographic theory to pesticide movement in soils. The slotted tube simulated a miniature field plot and utilized a chromatographic soil column. King and McCarty (1968) used a chromatographic model and a first order decay equation for pesticide degradation, to develop an elution curve for leaching studies with organo-

phosphate insecticides.

Leaching is one common method of studying pesticide movement in the laboratory. Commonly, the pesticide is applied to the top of the soil column and water is percolated through the soil column under saturated conditions. After leaching, the soil is sliced into sections and each segment is analyzed to obtain the distribution of pesticide in the profile. Rodgers (1968) found that the leaching of seven s-triazines in sandy loam corresponded poorly with solubility and that relative adsorption was a better predictor of s-triazine mobility. In Rodgers' experiment the order of leaching for the seven s-triazines was: atratone > propazine > atrazine > simazine > ipazine > ametryne > prometryne. Gray and Weierich (1968) found leaching was related to water solubility for five thiocarbamate herbicides. They also discovered the depth of leaching decreased as the clay and organic matter increased.

Harris (1969) studied the mobility of eleven insecticides in Hagerstown silty clay loam and Lakeland sandy loam by leaching through soil columns. He applied 2.5 cm of water to each soil column and after 3 days sliced the columns in sections and analyzed each section for the specific insecticide. His results revealed the organochlorine insecticides were immobile, phorate and disulfoton were only slightly mobile, and diazinon and thionazin were highly mobile. In an earlier study, Harris (1967) found s-triazines and substituted phenylureas were relatively immobile when compared to other herbicides. In comparing the two experiments, only thionazin showed as much mobility as the s-triazine and phenylurea herbicides.

Several research workers have studied pesticide movement in field

experiments. Dawson et al. (1968) applied simazine at 3 lb/A annually for 6 years on Warden silt loam in a low rainfall area (6-12 in/yr). They found simazine in the 4- to 8-inch depth 1 year after final application. In the same study, monuron and diuron were applied at a rate 7.2 lb/A. Monuron and diuron were recovered at the 8- to 12-inch depth. Higher concentrations of all three herbicides were found at the 0- to 4-inch depth.

Keys and Friesen (1968) found that most of the picloram applied to four different soils remained in the top 6 inches regardless of the application rate. Greater downward movement of picloram occurred in the low organic matter soils.

Several literature reviews of s-triazine movement in soil have been presented. Helling (1970) reviewed the literature through December 1968 and concluded that the s-triazines have low to moderate mobility, dependent on the soil adsorptive capacity and the triazine adsorptive strength. Harris et al. (1968) also concluded that the s-triazines were rather immobile in soil.

Molnau (1969) found initial soil moisture and environmental temperature were the most important parameters describing the movement of propachlor from a granule into Ida silt loam soil. For surface applied and incorporated granules, propachlor moved downward and laterally from the granule for soil at or below the wilting point. At higher soil moisture contents propachlor tended to move upward for incorporated granules, and horizontally for surface applied granules.

Mullins (1965) investigated the influence of initial soil moisture, air movement and surface applied water on the movement of CDAA from a

granule into soil. Movement of CDAA appeared to be either by gaseous diffusion or through water vapor acting as the transporting medium. For incorporated granules, it was found that movement was upwards for moist soils and downward for dry soils.

### C. Photochemical Degradation

Several investigators have demonstrated that s-triazines undergo photodecomposition. Comes and Timmons (1965) showed that atrazine and simazine on soil may be degraded by sunlight. They found soil sprayed with atrazine during the spring and exposed to sunlight lost 47 percent of the atrazine in 25 days and 73 percent in 60 days. Loss of atrazine from soil where light was excluded was negligible. In the summer, 65 to 80 percent of the atrazine was lost from soil in both the light and dark treatments. Soil temperatures in the summer ranged from 150° to 180°F, so volatilization of the herbicides may have occurred.

Jordon et al. (1970) observed loss of atrazine toxicity on soil irradiated with 311 m $\mu$  UV light for 240 hours. In an earlier study, Jordon et al. (1965) studied the effect on atrazine and simazine of UV light sources with peak emission at 254, 311, and 360 m $\mu$  for irradiation periods up to 500 hours. Loss of simazine and atrazine was rapid during the initial period of irradiation, but as time progressed, the rate of degradation decreased. The greatest loss of both herbicides occurred at 254 m $\mu$  and the least at 360 m $\mu$  of irradiation.

Many classes of herbicides besides the s-triazines undergo photochemical degradation. Crosby and Li (1969) have reviewed some of the different classes of herbicides that undergo photodecomposition. Sheets

(1963) has shown amiben, a benzoic acid derivative, will rapidly decompose in aqueous solution in the presence of sunlight or a fluorescent sunlamp. Picloram, also a benzoic acid derivative herbicide, is rapidly photolyzed under UV or sunlight irradiation in aqueous solution (Crosby and Li, 1969). Probst and Tepe (1969) discussed the photodecomposition of trifluralin. They postulated a portion of the reaction sequence of trifluralin photodecomposition based on identified degradation products. One of the intermediate products identified in the photodecomposition sequence was  $\alpha$ ,  $\alpha$ -trifluoro-6-nitro-2-nitroso-p-toludine.

There have been only a few field experiments that have successfully demonstrated pesticide photodecomposition. Slade (1966) demonstrated that paraquat decomposed photochemically to 1-methylpridinium-4-carboxylate on the leaves of different plants in sunlight. Kuwahara et al. (1965) showed that PCP was decomposed in rice-field water after several days exposure to sunlight.

#### D. Microbial Degradation

Degradation by soil microorganisms is an important factor affecting the persistence of pesticides in soils. Molecular configuration has an effect on the persistence and biodegradability of pesticides. Alexander and Aleem (1961) and Kaufman (1966) have tried to relate microbial degradation of pesticides to molecular structure. Kaufman (1966) found that the position, type, and number of halogen substituents are important factors affecting the microbial decomposition of both aliphatic and certain aromatic pesticides. Degradation of meta substituted chloro-

phenylcarbamates was more rapid than either ortho-chloro-, para-chloro-, or dichloro- substituted phenylcarbamates.

Kearney et al. (1967) stated that five conditions must be met before a pesticide molecule may be microbiologically degraded. These conditions are:

1. An organism that is effective in metabolizing a pesticide molecule must live in the soil or be capable of developing therein.
2. The compound must be in a form suitable for microbial degradation.
3. The chemical must be available to the organism.
4. The compound usually must be capable of inducing formation of the enzyme or enzymes appropriate for detoxication, because most enzymes require induction. Lack of induction may be caused by low solubility or low concentration of the pesticide.
5. Environmental conditions such as soil pH, soil temperature, and organic matter must be suitable, if the microorganism is to proliferate and the enzyme is to operate.

Kaufman and Kearney (1970) have presented an extensive review of microbial degradation of s-triazines. They concluded dealkylation and deamination are the major mechanisms of chloro-s-triazine biodegradation by microorganisms, although dehalogenation and hydroxylation have been reported. Hydroxy-s-triazines appear to be important degradation products of the chloro-s-triazines. Since they are non-phytotoxic, their formation represents a detoxication mechanism.

Harris et al. (1969) found residual phytotoxicities of s-triazines appear to follow the order of methoxy- > methylthio- > chloro-s-triazines. Kaufman and Kearney (1970) studied the utilization of methoxy-, methylthio- and chloro-analogues of simazine, atrazine, and propazine by asperigullus fumigatus. Chloro-s-triazines were most susceptible to utilization.

Degradation of s-triazines under anaerobic conditions has been observed, but is slow. Skipper (1966) observed that only small amounts of  $^{14}\text{CO}_2$  was evolved from chain-labelled atrazine treated soil under anaerobic conditions.

Bartha (1968) studied the biochemical transformations of several anilide herbicides. He found propanil, dicryl, and karsil were metabolized by soil microorganisms. Propanil was subject to the fastest degradation, dicryl decomposed more slowly and karsil was the most persistent.

Phenoxyalkanoic acids have been widely studied. Many organisms are capable of decomposing these herbicides. 2,4-D is the most quickly degraded of the phenoxyalkanoic acids, while MCPA persists somewhat longer, and soils receiving 2,4,5-T retain their toxicity longest (Kearney, 1966).

Patil et al. (1970) showed that twenty bacteria cultures that were capable of degrading dieldrin, also degraded endrin and DDT. Only thirteen of the different microbe populations were capable of degrading aldrin and none of the bacteria were able to degrade  $\gamma$ -BHC and Baygon.....

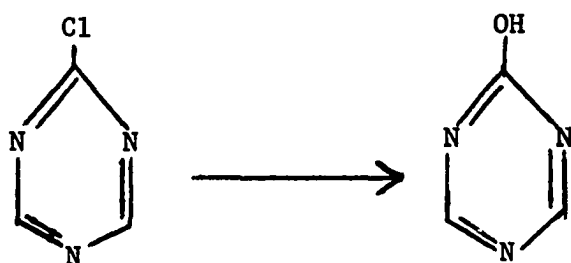
#### E. Chemical Degradation

A great amount of time and effort has been spent in recent years to identify the breakdown products of many pesticides. For some pesticides



detailed patterns of metabolic pathways have been constructed. In this section on chemical degradation, articles on biochemical and nonbiological degradation were reviewed.

Much evidence for the biochemical degradation of s-triazines by plants has been collected. Three major degradation pathways are evident: hydrolysis at C atom 2, N-dealkylation at C atoms 4 and 6, and splitting of the triazine ring (Knuesli et al., 1969). Of the three degradation pathways, the greatest breakdown of chlorotriazines is by chemical hydrolysis. Most in vivo degradation studies of s-triazines in plants have demonstrated the formation of hydroxytriazines.



Chemical hydrolysis of s-triazines also occurs in nonbiological systems. Skipper et al. (1967) showed that nonbiological hydrolysis was one of the major pathways of atrazine degradation. In greenhouse studies, they compared the loss of phytotoxicity of atrazine with  $^{14}\text{CO}_2$  evolution from ring-labelled and chain-labelled atrazine from microbial isolates and soil. Hydroxyatrazine accounted for approximately 20 percent of the extracted  $^{14}\text{C}$  activity after 2 or 4 weeks incubation of  $^{14}\text{C}$ -atrazine in nonsterile or sterile soils.

Jaworski (1969) proposed that two major mechanisms were responsible for the rapid detoxification of chloroacetoamide and chloroacetanilide

herbicides by plants. One mechanism involved a reaction of the  $\searrow$  halogen with endogenous substrates leading to the formation of water-soluble acidic metabolites, and the other involved the cleavage of the amide linkage and hydrolysis of the  $\searrow$  halogen.

Jaworski (1969) reported the results of some degradation studies of CDAA and 2-chloro-N-isopropylacetanilide (propachlor). Propachlor was taken up rapidly by both corn and soybean plants. In corn and soybeans it was metabolized to a water-soluble acidic metabolite. The absolute structure of this metabolite has not been defined, but it is known that the metabolite contains essentially the entire structure of the original herbicide, with the exception that the chloro-group appears to be displaced.

Geissbuhler (1969) stated that urea herbicides can undergo biochemical and enzymatic degradation by two pathways. The first mechanism is by N-dealkylation and the second major pathway is ring hydroxylation.

Methyl- and phenylcarbamate pesticides can undergo degradation by a number of pathways. Herrett (1969) proposes the major degradation mechanisms of these pesticides are by hydrolysis, hydroxylation, N-dealkylation, sulfur oxidation, and conjugate formation.

Konrad et al. (1967) found chemical hydrolysis was the main mechanism of degradation of diazinon in soils. Microbial degradation did not contribute to the breakdown of diazinon in the soils used by Konrad et al. (1967). Major breakdown products from chemical hydrolysis were 2-isopropyl-4-methyl-6-hydroxypyrimidine and diethylthiophosphoric acid.

## F. Plant Uptake and Translocation

Many pesticides are taken in by the plant roots and translocated to different areas of the plant. Some pesticides are biochemically degraded within the plant, which is one method of pesticide decontamination.

Toxicologists are concerned with pesticide residues in plants when they are used for animal feed. At harvest time, Caro (1971) found over 1.8 ppm of dieldrin in the lower leaves of corn plants. The corn plants were harvested from a watershed where 5 lb/A of dieldrin had been applied in the spring. Such high concentrations of dieldrin would make the corn plants unacceptable for dairy cattle fodder. He also found dieldrin concentrations increased in the corn plants as the growing season progressed. Heptachlor concentrations were much more constant over the season.

Nash et al. (1970) studied the uptake of DDT, dieldrin, endrin, and heptachlor by cotton and soybean plants. These plants did not provide an effective way of removing organochlorine insecticide residues from contaminated soils. No DDT was removed by cotton or soybeans from the soil, and only 1.5 percent of the heptachlor was removed by cotton plants. More endrin was removed from a sandy loam soil than a silty clay loam soil.

Triazine herbicides are taken up by different plant species. Sikka and Davis (1968) found cotton and soybeans absorbed essentially equal amounts of prometryne. Both cotton and soybean plants absorbed the most prometryne during the first 12 hours from a water solution and absorption stopped after 36 hours. After 2 days the shoots of cotton plants contained 37 percent of the prometryne and the roots contained 63 percent. For

soybean plants 23 percent of the pesticide was found in the roots and 77 percent in the shoots. Roeth and Lavy (1971) found concentrations of atrazine were two to three times greater in sudangrass and sorghum than in corn. Concentrations in all three types of plants reached a peak after 2 weeks of growth and then declined.

Lichtenstein et al. (1967) found aldrin, parathion and lindane present in pea roots and greens growing in sand when these chemicals were applied to the sand at concentrations 5 ppm. No diazinon was detected in the greens and only small amounts were detected in the roots at a dosage of 5 ppm. With a 25 ppm dosage, 0.27 ppm of diazinon was detected in the greens and 9.45 ppm were detected in the roots of the peas 15 days after the pesticide was applied. Kansouh and Hopkins (1968) found diazinon was readily absorbed from aqueous solutions by bean plant roots. Only small amounts of diazinon were translocated to the foliage where they were readily hydrolyzed. It appears diazinon will not accumulate to any dangerous levels in plant leaves that would make the foliage unsafe for animal consumption.

#### G. Volatilization

Volatilization influences the loss of pesticides from the soil. Pesticides like IPC and EPTC are incorporated into the soil upon application to prevent large losses by volatilization. The rate of loss is related to soil properties, moisture, temperature, and the physical and chemical properties of the pesticide (Jordon et al., 1970).

Several investigators have measured losses of organochlorine insecticides under field conditions. Willis et al. (1969) used a system comprised

of a stainless steel boom with regularly spaced ports, stainless steel regulating valve, vapor trap of ethylene glycol, pressure-vacuum pump, and flow meter to monitor atmospheric concentrations of endrin. They measured a maximum concentration of  $540 \text{ ng/m}^3$  air of endrin during a 3-day period after application to sugarcane at 4 feet above the soil surface. The concentrations in the atmosphere decreased asymptotically to  $30 \text{ ng/m}^3$ , 77 days later. Estimates based on a mean lateral air movement of 0.1 mph through the plot indicated a volatilization loss of 5 percent of the total endrin applied.

Willis et al. (1971), using the same vapor trapping apparatus used to monitor endrin, measured volatilization losses of DDT and DDD from flooded and nonflooded plots. Flooding treatment effectively retarded the volatilization of both pesticides. Cumulative recovery of DDT after 172 days, at 10 and 30 cm above the nonflooded plot was 20,335 and 13,520 ng, while corresponding values for the flooded plot were 4,960 and 2,639 ng. Cumulative recovery of DDD at the same time, 10 and 30 cm above the nonflooded plot was 15,985 and 7,090 ng while a total of 1,520 and 1,050 ng was recovered from the flooded plot.

Caro and Taylor (1971) found volatilization was the major pathway of dieldrin loss from soils under field conditions. Within one season horizontal filter traps collected 2.9 percent of the dieldrin applied to the underlying soil. The filter was not installed until 4 weeks after application, so total loss of dieldrin by volatilization probably would be greater than 2.9 percent.

Kearney et al. (1964) studied the volatility of seven s-triazine

herbicides from nickel planchets and soil surfaces. The herbicides volatilized more slowly from soils than from metal planchets. They found soil type influenced vapor loss of prometon, had less influence on atrazine, and had little effect on loss of simazine. Soil moisture also had an influence on the amounts of s-triazines volatilized. Simazine appeared to be more volatile from dry soil. Prometryne and ametryne, and to a lesser extent prometon, atrazine, and trietazine, were less volatile from a dry soil than a wet soil. Propazine volatility was not influenced by soil moisture.

Mullins (1965) found soil moisture influenced the volatilization of CDAA granules. In 48 hours, four times as much CDAA was lost by volatilization from a soil surface, initially at field capacity, than from an air dry soil surface. Losses were less for incorporated granules than for surface applied granules.

Several investigators have studied the volatilization of certain carbamate herbicides. Parochetti and Warren (1966) studied the vapor losses of IPC and CIPC from a soil surface as influenced by temperature, soil moisture, soil type, air-flow rate, and formulation. They found IPC was more volatile than CIPC. Vapor loss of both herbicides increased with increasing air-flow rate and temperature. An increase in percent clay, organic matter and cation exchange capacity increased losses from moist soil. They also found that vapor losses of IPC from granules were much higher than from a surface spray, while CIPC losses were about the same for granules as from a spray application.

Gray (1965) investigated the amount of EPTC lost by volatilization from six different soil types. On dry soils, the least loss of EPTC vapor

occurred from the soils highest in clay content, and the greatest loss occurred from sand. Large losses of EPTC occurred on all soil types when they were wet.

In another study, Gray and Weierich (1964) found the most important factor affecting the loss of EPTC from soil was the amount of moisture in the soil. EPTC vapor losses were 23, 49, and 69 percent after 1 day, and 44, 68, and 90 percent after 6 days on dry, moist, and wet soils, respectively.

#### H. Pesticides in Water and Sediment

In the past 10 years, many research workers have measured the concentrations of organochlorine insecticides in rivers. Only a few papers have been published in which investigators have analyzed surface runoff and sediment samples for herbicide residues.

White et al. (1967) measured atrazine losses in water and sediment from fallow plots of Cecil sandy loam soil. They found, using a rainfall simulator, that a 1 hour storm of 2.5 in/hr, occurring 96 hours after atrazine was applied at 3 lb/A caused atrazine losses of 7.3 percent. A storm of the same intensity and duration occurring 1 hour after atrazine application, caused atrazine losses of 18 percent. Losses of atrazine were lower for storms of less intensity. Atrazine concentrations were highest in the runoff and sediment during early stages of runoff. Concentrations were higher in the sediment than the water. However, most of the atrazine transported was associated with the water fraction because of the greater amounts of water lost as compared to soil.

Sheets and Lutz (1969) measured losses of picloram, dicamba, 2,4,5-T, and 2,4-D in surface runoff from two watersheds at 4.64 acres and 3.66 acres. Their results showed low concentrations of 2,4-D, 2,4,5-T, and picloram in the runoff water. Dicamba concentrations were less than 1 ppb in any of the runoff samples collected from the watersheds. The concentrations varied directly with the rate of application and percent of the area sprayed with pesticide.

Trichell et al. (1968) compared losses of dicamba, picloram and 2,4,5-T from fallow and from sod plots. Picloram and dicamba losses were greater from sod plots than from fallow plots, but 2,4,5-T losses were about equal from the two-plot types. The concentrations in runoff water from a sod plot after a simulated rainfall were 4.81, 3.30, and 2.17 ppm for dicamba, 2,4,5-T, and picloram, respectively.

Barnett et al. (1967) compared losses of ester and amino forms of 2,4-D in runoff and sediment mixtures from cultivated fallow plots of Cecil sandy loam soil. Concentrations of 2,4-D in the water and sediment were positively correlated with the rate applied, were greatest early in each storm, and decreased with duration of the storm. The ester formulation concentrations in washoff were more than 4 times the amine form.

Caro and Taylor (1971) found dieldrin losses in sediment and in runoff water reached 2.2 percent and 0.07 percent of the 5 lb/A application, respectively. Largest losses of dieldrin in the runoff water occurred in the first 2 months after application. Highest dieldrin concentrations in the water were 20 ppb shortly after application and were always less than 2 ppb in the second year of sampling.

Johnson and Morris (1971) found dieldrin, DDT, and DDE in a majority



of water samples taken from Iowa rivers from 1968-1970. Dieldrin was found in 40 percent of 179 water samples analyzed, DDT was detected in 19 percent, and DDE in 14.5 percent. The pesticide concentrations varied from year to year and from season to season. Concentrations were highest in rivers where heavy row-crop agriculture was located.

Haan (1970) studied the movement of aldrin, dieldrin, and DDT by runoff and erosion on small fallow sprinkled plots of Maury silt loam soil on a 1 to 2 percent slope. He found the total amount of pesticide carried in the sediment was more than twice the total amount carried in the water.

In another runoff study, Epstein and Grant (1968) reported DDT, endrin, and endosulfan concentrations were lower in runoff from plots in a potato, oat, sod rotation than from continuous potato plots. More pesticide was found in the water than in the settled muds.

Yule and Tomlin (1971) measured DDT concentrations in the Miramichi River of New Brunswick before, during, and up to 2 years after the final application of DDT to the forests in the area. Their results showed that the stream water contained less than 0.5 ppb DDT before the 1967 forest treatment. The amount in the water increased to 17 ppb during the aerial application of DDT, and declined within a few hours to a level similar to pre-spray amounts, where it remained relatively steady for the following 2 years.

Lichtenberg et al. (1970) summarized the results of 5 annual synoptic surveys (1964-68) for organochlorine pesticides in surface waters of the United States. Organochlorine pesticide concentrations reached a peak in 1966 and declined in 1967 and 1968. Dieldrin and DDT and its breakdown products DDE and DDD were the insecticides most frequently detected

throughout the 5-year period. Maximum concentrations detected did not exceed permissible limits as they relate to human intake directly from a domestic water supply.

Lauderdale (1969) found concentrations of 10.2, 46.9, 48.8, and 97.0 ppb of aldrin, dieldrin, chlordane, and DDT, respectively, in surface runoff from a storm that occurred 2 days after DDT, aldrin, and chlordane were applied to a grass watershed at rates of 3.87 lb/A, 7.74 lb/A, and 15.48 lb/A, respectively. In subsequent storms, the amounts of insecticide found in runoff samples were generally lower than the first concentrations by a factor of about ten. There was a significant increase in the concentrations of chlordane and dieldrin found in the surface runoff the following spring. Lauderdale concluded this could be due to the action of freezing and thawing which would expose more soil surface to leaching during the spring rains.

Zweig and Devine (1969) surveyed New York State groundwaters and natural watersheds for organophosphate pesticide contamination. From 1964-1966 they collected 82 water samples from different locations that showed no organophosphate pesticide contamination. In 1967 one water sample from a farm pond contained 0.13 ppb of ethion. Mud samples from the same pond showed ethion concentrations of 0.04 ppm (1966) and 0.21 ppm (1967). Frank et al. (1970) found dalapon, TCA, and 2,4-D present in irrigation waters, following bank applications of these herbicides for weed control. Concentrations of dalapon varied from 23 to 365 ppb from application rates of 6.7 to 20 lb/A. The maximum concentrations of TCA ranged from 31 to 128 ppb following applications of 3.8 to 5.9 lb/A.

Applications of 1.9 to 3 lb/A of 2,4-D produced maximum concentrations of 25 to 61 ppb.

## I. Pesticide Analysis

Pesticide residue analysis can be divided into three separate phases:

- (1) extraction of the pesticide from the source, (2) sample cleanup, and
- (3) identification and quantitative determination of the pesticide.

Manuals dealing with pesticide residue analysis compiled by Burchfield and Johnson (1965) and the United States Department of Health, Education, and Welfare (1968) give a complete discussion of each of the phases of pesticide residue analysis. Several volumes edited by Zweig (1964a, 1964b, 1967) on analytical methods for pesticides, plant growth regulators and food additives, also present analysis procedures for certain herbicides and insecticides. Thornburg (1969, 1971) has presented two literature reviews on pesticide residue analysis. Both articles have over 200 references.

### 1. Extraction of pesticides

Extraction procedures for soil, plant, water, and animal samples differ to some extent. Pesticides are easier to extract from soil and water samples than from plant and animal samples because fats, oils, and waxes are not present in soil and water samples as in animal and plant tissue.

Soxhlet extraction and some form of shaking are two methods of extracting pesticides from soils (Burchfield and Johnson, 1965).

Generally, a soxhlet extractor will give higher extraction efficiencies

but is more time consuming (McGlamery et al., 1967).

A variety of solvents are available for extracting pesticides from soils. Molnau (1969) used acetonitrile and mechanical shaking to extract propachlor from soil. He found the extraction efficiency varied with soil moisture content, but in all cases over 80 percent of the pesticide was recovered from the soil samples. Mullins (1965) used benzene, acetone, and a 4:1 hexane-benzene mixture for shaking extraction of CDAA from soil. He found acetone gave the highest extraction efficiency, but benzene absorbed no water and less organic matter than acetone and extracted 93 percent as much CDAA as acetone. The acetone extraction efficiencies varied from 58.9 percent for Luton soil to 67.0 percent for Ida silt loam soil. McGlamery et al. (1967) found methanol and chloroform gave extraction efficiencies of 91.9 and 87.5 percent for extracting atrazine from Drummer clay loam with a soxhlet extractor. Chloroform has also been used for extraction of other triazine herbicides (Childwell and Hughes, 1962). Some of the other solvents that have been used for soil extraction are hexane for organo-chlorine insecticides (Bowman et al., 1965), acetone for organophosphate insecticides (Getzin and Rosefield, 1966), and benzene for diazinon (Konrad et al., 1967).

There are fewer solvents available for extracting pesticides from water than from soils. Common solvents used for pesticide extraction from water are hexane, petroleum ether, benzene, ethyl ether, and chloroform. Generally, water samples also have fewer interferences than soil samples.

The United States Department of Interior, Federal Water Pollution Control Administration (1969) used a mixture of 15 percent ethyl ether in

hexane for extracting organochlorine insecticides from water samples. For an electron capture detector they use a 1-liter water sample and extract it twice with 60 ml of solvent. Extraction is carried out in a 2-liter separatory funnel and the water-solvent mixture is shaken vigorously for 2 minutes. Several authors discussed different methods for water extraction. Faust and Suffet (1966) presented in a comprehensive literature review, serial and continuous extraction procedures. Burchfield and Johnson (1965) also discussed a batch method that utilizes a separatory funnel and a continuous extraction method. The continuous extraction method reviewed in both references was developed by Kahn and Wayman (1964) for extraction of several organochlorine insecticides from natural waters with petroleum ether. Konrad and coworkers (1969) presented a method for extracting organophosphate and organochlorine insecticides from lake waters by use of benzene as solvent. By using 500 ml of water and 25 ml of benzene and shaking for 2 minutes in a separatory funnel, they obtain extraction efficiencies from 94 to 99 percent for organophosphate insecticides. Askew et al. (1969) found chloroform was the most suitable solvent for extracting a number of organophosphate insecticides from water.

## 2. Sample cleanup

In most cases, pesticide water samples do not require cleanup before being analyzed. The most elaborate cleanup procedures are used on pesticide residue samples of plants and animals. Morley (1966) has presented an extensive review of different adsorbents and their application to cleanup of pesticide residues. The most widely used adsorbents are alumina,

silica gel, florisil, carbon, and magnesia. Florisil is an excellent adsorbent for organochlorine residues but is not satisfactory for organophosphates.

McGlamery et al. (1967) tried several cleanup procedures for methanol extracts of atrazine from soils. They found that a cleanup procedure using grade IV or V basic alumina columns was the most successful. Other procedures tested were solvent partition methods that use acetonitrile and petroleum ether and aqueous methanol and carbon tetrachloride at 1:1 ratios.

Radomski and Rey (1970) used thin-layer chromatography to clean up animal tissue extracts of organochlorine insecticides. In this procedure the pesticides migrate further than the impurities on the thin-layer plates so they can then be separated for analysis by gas chromatography.

### 3. Detection of pesticides

The main methods used for identification and determining amounts of pesticide residues are gas chromatography, thin-layer chromatography, infrared spectroscopy, NMR, and colorimetric methods. Today for most routine pesticide analysis, gas chromatography is replacing many of the older colorimetric procedures.

The most common type of detectors used in gas chromatograph systems for pesticide analysis are electron-capture, flame ionization, and microcoulometric. The flame photometric detector, developed by Brody and Chaney (1966) is also gaining some popularity for analysis of organophosphates. The electron capture detector, which will detect chlorine, iron, phosphorus, sulfur and other ions that have an affinity for electrons, is the most

widely used detector. It is not a good detector for identifying unknown pesticide residues because of its lack of specificity. The source of free electrons in the electron capture detector is usually radioactive tritium or nickel-63. The main advantage of the nickel-63 source is that it can be operated at temperatures up to 400°C, whereas the maximum operating temperature for tritium is 225°C.

The microcoulometric detector has a great specificity for halogen- or sulfur-containing pesticides (Zweig, 1967). It is not as sensitive as the electron capture detector and the initial cost is higher, but it has greater specificity than the electron-capture detector.

The flame ionization detector is not as sensitive as the electron capture detector and is not very specific. It is an inexpensive detector, reasonably stable, moderately flow insensitive, and linear over a wide concentration range.

Many types of liquid phases and solid supports are available for columns for pesticide analysis by gas chromatography. Retention times and detection limits of many pesticides for a great variety of columns with different liquid phase are available in the literature. Burchfield and Johnson (1965) recommend 10 percent DC-200 on 80/90 mesh Anakron ABS in a six foot glass column and also a QF-1 and SE-30 mixture on 80/90 mesh Anakrom ABS for most pesticide residue analysis. The United States Department of Interior, Federal Water Pollution Control Administration (1969) recommends a 5 percent OV-17 on 60/80 mesh Gas-Chrom Q and a mixture of 5 percent QF-1 and 3 percent DC-200 on 60/80 Gas-Chrom Q for analysis of organochlorine pesticides in water.

Mattson et al. (1970) discussed the analysis of s-triazine herbicides

in soil. The three major methods for quantitative determination of triazine herbicides discussed were ultraviolet spectrophotometry, colorimetric spectrophotometry, and gas chromatography. The microcoulometric detector is the most common detector used for triazine analysis (Mattson et al., 1965). Today, it is replacing the ultraviolet method for triazine analysis in most laboratories. The ultraviolet method was one of the methods first used for triazine analysis. Knuesli et al., (1964) described this method for simazine analysis.

#### J. Summary

A vast amount of literature has appeared on the s-triazine pesticides in recent years. There has also been considerable work reported on organochlorine insecticides. Generally herbicides are more mobile in soils than insecticides. The chemical properties of the soil and environmental properties have a great influence on the movement of pesticides in soil. Pesticides would not be as mobile in soils with a high organic content or high clay content as in other soil types.

Most pesticides are degraded by soil microorganisms to some extent. The major degradation pathway for the s-triazine herbicides is by biochemical degradation by plants. The chlorotriazines like atrazine decompose mostly by chemical hydrolysis. Most organophosphates also are degraded by chemical hydrolysis.

More research has been done on the s-triazine herbicides than the chloroacetoamide and chloroacetanilide herbicides. Based on the results of most adsorption and pesticide movement studies, compounds like propachlor and CDAA will probably move more rapidly in the soil profile



than atrazine or other s-triazines. Propachlor and CDAA will also degrade more rapidly than atrazine. Organochlorine insecticides are the most persistent class of pesticides.

Concentrations of pesticides found in surface runoff and sediment will usually be small. Generally higher concentrations of pesticide are found in the sediment than in the surface runoff. Organochlorine insecticides may be detected in surface runoff and sediment several years after they are applied to the soil.

Table 1. Chemical and common names for pesticides mentioned in the literature review

Common Name	Chemical Name
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene
Ametryne	2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine
Amiben	3-amino-2,5-dichlorobenzoic acid
Atratone	2-(ethylamino)-4-(isopropylamino)-6-methoxy-s-triazine
Atrazine	2-chloro-4(ethylamino)-6-(isopropylamino)-s-triazine
Baygon	2-isopropoxyphenyl N-methyl-carbamate
CDAA	N,N-diallyl-2-chloroacetamide
Chlordane	1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
CIPC	Isopropyl N-(3-chloro-phenyl) carbamate
Dalapon	2,2-dichloropropionic acid
p,p'-DDD	2,2-bis-(p-chlorophenyl)-1,1-dichloroethane
p,p'-DDE	2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene
p,p'-DDT	1,1-bis-(p-chlorophenyl)-2,2,2-trichloroethane

Table 1 (Continued)

Common Name	Chemical Name
Diazinon	0,0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
Dicamba	3,6-dichloro-o-anisic acid
Dicryl	3',4'-dichloro-2 methylacrylanilide
Dieldrin	1,2,3,4,10,10-hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, exo-5,8-dimethanonaphthalene
Dimethoate	0,0-dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate
Diquat	1,1'-ethylene-2,2'-dipyridylum dibromide
Disulfoton	diethyl S-2-(ethylthio) ethyl phosphorodithioate
Diuron	3-(3-4-dichlorophenyl)-1,1-dimethylurea
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-endo-5,8-dimethanonaphthalene
EPTC	S-ethyl,N,N-dipropylthiolcarbamate
Ethion	0,0,0',0'-tetraethyl S,S'-methylene bisphosphorodithioate
Heptachlor	1,4,5,6,7,8,8a-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Ipazine	2-chloro-4-(diethylamino)-6-(isopropylamino)-s-triazine
IPC	Isopropyl-N-phenylcarbamate
Karsil	3',4'-dichloro-2-methylpentanilide
Lindane	1,2,3,4,5,6-hexachlorocyclohexane
MCPA	4-chloro-2-methylphenoxy-acetic acid
Monuron	3-(p-chlorophenyl)-1,1-dimethylurea
Paraquat	1,1'-dimethyl-4,4'-bipyridylum-ion
Parathion	0,0-diethyl 0-p-nitrophenyl phosphorothioate

Table 1 (Continued)

Common Name	Chemical Name
PCP	Pentachlorophenol
Phorate	0,0,-diethyl S-(ethylthio) methyl phosphorodithioate
Picloram	4-amino-3,5,6-trichloropicolinic acid
Prometone	2,4-bis(isopropylamino)-6-methoxy-s-triazine
Prometryne	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine
Propachlor	2-chloro-N-isopropylacetanilide
Propanil	3',4'-dichloropropionanilide
Propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine
Simazine	2-chloro-4,6-bis(ethylamino)-s-triazine
Simetryne	2-methylthio-4,6-bis-(ethylamino)-s-triazine
TCA	Trichloroacetic acid
Thionazin	0,0'-diethyl 0,2-pyrazinyl phosphorothioate
Trietazine	2-chloro-4-diethylamino-6-ethylamino-s-triazine
Trifluralin	$\alpha,\alpha,\alpha$ ,-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
$\gamma$ -BHC	Gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane
2,4-D	2,4-dichlorophenoxy-acetic acid
2,4,5-T	2,4,5-trichlorophenoxy-acetic acid

#### IV. ANALYTICAL METHODS

##### A. Atrazine

Atrazine is an s-triazine herbicide used to control many broadleaf and grassy weeds. Some of the chemical and physical properties of atrazine are given in Table 2.

##### 1. Extraction of atrazine from soil, water, and sediment samples

The extraction procedures used for soil, water, and sediment samples were similar to the techniques recommended by Geigy Chemical Corporation (1965). Chloroform was used as a solvent for both the water and soil samples. A mechanical shaker was used to obtain surface extraction for all of the soil and sediment samples. Atrazine water samples were shaken in a 500 ml separatory funnel.

The general procedure for extracting soil and sediment samples was as follows:

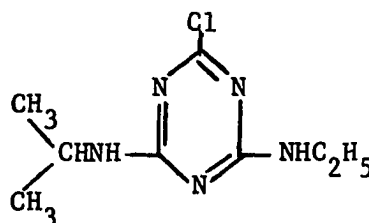
1. The clods were broken up and sieved with a number 8 sieve.
2. Forty grams of soil were selected for analysis and approximately 10 grams for a moisture content sample.
3. The soil moisture sample was dried at 105°C for 24 hours.
4. The 40 gram sample was extracted with 120 ml of chloroform for 30 minutes.
5. Two teaspoons of anhydrous sodium sulfate were added to the soil-chloroform mixture.
6. The soil-chloroform mixture was filtered with a Buchner funnel and filter flask.

Table 2. Chemical and physical properties of atrazine<sup>a</sup>

Chemical name: 2-chloro-4-ethylamino-6-isopropylamino-s-triazine

Trade name AAtrex

Formula:



Molecular weight: 215.7

Molecular formula:  $C_8H_{14}ClN_5$

Physical state: White, crystalline

Melting point: 173-175°C

Vapor pressure:	Temperature °C	mm Hg
	10	$5.7 \times 10^{-8}$
	20	$3.0 \times 10^{-7}$
	30	$1.4 \times 10^{-6}$
	50	$2.3 \times 10^{-5}$

Solubility:	Solvent	Temperature °C	Solubility (ppmw)
	Chloroform	27	52,000
	Methanol	27	18,000
	N-Pentane	27	360
	Petroleum ether	27	12,000
	Water	0	22
	Water	27	70
	Water	85	320

Toxicity LD<sub>50</sub> in rats, 3080 mg/kg  
LD<sub>50</sub> in mice, 1750 mg/kg

Formulations: wettable powder, 50%, 65%, and 80% granules, 2% dust, 8%

<sup>a</sup>Source: Weed Society of America, 1967; Farm Chemical Handbook, 1971

7. Eighty ml of the chloroform extract were saved for the hydroxy conversion process.

Less than 40 grams of soil and less than 120 ml of solvent were used for sediment samples, since in some cases there were not 40 grams of sediment available for analysis. For the laboratory experiments, the entire soil core was analyzed. Soil samples ranged from 65 to 108 grams and either 120 or 130 ml of solvent were used to extract the atrazine from the soil. Neither the soil, sediment, or water samples required any cleanup after extraction.

The general procedure used for extracting water samples was as follows:

1. Two hundred ml of the water sample were placed in a clean 500 ml separatory funnel.
2. Fifty ml of chloroform were added to the sample and the chloroform-water mixture was hand shaken for 90 seconds.
3. Upon separation of the two layers, the chloroform layer (bottom layer) was removed from the separatory funnel and placed in a clean flask.
4. A second 50 ml of chloroform was added to the water sample and again hand shaken for 90 seconds.
5. Upon separation of the two layers, the chloroform layer was removed from the separatory funnel and combined with the chloroform from the first extraction.
6. Two teaspoons of anhydrous sodium sulfate were added to the chloroform extract to remove any remaining water.

7. Eighty ml of the chloroform extract were saved for the hydroxy conversion process.

## 2. Ultraviolet method for atrazine analysis

In order to analyze chlorotriazine residues by the UV method, the triazine compound has to be converted to a hydroxytriazine. The method that was used to convert atrazine to its hydroxytriazine was similar to the methods described by Geigy Chemical Corporation (1965) for chlorotriazines, and by Knuesli et al. (1964) for simazine.

The procedure used for the conversion of atrazine to hydroxyatrazine was as follows:

1. Eighty ml of the chloroform extract were transferred to a 125 ml separatory funnel and 1 ml of 1:1 (50%) sulfuric acid was added to the separatory funnel.
2. The separatory funnel was shaken vigorously for 30 seconds every 15 minutes for 2 hours.
3. Nine ml of distilled water were added to the separatory funnel at the end of 2 hours and the solution shaken for 30 seconds.
4. Upon separation of the layers, the chloroform (bottom layer) was drawn off and discarded and the aqueous layer was transferred to a clean separatory funnel.
5. The aqueous solution was washed with 25 ml of ethyl ether by shaking for 30 seconds.
6. The aqueous layer (lower layer) was transferred to a 15 ml test tube and frozen until it was analyzed on the ultraviolet spectrophotometer.

The absorbance of the aqueous solution containing the atrazine is measured at 225, 240, and 255 m $\mu$ . The net absorbance (E) at 240 m $\mu$  is determined by using a baseline technique according to the equation:

$$E = A^{240} - \left( \frac{A^{225} + A^{255}}{2} \right) \quad (4-1)$$

where  $A^{240}$ ,  $A^{225}$ , and  $A^{255}$  are the actual absorbance readings at 240, 225, and 255 m $\mu$ , respectively. This baseline technique compensates for absorbance due to interfering organic materials.

The amount of atrazine in samples was determined from a calibration curve. Net absorbance values were obtained by dissolving known amounts of atrazine in chloroform that were carried through the hydroxy conversion process. A linear least squares analysis was applied to the known absorbance readings to obtain the calibration curve. A computer program was written to calculate the calibration curve and to analyze all data (Appendix A). Figure 2 shows a typical calibration curve. It was not necessary to determine a new calibration curve with every set of data since the net absorbance of a known amount of atrazine remained constant. The calibration curve was checked every one or two months, because the intensity of the hydrogen lamp on the ultraviolet spectrophotometer decreased with its hours of operation and the absorbance readings possibly reduced.

It was important to run reagent blanks with the soil and water samples. The net absorbance of the reagent blank was subtracted from the net absorbance of the soil or water sample to obtain the correct absorbance for the amount of atrazine in the sample. Reagent blanks did not change to any extent with different lots of chemicals, so it was not



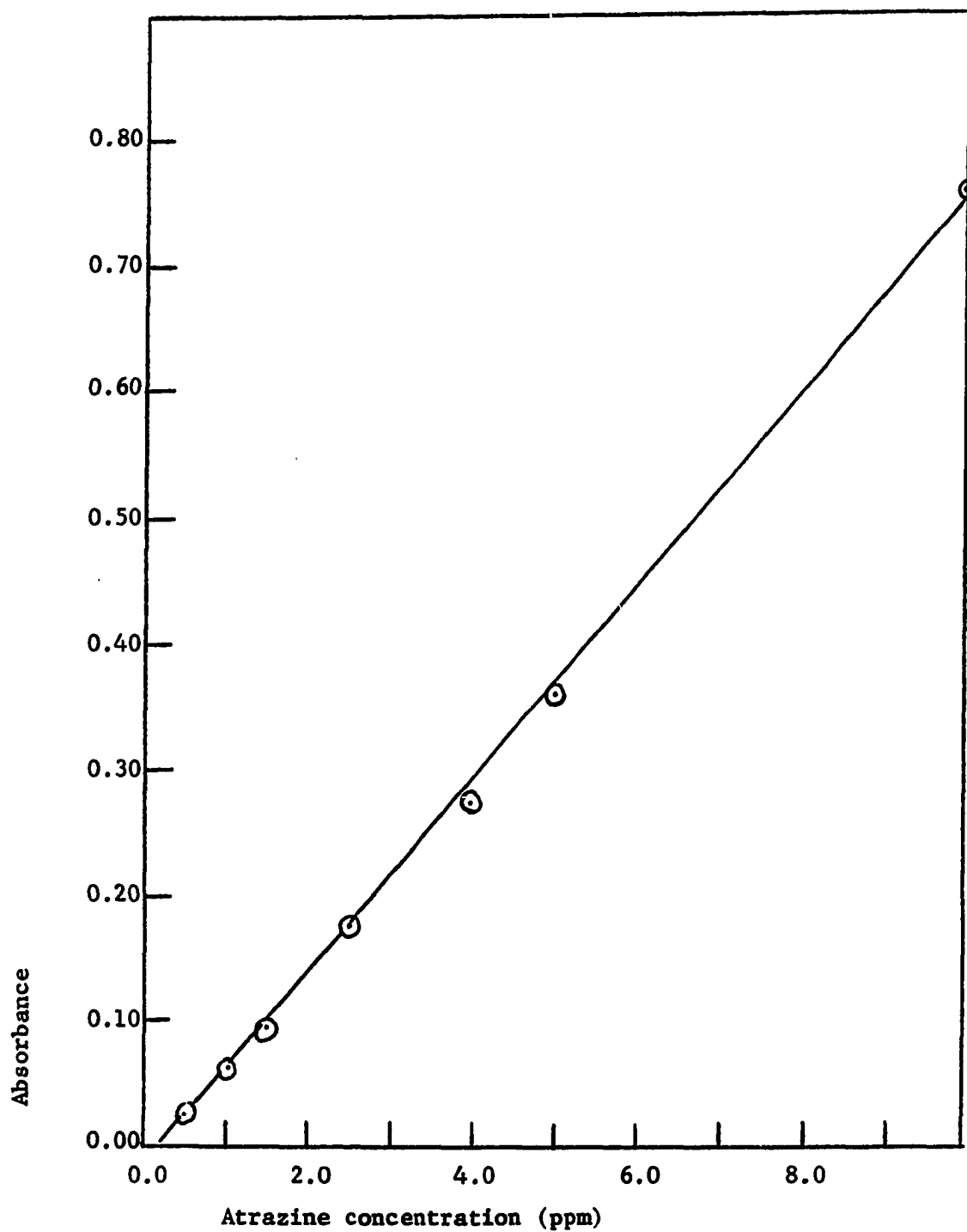


Figure 2. Calibration curve for atrazine on UV spectrophotometer

necessary to run reagent blanks every time a series of water or soil samples was analyzed.

Minimum detection limits were 0.2 ppm for soil samples and 0.02 ppm for water samples.

### 3. Extraction tests for soil and water samples

Extraction tests were conducted with soil and water samples that had known amounts of atrazine added. The general procedure used in the soil extraction tests was to add a known amount of atrazine dissolved in methanol or chloroform to several hundred grams of oven dried or air dried soil with an atomizer. After the soil and pesticide were mixed by hand, the solvent was allowed to evaporate for 5 to 6 hours before the desired amount of water was added with an atomizer. The soil was then wrapped tightly in aluminum foil and allowed to stand at room temperature for 24 hours to permit the moisture to become uniformly distributed. After 24 hours, 40 grams of soil were placed in flasks and extracted with chloroform. There was a large variation in the extraction efficiency tests on both air dried soil and soil at different moisture contents (Table 3). The average extraction efficiency for air dried soil was 79.2 percent, while soil at 18 percent and 13 percent moisture had average extraction efficiencies of 81.6 and 90.8 percent, respectively.

Several extraction tests with water were performed because over 100 percent extraction efficiencies were obtained on the first tests. The atrazine water extraction tests are summarized in Table 4. An average extraction efficiency of 106.9 percent was obtained on 13 water samples fortified with atrazine. The extraction efficiencies ranged from 118.5

Table 3. Extraction efficiency tests of atrazine in Ida silt loam soil at different moisture contents

Moisture Content (%)	Amount Added (ppm)	Amount Recovered (ppm)	Extraction Efficiency (%)	Average Extraction Efficiency (%)
Air Dry	0.61	0.47	77.0	
Air Dry	0.61	0.28	49.5	
Air Dry	0.61	0.37	60.7	
Air Dry	2.04	1.71	83.8	
Air Dry	2.04	1.54	75.5	
Air Dry	2.04	2.10	102.9	
Air Dry	4.08	2.97	72.8	
Air Dry	4.08	3.94	96.6	
Air Dry	4.08	3.82	93.6	79.2
18.63	4.00	3.37	84.2	
18.63	4.00	3.76	94.0	
18.63	4.00	2.89	72.2	
18.63	4.00	3.05	76.2	81.6
13.53	4.00	3.41	85.2	
13.53	4.00	3.30	82.5	
13.53	4.00	4.19	100.7	
13.53	4.00	3.79	94.7	90.8

Table 4. Summary of atrazine extraction from water by chloroform

Amount Added (ppm)	Amount Recovered (ppm)	Extraction Efficiency (%)
0.562	0.642	114.2
0.562	0.612	108.9
0.562	0.599	106.6
0.562	0.654	100.4
0.424	0.436	102.8
0.424	0.446	105.2
0.424	0.422	99.5
0.424	0.412	97.2
0.424	0.438	103.3
0.432	0.478	110.6
0.432	0.512	118.5
0.432	0.456	105.5
0.432	0.506	117.1
Average extraction efficiency--106.9%		

percent to 97.2 percent. Values of over 100 percent recovery on fortified samples are common (Molnau, 1969; Haan, 1970). Geigy (1965) obtained values ranging from 85 to 120 percent on cottonseed fortified with atrazine. Radomski and Rey (1970) had extraction efficiencies that varied from 64 to 107 percent for dieldrin and 57 to 99 percent for p,p'-DDT for fortified liver tissue.

In the water extraction tests, distilled water was "spiked" with atrazine by dissolving the atrazine in acetone and adding 1 ml of acetone to 1 liter of distilled water.

A test was also conducted to see if degradation of atrazine occurred in freezing soil samples. Samples containing 4.00 ppm were placed in standard soil sample bags and stored in the freezer. The results showed no significant amounts of degradation during the 138 days test period (Table 5).

Table 5. The effect of freezing on atrazine soil samples

Days Since Freezing	Concentration (ppm)	Amount Recovered (%)	Average Amount Recovered (%)
0	3.41	85.2	83.8
0	3.40	82.5	
28	4.33	108.2	100.3
28	3.70	92.5	
76	3.20	80.0	83.7
76	3.50	87.5	
138	4.27	106.7	96.6
138	3.46	86.5	

Because of the variation in extraction efficiency tests, no data was corrected for extraction efficiency. All values reported for atrazine, propachlor, and diazinon in this study are on an uncorrected basis. Also, all concentrations of pesticide in soil are expressed on a dry weight basis as micrograms of pesticide per gram of soil, or more commonly expressed as parts per million (ppm). This means that the actual concentrations in this study would be higher for the soil and sediment samples. Most of the pesticide concentrations reported for the water samples for atrazine and propachlor would be near the actual values but the diazinon water sample values would be slightly lower than the actual values.

#### B. Propachlor

Propachlor is a pre-emergence herbicide used to control annual grasses and some broadleaf weeds. Some of the chemical and physical properties of propachlor are given in Table 6.

##### 1. Extraction methods for soil, water, and sediment samples

Surface extraction techniques were also used for extracting propachlor soil samples. The extraction procedures developed by Molnau (1969) were used for extracting soil, water, and sediment samples.

The general procedure for analyzing soil and sediment samples was as follows:

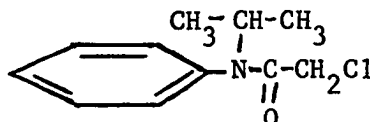
1. The clods were broken up and sieved with a number 8 sieve.
2. Fifteen to 30 grams of soil were removed for analysis and 8 to 12 grams of soil for a moisture content sample.
3. The soil moisture sample was dried at 105°C for 24 hours.

Table 6. Chemical and physical properties of propachlor<sup>a</sup>

Chemical name: 2-chloro-N-isopropylacetanilide

Trade name: Ramrod

Formula:



Molecular weight: 211.7

Molecular formula:  $C_{11}H_{14}ClNO$

Physical state: Light tan, solid

Melting point: 67-76°C

Boiling point: 110°C at 0.03 mm Hg

Vapor pressure: 0.03 mm Hg at 110°C

Solubility at 20°C

<u>Solvent</u>	<u>Solubility</u>
Acetone	30.9%
Benzene	50.0%
Carbon tetrachloride	14.8%
Ethyl ether	29.0%
Water	700 ppmw
Xylene	19.3%

Toxicity: LD<sub>50</sub> in rats, 1200 mg/kg

Formulations: 20% attapulgite clay granules  
65% wettable powder

<sup>a</sup>Source: Weed Society of America, 1967

4. The soil sample was extracted with 30 to 60 ml of acetonitrile for 15 minutes.
5. The soil-acetonitrile mixture was extracted with a Buchner funnel and filter flask.
6. Two teaspoons of anhydrous sodium sulfate were added to the filtrate to remove any moisture present.
7. A portion of the solvent was placed in a 15 ml test tube and stored in the freezer until the sample was analyzed by gas chromatography.

For the laboratory experiments, the entire diffusion cell soil sample was analyzed. Laboratory soil samples ranged from 65 to 108 grams and either 100 or 120 ml of acetonitrile were used for extraction.

The general procedure for extracting water samples was as follows:

1. Three hundred ml of the water sample were placed in a clean 500 ml separatory funnel.
2. Twenty-five ml of benzene were added and the mixture was hand shaken for 90 seconds.
3. After the two layers separated, the benzene (top layer) was removed from the separatory funnel and placed in a clean flask.
4. A second 25 ml of benzene were added and steps 2 and 3 were repeated, and the benzene from the two extractions combined.
5. A third 25 ml of benzene were added and steps 2 and 3 were again repeated, and the benzene from the third extraction combined with the benzene from the first two extractions.
6. Two teaspoons of anhydrous sodium sulfate were added to the

benzene.

7. A portion of the benzene was placed in a 15 ml test tube and stored in the freezer until the sample was analyzed by gas chromatography.

## 2. Detection by gas chromatography

For the early part of the research study, a Varian Aerograph 1520 gas chromatograph equipped with an electron-capture detector with a 150 millicurie tritium foil source was used to analyze the propachlor soil samples. Later a Microtek 220 gas chromatograph equipped with a nickel-63 electron-capture detector was purchased and used for all analysis.

With the Varian Aerograph 1520 gas chromatograph, 1/8-inch O.D. by 5-foot stainless steel spiral-shaped columns were used with a 5 percent Carbowax 20 M liquid support and 60/80 mesh acid-washed Chromosorb W solid support. The operating conditions were: column temperature 180° to 190°C, detector temperature 200° to 210°C, and injector temperature 230° to 250°C. Gas flow rates varied from 80 to 100 ml per minute of nitrogen.

For the Microtek 220 gas chromatograph, 1/4-inch O.D. by 6-foot glass U-shaped columns were used with the same liquid and solid supports used with the Varian Aerograph gas chromatograph. Operating conditions for the Microtek 220 gas chromatograph were: column temperature 190°C, detector temperature 275° to 300°C, injector temperature 270° to 280°C, and gas flow rates from 80 to 100 ml per minute. The minimum detectable quantity of propachlor ranged from 0.20 to 0.30 ppm for soil samples and 0.01 to 0.02 ppm for water samples for both instruments.

The propachlor peak was quite symmetrical so peak heights were used



to determine the amount of pesticide present. Figure 3 shows a propachlor peak from propachlor standards. A calibration curve was run each day the gas chromatograph was used. Standards were stored in the freezer and new standards were made up every 2 months. Benzene was used as a solvent for the standards. In most cases the calibration curve was linear, although at higher concentrations the upper part of the calibration curve was sometimes curved. Figure 4 shows a typical calibration curve. A computer program was written to determine either a linear or parabolic curve and to compute the amount of propachlor present in the sample (Appendix A).

### 3. Extraction tests for soil and water samples

Molnau (1969) found that the extraction efficiency of propachlor from Ida silt loam soil (extracted with acetonitrile) varied with the moisture content of the soil. Molnau's extraction efficiency tests are summarized in Table 7. The extraction efficiency varied from 81.4 percent to 109.3 percent. The procedure used in the extraction efficiency tests was to place about 1 gram of soil in a 25 ml test tube and add 1.0 ml benzene containing a known amount of propachlor. The soil was allowed to dry for a day at room temperature and then the desired amount of water was added before the sample was extracted with acetonitrile.

Molnau (1969) also found that no noticeable degradation of propachlor occurred when soil samples were stored in the freezer (Table 8). From these tests it was concluded that freezing the soil samples would create no serious problems with the experimental results. An average of 96.6 percent of the propachlor was recovered from fortified distilled water samples that were extracted with benzene (Table 9).

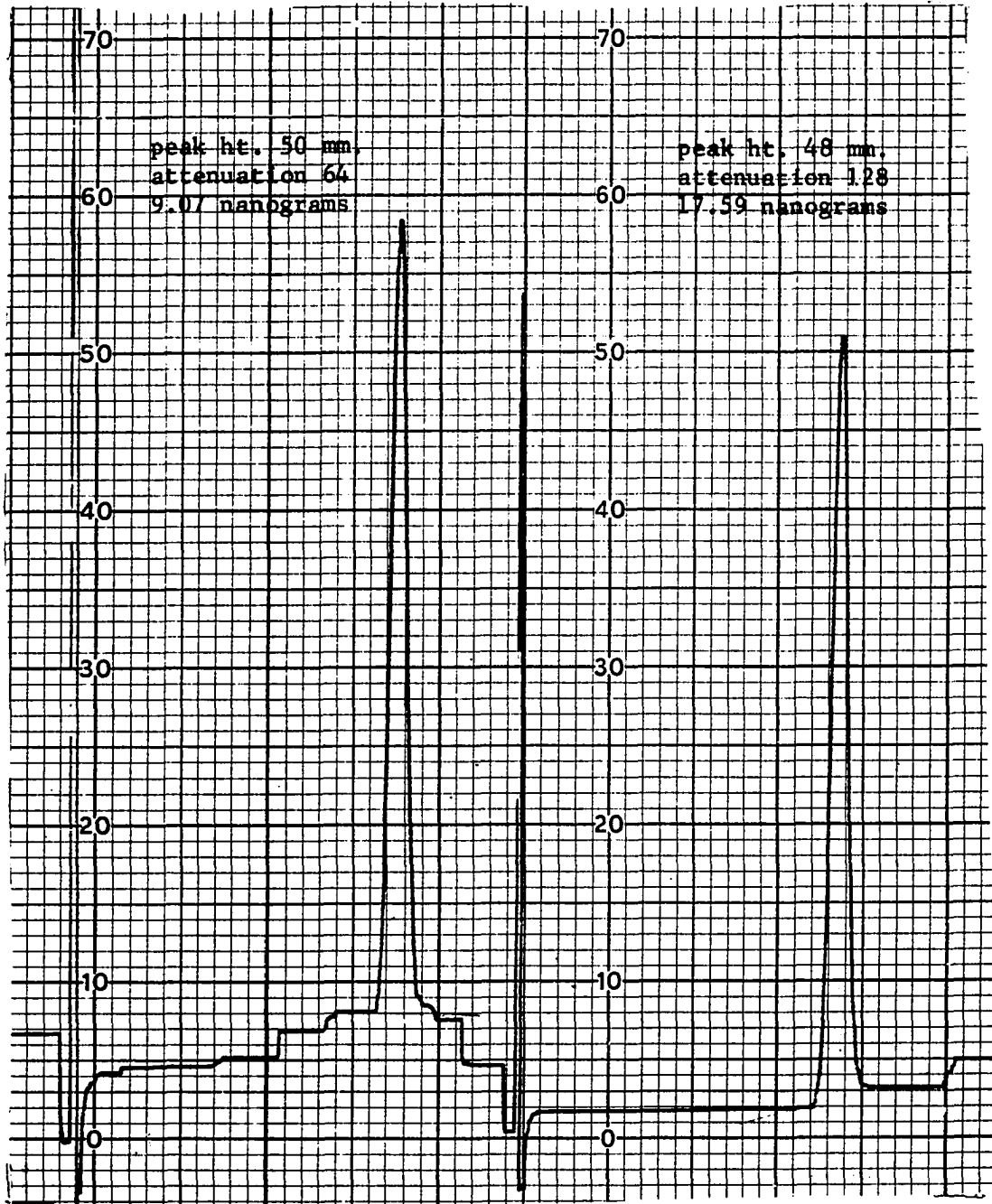


Figure 3. Chromatogram of propachlor standards with a 5 percent Carbowax 20 M column

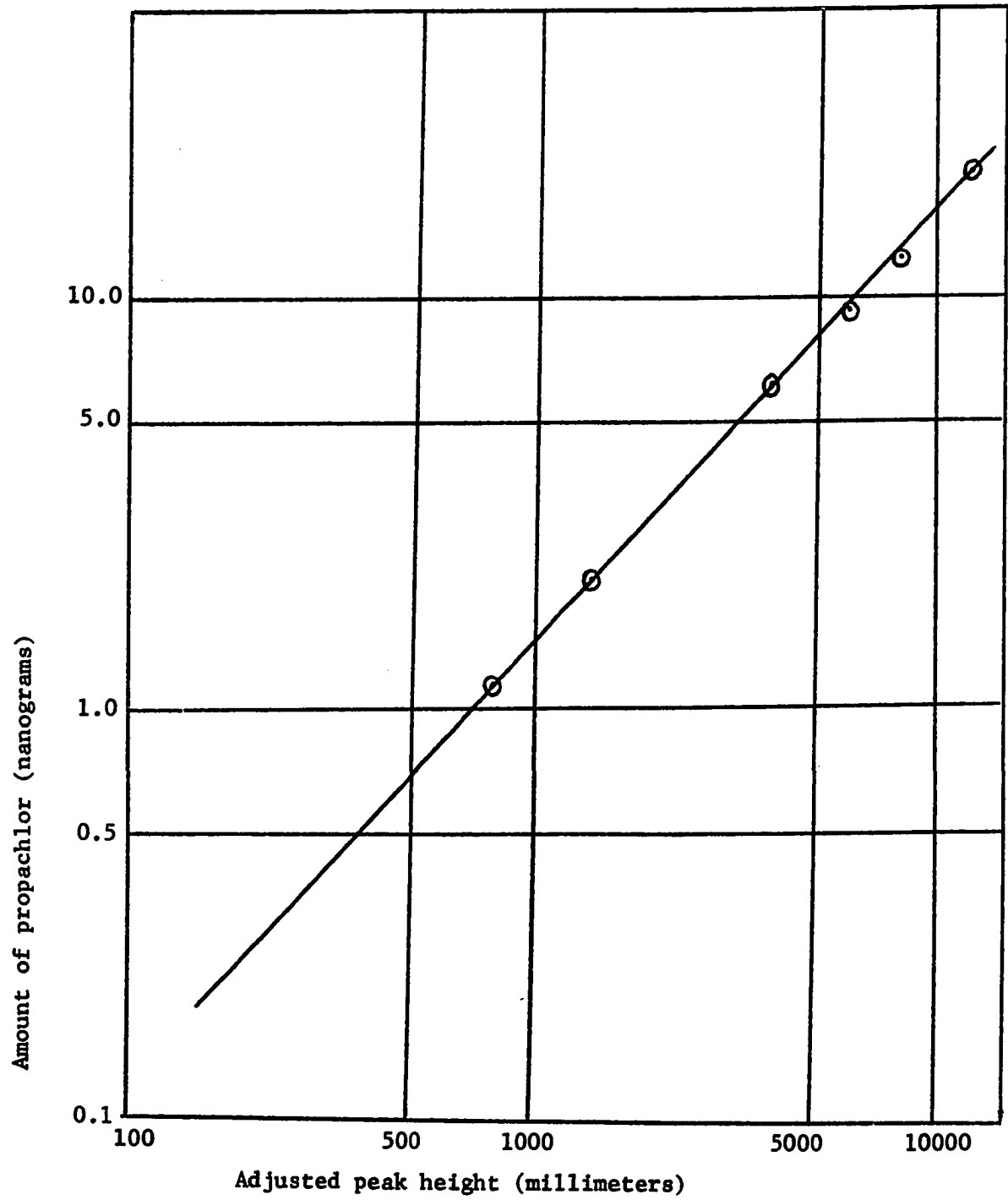


Figure 4. Calibration curve for propachlor, for gas chromatograph

Table 7. Summary of extraction efficiency of propachlor from soil using acetonitrile<sup>a</sup>

Moisture	Extraction Efficiency (%)
Air dry	96.4
Air dry	81.4
One drop	88.6
Two drops	92.7
Three drops	96.1
Four drops	103.8
Air dry	107.4
2.5%	109.3
15.8%	90.7
27.0%	95.3
35.6%	100.0

<sup>a</sup>Source: Molnau, 1969

Table 8. Effect of freezing on propachlor degradation<sup>a</sup>

Days Frozen	Percent Recovered
7	96
33	95
47	96
61	86
68	103
80	88

<sup>a</sup>Source: Molnau, 1969

Table 9. Extraction efficiency tests for propachlor extracted from water with benzene

Amount Added (ppm)	Amount Recovered (ppm)	Extraction Efficiency (%)
0.741	0.710	95.8
0.741	0.694	93.5
0.741	0.747	100.6
Average extraction efficiency, 96.6%		

The procedure used in the water extraction efficiency tests was to add 1 ml of acetone containing 0.741 mg of propachlor to 1 liter of distilled water. Three samples of 300 ml of water were then extracted three times with 25 ml portions of benzene. The benzene from the three extractions was combined for final analysis on the gas chromatograph.

### C. Diazinon

Diazinon is an organophosphate insecticide used for insect control. Some of the properties of diazinon are given in Table 10.

#### 1. Extraction methods for soil, water, and sediment samples

Surface extraction by shaking on a mechanical shaker was used for all soil and sediment samples. Several solvents were tried using both air dried soil and soil at different moisture contents. Acetonitrile gave the highest extraction efficiency with air dried soil and the extraction efficiency decreased with increasing moisture content (Table 11). No diazinon was recovered from air dried soils extracted with hexane, benzene, and petroleum ether, so it was decided to use acetonitrile for extracting all soil samples containing diazinon residues. On these extraction efficiency tests about 1 gram of air dried soil was placed in a 25 ml test tube and 1.0 ml of benzene containing a known amount of diazinon was added. The soil was allowed to dry for a day at room temperature and then the desired amount of water was added to some of the samples before extracting with solvent.

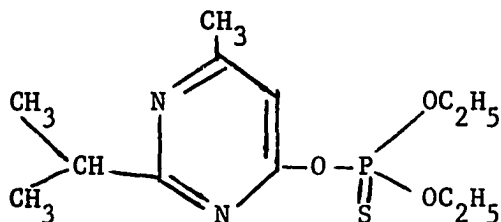
The general procedure for extracting soil and sediment samples was as follows:

Table 10. Chemical and physical properties of diazinon<sup>a</sup>

Chemical name: 0, 0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate

Trade name: Diazinon

Formula:



Molecular weight: 304.3

Molecular formula:  $C_{12}H_{21}N_2O_3PS$

Physical state: Colorless liquid

Boiling point: 83-84°C at 0.002 mm Hg

Vapor pressure:  $1.4 \times 10^{-4}$  mm Hg at 20°C  
 $6.6 \times 10^{-3}$  mm Hg at 60°C

Solubility: 4 ppm. in water at room temperature  
 miscible with acetone, alcohol, xylene  
 soluble in petroleum oils

Toxicity: LD<sub>50</sub> in rats, 108 mg/kg

Formulations: wettable powder, 40%  
 emulsifiable concentrate, 25% and 60%  
 dust, 4%  
 granules, 5%

<sup>a</sup>Source: Canadian Department of Agriculture, 1968

Table 11. Effect of solvent and soil moisture content on the extraction efficiency of diazinon

Solvent	Moisture Content (%)	Amount Recovered (ppm)	Extraction Efficiency (%)
Acetonitrile	Air Dry	1.62	99.4
	Air Dry	1.41	86.5
	Air Dry	1.57	96.3
	Air Dry	1.16	71.2
	Air Dry	1.26	77.3
	5.40	0.97	59.5
	16.60	0.52	31.9
	20.10	0.44	27.0
	31.00	0.38	23.3
Benzene	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	5.10	1.21	74.2
	16.20	0.72	44.2
	21.50	0.51	31.3
	28.40	0.19	11.6
Hexane	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	4.20	0.56	34.4
	16.20	0.71	43.6
	27.50	0.44	27.0
	28.00	0.38	23.3
Petroleum Ether	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	Air Dry	0.00	0.0
	4.50	0.81	49.7
	17.30	0.80	49.1
	22.10	0.56	34.4
	31.40	0.97	59.5

1. The clods were broken up and sieved with a number 8 sieve.
2. Fifteen to 40 grams of soil were removed for analysis and 8 to 12 grams of soil for a moisture content sample.
3. The soil moisture sample was dried at 105°C for 24 hours.
4. The soil sample was extracted with 30 to 75 ml of acetonitrile for 30 minutes.
5. The soil-solvent mixture was filtered with a Buchner funnel and filter flask.
6. Two teaspoons of anhydrous sodium sulfate were added to the filtrate.
7. A portion of the solvent was placed in a 15 ml test tube and stored in the freezer until the sample was analyzed by gas chromatography.

For the laboratory experiments the entire diffusion cell soil sample was analyzed. Soil samples ranged from 65 to 108 grams and either 100 or 120 ml of acetonitrile were used for extraction.

The general procedure for extracting water samples was as follows:

1. Two hundred or 300 ml of the water sample were placed in a clean 500 ml separatory funnel.
2. Fifty ml of hexane were used and the water and hexane were hand shaken for 90 seconds.
3. After the hexane and water had separated, the hexane (top layer) was removed from the separatory funnel and placed in a clean flask.
4. A second 50 ml of hexane was added and steps 2 and 3 were repeated, and the hexane was combined from the two extractions.



5. Two teaspoons of sodium sulfate were added to the hexane.
6. A portion of the hexane extract was placed in a 15 ml test tube and stored in the freezer until the sample was analyzed by gas chromatography; or 75 to 100 ml of the hexane extract was concentrated to less than 10 ml in a flask on a hot water bath. If the hexane extract was concentrated, the final volume was diluted to 10 ml in a volumetric flask and stored in the freezer.

## 2. Detection by gas chromatography

The Varian Aerograph 1520 gas chromatograph with an electron-capture detector was also used to analyze some of the diazinon samples. Later, the Microtek 220 gas chromatograph with the electron-capture detector was used. The same size and type of columns as used for the propachlor analysis were also used for diazinon. A 5 percent Carbowax 20 M liquid support and 60/80 mesh acid-washed Chromosorb-W solid support was used in the columns for most of the samples. A 10 percent DC-200 and 5 percent SE-30 liquid support on Chromosorb-W was used for a few diazinon samples.

The operating conditions for the Varian Aerograph 1520 gas chromatograph were: column temperature 180° to 190°C, detector temperature 200° to 210°C, injector temperature 215° to 240°C, and gas flow rates of from 80 to 90 ml per minute. For the Microtek 220 gas chromatograph, operating conditions were: column temperature 190°C, detector temperature 275° to 300°C, injector temperature 270° to 280°C, and gas flow rates from 80 to 90 ml per minute of nitrogen.

The minimum detectable quantity ranged from 0.05 to 0.15 ppm for soil and sediment samples, and 10 parts per billion (ppb) for water samples.

The diazinon peak was also quite symmetrical, so peak heights were used to determine the amount of pesticide present. Figure 5 shows a chromatogram from diazinon standards. With the 5 percent Carbowax 20 M on 60/80 acid-washed Chromosorb-W, the retention times were longer for diazinon than propachlor with the same operating conditions. Benzene was used as a solvent for diazinon standards. In most cases, the diazinon calibration curve was linear. The computer program used for the propachlor data was also used for the diazinon data.

### 3. Extraction tests for soil and water samples

After the initial soil sample extraction tests with different solvents were completed, more extraction tests with acetonitrile were conducted. The technique used for the atrazine soil extraction tests was used for the diazinon extraction tests with acetonitrile. Hexane was used as a solvent to apply the diazinon to the soil. Higher extraction efficiencies were generally obtained with the drier soil. The extraction efficiency tests are summarized in Table 12. An average of 69.4 percent of the diazinon was recovered from three soil samples at 8.0 percent moisture and 51.0 percent of the diazinon was recovered from three soil samples at 24.0 percent moisture. One set of tests at 9.0 percent moisture had an average extraction efficiency of 78.9 percent, however, the extraction efficiency of 105.3 percent from one replication raised the average for the three replications. Some of the variation in the data was caused by not having the pesticide mixed uniformly in the soil.

Extraction tests were conducted with distilled water that was "spiked" with diazinon. Each water sample was extracted twice with 50 ml portions

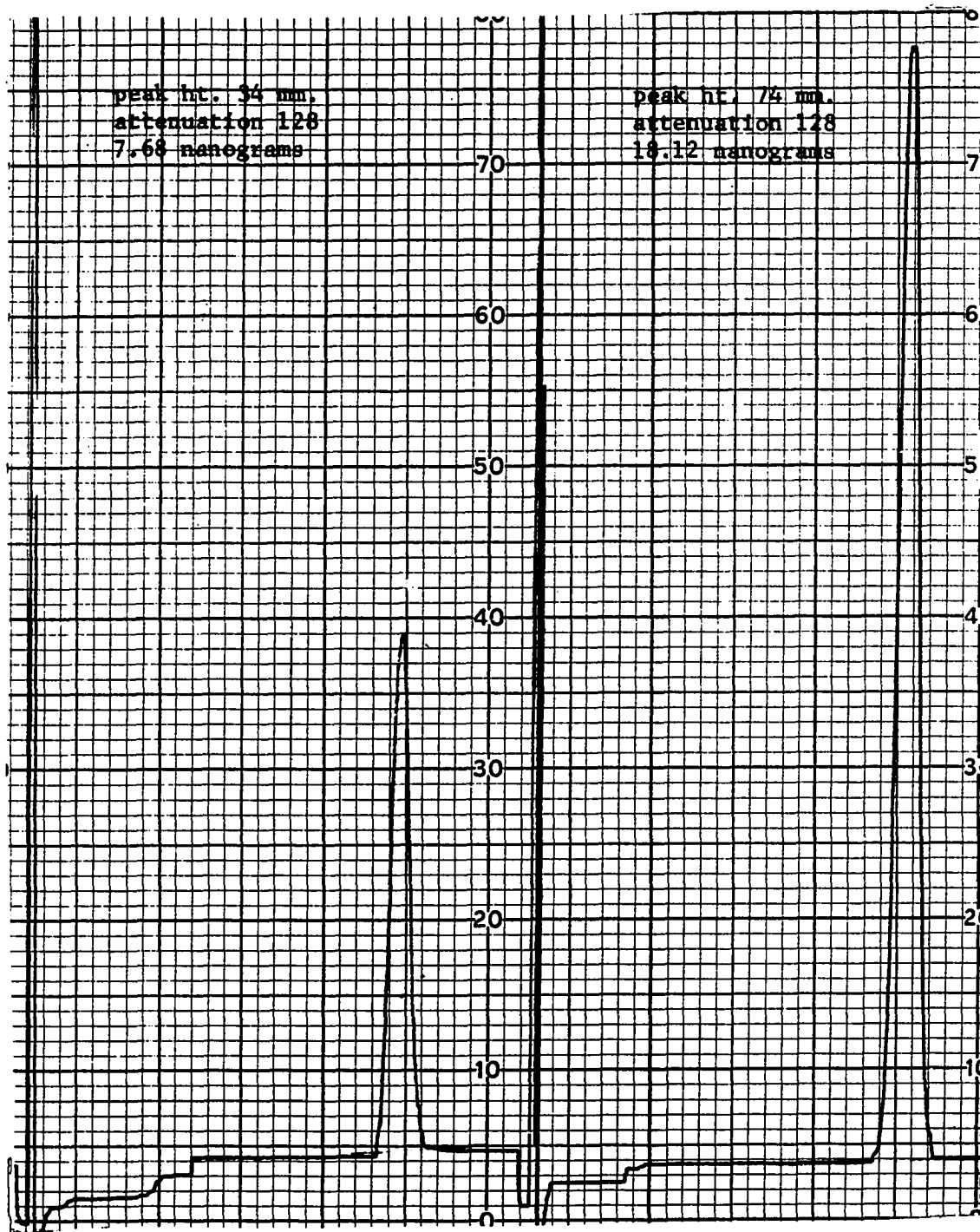


Figure 5. Chromatogram of diazinon standards with a 5 percent Carbowax 20 M column

of hexane. The two extractions were combined for final analysis on the gas chromatograph. The average extraction efficiency of three water samples fortified with 0.187 ppm of diazinon was 77.6 percent (Table 13).

Table 12. Extraction efficiency tests of diazinon in Ida silt loam soil at different moisture contents with acetonitrile

Moisture Content (%)	Amount Added (ppm)	Amount Recovered (ppm)	Extraction Efficiency (%)	Average Extraction Efficiency (%)
8.28	10.0	6.78	67.8	62.5
8.28	10.0	5.98	59.8	
8.28	10.0	5.98	59.8	
14.90	20.0	10.52	52.6	52.0
14.90	20.0	9.98	49.9	
14.90	20.0	10.67	53.4	
24.58	10.0	6.94	69.4	62.1
24.58	10.0	6.39	63.9	
24.58	10.0	5.29	52.9	
15.92	10.0	5.14	51.4	63.1
15.92	10.0	6.89	68.9	
15.92	10.0	6.90	69.0	
9.03	10.0	10.53	105.3	78.9
9.03	10.0	6.98	69.8	
9.03	10.0	6.17	61.7	
8.00	10.0	6.72	67.2	69.4
8.00	10.0	7.62	76.2	
8.00	10.0	6.47	64.7	
16.76	10.0	7.10	71.0	66.9
16.76	10.0	6.29	62.9	
16.76	10.0	6.68	66.8	
24.05	10.0	4.93	49.3	51.0
24.05	10.0	5.33	53.3	
24.05	10.0	5.03	50.3	

Table 13. Diazinon extraction from water by hexane

Amount Added (ppm)	Amount Recovered (ppm)	Extraction Efficiency (%)
0.187	0.150	80.3
0.187	0.144	77.0
0.187	0.141	75.3
Average Efficiency, 77.6%		

## V. FIELD EXPERIMENT

### A. Description of the Experiment

The experiment was conducted on the Gingles Watersheds located 1 mile west of the Western Iowa Experimental Farm near Castana in Monona County, Iowa. There are six watersheds ranging in size from 1.3 to 3.8 acres. Three soil types predominate on each watershed; Ida silt loam, Monona silt loam, and Napier silt loam. Precipitation, surface runoff, pan evaporation, water table elevation, wind travel, total solar radiation, soil moisture, humidity, and maximum and minimum temperature records were collected during the growing season. Soil temperature records were also available for the general area, from measurements taken at the Western Experimental Farm. Four of the watersheds were used for the pesticide studies. These watersheds are referred to as the northmiddle (NM), southmiddle (SM), northeast (NE), and southwest (SW) watersheds. Figure 6 shows a contour map of all six watersheds.

The experimental program to study pesticide movement in the soil profile and losses of pesticides in surface runoff and sediment was initiated in 1967. In 1967, all four watersheds were in surface planted contoured corn. At the first cultivation, ridges were established on the northmiddle and southwest watersheds. In 1968, 1969, and 1970 the northmiddle and southwest watersheds were in ridge planted corn, and the northeast and southmiddle watersheds were in surface planted contoured corn. Figure 7 is an overall view of the southwest watershed, and Figure 8 shows the ridges at planting time.

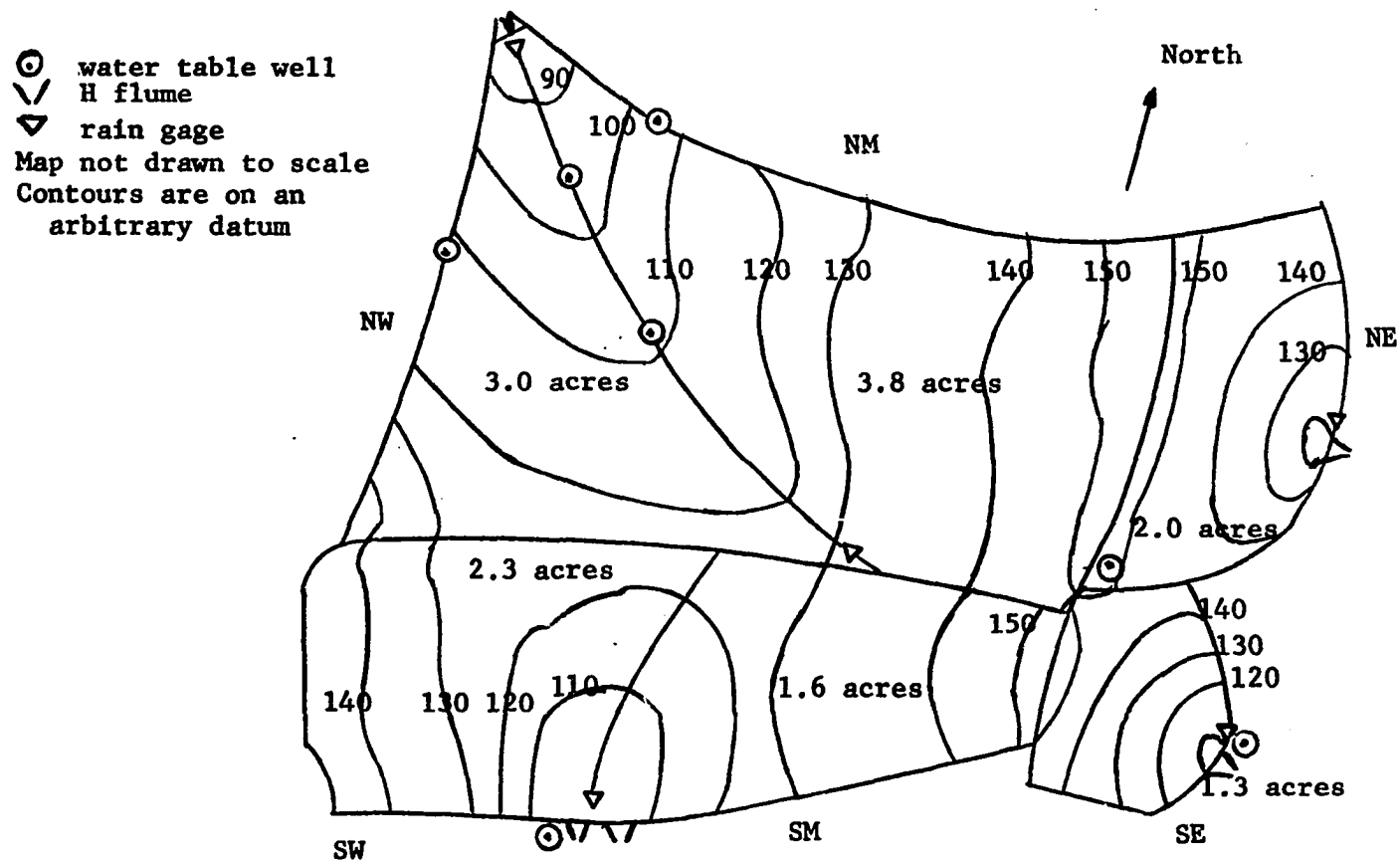


Figure 6. Map of Gingles Watersheds

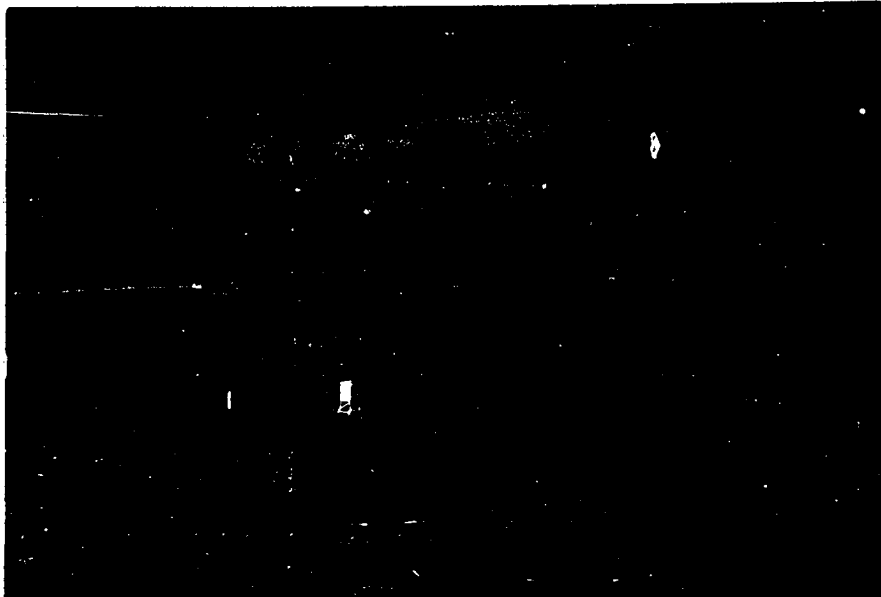


Figure 7. A view of the southwest watershed





Figure 8. The ridges on the northmiddle watershed at planting time

Each year the stalks were chopped on the surface contoured watersheds before planting, and the watersheds were plowed, disked, and harrowed. After planting the corn, the surface contoured watersheds were cultivated once around the middle of June. The stalks were chopped on the ridged watersheds before planting. The corn was then planted on the ridged watersheds without any tillage before planting. After planting the corn, the ridged watersheds were cultivated once around the middle of June and the ridges were reshaped with a ridge cultivator. It was also necessary to reshape some of the ridges on the northmiddle watershed before planting in 1968, 1969, and 1970, where breakover of the ridges occurred.

Atrazine was applied to the northmiddle and southmiddle watersheds in a wettable powder formulation with 20 gallons of water per acre at planting time each year, and propachlor was applied to the southwest and northeast watersheds in a wettable powder formulation with 20 gallons of water per acre at planting time each year. Diazinon was applied to all four watersheds each year at the first cultivation in a granular formulation. In 1969 and 1970 atrazine and oil were applied to the southwest watershed the first week in June at a rate of 1 lb/A. Atrazine and propachlor were applied broadcast with a sprayer while diazinon was incorporated in a band application along the corn rows at a depth of 1 to 2 inches. Table 14 gives the amounts of active ingredient of each pesticide applied each year to the different watersheds.

Table 14. Amount of active ingredient of pesticides applied to the Gingles Watersheds

Year	Amount of Pesticide lb/A		
	Atrazine	Propachlor	Diazinon
1967	2	4	1
1968	2	4	1
1969	3	6	1
1970	3	6	1

#### B. Collection of Water, Sediment, and Soil Samples

Molnau (1969) developed sampling procedures for collecting water, sediment, and soil samples to analyze for propachlor (CIPA) from the northeast and southwest watersheds in 1967 and 1968. The same procedures used by Molnau (1969) were used for sampling water, sediment, and soil samples on the northmiddle and southmiddle watersheds from 1967-1970.

Water and sediment samples were obtained from all four watersheds by single-stage samplers (Figure 9). The sampler originally was tapped into the side of the flume in 1967 (Figure 10) with 3/8 inch copper tubing through the side of the flume and through the rubber stopper on the bottle. One liter polyethylene bottles were used in 1967, but one quart glass bottles were substituted in 1968 because there was a possibility that the pesticides might be adsorbed to the polyethylene.

In 1969 additional single-stage samplers were installed and all of the copper tubing intake nozzles were changed from 3/8 inch to 1/2 inch

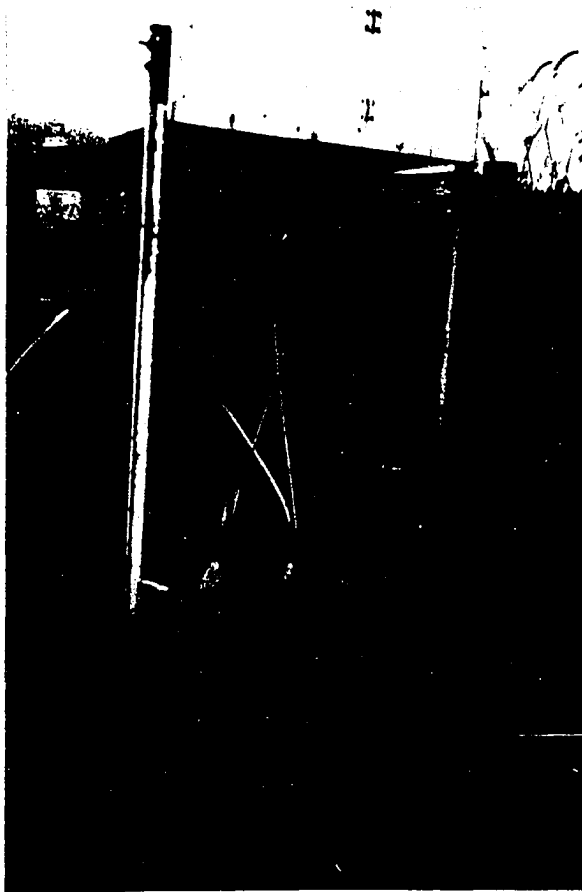


Figure 9. Single-stage sediment samplers

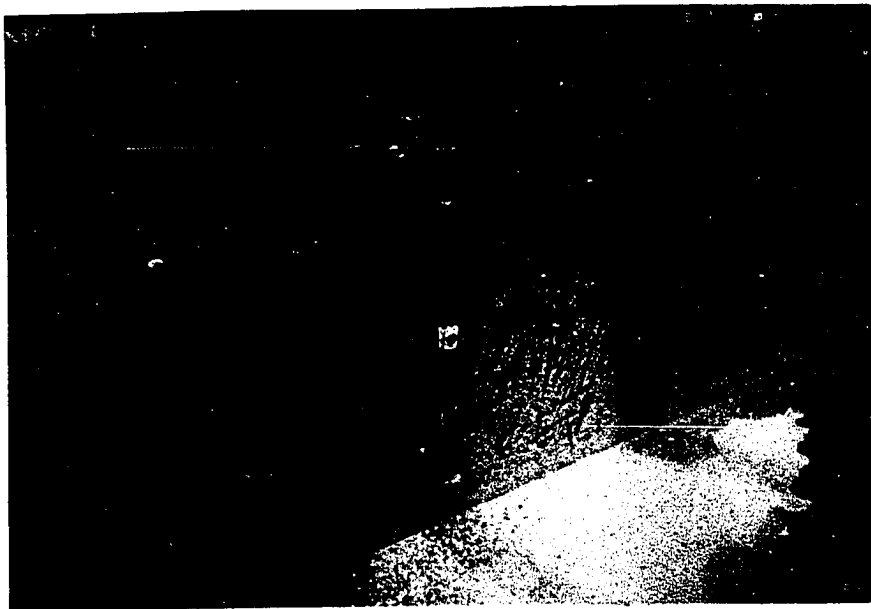


Figure 10. Intake nozzles of single-stage sediment samplers

diameter. This eliminated some of the problems encountered with fine trash and sediment clogging the smaller diameter nozzles.

Water and sediment samples were also obtained from the southmiddle and southwest watersheds by use of a 2 foot diameter Coshocton runoff sampler (Parsons, 1954) (Figure 11). Water collected by the sampler ran to a 55 gallon drum, which contained two cans of 20 and 5 gallon capacity. Laboratory tests showed that at the sampler offset used, the sampler collected 0.15 percent of the flume discharge for flows less than 1 cfs and 0.23 percent for flows of 2 cfs (Molnau, 1969). Use of the Coshocton runoff samplers created several problems, so the samplers were not used in 1970. If the water and sediment were not completely mixed when a sample was taken out of the drum, large errors in the sediment concentrations resulted.

All water and sediment were frozen in polyethylene bottles immediately after collecting. The samples remained frozen until they were analyzed for pesticide residues. At that time, the entire sample was weighed, the water removed for separate analysis and the sediment allowed to air dry. The air dried sediment was weighed and separated into two parts. One part was used for a moisture determination and the other for residue analysis.

Sample points were located on the watersheds by laying out a 125 foot by 125 foot grid system on the six watersheds. This system resulted in having six sampling locations on the southwest watershed, five sample points on the southmiddle watershed, seven sample points on the northeast watershed, and twelve sample points on the northmiddle watershed.

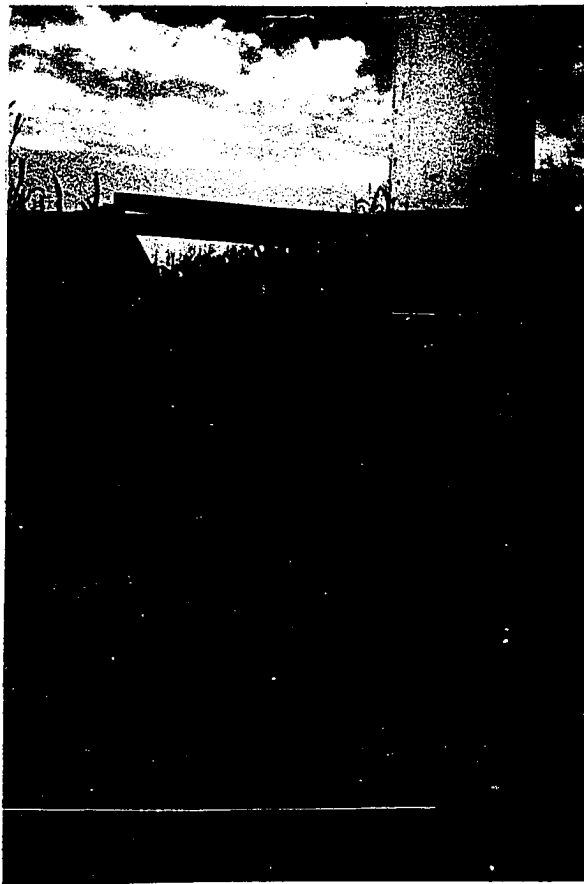


Figure 11. Coshocton runoff sampler

Figure 12 shows the 3/4 inch inside diameter hollow probe used for taking the soil samples. Seven individual soil cores were taken normal to the corn row and composited into a single sample. In 1967, the 0 to 4 and 4 to 8 inch depth of sampling did not give a clear picture of pesticide movement in the soil profile. The sample depths used in 1968 through 1970 were changed to 0 to 1, 1 to 3, and 3 to 5 inches for the first few samplings. Later in the growing season, sampling depths were changed to 0 to 2, 2 to 4, and 4 to 6 inches. In September and October soil samples were also taken at 6 to 8 and 8 to 10 inches for atrazine analysis.

Soil samples containing atrazine were taken throughout the growing season, while soil samples for diazinon and propachlor were collected for 4 to 6 weeks after application. All soil samples were collected in soil sample bags and frozen immediately after collection.

### C. Water and Sediment Losses

Total amounts of runoff from each storm event were calculated from runoff hydrographs obtained from time and water stage data recorded for each storm. Sediment concentrations were obtained from the single-stage sediment samplers for the rising limb of the runoff hydrograph; no sediment samples were collected on the falling limb of the hydrograph because the single-stage samplers took a sample only on the rising stage. No samplers were installed to sample the falling stage. The sediment concentrations on the falling limb of the hydrograph were estimated. Judgement was based on sediment measurements taken by Doty and Carter (1964), Dragoun and Miller (1964) and personnel of the United States





Figure 12. Soil sampling probe used to take soil samples

Department of Agriculture (1971), who were also studying runoff from loessial soils. For most storm events the peak sediment concentrations occurred before the maximum discharge occurred; then the sediment concentrations decreased quickly on the falling limb of the hydrograph.

In order to calculate total sediment loads the continuous sediment concentration curve was superimposed on the runoff hydrograph and the areas under the two curves were summed by increments of time. Figure 13 shows a typical runoff hydrograph and sediment concentration curve. The formula used for calculating total pounds of sediment was:

$$Q_s = Q_w \cdot C_s \cdot T \cdot K \quad (5-1)$$

where  $Q_s$  is the sediment load in pounds,  $Q_w$  is the average water discharge in cfs for the time interval,  $T$ .  $C_s$  is the sediment concentration in ppm, and  $K$  is a conversion factor for units and for converting sediment concentrations to a pure water basis.

Table 15 shows the total surface runoff for 1967 to 1970 for the two ridged watersheds, and the two surface contoured watersheds. The total runoff for each storm event for each year is given in Tables 27 to 30 of Appendix B. The total runoff was estimated by correlation for some storms when the clock stopped or the inking pens failed.

The total runoff was significantly lower for the ridged watersheds than the surface contoured watersheds. Runoff from the northmiddle watershed was higher than from the other ridged watershed. The northmiddle watershed is 3.8 acres in size compared to 2.3 acres for the southwest watershed and some problem of breakover of the ridges was encountered

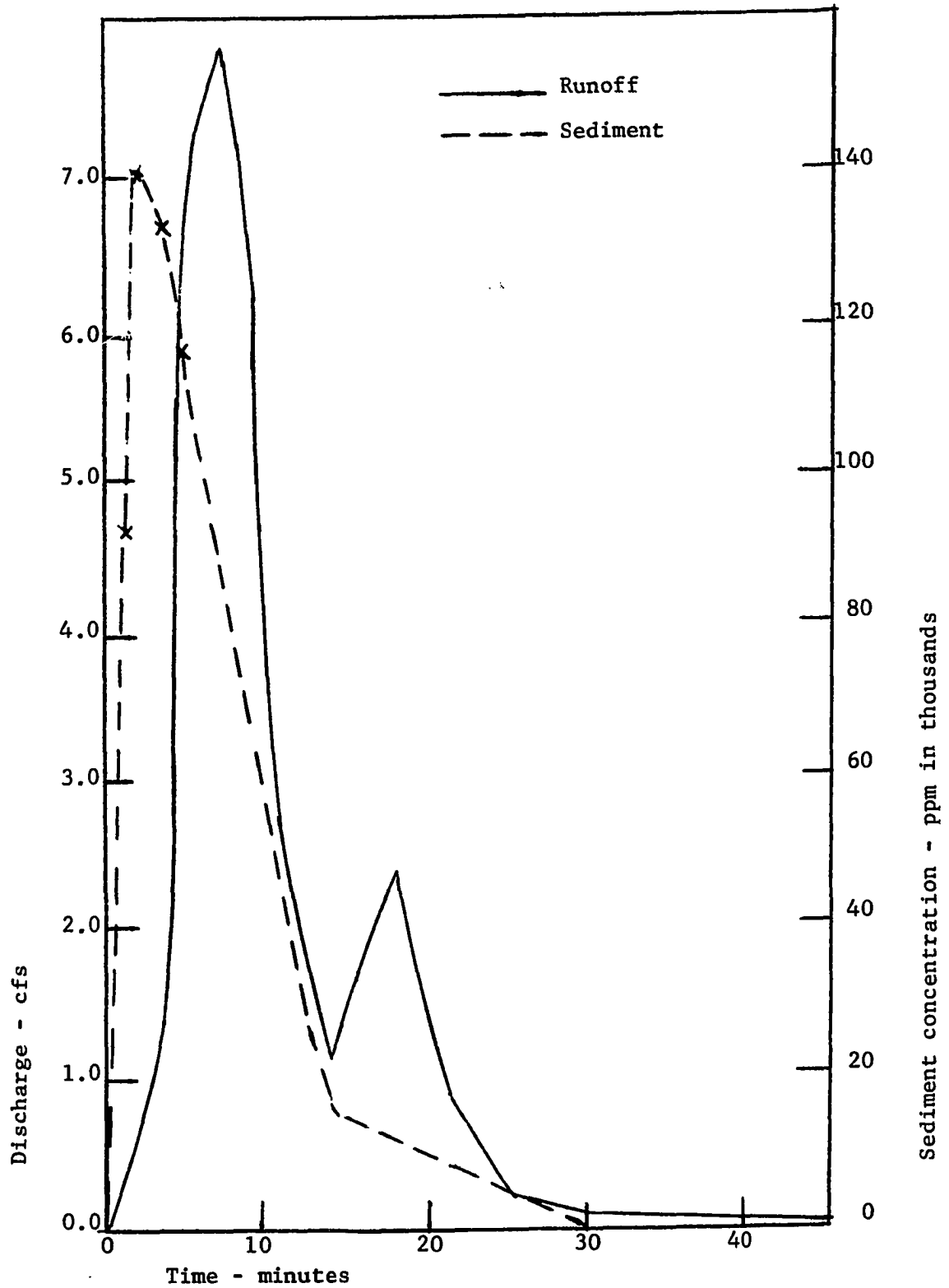


Figure 13. Runoff hydrograph and sediment concentration curve for a storm July 7, 1969, on the southmiddle watershed

Table 15. Total annual surface runoff for the ridge planted corn and surface planted contoured corn watersheds

Year	Ridged		Total Runoff (inches)	
	NM	SW	Surface Contoured SM	NE
1970	0.39	0.02	1.26	0.97
1969	1.85	0.46	3.07	1.71
1968	0.93	0.22	1.62	1.42
1967 <sup>a</sup>	4.50	3.04	3.95	4.30

<sup>a</sup>All four watersheds in surface contoured corn

on the northmiddle watershed. This accounted for the larger amounts of surface runoff on the northmiddle watershed relative to the southwest watershed.

Total sediment losses for the northmiddle, southmiddle, and northeast watersheds for certain storm events in 1968, 1969, and 1970 are given in Table 16. Total yearly sediment losses could not be calculated because sediment losses from some storm events were not recorded. For some storms the total runoff for individual watersheds was estimated so no runoff hydrograph was available to calculate sediment loads; for other storms, trash and sediment plugged the intake nozzles. The sediment losses for 1968 on the southmiddle watershed were estimated from the Coshocton runoff sampler data since no other data was available. All other sediment losses were based on data collected with the single-stage samplers. No sediment losses from the southwest watershed were presented because generally only one sample was obtained in each storm. Sediment concentrations were usually less than 1500 ppm on the southwest watershed, so sediment losses would be negligible.

Table 16. Sediment losses from the Gingles Watersheds, 1968-1970, (T/A)

Date of Storm	SM Watershed (Surface Contoured)	NE Watershed	NM Watershed (Ridged)
5-13-70	12.18	6.47	0.29
5-30-70	2.04	1.83	0.25
6-11-70	0.91	1.08	0.04
6-11-69	6.94	2.69	0.75
6-11-69	5.40	1.80	0.24
6-22-69	0.39		0.45
6-28-69	2.84	1.12	0.95
7- 7-69	6.16		
8- 6-69	2.37	0.57	0.57
8- 8-69	1.02	0.32	0.47
6-23-68	0.04		
6-24-68		1.26	0.63
6-25-68	7.92	2.10	0.36
6-29-68	0.44	0.88	
7-17-68	0.006	0.007	
8- 8-68	0.50	0.15	
8-27-68	0.14		

Sediment losses given in Table 16 are smaller than the actual sediment losses from the tillage area. Large amounts of sediment were deposited in and above the flumes on the southmiddle and northeast watersheds. Figure 14 shows the sediment deposited in the flume of the southmiddle watershed after a storm. Some sediment was also deposited in the flume and grassed waterway of the northmiddle watershed. The volume of sediment deposited in the flume and grassed waterway of the northmiddle watershed was small compared to the sediment deposited on the southmiddle and northeast watersheds.

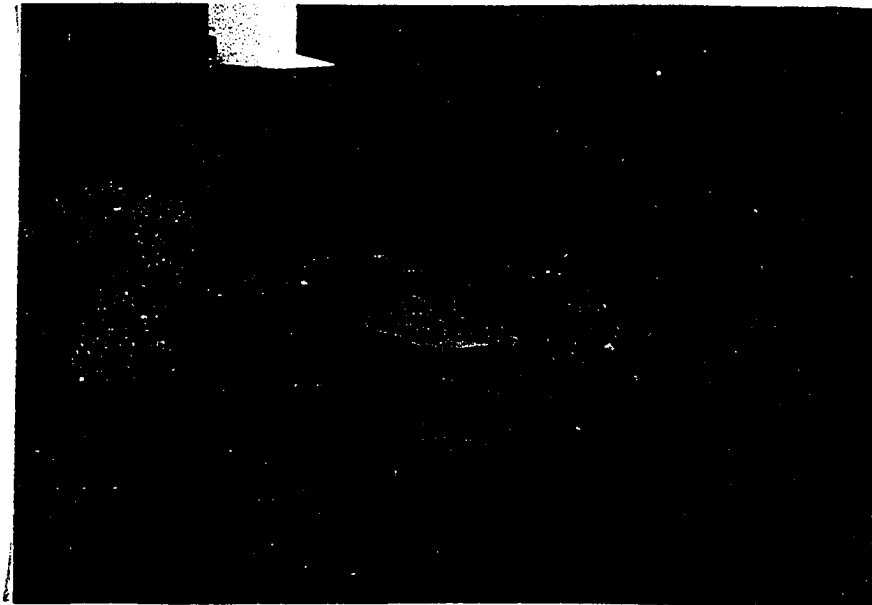


Figure 14. Sediment deposited in the flume of the southmiddle watershed after a storm

Sediment losses from the two surface contoured watersheds were usually greater than sediment losses from the ridged watersheds. The sediment losses from the southwest watershed were negligible and from the north-middle watershed were less than 1 T/A for all storms. Highest sediment losses occurred on the southmiddle watershed, with 12.18 T/A of sediment lost from the storm on May 13, 1970.

The calculated sediment loads presented in Table 16 are only an estimate of the true sediment losses. Since the sediment samples were obtained only on the rising limb of the hydrograph, the sediment losses may be overestimated or underestimated by as much as 25 percent. It is uncertain whether the sediment is uniformly distributed with depth in the surface runoff, and the concentration of sediment obtained with the single-stage sediment sampler representative of the average sediment concentration for that particular time in the storm. Sediment distribution curves of the dominant sizes indicate nearly uniform distribution. With the field personnel and equipment available the above estimates of sediment losses are the best obtainable from the Gingles Watersheds.

#### D. Pesticides in Runoff Water and Sediment

##### 1. Atrazine

Runoff and sediment samples were collected in 1967, 1968, 1969, and 1970 from the southmiddle and northmiddle watersheds and analyzed for atrazine residues by the methods described in Chapter IV. A total of sixty water samples from the southmiddle watershed and thirty-four water samples from the northmiddle watershed were analyzed for atrazine residues

from 1967 to 1970. Detectable concentrations of atrazine were found in eighty-two of the water samples. The minimum detectable concentration of atrazine in water was approximately 0.02 ppm. Forty-three sediment samples from the southmiddle watershed and twenty-one sediment samples from the northmiddle watershed were analyzed for atrazine residues. Fifty-seven of the sediment samples contained detectable amounts of atrazine. The minimum detectable concentration of atrazine in the sediment depended upon the amount of sediment available for analysis, but generally was from 0.10 to 0.30 ppm. More water samples than sediment samples were analyzed for atrazine because there was not always enough sediment available to perform an analysis. This usually occurred for storms later in the season on the surface contoured watersheds when sediment concentrations were lower, and for storms on the ridged watershed where sediment concentrations and total runoff were low for the entire season.

Table 17 presents the average concentrations of atrazine in the water and sediment, and total losses of atrazine in the water and sediment (best estimates) from the southmiddle (surface contoured) and northmiddle (ridged) watersheds for data collected from 1967 to 1970. The concentration of atrazine in each water and sediment sample analyzed is given in Tables 31 to 34 of Appendix B. For some dates runoff occurred more than once. In these cases the average concentration of pesticide for the first runoff event was used for the second storm and the total load for the two storms was summed for that date.

From a storm which occurred on May 13, 1970, 7 days after the atrazine was applied, approximately 0.448 lb/A or about 15 percent of the



Table 17. Total losses of atrazine in the water and sediment from the southmiddle and northmiddle watersheds, 1967-1970<sup>a</sup>

Date of Storm	SM Watershed				NM Watershed			
	Water		Sediment		Water		Sediment	
	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)
5-13-70	2.87	0.339	4.47	0.109	1.68	0.061	8.55	0.005
5-30-70	0.31	0.020	0.21	0.001	0.35	0.009	1.87	0.001
6-11-70	0.15	0.008	0.18	0.0003	0.39	0.005		
5-16-69	0.97	0.002						
6-11-69	0.43	0.087	0.76	0.019	0.55	0.056		
6-22-69	0.21	0.002	0.31	0.0002	0.19	0.002	1.19	0.001
6-28-69	0.13	0.012	0.26	0.014	0.11	0.006	0.20	0.0004
7- 7-69	0.14	0.019	0.23	0.003	0.11	0.009	0.18	
8- 6-69	0.02	0.003	0.12	0.001	0.01	0.001		
8- 8-69	0.01	0.002	T <sup>b</sup>	0.000	0.01	0.001		
6-25-68	0.07	0.007	0.28	0.004	0.02	0.001	0.19	
6-29-68					0.03	0.001		
8- 8-68	0.03	0.002						
6-11-67	0.07	0.003	0.45					
6-13-67	0.04	0.004	0.34		0.10	0.014	0.51	
6-14-67	0.05	0.007	0.66		0.06	0.010	0.45	
6-15-67	0.12	0.0003	0.49		0.06	0.0004	0.66	
6-19-67	0.07	0.009	0.27				0.39	
6-24-67	0.10	0.008	0.31		0.06	0.007	0.47	
6-27-67	0.02	0.0003	T		0.03	0.001		

<sup>a</sup> Atrazine applied 5-6-70, 5-8-69, 4-30-68, 5-22-67

<sup>b</sup> Trace

total amount of atrazine applied to the southmiddle watershed was lost in the surface runoff and sediment. Of the total 0.45 lb/A lost, 0.11 lb/A was carried in the sediment and 0.34 lb/A was carried in the water. For the same storm, the total atrazine lost from the northmiddle watershed (ridged) was approximately 0.066 lb/A or 2.2 percent of the total amount of atrazine applied to the watershed. For this storm total runoff was 0.58 inches on the southmiddle watershed and 0.16 inches on the northmiddle watershed. The total rainfall for the storm on May 13 was 1.15 inches. In general, the amount of atrazine lost in the water and sediment decreased with time after application. For storms occurring 2 months after application, the amounts of atrazine lost in the water and sediment were insignificant.

The results indicate that if a storm occurs shortly after the atrazine is applied, significant amounts of atrazine may be lost in the surface runoff and sediment.

In 1970 approximately 0.48 lb/A or 16 percent of the total amount of atrazine applied to the southmiddle watershed was lost in the surface runoff and sediment. Of this amount, 0.37 lb/A was lost in the surface runoff and 0.11 lb/A was attached to the sediment. In 1969, 0.13 lb/A was lost in the surface runoff and 0.04 lb/A was lost in the sediment from the southmiddle watershed, about 6 percent of the total amount applied to the watershed. The data for 1967 and 1968 for the southmiddle watershed, and data for all 4 years for the northmiddle watershed is incomplete; thus the total amount of atrazine lost during the year cannot be estimated.

In comparing the two tillage systems on an individual storm basis,

more atrazine was lost from the surface contoured watershed than from the ridged watershed. This difference is due to the fact that water and sediment losses from the surface contoured watershed were greater than from the ridged watershed.

In general, the atrazine concentrations were higher in the sediment than the water, but greater losses of atrazine occurred in the water. Highest concentrations of atrazine in both the water and sediment were found in samples taken at the beginning of the runoff. Table 18 shows the concentrations of atrazine in the water and sediment for the storm of May 13, 1971 on the southmiddle watershed at different times since the beginning of the runoff. The atrazine concentration in the water for the first sample was 4.91 ppm and dropped to 1.17 ppm by the time the last sample was collected. These results are similar to the concentration patterns observed by White *et al.* (1967), who measured atrazine losses from small runoff plots where a rainfall simulator was used to produce runoff.

Table 18. Concentration of atrazine in the water and sediment for the storm May 13, 1970, on the southmiddle watershed

Time Since Beginning of Runoff (Min.)	Concentration in Water (ppm)	Concentration in Sediment (ppm)
6.0	4.91	7.25
7.0	4.38	7.35
10.0	2.45	4.66
10.5	1.44	3.39
11.0	1.17	1.77
11.4		2.38

## 2. Propachlor

Molnau (1969) analyzed thirty water and sediment samples for propachlor which were collected in 1967. The first samples were collected 14 days after the propachlor was applied and the last samples were collected 25 days after the propachlor was applied. No runoff occurred in 1968 or 1969 before propachlor completely degraded. Runoff and sediment samples collected in 1970 were analyzed for propachlor residues.

Molnau (1969) found no detectable amounts of propachlor in the water or sediment. The minimum detectable quantity of propachlor was 0.05 ppm in the water and 0.2 to 0.3 ppm in the sediment.

Table 19 shows the average concentrations of propachlor in the water and sediment, and total losses of propachlor in the water and sediment from the northeast watershed for 1970. The concentration of propachlor in each of the ten water and sediment samples is given in Tables 35 and 36 of Appendix B.

From the storm on May 13, 1970, 0.116 lb/A of propachlor was lost in the water and .039 lb/A was lost with the sediment from the surface contoured watershed. Propachlor found in the water and sediment from this storm was 2.6 percent of the amount applied to the watershed. The amount of propachlor lost in the surface runoff and sediment was lower than the amount of atrazine lost from the other surface contoured watershed for this storm. Since propachlor and atrazine were applied to the watersheds on successive days in 1970, it appears larger amounts of atrazine than propachlor would be lost in the surface runoff and sediment for a storm occurring shortly after the chemicals were applied. Small amounts of

propachlor were found in the surface runoff from storms on May 30 and June 11, but no detectable amounts of propachlor were found in the sediment.

Table 19. Total losses of propachlor in the water and sediment for the northeast watershed, 1970<sup>a</sup>

Date of Storm	Water		Sediment	
	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)
5-13-70	1.28	0.116	3.01	0.039
5-30-70	0.29	0.017	0.00	0.000
6-11-70	0.23	0.014	0.00	0.000

<sup>a</sup>Propachlor applied 5-5-70

### 3. Diazinon

Runoff and sediment samples collected in 1968 and 1969 were analyzed for diazinon residues. A total of sixty-six water samples and eighteen sediment samples were analyzed for diazinon. Detectable concentrations of diazinon were found in nineteen of the water samples, with a maximum concentration of 82 ppb. Eight of the sediment samples contained diazinon with a maximum concentration of 0.17 ppm. Table 20 shows the average concentrations of diazinon in the water and sediment and total losses of diazinon in the water and sediment from the southmiddle and northeast watersheds. A summary of the concentrations of diazinon in individual samples is given in Tables 37 to 42 of Appendix B.

Table 20. Total losses of diazinon in the water and sediment for the southmiddle and northeast watersheds, 1968-1969<sup>a</sup>

Date of Storm	SM Watershed				NE Watershed			
	Water		Sediment		Water		Sediment	
	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)	Average Concentration (ppm)	Total Loss (lb/A)
6-22-69	0.08	0.001	0.00	0.00	-- <sup>c</sup>	--	--	--
6-28-69	0.06	0.001	--	--	0.05	0.004	--	--
7- 7-69	0.00	0.000	0.00	0.00	0.04	0.001	T <sup>b</sup>	0.000
8- 6-69	0.00	0.000	0.00	0.00	0.01	0.001	0.00	0.000
8- 8-69	--	--	0.00	0.00	0.00	0.000	--	--
6-25-68	0.00	0.000	--	--	0.03	0.002	0.02	0.0001
6-29-68	0.00	0.000	--	--	0.00	0.001	0.00	0.000
7-17-68	0.00	0.000	--	--	0.00	0.000	--	--
8- 8-68	0.00	0.000	--	--	0.00	0.000	--	--
8-27-68	--	--	--	--	0.00	0.000	--	--

<sup>a</sup>Diazinon applied 6-19-69, 6-19-68

<sup>b</sup>Trace

<sup>c</sup>No data collected

Diazinon occurred in water samples collected from the surface contoured watersheds more frequently than in samples collected from the ridged watersheds. There was only one water sample collected from the ridged watersheds that contained detectable diazinon. Since diazinon was applied in a band application at 1 lb/A in the corn rows, water flowing between the ridges would not have as much contact with the diazinon as water flowing over the surface contoured watersheds. This may explain why more diazinon was found in runoff samples collected from the surface contoured watersheds. The highest concentrations of diazinon were found in runoff and sediment samples collected 4 to 10 days after the diazinon was applied. In 1969, 4 days after the diazinon was applied, only 0.1 percent of the diazinon was lost in the surface runoff and sediment from the southmiddle watershed. For the cultural practices used in this experiment, no large amounts of diazinon would be lost in surface runoff and sediment.

#### E. Pesticide Movement and Degradation in the Soil Profile

##### 1. Atrazine

Soil samples taken in 1967, 1968, 1969, and 1970 on the southmiddle and northmiddle watersheds were analyzed for atrazine.

All the data is summarized in Tables 43 to 50 in Appendix B. The average concentrations for each sample date for the data collected from 1967 to 1970 are plotted on logarithmic paper to show the degradation pattern and movement in soil profile (Figures 15 to 22). The data was coded by adding 0.1 to the concentrations and 1 to each time value to facilitate logarithmic plotting.

Figures 15 to 22 show a general downward trend of concentration. Atrazine moved slowly in the soil profile with time. Samples taken at 6 to 8 inches below the surface 80 to 90 days after the atrazine was applied contained small amounts of atrazine. The atrazine concentrations at the greater depths generally increased with time, which indicates atrazine was moving downward in the soil profile. In 1969, soil samples taken from 8 to 10 inches in November had average concentrations of atrazine of 0.19 ppm on the northmiddle watershed and 0.22 ppm on the southmiddle watershed. No soil samples were taken at depths greater than 10 inches, but it appears from the small concentrations detected at the 8- to 10-inch depth, only very small amounts of atrazine would move below a depth of 10 inches.

All of the data showed atrazine present in the 1- to 3-inch depth shortly after application. One would not expect atrazine to move that quickly within the soil profile, since samples were always taken within a day after the application of the atrazine. The surface of the soil was rough at sampling time which made it difficult to define the surface inch, and 1- to 3-inch depth. The rough surface also may have allowed the spray to penetrate to the 1- to 3-inch depth.

Generally higher concentrations of atrazine were detected on the surface contoured watershed than on the ridged watershed immediately after application although the same amount of atrazine was applied to both watersheds. Some of the spray landed on the trash on the ridged watershed and would not have reached the soil profile. This could account for the lower concentrations of atrazine observed on the ridged watershed.



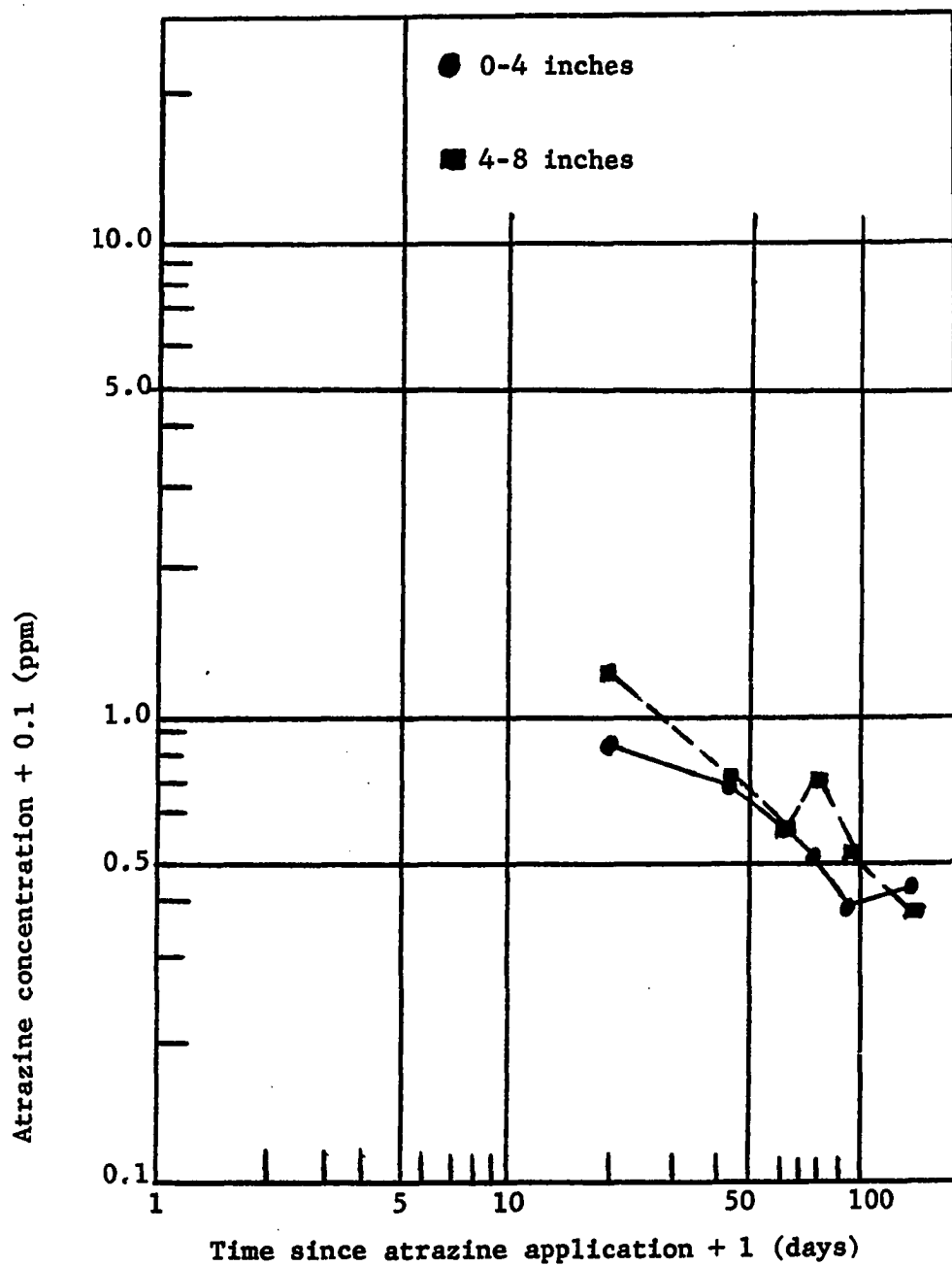


Figure 15. Concentration of atrazine in soil profile for southmiddle watershed, 1967

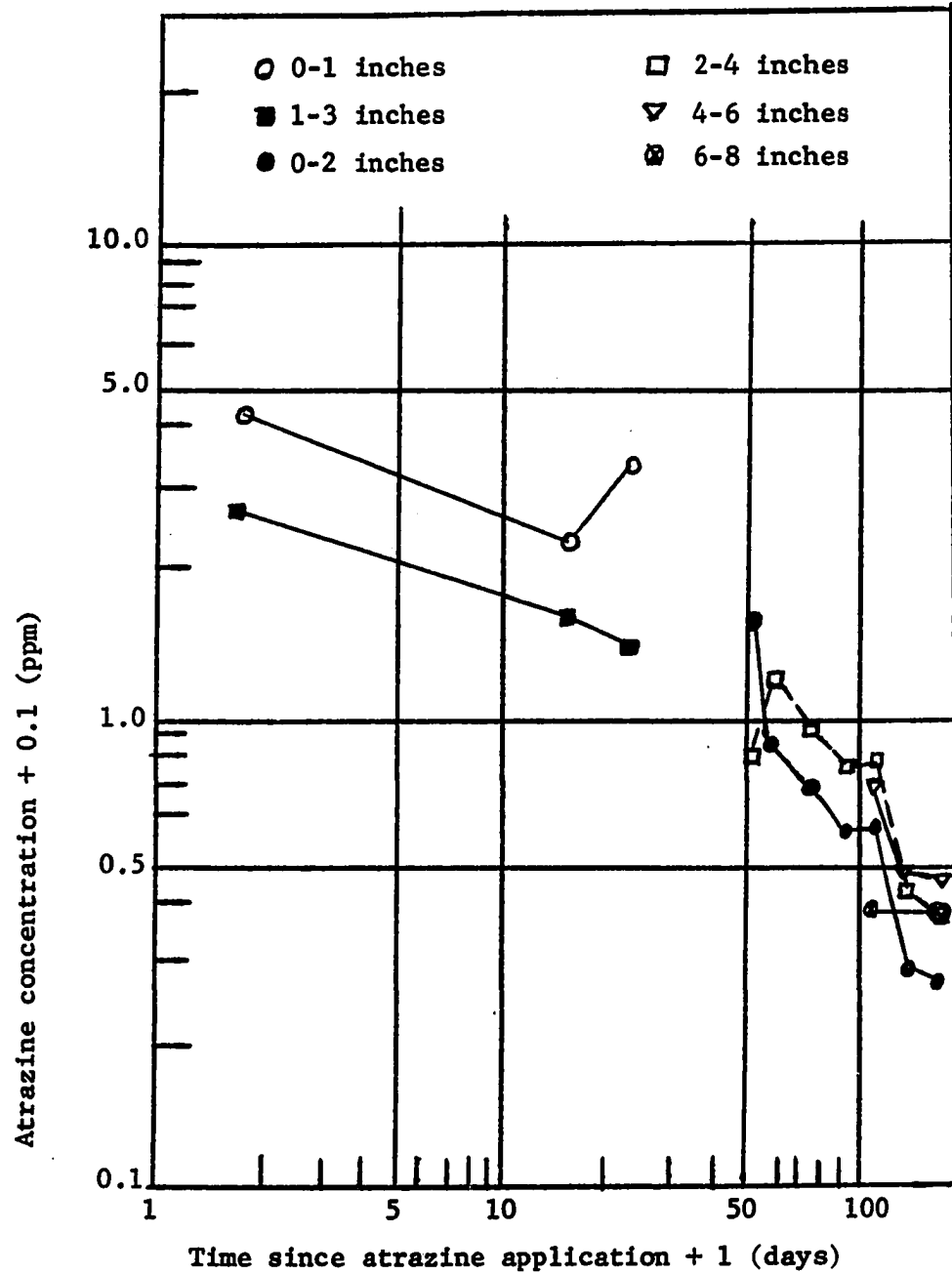


Figure 16. Concentration of atrazine in soil profile for southmiddle watershed, 1968

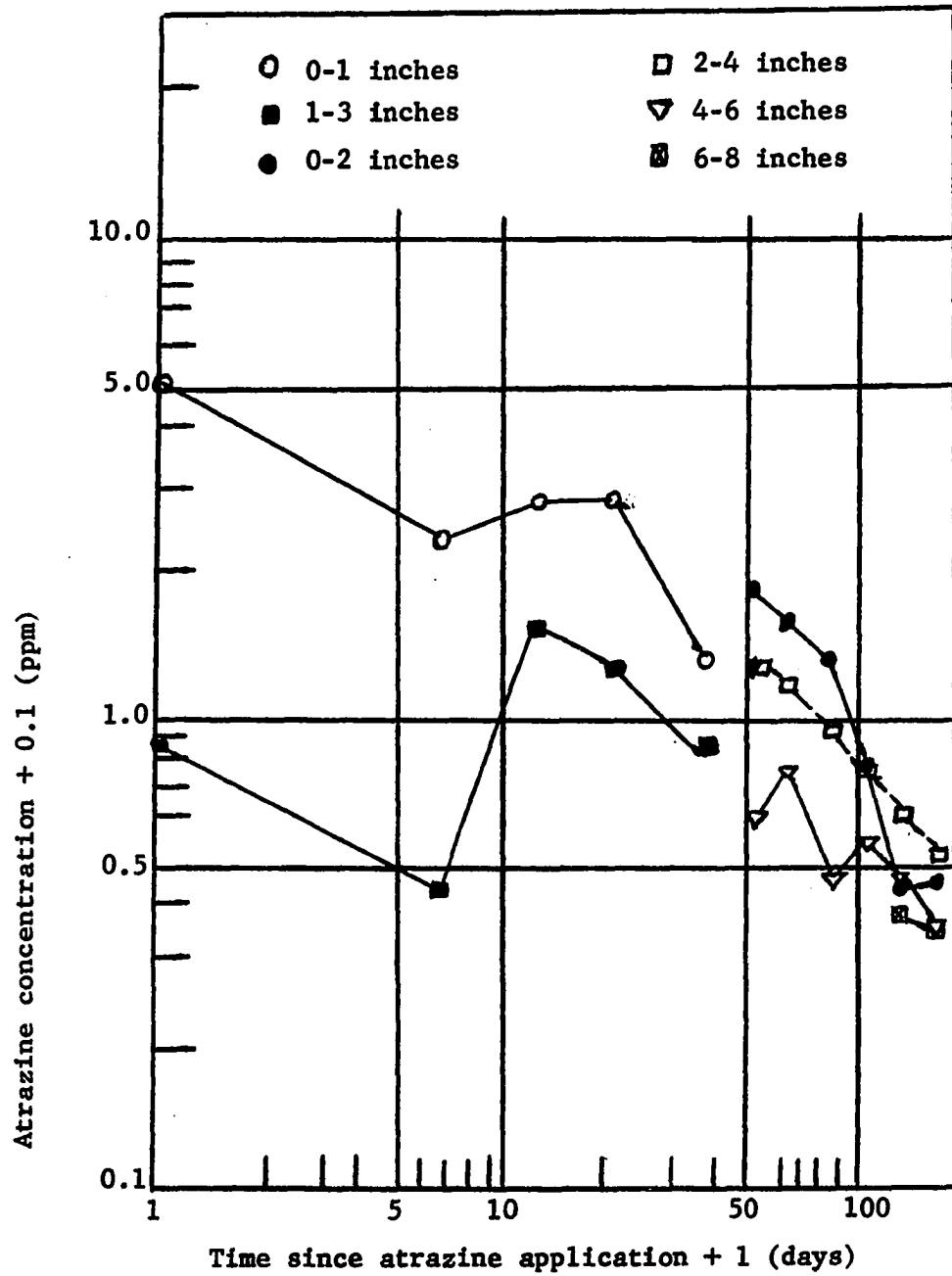


Figure 17. Concentration of atrazine in soil profile for southmiddle watershed, 1969

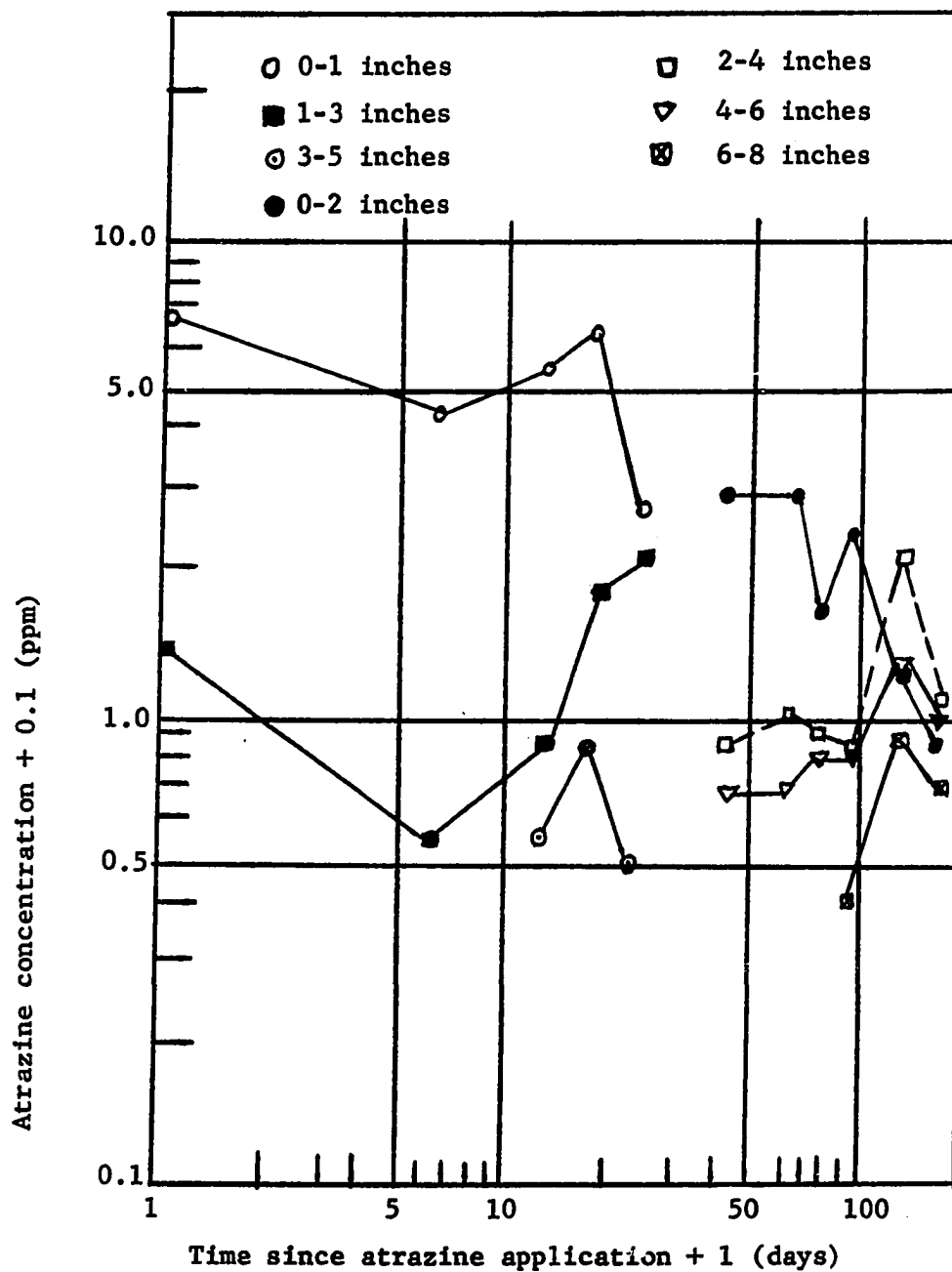


Figure 18. Concentration of atrazine in soil profile for southmiddle watershed, 1970

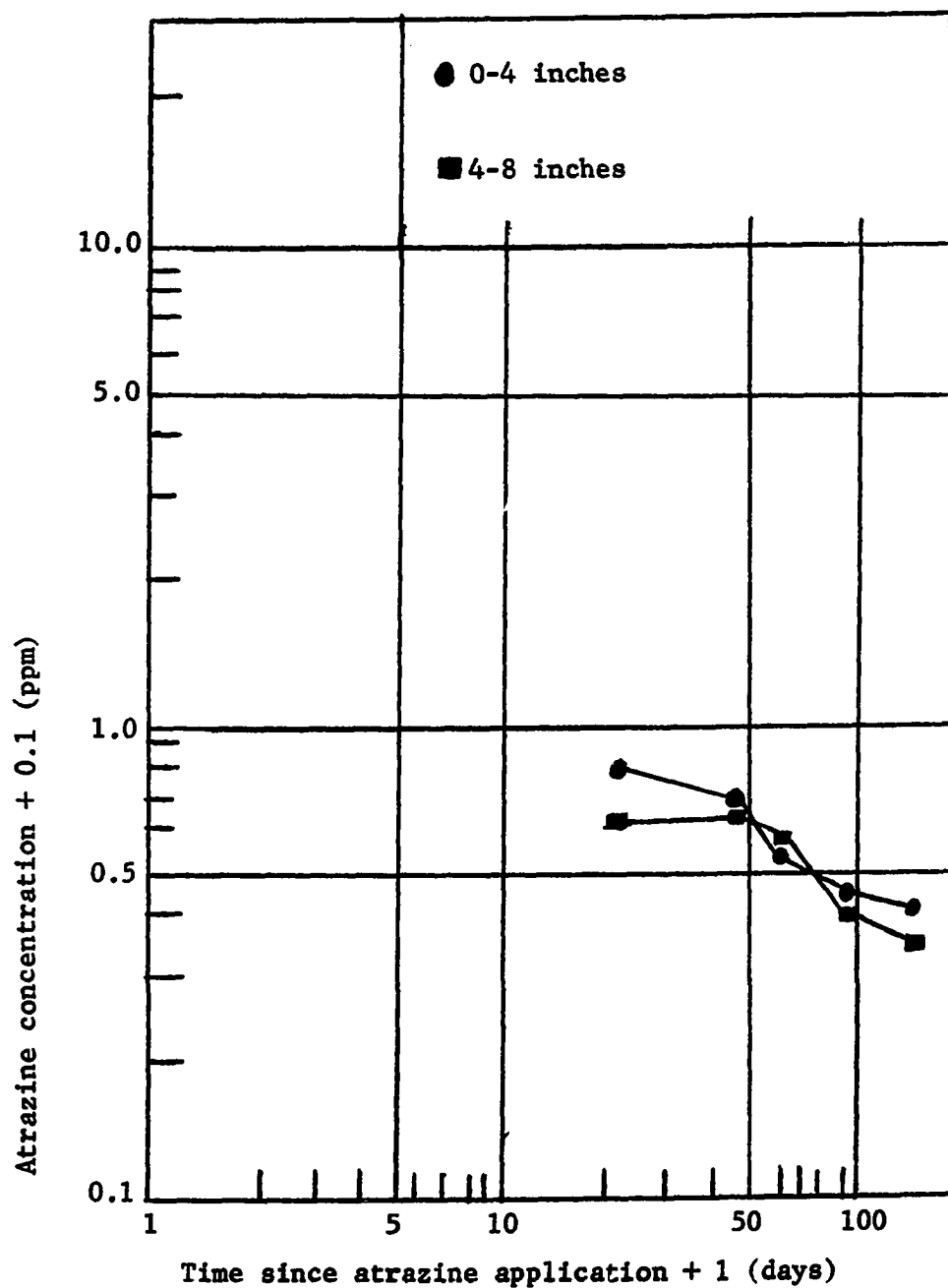


Figure 19. Concentration of atrazine in soil profile for northmiddle watershed, 1967

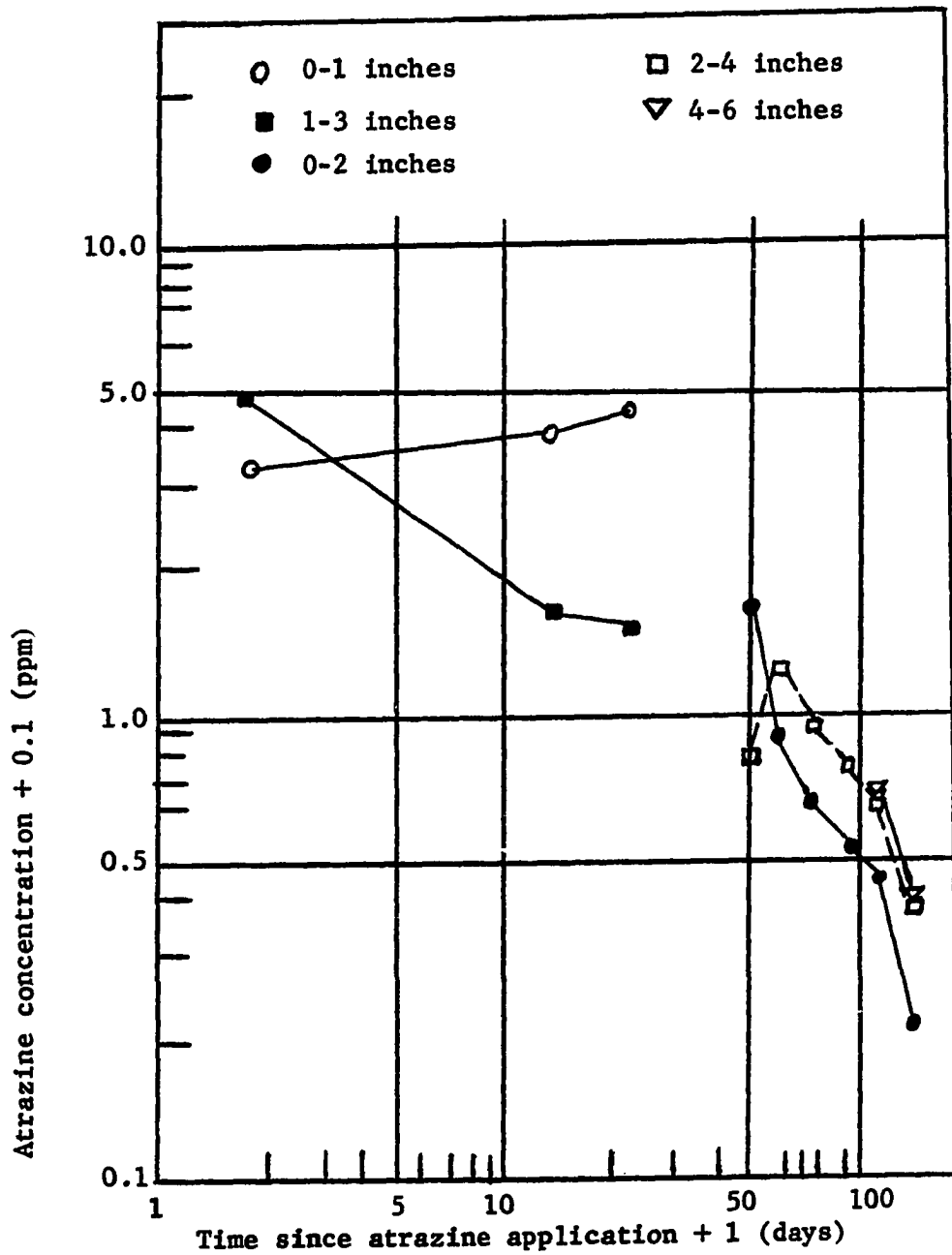


Figure 20. Concentration of atrazine in soil profile for northmiddle watershed, 1968

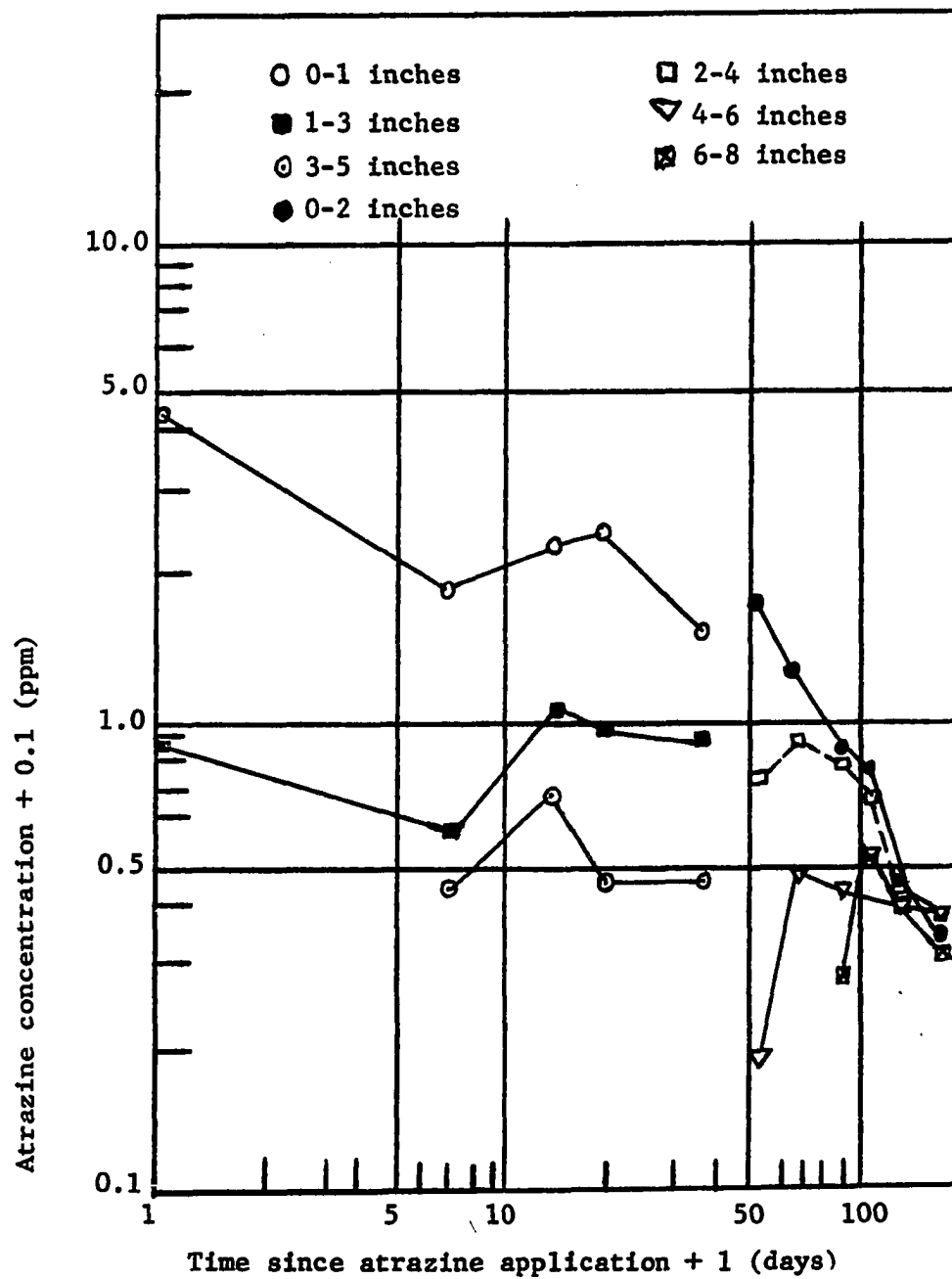


Figure 21. Concentration of atrazine in soil profile for northmiddle watershed, 1969

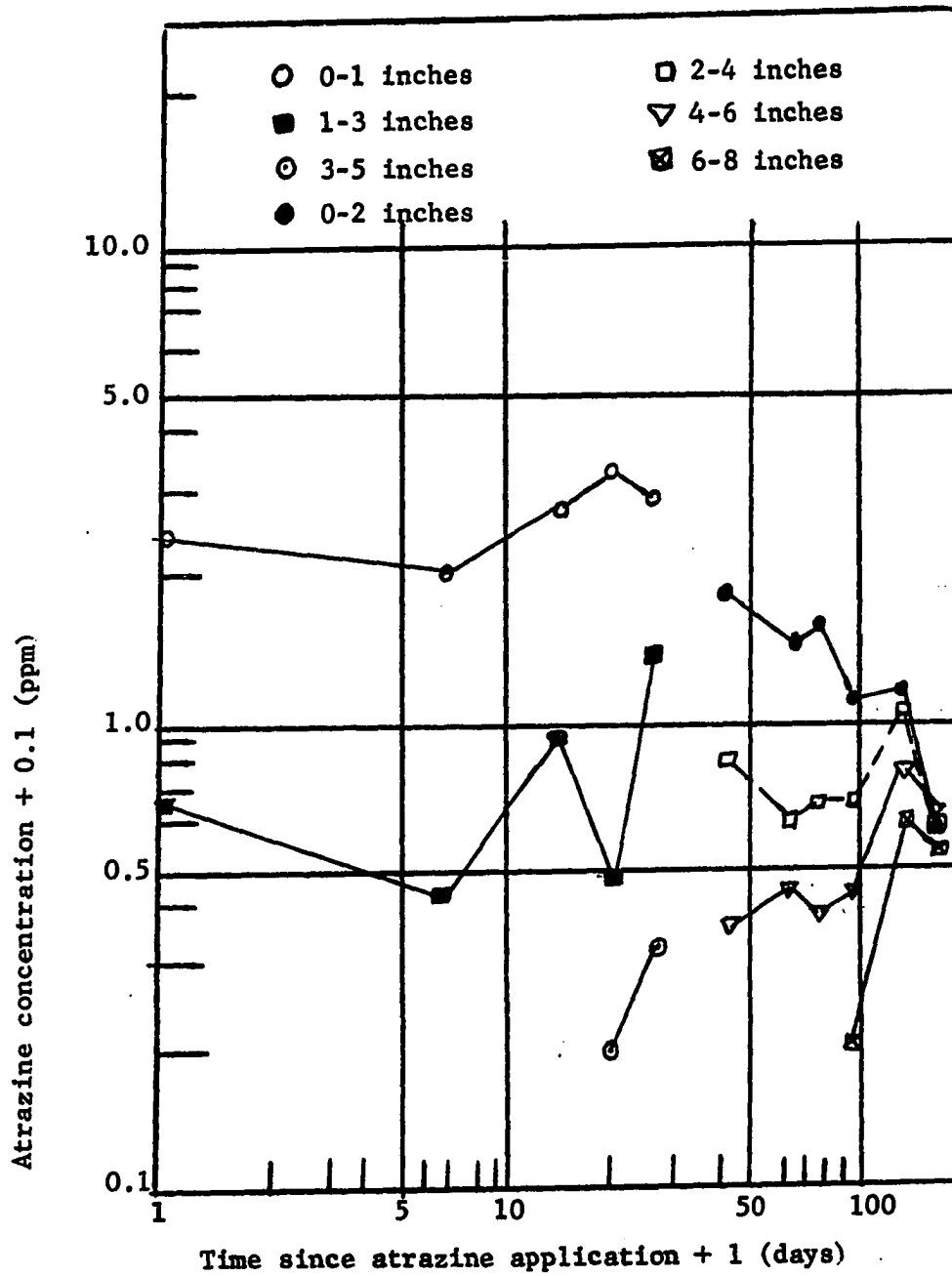


Figure 22. Concentration of atrazine in soil profile for northmiddle watershed, 1970



In some instances there was not a smooth downward trend of concentration with time. This was especially true in the first few sampling dates. On the southmiddle watershed the average concentration increased from 4.02 ppm on May 12, 1970 to 5.34 ppm on May 19 for the 0- to 1-inch depth and from 0.44 ppm to 0.72 ppm for the 1- to 3-inch depth. Most of this variation was due to sampling error. The exact same location was not sampled each time. Samples were taken in the same general area as the previous sample. There was a great variation in concentration at each sample location (Tables 43 to 50). Figure 23 shows the variation in concentration with time for each sample point on the southmiddle watershed for 1970. For samples taken a few hours after application on May 6, 1970, the concentrations ranged from a maximum of 10.37 ppm for location 7 to a minimum of 3.36 ppm for location 11 on the southmiddle watershed. On the northmiddle watershed the concentrations ranged from 4.15 ppm at location 26 to 0.21 ppm at location 29 for samples taken May 6, 1970. Caro and Taylor (1971) also found great variability in soil samples taken from a watershed treated with dieldrin. They were not able to show statistically that there was any loss of dieldrin from the soil over 41 months. Nash and Woolson (1967) often found the quantity of organochlorine pesticides in a soil "increased" between samplings taken 3 to 5 years apart.

There was no significant difference in the rate of degradation or the amount of movement in the soil profile for the two tillage systems. In 1969, under both tillage systems only small concentrations of atrazine were found in the 8- to 10-inch depth 181 days after the atrazine was

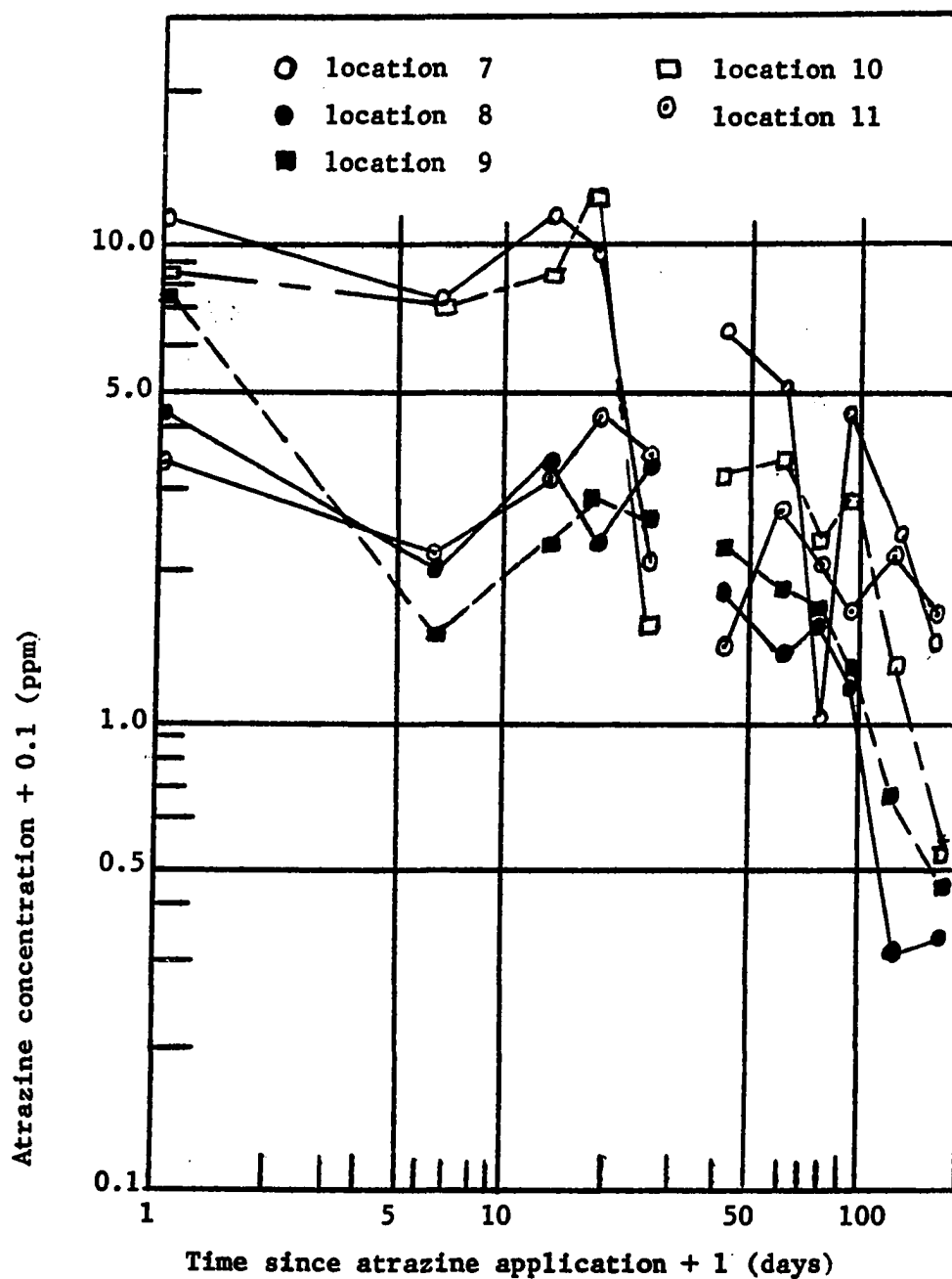


Figure 23. Concentration of atrazine for 0 to 1 inch and 0 to 2 inch depths for different sampling locations on the southmiddle watershed, 1970

applied. No exact rates of degradation can be determined because of the variability in the data and the environmental factors that affect atrazine degradation, but some idea of the amount of atrazine remaining after certain periods of time can be determined. Table 21 shows the percent atrazine remaining at different times for the northmiddle and southmiddle watersheds. Generally, 30 to 40 days after the atrazine had been applied, less than 50 percent of it remained. The atrazine degraded faster in 1968 than 1969 or 1970. In 1969 and 1970, 3 lb/A of atrazine were applied to both watersheds, while in 1968 2 lb/A were applied. The application rate may have had an effect on the percent of atrazine remaining. In 1970, after 40 days, 94.1 percent of the atrazine remained in the soil profile on the northmiddle watershed and 50.5 percent remained on the southmiddle watershed. Part of this difference is due to the great variation in the data; also more atrazine was lost in the surface runoff and sediment from storms in May on the southmiddle watershed than on the northmiddle watershed.

Some atrazine carryover was found on both watersheds (see Table 22). Samples taken in April 1969 showed atrazine concentrations ranging from 0.13 to 0.34 ppm on the southmiddle watershed and from 0.15 to 0.57 ppm on the northmiddle watershed for depths of 0 to 8 inches. In 1970 the concentrations ranged from 0.00 to 0.99 ppm on the southmiddle watershed and from 0.00 to 0.66 ppm on the northmiddle watershed in the top 10 inches of the soil profile.

Table 21. The percent atrazine remaining in the soil profile at various times since application

Year	SM Watershed (Surface Contoured)		NM Watershed (Ridged)	
	Days Since Application	Percent Atrazine Remaining	Days Since Application	Percent Atrazine Remaining
1970	40	50.5	40	94.1
	97	47.8	97	67.8
1969	36	42.1	36	50.3
	102	34.7	102	39.4
1968	51	32.8	49	26.3
	107	30.2	107	19.9

Table 22. Carryover concentrations of atrazine in soil profile for samples taken in April 1969 and 1970

Date of Sampling	Depth of Sampling (inches)	SM Watershed (Surface Contoured) Concentration (ppm)			NM Watershed (Ridged) Concentration (ppm)		
		Avg	Max	Min	Avg	Max	Min
April 21, 1970	0- 2	0.56	0.95	0.31	0.34	0.60	0.26
	2- 4	0.20	0.30	0.00	0.48	0.66	0.00
	4- 6	0.19	0.36	0.00	0.33	0.47	0.00
	6- 8	0.33	0.99	0.00	0.34	0.41	0.19
	8-10	0.00	0.00	0.00	0.25	0.44	T <sup>a</sup>
April 29, 1969	0- 2	0.28	0.34	0.24	0.20	0.27	0.15
	2- 4	0.19	0.25	0.13	0.34	0.57	0.19
	4- 6	0.23	0.30	0.16	0.38	0.52	0.30
	6- 8	0.20	0.24	0.15	0.34	0.47	0.25

<sup>a</sup>Trace

## 2. Propachlor

Soil samples taken in 1969 and 1970 from the northeast and southwest watersheds were analyzed for propachlor residues. The average concentrations for each sample date for 1969 and 1970 were plotted on logarithmic paper in a manner similar to the atrazine data (Figures 24 to 27). Summaries of all the propachlor soil sample data are presented in Tables 51 to 54 in Appendix B.

Figures 24 to 27 show a general downward trend of concentration. Very little propachlor moved below the 3-inch depth (Tables 51 to 54). In 1970 on the northeast watershed no propachlor was found at the 1- to 3-inch or 3- to 5-inch depth 20 days after propachlor was applied to the watershed. Twenty-eight days after the application date the average concentrations from 0 to 1 inches, 1 to 3 inches, and 3 to 5 inches, were 2.43, 0.27, and 0.04 ppm, respectively.

The propachlor soil sampling program was continued only for 3 or 4 weeks after the date of application in 1969 and 1970, because atrazine and oil were applied to the southwest watershed for broadleaf weed control since it was necessary to have uniform weed control on all watersheds. It was suspected that atrazine and oil would interfere with the detection of propachlor on the gas chromatograph.

In 1970 propachlor was present 37 days after the application date on the northeast watershed because small amounts of propachlor were detected in the surface runoff from a storm on June 11. At the last sampling date, which was 28 days after the date of application, approximately 80 percent of the propachlor had disappeared. In 1968, Molnau (1969) found small

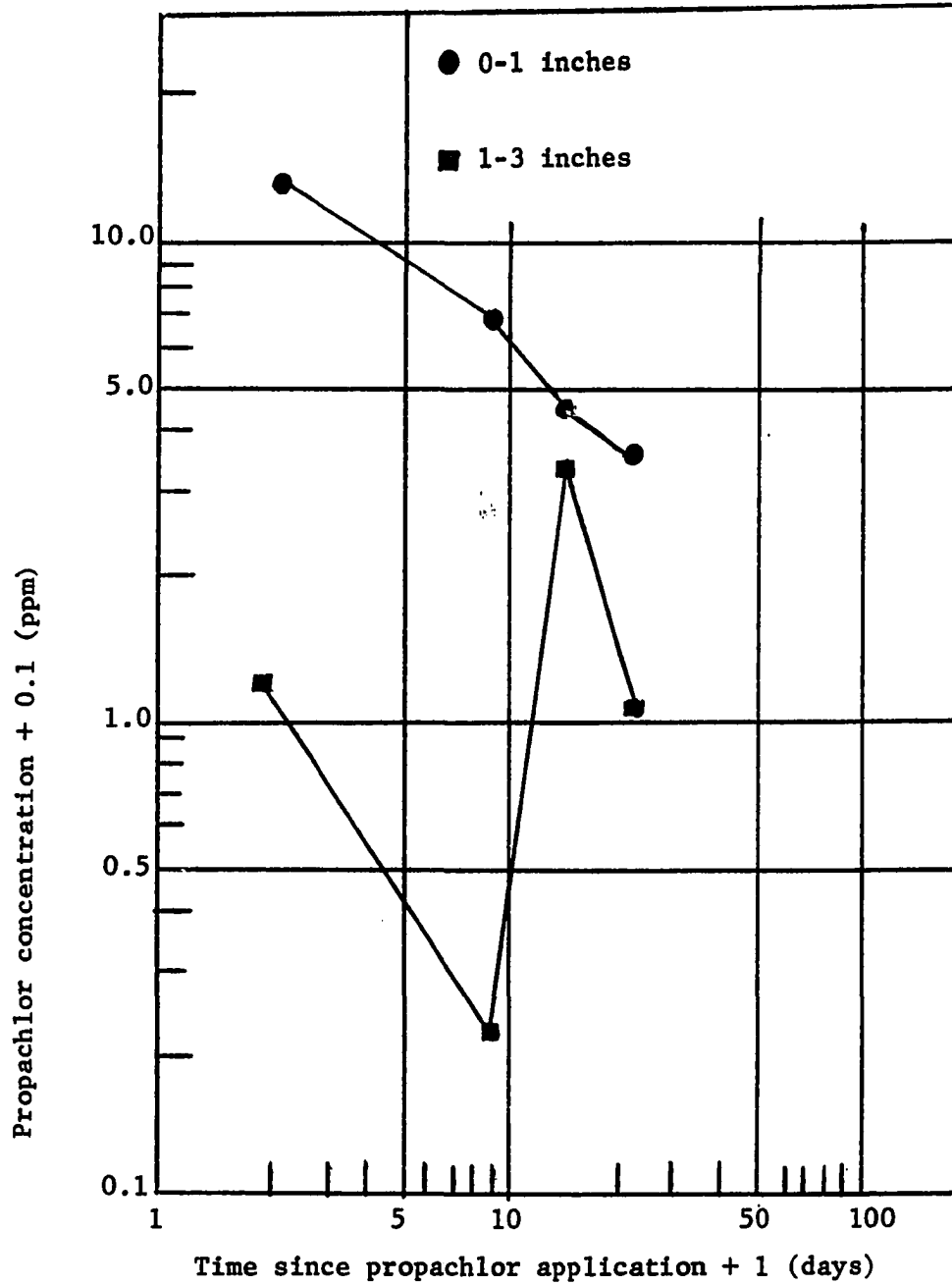


Figure 24. Concentration of propachlor in soil profile for northeast watershed, 1969

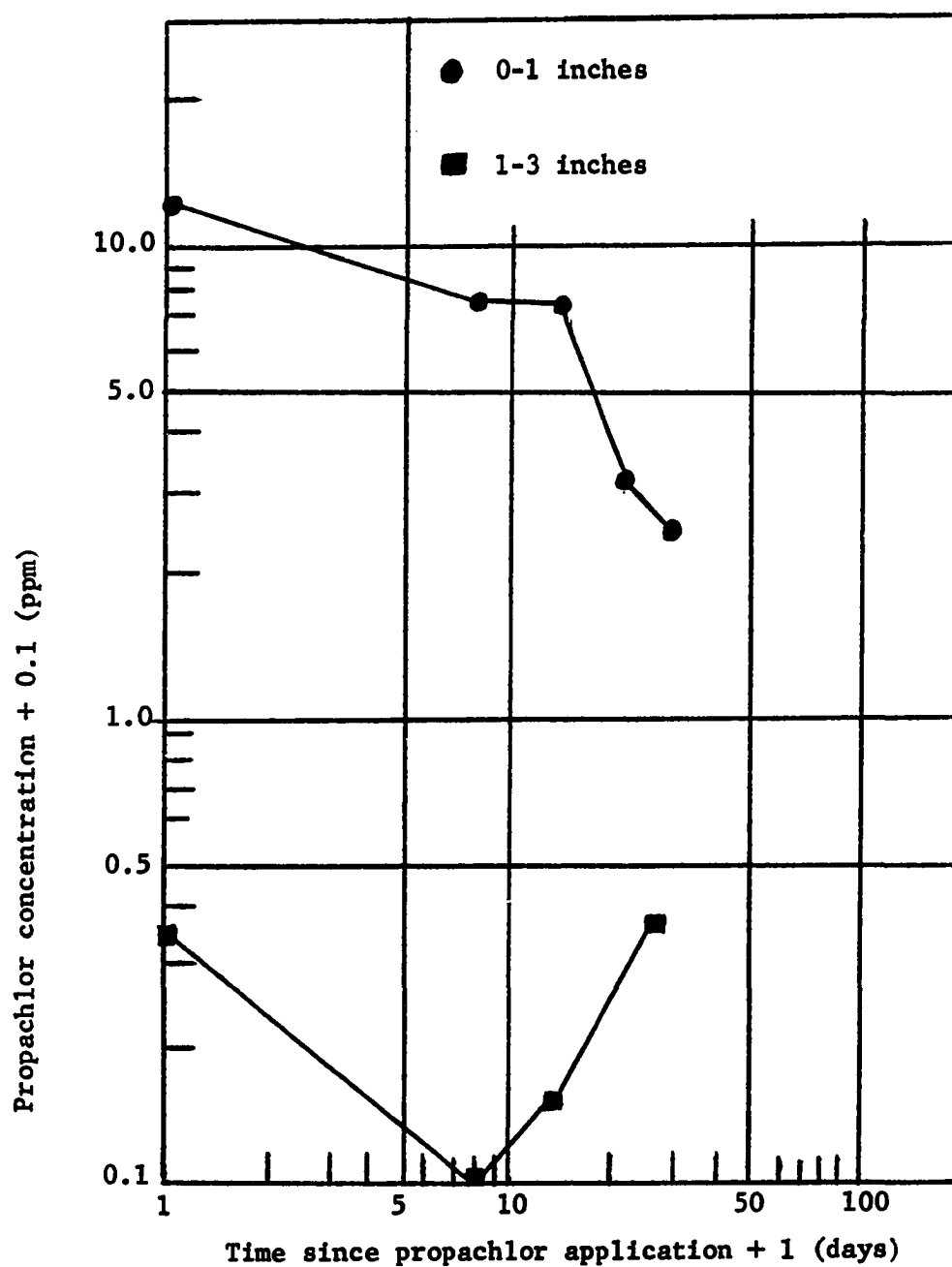


Figure 25. Concentration of propachlor in soil profile for northeast watershed, 1970

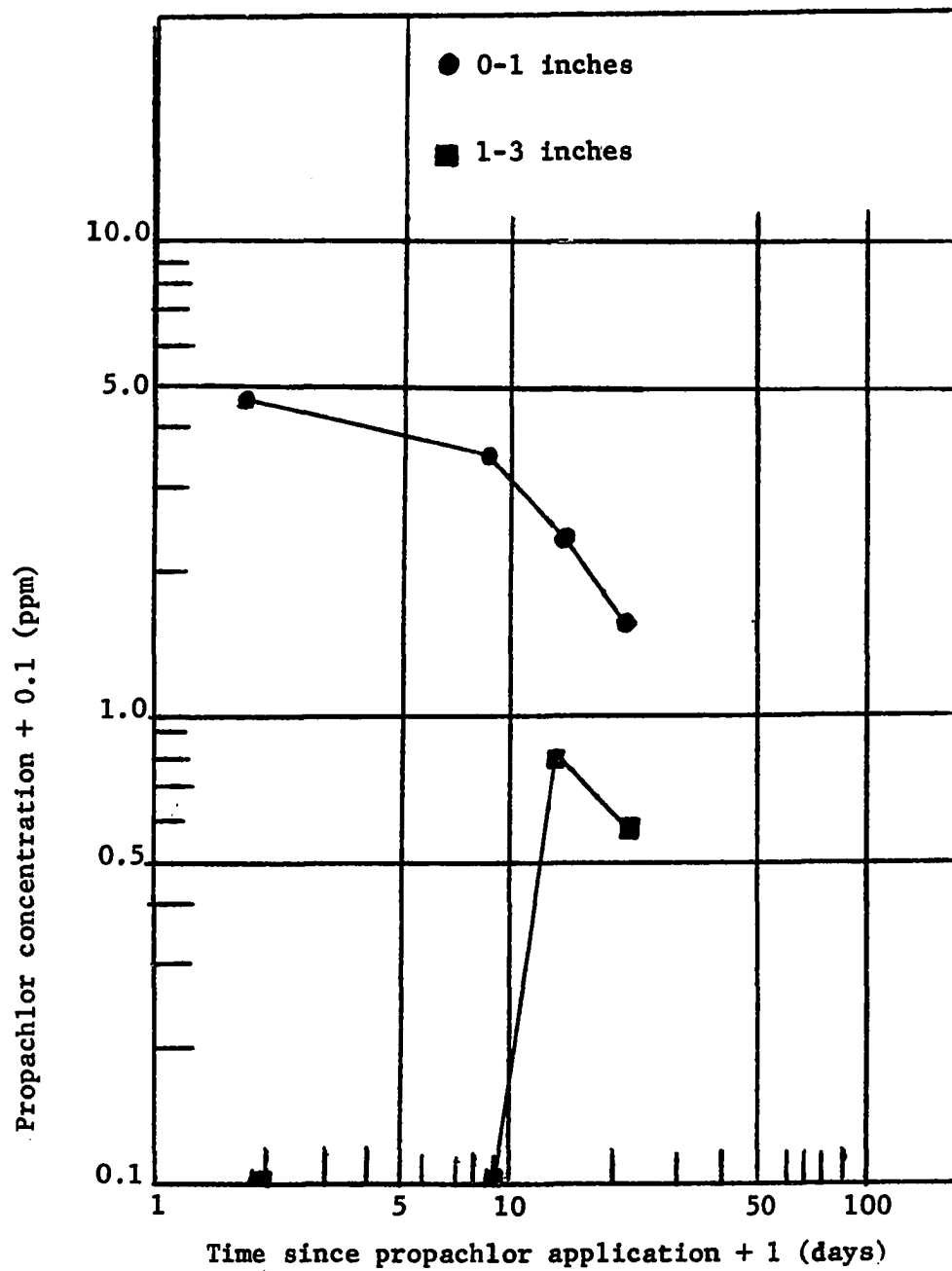


Figure 26. Concentration of propachlor in soil profile for southwest watershed, 1969



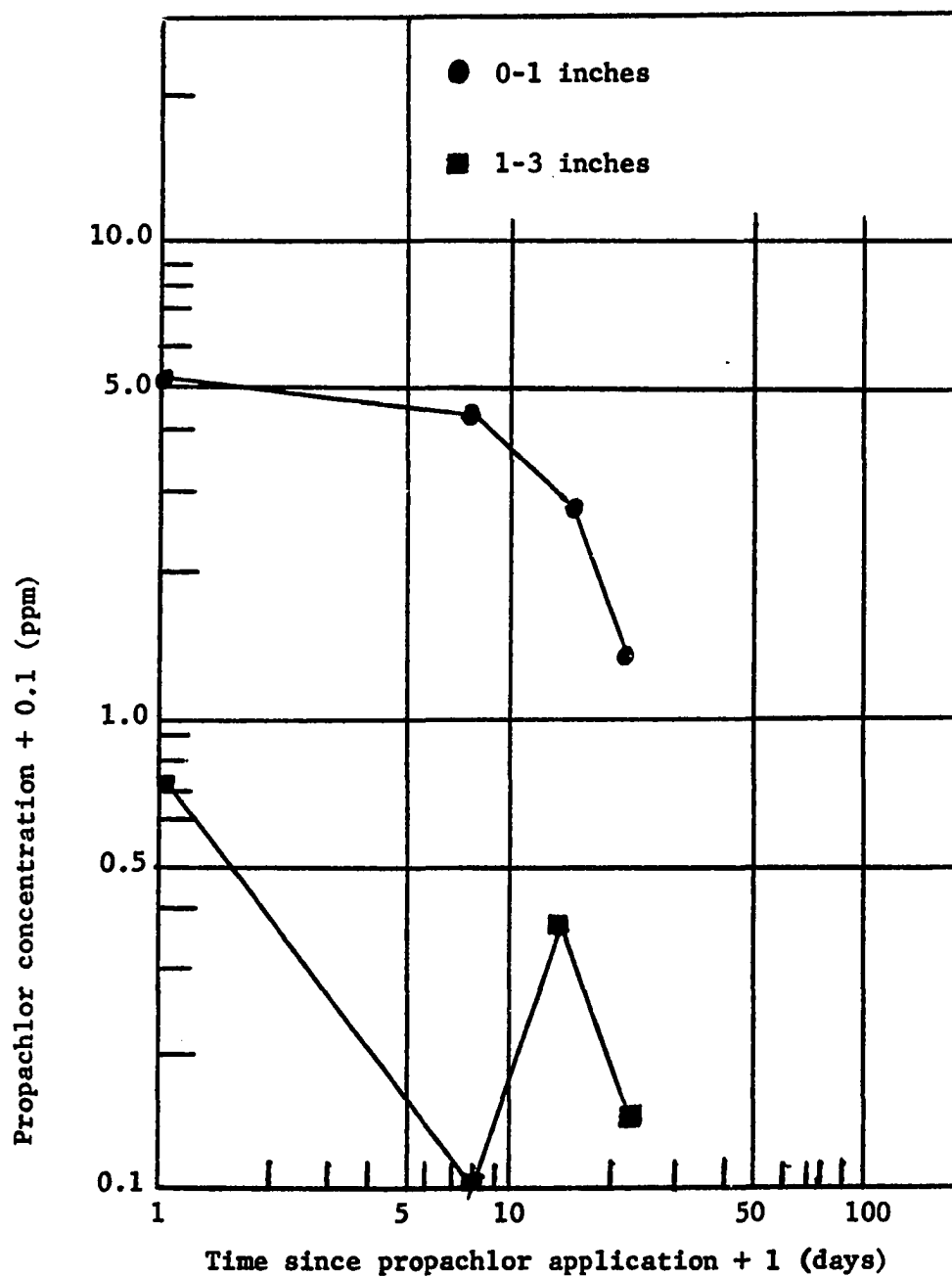


Figure 27. Concentration of propachlor in soil profile for southwest watershed, 1970

amounts of propachlor residues in the soil on the southwest watershed 36 days after application, but all of the propachlor had degraded on the northeast watershed.

The propachlor data also showed a great variation in concentration at each sample location for the two tillage systems. Figure 28 shows the great variation in concentration with time for each sample location on the southwest watershed for 1969. Concentrations ranged from 8.59 ppm at location 5 to 2.33 ppm at location 4 for samples taken 1 day after the propachlor was applied. In 1970, soil samples taken at three of the six sample locations on the day of application did not contain detectable propachlor residues.

### 3. Diazinon

Soil samples were collected in 1968, 1969, and 1970 from all four watersheds and analyzed for diazinon. Only small concentrations of diazinon were detected in any of the soil samples that were analyzed from the four watersheds. Samples collected a few hours after the diazinon was applied contained less than 1.0 ppm of diazinon; in some of the samples no diazinon was detected. Fourteen soil samples taken on the northeast watershed in 1970 the day the diazinon was applied had concentrations ranging from 0.21 ppm to 0.00 ppm for depths of 0 to 2 inches and 2 to 4 inches, respectively. Soil samples taken 21 days after the diazinon was applied showed no detectable amounts of diazinon present.

After analyzing several hundred soil samples from the different watersheds that were collected in 1968, 1969, and 1970, it was decided not to analyze the rest of the soil samples because of the small concentrations

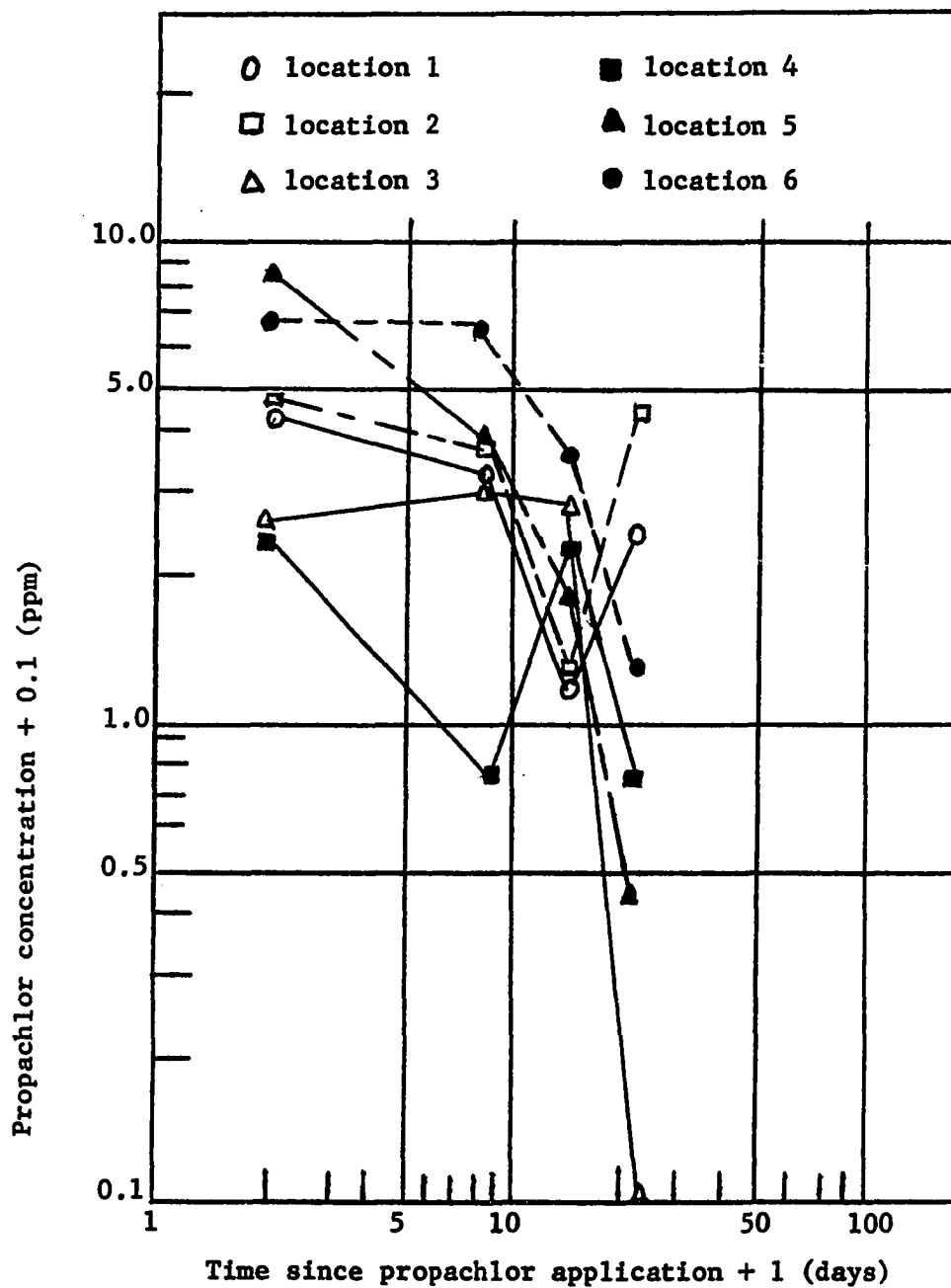


Figure 28. Concentration of propachlor for 0 to 1 inch depth for different sampling locations on the southwest watershed, 1969

of diazinon detected in the samples and because of the time and expense involved in the chemical analysis. With such small concentrations and variation in the data, no conclusions can be drawn from the data that was analyzed. All soil samples contained much smaller concentrations of diazinon than was theoretically applied to the watersheds. The diazinon may have degraded in the soil samples while they were stored in the freezer. All of the soil samples were kept frozen from 9 to 24 months before they were analyzed. Since it was decided to analyze the atrazine and propachlor soil samples first, it was impossible to analyze the diazinon soil samples at an earlier date with the personnel and equipment available. The diazinon may have degraded rapidly in the field. The laboratory experiments which will be discussed in the next chapter showed diazinon degraded rapidly at high temperatures.

## VI. LABORATORY EXPERIMENT

## A. Theory of Pesticide Diffusion in Soils

Ehlers et al. (1969b) studied lindane diffusion in soils and developed equations to describe the diffusion process. Their development was similar to the one Jackson (1964) used to develop diffusion equations to describe water movement through the soil in the combined vapor and liquid states. The following development of pesticide diffusion theory is taken from Ehlers et al. (1969b).

The steady-state vapor diffusion is described by:

$$q_v = - (D_v S^{10/3} S_t^2) \left( \frac{\partial \rho}{\partial x} \right) \quad (6-1)$$

where  $q_v$  is the vapor flux ( $\text{g cm}^{-2} \text{ sec}^{-1}$ ),  $D_v$  is the vapor diffusion coefficient in air ( $\text{cm}^2 \text{ sec}^{-1}$ ),  $S$  and  $S_t$  are the air-filled and total porosity of the soil, respectively, ( $\text{cm}^3 \text{ cm}^{-3}$ ) and  $\rho$  is the vapor density ( $\text{g cm}^{-3}$ ).

Combining the continuity equation

$$\frac{\partial \rho}{\partial t} = - \frac{1}{S} \left( \frac{\partial q_v}{\partial x} \right) \quad (6-2)$$

and equation 6-1, gives the transient-state equation

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left[ (D_v S^{7/3} S_t^2) \left( \frac{\partial \rho}{\partial x} \right) \right] \quad (6-3)$$

Equation 6-3 is valid for a non-adsorbing media. Sorption may be account-

ed for by adding the term  $-(\frac{B}{S}) (\frac{\partial C}{\partial t})$  to the right-hand side of equation 6-3 where  $B$  is the soil bulk density ( $\text{g cm}^{-3}$ ) and  $C$  is the total nonvapor concentration of the pesticide (g per g soil).

By adding the term  $-(\frac{B}{S}) (\frac{\partial C}{\partial t})$  and rearranging equation 6-3

$$\frac{\partial C}{\partial t} + (\frac{S}{B}) (\frac{\partial \rho}{\partial t}) = \frac{\partial}{\partial x} (D_v S^{10/3} / B S_t^2) (\frac{\partial \rho}{\partial x}) \quad (6-4)$$

Since  $\frac{\rho S}{B}$  is extremely small compared to  $C$ , it is assumed that  $(\frac{S}{B}) (\partial \rho / \partial t)$  is negligible compared with  $\frac{\partial C}{\partial t}$  in equation 6-4 and can be eliminated.

The vapor flux can be expressed in terms of the nonvapor concentration gradients by using the following relation:

$$\frac{\partial \rho}{\partial x} = (\frac{\partial \rho}{\partial C}) (\partial C / \partial x) \quad (6-5)$$

Combining equations 6-4 and 6-5

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ \left( (D_v S^{10/3} / B S_t^2) (\partial \rho / \partial C) \right) \frac{\partial C}{\partial x} \right] \quad (6-6)$$

Equation 6-6 accounts for diffusion in the vapor state.

"Nonvapor" diffusion through soils can be described by ionic diffusion. The steady-state linear diffusion is given by:

$$q_C = - B \theta (L/L_e)^2 (1 - Y) D_s (\frac{\partial C}{\partial x}) \quad (6-7)$$

where  $q_C$  is the "nonvapor" phase flux ( $\text{g cm}^{-2} \text{ sec}^{-1}$ ),  $\theta$  is the volumetric water content,  $(L/L_e)^2$  is the tortuosity factor,  $Y$  is the interaction term between the pesticide and soil, and  $D_s$  is the solution diffusion

coefficient of the compound.

Combining equation 6-7 with the continuity equation

$$\frac{\partial C}{\partial t} = - \frac{1}{B} \left( \partial q_C / \partial x \right) \quad (6-8)$$

gives

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ \theta \left( \frac{L}{L_e} \right)^2 (1 - Y) D_s \left( \frac{\partial C}{\partial x} \right) \right] \quad (6-9)$$

Total diffusion is equal to the summation of the vapor and "nonvapor" diffusion. Combining equations 6-7 and 6-9 gives the total diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ \left[ (D_v S^{10/3} / B S_t^2) \left( - \frac{\partial \rho}{\partial C} \right) + \theta \left( \frac{L}{L_e} \right)^2 (1 - Y) D_s \right] \frac{\partial C}{\partial x} \right] \quad (6-10)$$

Ehlers et al. (1969b) define the apparent vapor phase diffusion coefficient,  $D_v'$ , and apparent "nonvapor" diffusion coefficient  $D_s'$ , by the equations

$$D_v' = (D_v S^{10/3} / S_t^2) \left( - \frac{\partial \rho}{\partial C} \right) \quad (6-11)$$

$$D_s' = \left( L / L_e \right)^2 (1 - Y) D_s \quad (6-12)$$

The total apparent diffusion coefficient  $D_{vs}$  is defined as

$$D_{vs} = D_v' + D_s' \quad (6-13)$$

If  $D_v$  and  $D_s$  are considered constants, equation 6-10 can be written as Fick's second law of diffusion

$$\frac{\partial C}{\partial t} = D_{vs} \partial^2 C / \partial x^2 \quad (6-14)$$

By imposing specific boundary conditions, equation 6-14 can be solved for  $D_{vs}$ . To determine the relative diffusion in the vapor and "nonvapor" phase, the ambient pressure can be varied. Vapor diffusion is influenced by ambient pressure, whereas "nonvapor" diffusion is not. Jackson (1965) relates  $D_{vs}$  to pressure by the equation:

$$D_{vs} = D_s' + D_v' (P_o/P) \quad (6-15)$$

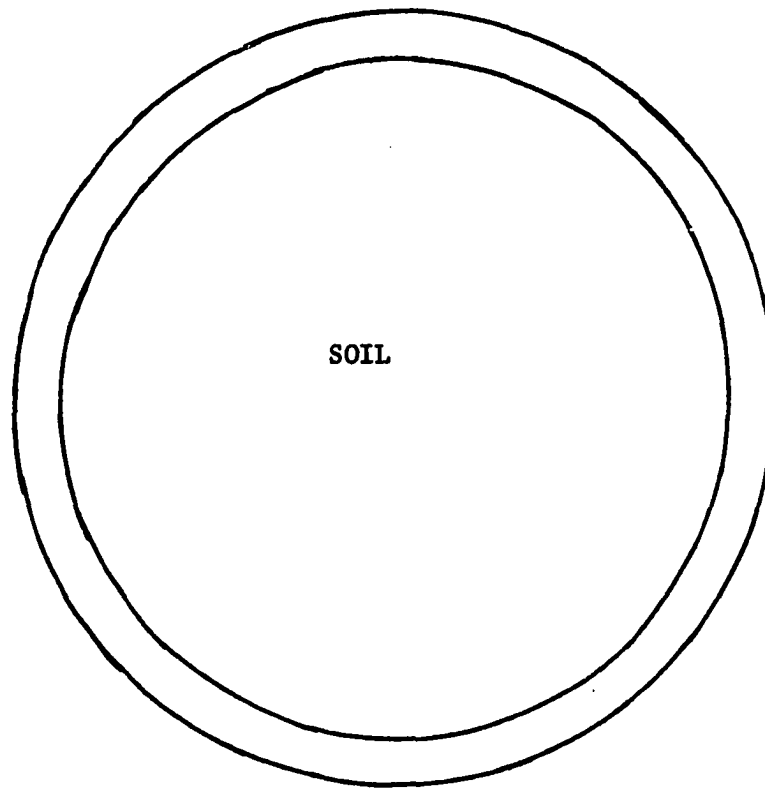
where  $P$  is the ambient pressure and  $P_o$  is the reference pressure. A plot of  $D_{vs}$  versus  $P_o/P$  should yield a straight line with the slope equal to  $D_v'$  and the intercept at  $D_s'$ .

#### B. Description of the Experiment

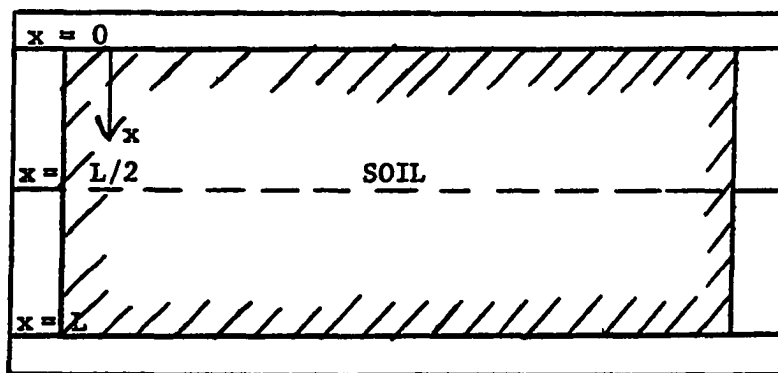
The laboratory experiment was designed to study the movement of propachlor, atrazine, and diazinon in soil by molecular diffusion. The technique used by Ehlers et al. (1969b) to study the movement of lindane through soil by molecular diffusion was used in the laboratory study. The diffusion system consisted of a half-cell that was filled with soil containing the pesticide in contact with a half-cell filled with untreated soil. Ehlers et al. (1969b) used radioactive lindane and cells constructed of acrylic plastic which were 15 mm in diameter and 9 mm in total depth. In order to have a large enough soil sample for atrazine analysis by the UV method, the diffusion system half-cells were constructed of acrylic plastic 7.6 cm in diameter and 1.5 cm in depth. Figure 29 shows a sketch of the diffusion cell used in the experiment.

The solution to the diffusion equation (equation 6-14) developed in





Top View



Side View

Figure 29. Diagram of the diffusion cell

the previous section of this chapter for the diffusion system and conditions used in the experiment is (Crank, 1951; Ehlers et al., 1969b)

$$\frac{M_{L/2}}{M_L} = \frac{1}{2} - \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left[ -(2n-1)^2 \pi^2 D_{vs} \frac{t}{L^2} \right] \quad (6-16)$$

where  $M_{L/2}$  is the amount of pesticide in the initially untreated half-cell after the half-cells have been united for time  $t$ ,  $M_L$  is the total amount of pesticide in the diffusion cell,  $D_{vs}$  is the diffusion coefficient as defined in equation 6-13 and  $L$  is the total depth of the diffusion cell. A graph similar to the graph in Figure 30 for solutions of equation 6-16 for  $L = 30$  mm was used to obtain values of  $D_{vs}$  from measured values of  $M_{L/2}$ ,  $M_L$ , and  $t$ . In order to obtain the curve in Figure 30, a computer program was written to solve equation 6-16 for  $M_{L/2}/M_L$  for given values of  $D_{vs} t$  and  $L = 30$  mm.

Ida silt loam soil obtained from the Gingles Watersheds was used in the laboratory experiment. The Ida soil on the Gingles Watersheds is composed of less than 20 percent clay and less than 20 percent sand. Figure 31 shows a textural profile of the Ida silt loam soil. Laboratory analysis of the soil showed the following chemical and physical properties: 2 percent organic matter, a pH of 7.3, a 15 atmosphere moisture percentage of 7.6, and a 1/3 atmosphere moisture of 24 percent (Molnau, 1969).

According to the model developed by Ehlers et al. (1969b), diffusion is a function of soil moisture content, soil temperature, soil structure, and chemical properties of the soil and pesticide. To use the model developed by Ehlers et al. (1969b), an experiment was designed for which soil temperature, soil moisture, and bulk density could be varied.

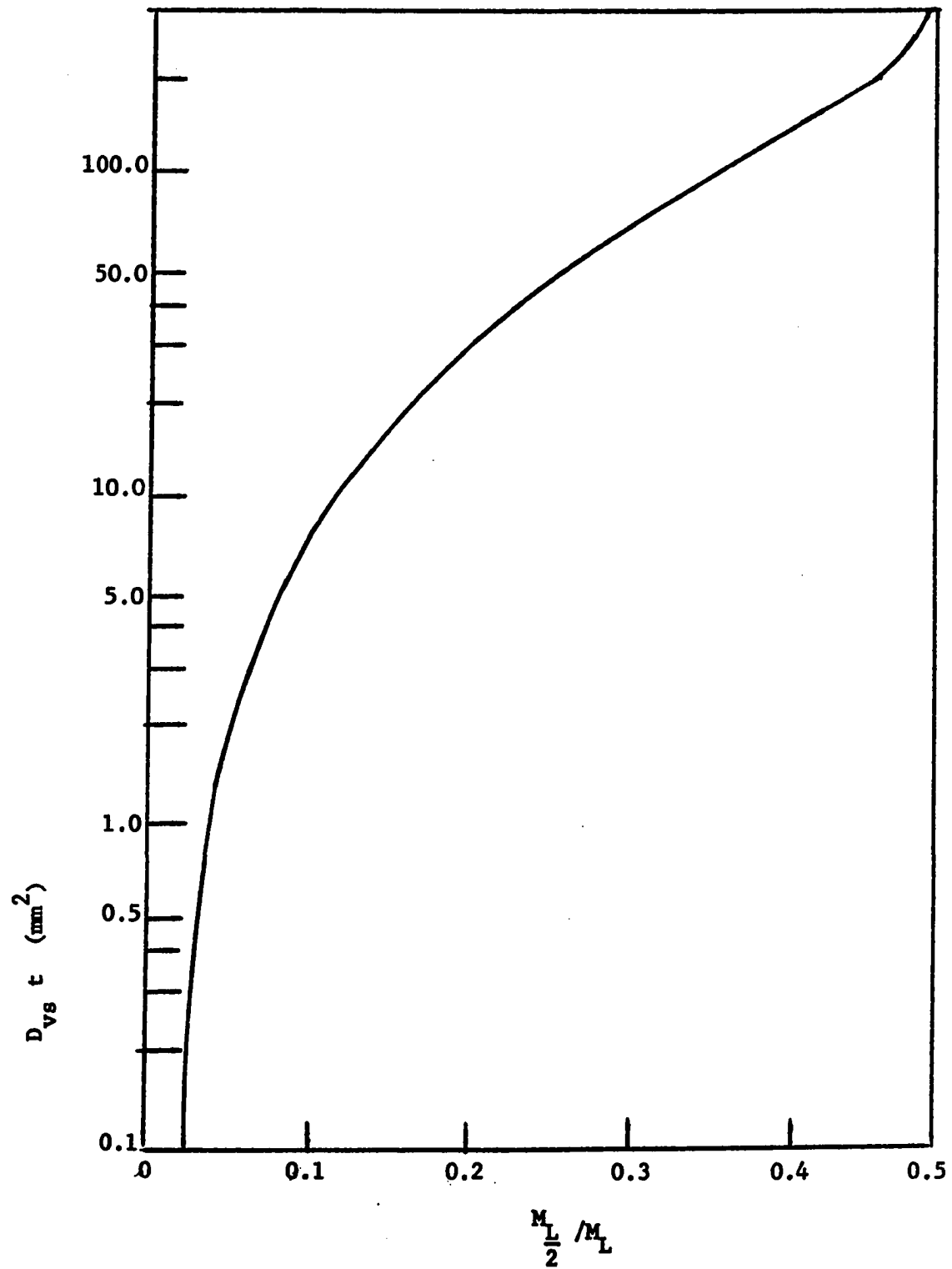


Figure 30. Plot of the diffusion equation

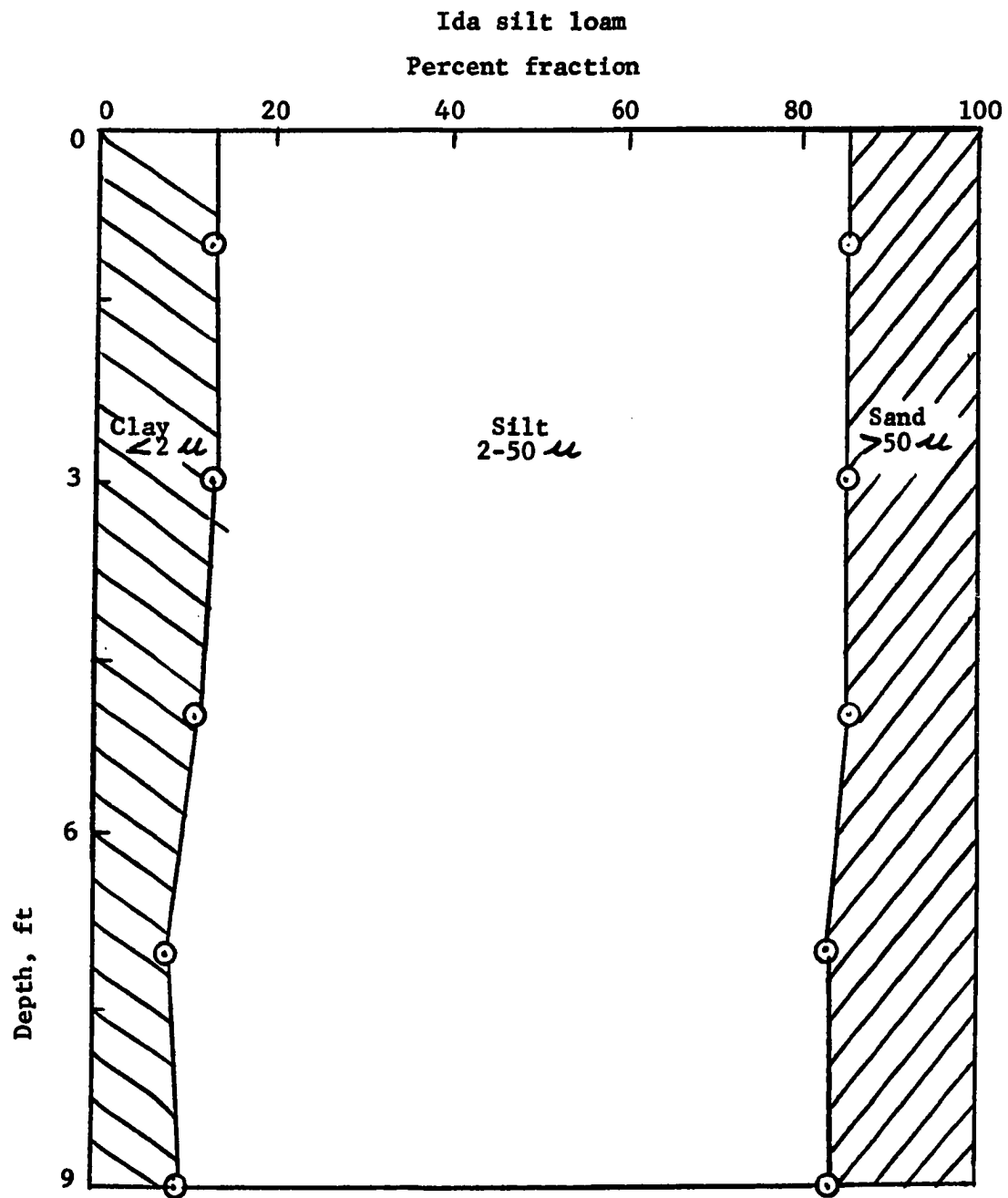


Figure 31. Textural profile of Ida silt loam soil (Melvin, 1970)

Three soil moisture contents in the available soil moisture range were used. The soil moisture contents chosen were: 8 percent which is near the wilting point, 23 percent which is near field capacity, and 15 percent.

The bulk densities chosen were of 0.90 grams per cubic cm and 1.30 grams per cubic cm. The low bulk density would represent a condition where the field was freshly plowed, disked, and harrowed and the high bulk density would represent a situation found at planting time when no plowing was done.

Three temperatures to represent average and extreme conditions were used in the experiment. The temperatures chosen were 50°, 80°, and 110°F.

All soil used for the experiment was sieved through a number 8 sieve and dried in the oven for 24 hours at 100° to 105°C. The pesticide was dissolved in an organic solvent. The soil treated with pesticide was prepared by hand mixing the oven dried soil with the organic solvent containing the dissolved pesticide. The solvent containing the pesticide was applied to the soil with an atomizer. Twenty ml of solvent were used with 100 grams of soil. The soil was exposed to the air for 5 or 6 hours to allow the solvent to evaporate. Hexane was used as the solvent for applying diazinon and propachlor to the soil and either chloroform or methanol was used for atrazine. For all of the tests 10 ppm of pesticide were added to the oven dried soil.

After the solvent had evaporated, enough water was added to the treated and untreated soil with an atomizer to obtain the desired moisture content. The soil was then sealed tightly in aluminum foil and allowed to stand for 24 hours in a constant temperature room. After 24 hours the

treated and untreated soil was removed from the constant temperature room and placed in the acrylic plastic half-cells and compacted to the desired bulk density. The treated and untreated half-cells were then placed in contact with one another, sealed with masking tape to prevent moisture loss. The sealed cells were then placed in the constant temperature room for 8 days. Preliminary tests with atrazine at 80°F showed that detectable amounts of atrazine had diffused into the initially untreated half-cell in 8 days. Since diazinon and propachlor degraded rapidly in the field, it was decided to use a test duration of 8 days for all tests. Four replications were used for each test. Three of the replications were analyzed for pesticide and a fourth was used for soil moisture determinations. The entire initially treated and untreated samples were analyzed for pesticide. After the diffusion period the cells were separated with the aid of a sharp piece of plastic and the soils were either analyzed immediately or placed in soil sample bags and frozen. No samples were kept in the freezer for more than 3 weeks before they were analyzed.

### C. Diffusion Results and Discussion

A discussion of the laboratory study of the movement of diazinon, propachlor, and atrazine in soil by molecular diffusion is presented in this section. All of the data used in the discussion is given in Tables 55 to 57 of Appendix B. The results of the analysis of variance for atrazine, propachlor, and diazinon are given in Tables 58 to 60 of Appendix B.

In order to explain some of the results in the diffusion tests for propachlor and diazinon, it is important to discuss the degradation of diazinon and propachlor that occurred during the diffusion tests. The

degradation of propachlor and diazinon will be discussed before the diffusion test results.

#### 1. Degradation of diazinon and propachlor

It was discovered during the diffusion tests that a considerable amount of diazinon degraded within 9 days. The amount of diazinon degradation was influenced by soil moisture content and temperature. An analysis of variance of the data showed that both temperature and soil moisture content had a significant effect on degradation (Table 61, Appendix B). Under field conditions high moisture contents and high temperatures would make diazinon less effective in controlling insects. At 110°F, less than 2 percent of the diazinon was recovered after 9 days at a soil moisture content of 23 percent. The actual time available to degrade would be 9 days since the soil was sealed in aluminum foil for 24 hours before it was placed in the diffusion cells. The average amount of diazinon recovered in the three replicates is given in Table 23. When the temperature was increased from 80°F to 110°F, the rate of diazinon degradation was greatly accelerated. In all tests at 110°F, less than 5 percent of the diazinon was recovered. Actual amounts of diazinon recovered is somewhat greater than indicated in Table 23 since none of the values are corrected for extraction efficiency. The diazinon probably degraded by hydrolysis. Konrad et al. (1967) found that diazinon degraded rapidly in soil by chemical hydrolysis. They also found that degradation was closely related to the amount of diazinon that was initially adsorbed to the soil. This would explain why diazinon degradation increased at higher moisture contents, because water would occupy more of the adsorption sites and the

Table 23. Amount of diazinon recovered in diffusion tests

Temperature (°F)	Moisture Content (%)	Bulk Density (g/cm <sup>3</sup> )	Amount Recovered (%)
50	8	0.90	23.7
	15	0.90	24.9
	23	0.90	17.3
	8	1.30	52.9
	15	1.30	20.8
	23	1.30	9.9
80	8	0.90	42.0
	15	0.90	21.1
	23	0.90	26.5
	8	1.30	50.1
	15	1.30	20.6
	23	1.30	20.1
110	8	0.90	5.5
	15	0.90	2.7
	23	0.90	0.9
	8	1.30	5.2
	15	1.30	3.7
	23	1.30	0.6

total amount of diazinon adsorbed to the soil particle would be less.

Konrad et al. (1967) found the degradation rates of diazinon in three different soils were 11, 7, and 6 percent per day for an initial concentration of 10 ppm.

Because the results from the field tests and diffusion tests indicated rapid degradation, the rate of diazinon degradation in Ida silt loam at 110°F and a soil moisture content of 23 percent was studied. The soil was initially treated with 10 ppm of diazinon and placed in soil sample bags in



the constant temperature room for 3, 4, 6, and 8 days, respectively. The results of this test are plotted in Figure 32. Each data point is an average of two replications. Diazinon degraded rapidly, with less than 20 percent recovered after 3 days. After 8 days, only 3.5 percent of the diazinon was recovered from the soil. The data in Figure 32 was not corrected for extraction efficiencies.

The degradation tests show diazinon could have degraded rapidly when applied to the Gingles Watersheds in June. Table 24 shows the soil temperatures at 1.0 inch depth and 2.25 inches depth at the Western Iowa Experimental Farm from June 15 to 23, 1970. Soil temperatures reached a high of 95°F during this period. Since a considerable amount of rainfall occurred in June during the field experiment, the soil moisture content ranged from 12 to 24 percent for most of the soil samples taken in June. The high soil moisture content combined with the high soil temperatures may have caused diazinon to degrade rapidly in the soil profile.

Degradation also occurred in the propachlor diffusion tests. At 50°F very little degradation occurred, but at 110°F less than 35 percent of the propachlor was recovered after 8 days for all tests. The amount of propachlor recovered in the diffusion tests is summarized in Table 25. Both temperature and soil moisture content had a significant effect on the rate of degradation (Table 62, Appendix B). Generally, at higher moisture contents more propachlor degraded than at a soil moisture content of 8 percent. At 50°F no noticeable amounts of propachlor degraded except in one case. The low amount recovered could have been the result of experimental error since in all other tests at 50°F more than 90 percent of the

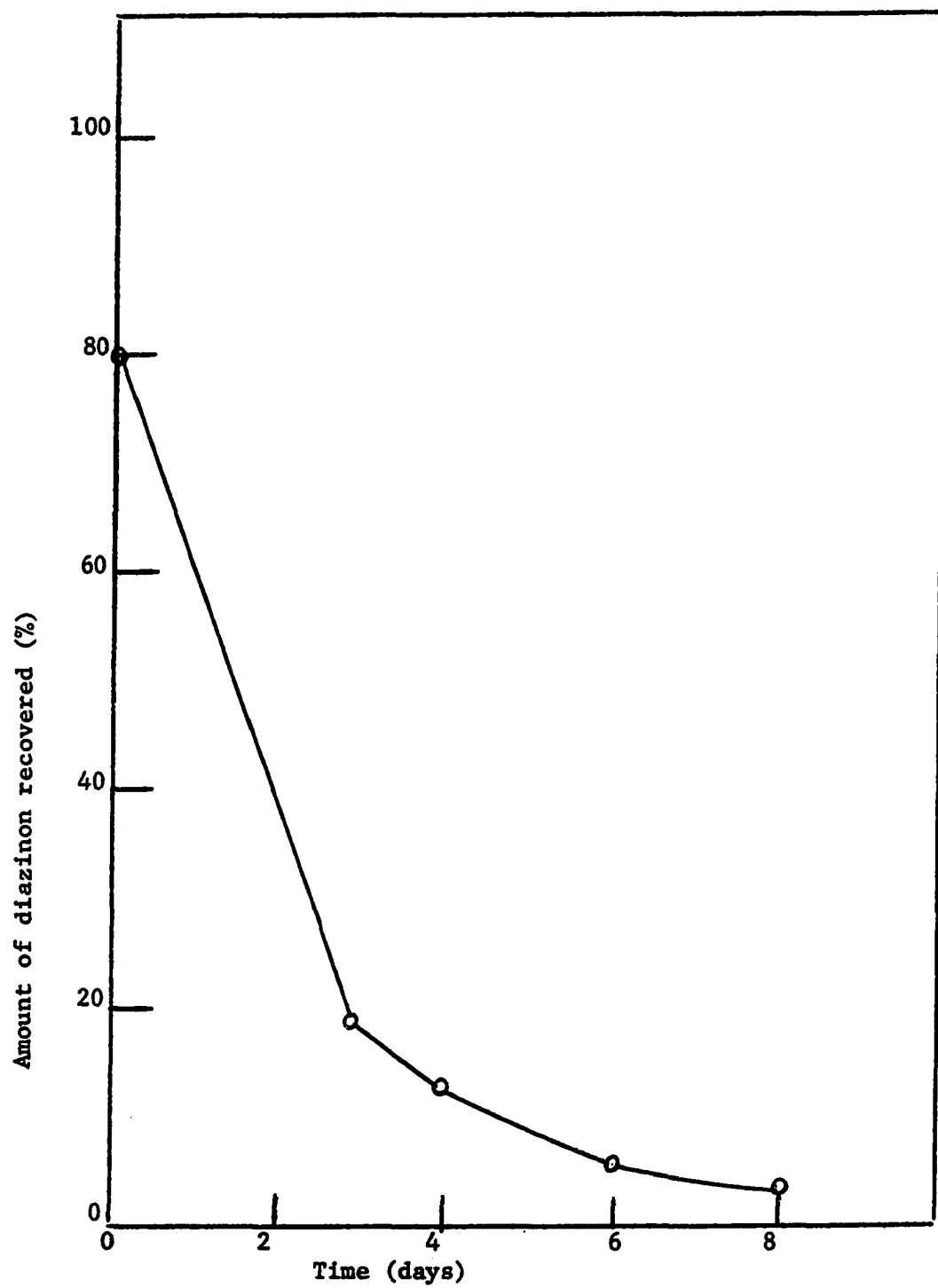


Figure 32. Degradation of diazinon at 110°F and soil moisture content of 23 percent

propachlor was recovered.

There was no noticeable degradation of atrazine in the diffusion tests.

Table 24. Soil temperatures at the Western Iowa  
Experimental Farm from June 15 to 23, 1970

Date	Temperature (°F)					
	1 inch			2.25 inches		
	8:00 am	12:00 pm	5:00 pm	8:00 am	12:00 pm	5:00 pm
15	70	94	95	70	87	92
16	69	83	88	68	78	87
17	70	84	88	70	77	86
18	64	76	88	64	73	82
19	58	87	84	50	79	88
20	62	73	92	62	69	70
21	53		70	54		77
22	61	88	76	60	81	88
23	62	90	92	61	80	87

Table 25. Amount of propachlor recovered in  
diffusion tests

Temperature (°F)	Moisture Content (%)	Bulk Density (g/cm <sup>3</sup> )	Amount Recovered (%)
50	8	0.90	94.4
	15	0.90	58.1
	23	0.90	89.4
	8	1.30	97.0
	15	1.30	98.7
	23	1.30	98.6
80	8	0.90	60.5
	15	0.90	47.6
	23	0.90	62.2
	8	1.30	72.4
	15	1.30	45.5
	23	1.30	41.6
110	8	0.90	34.5
	15	0.90	17.3
	23	0.90	23.1
	8	1.30	22.1
	15	1.30	13.7
	23	1.30	19.5

## 2. Temperature

Figure 33 shows the effect of temperature on the diffusion coefficients for atrazine, propachlor, and diazinon. The diffusion coefficients presented in Figure 33 are an average of the diffusion coefficients obtained for the two bulk densities and three soil moisture contents at each temperature. No diffusion coefficients were measured at 110°F for diazinon because of the rapid degradation of diazinon at the high temperature.

Temperature had a large influence on the diffusion coefficients for all three pesticides. The effect of temperature on the diffusion coefficients was significant at the 1 percent level for all three pesticides. The F values obtained for temperature were much greater than the F values for the other main effects of bulk density and soil moisture content. Diffusion coefficients increased more rapidly for atrazine and propachlor when the temperature was increased from 80°F to 110°F than when the temperature was increased from 50°F to 80°F. The average diffusion coefficient for propachlor increased from 1.46 mm<sup>2</sup>/day to 1.90 mm<sup>2</sup>/day when the temperature was increased from 50°F to 80°F, and from 1.90 mm<sup>2</sup>/day to 6.99 mm<sup>2</sup>/day when the temperature increased from 80°F to 110°F. The average diffusion coefficient for atrazine increased from 0.40 mm<sup>2</sup>/day to 1.36 mm<sup>2</sup>/day when the temperature was increased from 50°F to 80°F and from 1.36 mm<sup>2</sup>/day to 3.00 mm<sup>2</sup>/day when the temperature increased from 80°F to 110°F. Essentially no movement by diffusion was detected for diazinon at 50°F. The only tests in which any movement was measured at 50°F for diazinon was at a soil moisture content of 8 percent and a bulk density of

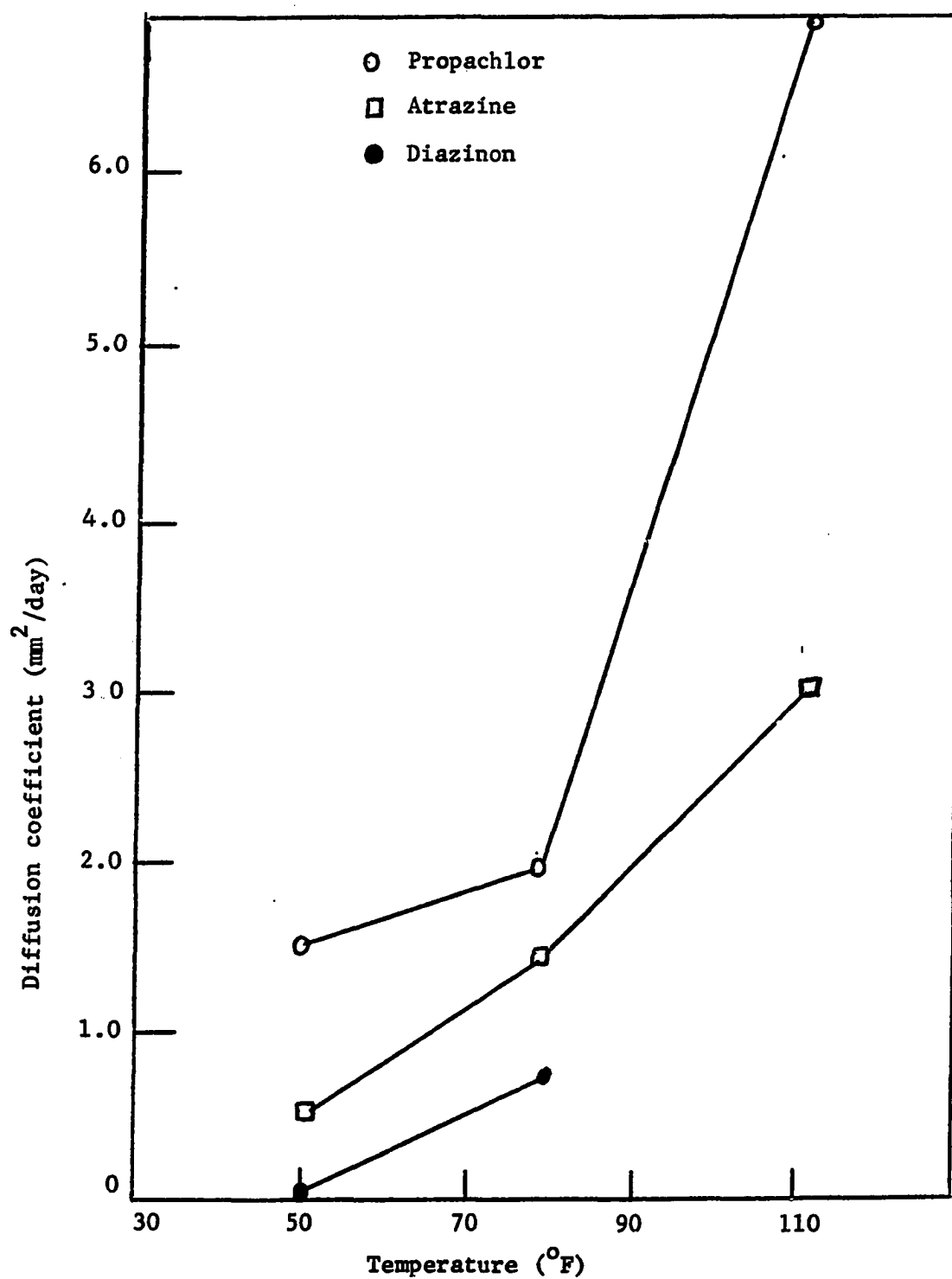


Figure 33. Effect of temperature on the diffusion coefficients for atrazine, propachlor, and diazinon

0.90 g/cm<sup>3</sup>.

Temperature will affect diffusion in both the vapor and "nonvapor" phases. In examining equations 6-11 and 6-12, the temperature-dependent components of  $D_v'$  would be  $D_v$  and  $\partial \rho / \partial c$ , and the temperature-dependent components of the "nonvapor" phase would be  $D_s$  and  $\gamma$  (Ehlers et al., 1969b).

Figure 33 also shows there is a difference in the rate of movement by diffusion for the three pesticides. For all temperatures, propachlor had the largest diffusion coefficients and diazinon the smallest diffusion coefficients. Propachlor is more soluble in water than either atrazine or diazinon (Table 26). Diazinon and propachlor are more volatile than atrazine. None of the three pesticides can be considered volatile compounds. It appears the rate of movement by diffusion is related to the water solubility of the pesticide and is not related to the vapor pressure. Since it appears the rate of diffusion is related to the water solubility of the pesticide for atrazine, propachlor, and diazinon, probably the greatest amount of pesticide that moved by diffusion was in the liquid phase.

Table 26. Solubility and vapor pressure for atrazine, propachlor, and diazinon

Pesticide	Vapor Pressure mm Hg	Water Solubility (ppm)
Atrazine	$3.0 \times 10^{-7}$ at 27°C <sup>a</sup>	70 at 27°C <sup>a</sup>
Propachlor	$1.0 \times 10^{-4}$ at 20°C <sup>c</sup>	700 at 20°C <sup>a</sup>
Diazinon	$1.4 \times 10^{-4}$ at 20°C <sup>b</sup>	4 at 20°C <sup>b</sup>

<sup>a</sup>Weed Society of America, 1967

<sup>b</sup>Canadian Department of Agriculture, 1968

<sup>c</sup>Personal communication with Monsanto Chemical Company

### 3. Soil moisture content and bulk density

The effect of soil moisture content on the diffusion coefficients for atrazine, propachlor, and diazinon is plotted in Figure 34. The diffusion coefficients presented in Figure 34 are an average of all values obtained at the three temperatures and two bulk densities. The statistical analysis showed that soil moisture content was significant at the 1 percent level for both atrazine and propachlor. For atrazine and propachlor, the rate of diffusion increased as the moisture content increased. Soil moisture had no significant effect on the diffusion coefficients for diazinon. This may have been the result of the variability in the data or the low water solubility of diazinon.

The effect of bulk density averaged across the other variables for the diffusion coefficients for propachlor, atrazine, and diazinon, is plotted in Figure 35. In Figure 35 the mean values for the three temperatures and three soil moisture contents are plotted. For all three pesticides the diffusion coefficient decreased slightly with an increase in bulk density. The analysis of variance showed bulk density was significant at the 1 percent level for atrazine and at the 5 percent level for propachlor. Even though bulk density was significant for atrazine and propachlor, it was difficult to draw any conclusions about the effect of bulk density on the diffusion coefficients because only two bulk densities were used in the diffusion tests. However, a decrease in the diffusion coefficient would be expected with increased soil density.

Figures 36 and 37 show the relationship between soil moisture content and temperature on the diffusion coefficients for atrazine and propachlor.

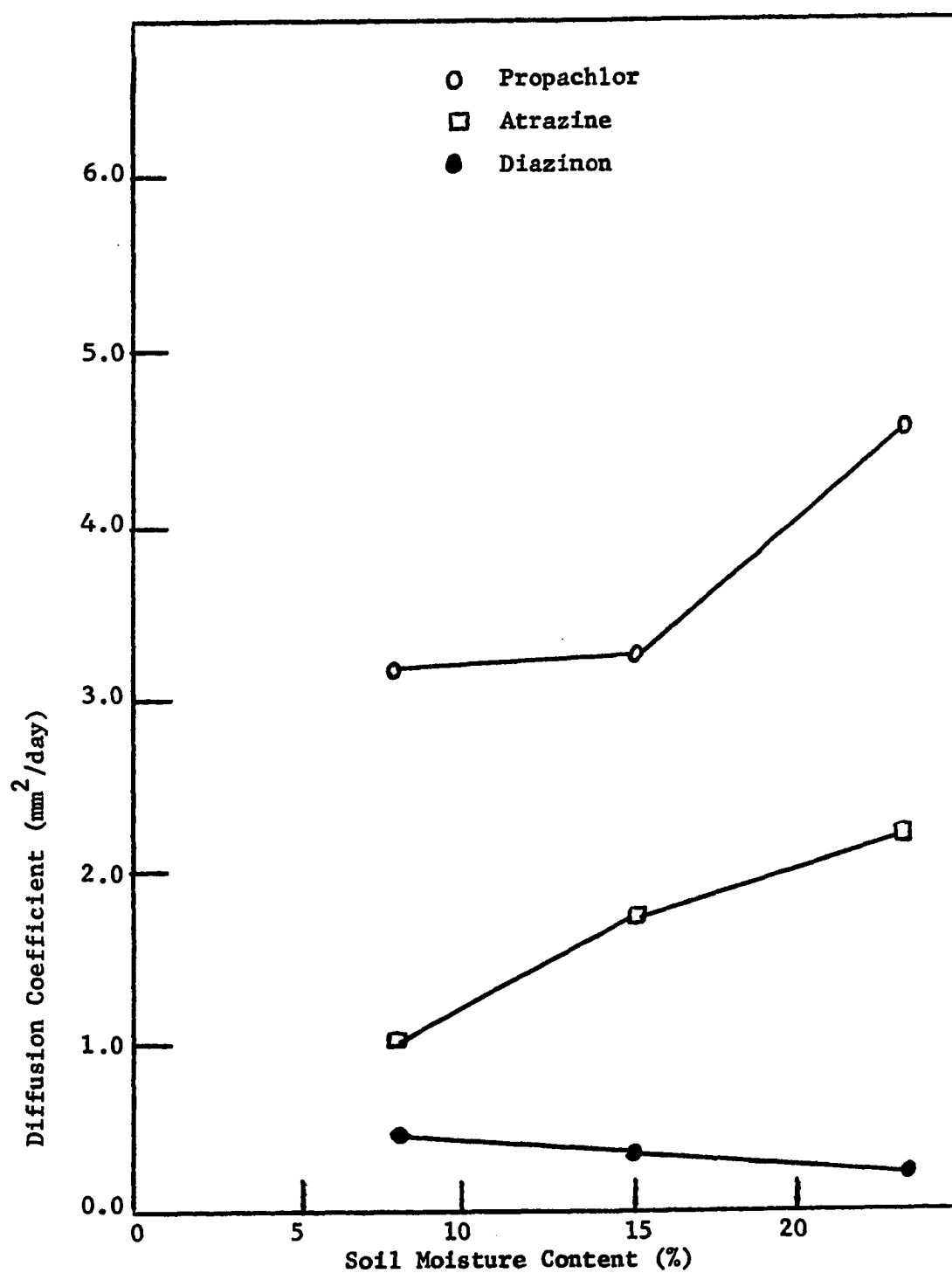


Figure 34. Effect of soil moisture content on the diffusion coefficients for atrazine, propachlor, and diazinon.



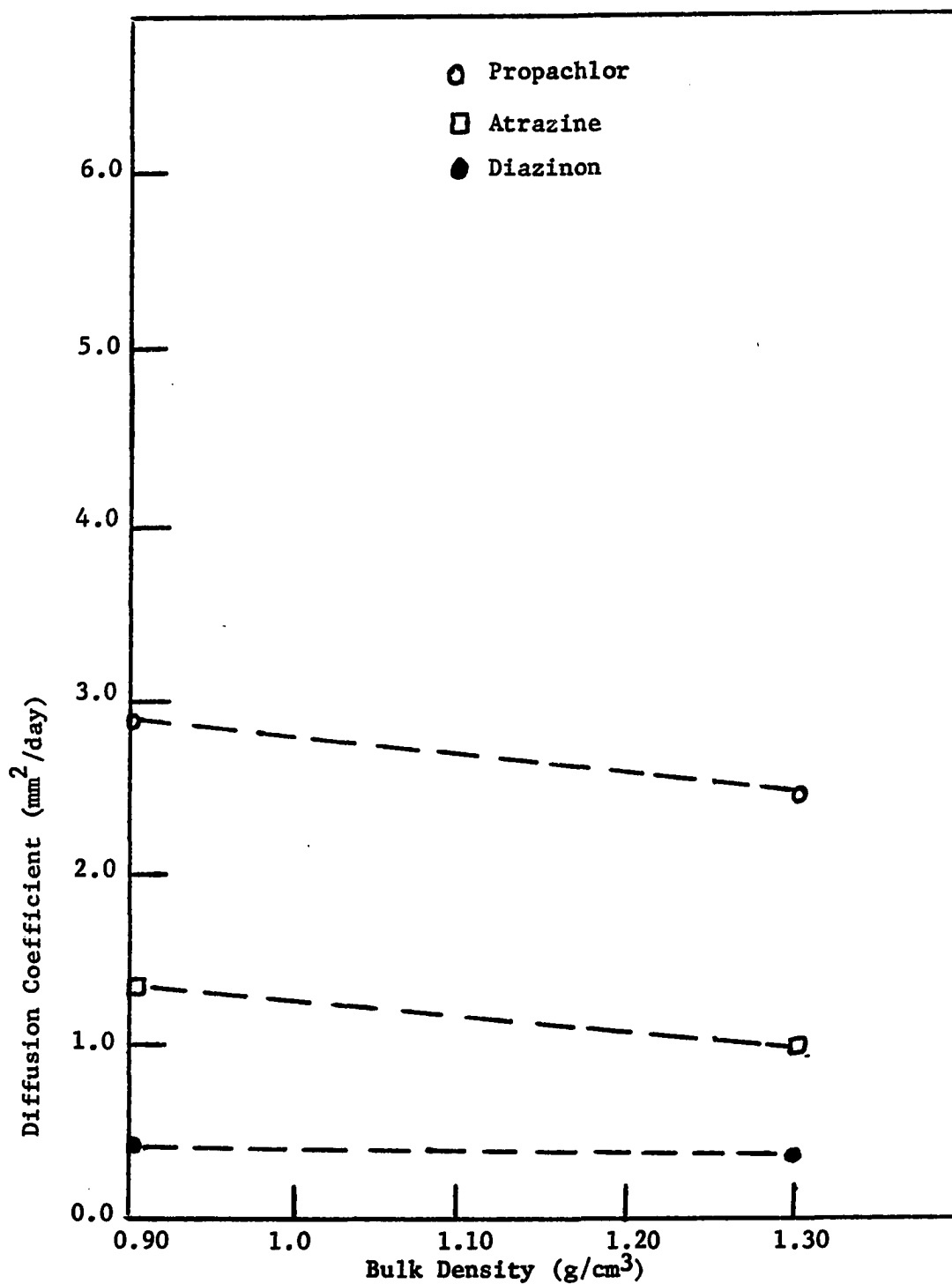


Figure 35. Effect of bulk density on the diffusion coefficients for atrazine, propachlor, and diazinon

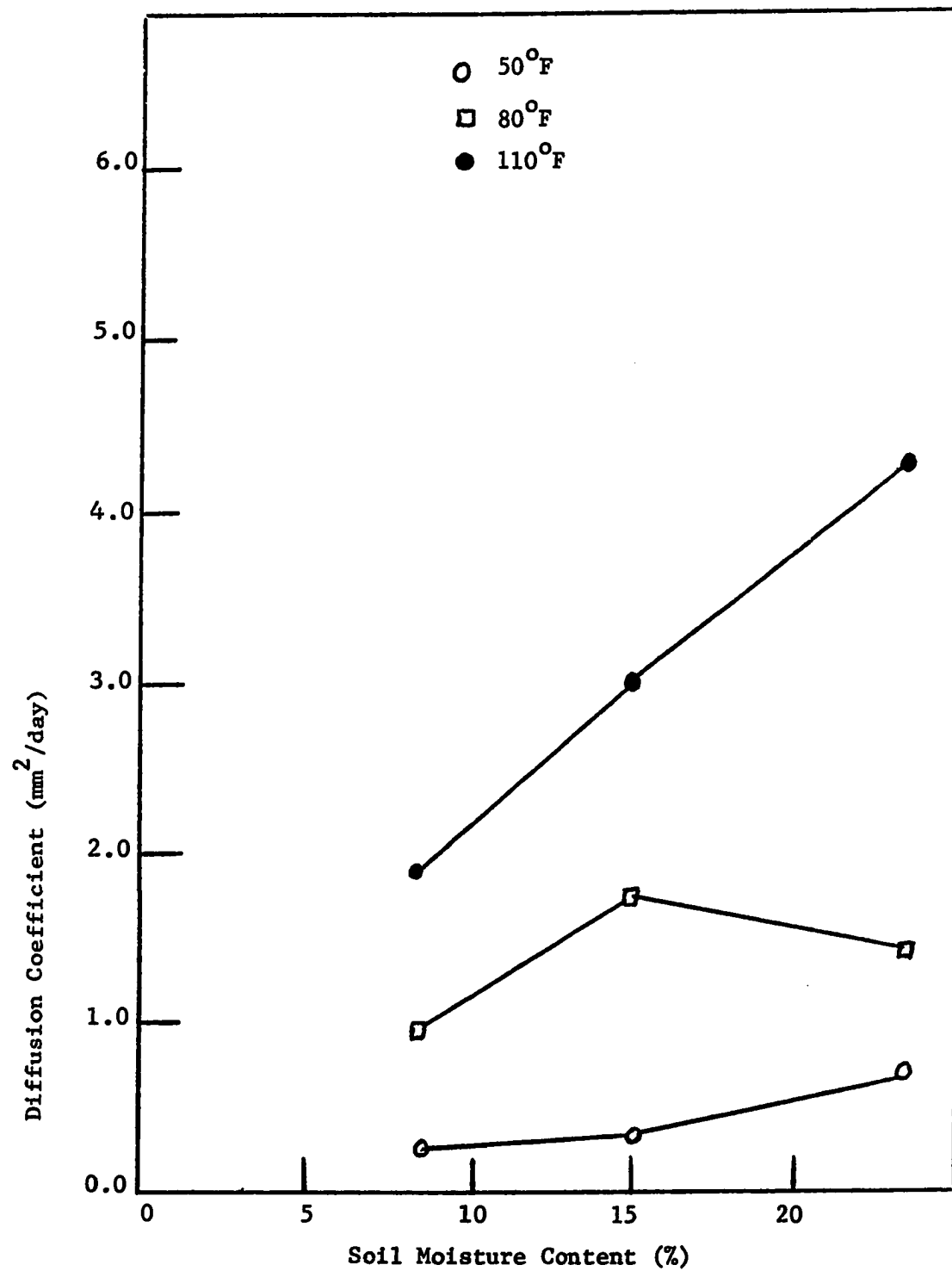


Figure 36. Effect of temperature and soil moisture content on the diffusion coefficients for atrazine

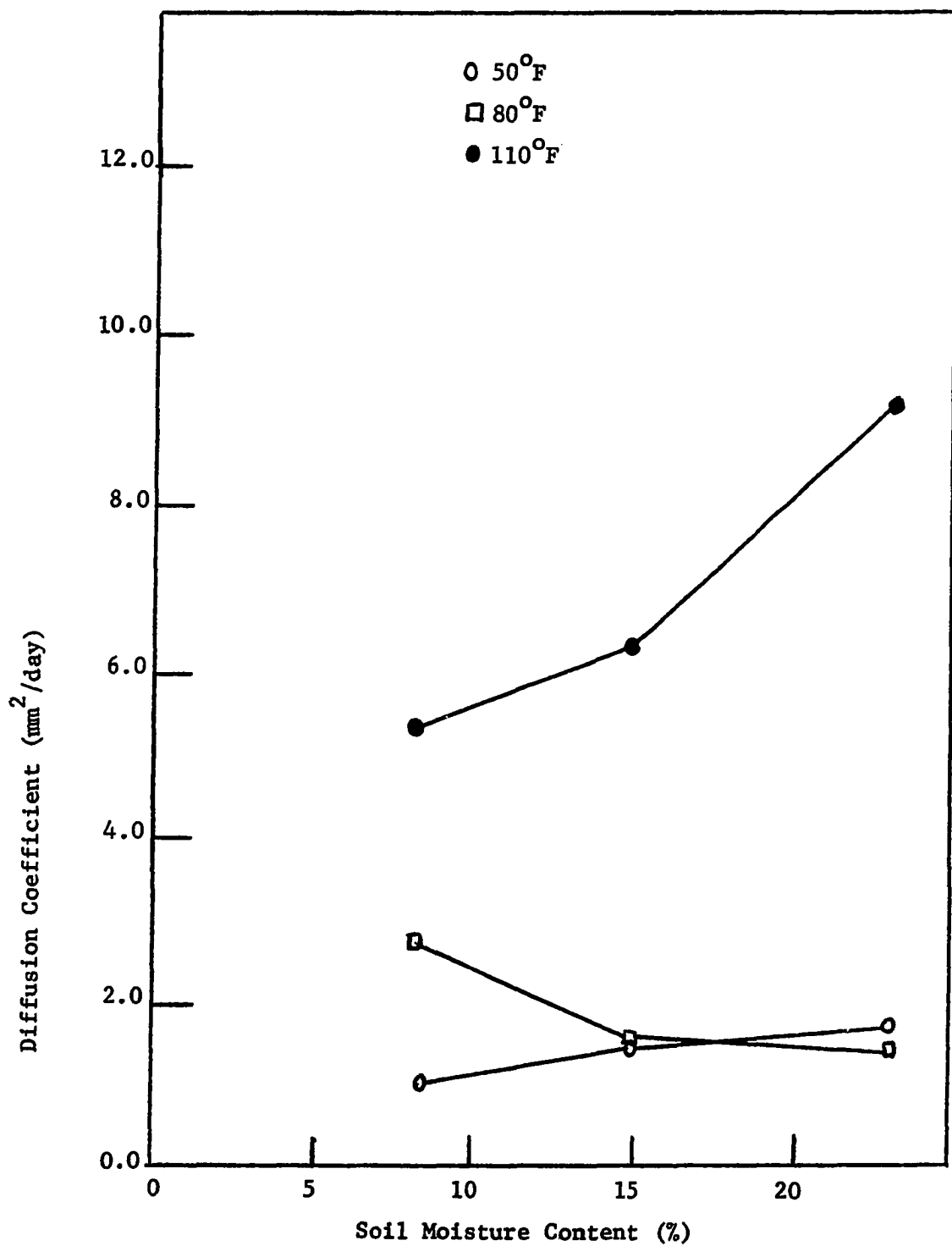


Figure 37. Effect of temperature and soil moisture content on the diffusion coefficients for propachlor

In both diagrams the mean values for the two bulk densities and three replications at each temperature are plotted. The statistical analysis showed the interaction of soil moisture and temperature was significant at the 1 percent level for propachlor and atrazine. Soil moisture content had a more pronounced effect on the diffusion coefficients for atrazine and propachlor at 110°F than at the lower temperatures. There was considerable scatter in the data as shown in Tables 57 to 59 of Appendix B. This variability in the data could account for the shape of the curves in Figures 36 and 37 at 50°F and 80°F.

There are many things that may have contributed to the variability in the data. The rapid degradation of propachlor and diazinon after 8 days as discussed in the previous section of this chapter could have caused the great variability in the propachlor and diazinon results. With the rapid degradation and slow movement of pesticide by diffusion, most of the initially untreated soil samples contained small amounts of pesticide. This small amount of pesticide was near the minimum detectable limits for propachlor and diazinon which made accurate analysis impossible. In this range of concentrations the peaks for propachlor and diazinon on the chromatogram were not very symmetrical.

The initially treated and untreated half-cells may not have been separated at exactly the same surface, some of the initially treated soil may have been included in the initially untreated sample. Some difficulty was encountered in separating the half-cells for tests at the low soil moisture content and low bulk density because of the loose condition of the soil.

Some difficulty was also encountered in mixing the pesticide uniformly with the soil. There was also a slight possibility that the soil had somewhat different chemical and physical properties since soil was obtained from the Gingles Watersheds three times at two different locations. Both factors also could have contributed to the scatter in the data.

In studying the movement of pesticides like diazinon and propachlor that degrade rapidly, higher concentrations and shorter time periods should be used. This should eliminate some of the variability in the results.

Other research workers have found that soil moisture content influenced diffusion of some pesticides but had little effect on other pesticides. Graham-Bryce (1969) found for a silt loam soil that soil moisture content influenced the diffusion coefficients of dimethoate but had little effect on the diffusion coefficients of disulfoton. Graham-Bryce (1969) measured diffusion coefficients at 20°C for dimethoate from  $2.7 \times 10^{-8} \text{ cm}^2/\text{sec}$  at a volumetric moisture content of 10.4 percent to  $159.1 \times 10^{-8} \text{ cm}^2/\text{sec}$  at a volumetric moisture content of 42.9 percent. Diffusion coefficients for disulfoton ranged from  $2.3 \times 10^{-8} \text{ cm}^2/\text{sec}$  to  $4.6 \times 10^{-8} \text{ cm}^2/\text{sec}$ . Diffusion coefficients for disulfoton were in the same range as the diffusion coefficients measured for propachlor at 80°F. The latter ranged from  $4.40 \times 10^{-8} \text{ cm}^2/\text{sec}$  to  $0.51 \times 10^{-8} \text{ cm}^2/\text{sec}$ . Lavy (1970) found that soil moisture content had an effect on the diffusion coefficients of atrazine, propazine, and simazine. Average diffusion coefficients at 5°C for the three s-triazine herbicides on six different soils increased from  $0.5 \times 10^{-8} \text{ cm}^2/\text{sec}$  at a soil moisture content of 0.5 of field capacity to  $1.83 \times 10^{-8} \text{ cm}^2/\text{sec}$  at field capacity. Lavy (1970)

used an autoradiographic technique for measuring diffusion coefficients with concentrations of 424, 342, and 224 ppm for atrazine, propazine, and simazine, respectively. In another experiment at a soil moisture content of 0.8 field capacity at 25°C, Lavy (1970) found that the average diffusion coefficient for atrazine on eight different soil types was  $15.2 \times 10^{-8} \text{ cm}^2/\text{sec}$ . For this study the average diffusion coefficient for atrazine at 23 percent moisture content (field capacity) and a bulk density of  $0.90 \text{ g/cm}^3$  at 110°F for the Ida silt loam soil was  $5.78 \times 10^{-8} \text{ cm}^2/\text{sec}$ . Different extraction and analysis techniques and different concentrations of pesticide were used in the studies. Lavy (1970) used an unusually high concentration of atrazine in his experiments.

#### 4. Distance moved by diffusion

Several tests were conducted to determine the distance the pesticide had moved in 8 days by diffusion. Acrylic plastic columns 7.5 cm long and 5.0 cm diameter were used for these tests. The lower 5 cm of the columns were filled with untreated soil; the top 2.5 cm were filled with soil that was treated with pesticide. After 8 days the soil cores were sliced at the interface of the initially treated and untreated soil. The initially untreated soil was sliced into 1 cm lengths. Soil cores for atrazine and propachlor at an initial concentration of 10 ppm, 110°F, a soil moisture content of 15 percent, and bulk density of  $1.30 \text{ g/cm}^3$ , were sliced and analyzed for pesticide residues. Diazinon tests were conducted at 80°F with the same initial concentration, soil moisture content, and bulk density as the tests for propachlor and atrazine. Two soil cores for each pesticide were analyzed. In all of the soil cores no pesticide moved

beyond the first 1 cm slice. This means that the distance moved by diffusion was less than 1 cm for the 8 day period for all three pesticides.

The results of these tests indicate that for short periods of time, diffusion does not contribute significantly to the movement of these pesticides in the soil profile for distances greater than 1 cm. Diffusion may be important in bringing about the transfer of atrazine and propachlor from the soil surface into the soil after application, and in the micro-movement of the pesticide in the soil required for effective weed control.

## VII. SUMMARY AND CONCLUSIONS

The main objectives of the research were to measure losses of selected pesticides in runoff water and sediment under field conditions and to gain a better understanding of the factors that affect pesticide movement in soils.

Atrazine, propachlor, and diazinon losses in sediment and surface runoff were measured on four watersheds ranging in size from 1.9 acres to 3.8 acres and located in the loessial soil region of Western Iowa. Two of the watersheds were in ridged planted corn and two were in surface contoured planted corn. Movement of atrazine, propachlor, and diazinon in the soil profile and degradation of these pesticides were measured on the four watersheds.

Sixteen percent (0.48 lb/A) of the atrazine in the original chemical form which was applied to the surface contoured watershed was lost in the surface runoff and sediment from a storm that occurred 7 days after the pesticide was applied. Atrazine losses decreased for storms occurring later in the season. Propachlor losses in the surface runoff and sediment on the surface contoured watershed for a storm that occurred 8 days after it was applied were 0.155 lb/A or 2.6 percent of the amount that was applied. No significant amounts of diazinon were lost in the surface runoff and sediment from a storm occurring 4 days after the diazinon was applied. Pesticide losses in the water and sediment were much greater from the surface contoured watersheds than from the ridged watersheds. Generally, pesticide concentrations were higher in the sediment than the runoff water, but greater losses were associated with the water because



of the greater volume.

Atrazine and propachlor moved slowly in the soil profile. After 175 to 200 days following application, small concentrations of atrazine were detected in the 8- to 10-inch depth. Small concentrations of propachlor were detected at a depth of 3 to 5 inches 3 to 4 weeks after the propachlor was applied. Generally 30 to 40 days after the atrazine was applied, less than 50 percent remained in the 0- to 6-inch depth of the soil profile. Only small concentrations of propachlor were detected in the soil profile at the 0- to 5-inch depth 3 to 4 weeks after it was applied.

Movement of atrazine, propachlor, and diazinon by diffusion in Ida silt loam soil was studied in the laboratory. A model developed by Ehlers et al. (1969b) was used to evaluate diffusion coefficients. Temperature, soil moisture content, and bulk density were varied in the diffusion tests.

Temperature had a statistically significant effect at the 1 percent level on the diffusion coefficients for atrazine, propachlor, and diazinon. Soil moisture content also had a statistically significant effect at the 1 percent level for atrazine and propachlor diffusion. The atrazine and propachlor diffusion coefficients increased with an increase in soil moisture content. Propachlor moved more rapidly by diffusion than atrazine or diazinon. At 50°F, no significant movement by diffusion of diazinon was observed. Average diffusion coefficients for propachlor, atrazine, and diazinon at 80°F were 1.90, 1.36, and 0.63 mm<sup>2</sup>/day, respectively.

Diazinon degraded rapidly at 110°F. Less than 6 percent of the diazinon was recovered after 9 days for all diazinon diffusion tests at 110°F. Degradation probably occurred by hydrolysis.

The following conclusions were drawn from this study:

1. Significant amounts of atrazine and propachlor may be lost in surface runoff and sediment if a storm occurs shortly after the pesticide is applied.
2. No significant amounts of diazinon would be lost in the surface runoff and sediment if applied to a watershed at the recommended rates when the diazinon is incorporated in the soil.
3. Ridge farming greatly reduces the amounts of pesticide lost in surface runoff and sediment as compared to a conventional tillage system.
4. Higher concentrations of pesticide will occur in the sediment than the water, but larger amounts of the above pesticides may be lost in the water if the volume of runoff is large compared to the volume of sediment.
5. Atrazine moves slowly in the soil profile and will not be found at depths greater than 8 to 10 inches in measurable amounts after 1 year from application in loessial soils.
6. Small concentrations of atrazine will be detected in the soil profile 1 year after the atrazine is applied, if atrazine is applied to a watershed at the recommended rates.
7. Propachlor will not move to a depth greater than 3 to 5 inches in any significant amounts before it is completely degraded. Only small concentrations of propachlor will remain in the soil profile 3 to 4 weeks after it is applied.
8. A wide range of concentrations of pesticide in the surface inch of soil will result when the pesticide is applied to the soil in a conventional manner.

9. Soil moisture content has a significant effect on the movement of atrazine and propachlor by diffusion, but has little influence on diazinon diffusion rates. Diffusion rates for atrazine and propachlor will increase with an increase in soil moisture content.
10. The rate of movement by diffusion for atrazine, propachlor, and diazinon increases as the temperature increases.
11. Atrazine, propachlor, and diazinon move less than 1 cm in the soil in 8 days by diffusion under the conditions tested.
12. Diazinon degrades rapidly in the soil at high temperatures.

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## IX. ACKNOWLEDGMENTS

The author would like to express his appreciation to:

Iowa State University of Science and Technology for providing the facilities and support for this study.

Dr. H. P. Johnson and Dr. J. L. Cleasby for serving as major professors and for their assistance.

Mr. W. G. Lovely of the United States Department of Agriculture for his guidance in conducting this research.

Dr. C. W. Bockhop, Dr. C. S. Oulman, and Dr. D. W. Staniforth for serving on the author's committee.

Monsanto Chemical Company, St. Louis, Missouri for supplying the propachlor standards.

Geigy Chemical Company, Ardsley, New York for supplying the atrazine and diazinon standards.

The author also wishes to thank his wife, Carol-Anne, for typing this manuscript.

**X. APPENDIX A. COMPUTER PROGRAMS FOR DATA REDUCTION**

**A. Computer Program for Atrazine Analysis on UV Spectrophotometer**

C		0010
C	-----	0020
C		0030
C	PROGRAM TO DETERMINE AMOUNT OF PESTICIDE IN SAMPLES ANALYZED ON UV	0040
C	SPECTROPHOTOMETER	0050
C	CALIBRATION CURVED OBTAINED BY SIMPLE REGRESSION	0060
C	1ST CARD OF EACH DATA SET IS AN IDENTIFICATION CARD WITH THE	0070
C	FOLLOWING CODE PUNCHED IN COLUMN 1, ICARD	0080
C	ICARD =0, END OF DATA	0090
C	ICARD =1, WATER SAMPLES FROM WATERSHED	0100
C	ICARD =2, SEDIMENT SAMPLES FROM WATERSHED	0110
C	ICARD =3, SOIL SAMPLES FROM WATERSHED	0120
C	ICARD =4, SPECIAL TEST	0130
C	ICARD=5, DIFFUSION TEST	
C	1ST CARD ALSO IDENTIFIES PESTICIDE BEING ANALYZED, PEST, 2A4	0140
C	COL 3-10 PESTICIDE BEING ANALYZED, PEST, 2A4	0150
C		0160
C	IF DATA SET IS WATER SAMPLES OR SEDIMENT SAMPLES THE 2ND CARD IS	0170
C	COL 7-10 MONTH RAINFALL OCCURRED, A4, MMSAMP	0180
C	12-17 DAY RAINFALL OCCURRED, I6, MDSAMP	0190
C	19-24 YEAR RAINFALL OCCURRED, I6, MYSAMP	0200
C		0210
C	IF DATA SET IS SOIL SAMPLES THE 2ND CARD IS	0220
C	COL 2-5. WATERSHED, A4, WAT	0230
C	7-10 DAYS SINCE APPLICATION, A4, MDAYS	0240
C	12-15 MONTH OF SAMPLING, A4, MMSAMP	0250
C	16-21 DAY OF SAMPLING, I6, MDSAMP	0260
C	22-27 YEAR OF SAMPLING, I6, MYSAMP	0270
C		0280
C	IF DATA SET IS A SPECIAL TEST THE 2ND AND 3RD CARDS DESCRIBE THE TEST	0290
C	ARE READ UNDER THE FORMAT 20A4, ITITLE, TITLE	0300
C		0310
C	IF DATA SET IS A DIFFUSION TEST THE 2ND AND 3RD CARDS DESCRIBE THE	
C	TEST AND ARE READ UNDER THE FORMAT 20A4, ITITLE, TITLE	
C	THE 4TH CARD FOR THE DIFFUSION TEST DESCRIBES THE OPERATING	



C	PARAMETERS OF THE DIFFUSION TEST	
C	COL 1-5 TEMPERATURE,F5.0,TEMP	
C	6-10 SOIL MOISTURE CONTENT,F5.2,ST	
C	11-15 SOIL BULK DENSITY,F5.2,DEN	
C	16-20 LENGTH OF TEST,F5.2,TIME	
C	21-36 DATE TEST PERFORMED,4A4,DATE	
C	37 INDICATES TEST IS A SOIL SAMPLE,IND=2,I1,IND	
C		
C	3RD DATA CARD IS FOR A CALIBRATION CURVE,I1,INT	0320
C	IF INT=1,CALILIBRATION DATA FOLLOWS AND IS READ IN BY SUBROUTINE	0330
C	CALIB(ANS(1),B(J))	0340
C	IF DATA SET USES SAME CALIBRATION CURVE AS PREVIOUS DATA SET IND=0	0350
C		0360
C	AFTER CALIBRATION CURVE NEXT DATA CARD CONTAINS A BLANK CORRECTION	0370
C	FOR ABSORBANCE,F5.3,CORR	0380
C		0390
C	IF A SPECIAL TEST NEXT CARD DETERMINES IF SPECIAL TEST IS A WATER	0400
C	OR SOIL TEST,I1,IND	0410
C	IND=1,IS A WATER TEST	0420
C	IND=2 IS A SOIL TEST	0430
C		0440
C	DATA CARDS FOLLOW CORR OR IND	0450
C	IF WATER SAMPLE DATA	0460
C	COL 2-5 SAMPLE IDENTIFICATION,A4,ID(I)	0470
C	6-10 ABSORBANCE,F5.3,CONC(I)	0480
C	11-15 AMOUNT OF SOLVENT USED FOR EXTRACTION,F5.1,EXT(I)	0490
C	16-20 AMOUNT OF SOLVENT CONVERTED,F5.1,CONV(I)	0500
C	21-26 AMOUNT OF WATER EXTRACTED,F6.1,WD(I)	0510
C	27-29,TELLS PROGRAM WHAT TO DO,I3,IFLAG(I)	0520
C	IF IFLAG(I)=1, LAST DATA CARD OF SET	0530
C	IF WANT PROGRAM TO PRINT OUT TRACE INSTEAD OF PPM,IFLAG(I)=2	0540
C	IF WANT PROGRAM TO PRINT OUT TRACE INSTEAD OF PPM AND LAST CARD OF DATA	
C	SET,IFLAG(I)=3	0560
C	31 VOLUME OF SAMPLE USED FOR ABSORBANCE READING,I1,IM(I)	0570
C	IF IM(I)=0,VOLUME IS 10 ML	0580

C	IF IM(I)=1,VOLUME IS 20 ML	0590
C	IF IM(I)=2,VOLUME IS 30 ML	0600
C	IF IM(I)=3,VOLUME IS 40 ML	0610
C	IF IM(I)=4,VOLUME IS 50 ML	0620
C	IF IM(I)=5,VOLUME IS 60 ML	0630
C	IF IM(I)=6,VOLUME IS 120 ML	0640
C	IF IM(I)=7,VOLUME IS 150 ML	0650
C	IF IM(I)=9,VOLUME IS 110 ML	
C		0660
C	IF SOIL SAMPLE DATA	0670
C	COL 2-5 SAMPLE IDENTIFICATION,A4,ID(I)	0680
C	6-10 MOISTURE CONTENT,F5.2,MC(I)	0690
C	11-15 ABSORBANCE,F5.3,CONC(I)	0700
C	16-20 AMOUNT SOLVENT USED FOR EXTRACTION,F5.1,EXT(I)	0710
C	21-25 AMOUNT SOLVENT CONVERTED,F5.1,CONV(I)	0720
C	27-31 WET WEIGHT OF SAMPLE,F5.2,WT(I)	0730
C	32-34,TELLS PROGRAM WHAT TO DO,I3,IFLAG(I)	0740
C	IF IFLAG(I)=1, LAST DATA CARD OF SET	0750
C	IF WANT PROGRAM TO PRINT OUT TRACE INSTEAD OF PPM,IFLAG(I)=2	0760
C	IF WANT PROGRAM TO PRINT OUT TRACE INSTEAD OF PPM AND LAST CARD OF DATA	
C	SET,IFLAG(I)=3	0780
C	35 VOLUME OF SAMPLE USED FOR ABSORBANCE READING,I1,IM(I)	0790
C	IF IM(I)=0,VOLUME IS 10 ML	0800
C	IF IM(I)=1,VOLUME IS 20 ML	0810
C	IF IM(I)=2,VOLUME IS 30 ML	0820
C	IF IM(I)=3,VOLUME IS 40 ML	0830
C	IF IM(I)=4,VOLUME IS 50 ML	0840
C	IF IM(I)=5,VOLUME IS 60 ML	0850
C	IF IM(I)=6,VOLUME IS 120 ML	
C	IF IM(I)=7,VOLUME IS 150 ML	
C	IF IM(I)=9,VOLUME IS 110 ML	
C		0860
C	-----	0870
C		0880
C	DIMENSION AB(50),CONC(50),EXT(50),CONV(50),WT(50),AMT(50),PPM(50),	0890

	CID(50),IFLAG(50),CC(50),WD(50),ANS(50),DMT(50),B(50),PEST(8),	0900
	CITITLE(20),TITLE(20),IM(50),SMT(50),DATE(4),W(50),DIF(50),CMT(50)	
	REAL MC(100)	0920
	ZZ=4.0/(3.1416**2)	
650	READ(5,508)ICARD,PEST	0930
	IF(ICARD.EQ.0)GO TO 506	0940
	GO TO(502,502,503,504,505),ICARD	
502	READ(5,507)MMSAMP,MDSAMP,MYSAMP	0960
	GO TO 520	0970
503	READ(5,900)WAT,MDAYS,MMSAMP,MDSAMP,MYSAMP	0980
	GO TO 520	0990
504	READ(5,509)ITITLE	1000
	READ(5,509)TITLE	1010
	GO TO 520	
505	READ(5,509)ITITLE	
	READ(5,509)TITLE	
	READ(5,771)TEMP,ST,DEN,TIME,DATE,IND	
520	READ(5,511)INT	1020
	IF(INT.EQ.0) GO TO 521	1030
	CALL CALIB(ANS,B)	1040
	DN=ANS(1)/B(1)	1050
521	READ(5,522)CORR	1060
	IF(ICARD.EQ.1)GO TO 550	1070
	IF(ICARD.EQ.2)GO TO 551	1080
	IF(ICARD.EQ.3)GO TO 551	1090
	IF(ICARD.EQ.4)GO TO 552	1100
	IF(ICARD.EQ.5)GO TO 551	
C		1110
C	DATA CARD TO SEE IF SPECIAL TEST A WATER OR SOIL TEST,IND	1120
C		1130
552	READ(5,553)IND	1140
	IF(IND.EQ.1)GO TO 550	1150
	IF(IND.EQ.2)GO TO 551	1160
550	M=0	1170
	DO 560 I=1,100	1180

READ(5,561)ID(I),CONC(I),EXT(I),CONV(I),WD(I),IFLAG(I),IM(I)	1190
M=M+1	1200
IF(IFLAG(I).EQ.1)GO TO 100	1210
IF(IFLAG(I).EQ.3)GO TO 100	1220
560 CONTINUE	1230
551 M=0	1240
DO 50 I=1,100	1250
READ(5,6) ID(I),MC(I),CONC(I),EXT(I),CONV(I),WT(I),IFLAG(I),IM(I)	1260
M=M+1	1270
IF(IFLAG(I).EQ.3)GO TO 100	1280
IF(IFLAG(I).EQ.1)GO TO 100	1290
50 CONTINUE	1300
100 DO 65 I=1,M	1310
CC(I)=CONC(I)-CORR	1320
AMT(I)=(CC(I)- ANS(1))/B(1)	1330
IF(AMT(I).LE.DN)AMT(I)=0.00	1340
IF(AMT(I).LE.0.0)AMT(I)=0.0	1350
65 CONTINUE	1360
DO 499 I=1,M	1370
IF(IM(I).EQ.0)CMT(I)=AMT(I)*10.0	1380
IF(IM(I).EQ.1)CMT(I)=AMT(I)*20.0	1390
IF(IM(I).EQ.2)CMT(I)=AMT(I)*30.0	1400
IF(IM(I).EQ.3)CMT(I)=AMT(I)*40.0	1410
IF(IM(I).EQ.4)CMT(I)=AMT(I)*50.0	1420
IF(IM(I).EQ.5)CMT(I)=AMT(I)*60.0	1430
IF(IM(I).EQ.6)CMT(I)=AMT(I)*120.0	1440
IF(IM(I).EQ.7)CMT(I)=AMT(I)*150.0	1450
IF(IM(I).EQ.9)CMT(I)=AMT(I)*110.0	1460
DMT(I)=CMT(I)*(EXT(I)/CONV(I))	1470
499 CONTINUE	1480
IF(ICARD.EQ.1)GO TO 570	1490
IF(ICARD.EQ.2)GO TO 571	1500
IF(ICARD.EQ.3)GO TO 571	1510
IF(ICARD.EQ.4)GO TO 770	1520
770 IF(IND.EQ.1)GO TO 570	1530

	IF(IND.EQ.2)GO TO 571	1540
C		1550
C	CALCULATION OF AMOUNT OF PESTICIDE IN WATER SAMPLE	1560
C		1570
	570 DO 572 I=1,M	1580
	572 PPM(I)=DMT(I)/WD(I)	1590
	GO TO 580	1600
C		1610
C	CALCULATION OF AMOUNT OF PESTICIDE IN SOIL SAMPLE	1620
C		1630
	571 DO 75 I=1,M	1640
	75 PPM(I)=(DMT(I))/(WT(I)/((MC(I)/100.0)+1.0))	1650
	580 IF(ICARD.EQ.1)GO TO 590	1660
	IF(ICARD.EQ.2)GO TO 591	1670
	IF(ICARD.EQ.3)GO TO 592	1680
	IF(ICARD.EQ.4)GO TO 593	1690
	IF(ICARD.EQ.5)GO TO 593	
	590 WRITE(6,700)MMSAMP,MDSAMP,MYSAMP	1700
	GO TO 705	1710
	591 WRITE(6,701)MMSAMP,MDSAMP,MYSAMP	1720
	GO TO 706	1730
	592 WRITE(6,500)WAT,MMSAMP,MDSAMP,MYSAMP,MAYS	1740
	GO TO 706	1750
	593 WRITE(6,702)ITITLE,TITLE	1760
	IF(IND.EQ.1)GO TO 705	1770
	IF(IND.EQ.2)GO TO 706	1780
	705 WRITE(6,710)	1790
C		1800
C	PRINT ONLY 28 LINES OF DATA PER PAGE	1810
C		1820
	DO 711 I=1,M	1830
	IF(IFLAG(I).EQ.2)WRITE(6,798)ID(I),PEST,WD(I),EXT(I),CONV(I)	1840
	IF(IFLAG(I).EQ.2)GO TO 88	1850
	IF(IFLAG(I).EQ.3)WRITE(6,798)ID(I),PEST,WD(I),EXT(I),CONV(I)	1860
	IF(IFLAG(I).EQ.3)GO TO 88	1870

1000	WRITE(6,712) ID(I),PEST,WD(I),EXT(I),CONV(I),DMT(I),PPM(I)	1890
88	IF(I.EQ.28.AND.ICARD.EQ.1)WRITE(6,700)MMSAMP,MDSAMP,MYSAMP	1890
	IF(I.EQ.28.AND.ICARD.EQ.4)WRITE(6,702)ITITLE,TITLE	1900
	IF(I.EQ.28)WRITE(6,710)	1910
	IF(I.GE.28)GO TO 888	1920
711	CONTINUE	1930
	GO TO 650	1940
888	DO 887 I=29,M	1950
	IF(IFLAG(I).EQ.2)WRITE(6,798)ID(I),PEST,WD(I),EXT(I),CONV(I)	1960
	IF(IFLAG(I).EQ.2)GO TO 887	1970
	IF(IFLAG(I).EQ.3)WRITE(6,798)ID(I),PEST,WD(I),EXT(I),CONV(I)	1980
	IF(IFLAG(I).EQ.3)GO TO 887	1990
1001	WRITE(6,712) ID(I),PEST,WD(I),EXT(I),CONV(I),DMT(I),PPM(I)	2000
887	CONTINUE	2010
	GO TO 650	2020
706	WRITE(6,501)	2030
	DO 730 I=1,M	2040
	IF(IFLAG(I).EQ.2)WRITE(6,799)ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I)	2050
	IF(IFLAG(I).EQ.2)GO TO 89	2060
	IF(IFLAG(I).EQ.3)WRITE(6,799)ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I)	2070
	IF(IFLAG(I).EQ.3)GO TO 89	2080
1002	WRITE(6,731) ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I),DMT(I),PPM(I)	2090
89	IF(I.EQ.28.AND.ICARD.EQ.2)WRITE(6,701)MMSAMP,MDSAMP,MYSAMP	2100
	IF(I.EQ.28.AND.ICARD.EQ.3)WRITE(6,500)WAT,MMSAMP,MDSAMP,MYSAMP,	2110
	CMDAYS	2120
	IF(I.EQ.28.AND.ICARD.EQ.4)WRITE(6,702)ITITLE,TITLE	2130
	IF(I.EQ.28)WRITE(6,501)	2140
	IF(I.GE.28)GO TO 889	2150
730	CONTINUE	2160
	IF(ICARD.EQ.5)GO TO 772	
	GO TO 650	2170
889	DO 890 I=29,M	2180
	IF(IFLAG(I).EQ.2)WRITE(6,799)ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I)	2190
	IF(IFLAG(I).EQ.2)GO TO 890	2200
	IF(IFLAG(I).EQ.3)WRITE(6,799)ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I)	2210

IF(IFLAG(I).EQ.3)GO TO 890	2220
1003 WRITE(6,731) ID(I),PEST,WT(I),MC(I),EXT(I),CONV(I),AMT(I),PPM(I)	2230
890 CONTINUE	2240
6 FORMAT(1X,A4,F5.2,F5.3,F5.1,F5.1,F6.2,I3,I1)	2250
900 FORMAT(3(1X,A4),2I6)	2260
508 FORMAT(I1,1X,8A1)	2270
507 FORMAT(6X,A4,1X,I6,1X,I6)	2280
702 FORMAT('1',////////,15X,20A4,/,15X,20A4)	2290
509 FORMAT(20A4)	2300
511 FORMAT(I1)	2310
522 FORMAT(F5.3)	2320
553 FORMAT(I1)	2330
561 FORMAT(1X,A4,F5.3,F5.1,F5.1,F6.1,I3,1X,I1)	2340
700 FORMAT('1',////////,15X,'PESTICIDE IN WATER SAMPLES FROM STORM ',	2350
CA4,',',I2,',',I4,',',ON GINGLES WATERSHEDS')	2360
701 FORMAT('1',////////,15X,'PESTICIDE IN SEDIMENT SAMPLES FROM STORM '	2370
C,A4,',',I2,',',I4,',',ON GINGLES WATERSHEDS')	2380
500 FORMAT('1',////////,15X,'PESTICIDE ON',A4,' WATERSHED,SAMPLED ON ',	2390
CA4,I3,',',I4,',',A4,' DAYS SINCE APPLICATION')	2400
710 FORMAT(13X,80(1H-),/,27X,'PESTI',5X,'SAMPLE',5X,'SOLVENT',6X,'SOLV	2410
CENT',7X,'AMOUNT IN SAMPLE',/,16X,'REMARKS',4X,'-CIDE',5X,'SIZE',7X	2420
C,'USED',8X,'CONVERTED -----',/,38X,'(ML)',7X,'(ML	2430
C)',10X,'(ML)',5X,'MICROGRAMS PPMW',/,13X,80(1H-))	2440
712 FORMAT(17X,A4,4X,8A1,3X,F7.2,5X,F7.2,5X,F7.2,3X,F9.2,4X,F6.2)	2450
501 FORMAT(13X,83(1H-),/,26X,'PESTI',4X,'WET MOIST SOLVENT	2460
CSOLVENT AMOUNT IN SAMPLE',/,15X,'REMARKS -CIDE WEIGHT	2470
C-URE USED CONVERTED -----',/,35X,'(GM)	2480
C (%) (ML) (ML) MICROGRAMS PPMW',/,13X,83(1H-))	2490
798 FORMAT(17X,A4,4X,8A1,3X,F7.2,5X,F7.2,5X,F7.2,17X,'TRACE')	2500
799 FORMAT(16X,A4,4X,8A1,2X,F6.2,3X,F6.2,5X,F5.2,5X,F6.2,15X,'TRACE')	2510
731 FORMAT(16X,A4,4X,8A1,2X,F6.2,3X,F6.2,5X,F6.2,5X,F6.2,2X,F9.2,3X,F7	2520
C.2)	2530
771 FORMAT(F5.0,3F5.2,4A4,I1)	
772 DO 977 I=1,M	
977 SMT(I)=DMT(I)	





2	FORMAT(F8.4,F7.3)	2740
3	FORMAT (27H1POLYNOMIAL REGRESSION.....,A4,A2/)	2750
4	FORMAT (23H0NUMBER OF OBSERVATIONS,I6//)	2760
5	FORMAT (32H0POLYNOMIAL REGRESSION OF DEGREE,I3)	2770
6	FORMAT (12H0 INTERCEPT,F15.5)	2780
7	FORMAT (26H0 REGRESSION COEFFICIENTS/(10F15.8))	2790
8	FORMAT (1H0/24X,24H0ANALYSIS OF VARIANCE FOR,I4,I9H DEGREE POLYNOM	2800
	1IAL/)	2810
9	FORMAT (1H0,5X,19H0SOURCE OF VARIATION,7X,9H0DEGREE OF,7X,6H0SUM OF,9	2820
	1X,4H0MEAN,10X,1HF,9X,20H0IMPROVEMENT IN TERMS/33X,6HFREDJM,8X,7HSQUA	2830
	2RES,7X,6HSQUARE,7X,5H0VALUE,8X,17H0F SUM OF SQUARES)	2840
10	FORMAT (20H0 DUE TO REGRESSION,12X,I6,F17.5,F14.5,F13.5,F20.5)	2850
11	FORMAT (32H DEVIATION ABOUT REGRESSION ,I6,F17.5,F14.5)	2860
12	FORMAT (8X,5HTOTAL,19X,I6,F17.5///)	2870
13	FORMAT (17H0 NO IMPROVEMENT)	2880
14	FORMAT(1H0,/,27X,18HTABLE OF RESIDUALS,/,16H OBSERVATION NO.,	2890
	15X,74X VALUE,7X,7HY VALUE,7X,10HY ESTIMATE,7X,8HRESIDJAL,/)	2900
15	FORMAT(1H0,3X,I6,F18.5,F14.5,F17.5,F15.5)	2910
100	READ(5,1)PR,PR1,N,M,NPLOT	2920
	IF(N)260,260,270	2930
270	WRITE(6,3)PR,PR1	2940
	WRITE(6,4)N	2950
	L=N*M	2960
	DO 110 I=1,N	2970
	J=L+I	2980
110	READ(5,2)X(I),X(J)	2990
	CALL GDATA(N,M,X,XBAR,STD,D,SUMSQ)	3000
	MM=M+1	3010
	SUM=0.0	3020
	NT=N-1	3030
	DO 200 I=1,M	3040
	ISAVE(I)=I	3050
	CALL ORDER (MM,D,MM,I,ISAVE,DI,E)	3060
	CALL UMINV (DI,I,I,DET,LL,MMM)	3070
	CALL MULTR (N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,SB,T,ANS)	3080

WRITE (6,5)I	3090
SUMIP=ANS(4)-SUM	3100
IF (SUMIP)140,140,150	3110
140 WRITE (6,13)	3120
GO TO 210	3130
150 WRITE (6,6)ANS(1)	3140
WRITE(6,7)(B(J),J=1,I)	3150
WRITE(6,8)I	3160
WRITE(6,9)	3170
SUM=ANS(4)	3180
WRITE (6,10)I,ANS(4),ANS(5),ANS(10),SUMIP	3190
NI=ANS(8)	3200
WRITE(6,11)NI,ANS(7),ANS(9)	3210
WRITE(6,12)NT,SUMSQ(MM)	3220
COE(1)=ANS(1)	3230
DO160 J=1,I	3240
160 COE(J+1)=B(J)	3250
LA=I	3260
200 CONTINUE	3270
C	3280
C TEST IF PLOT AND RESIDUALS ARE REQUIRED	3290
C	3300
210 IF(NPLOT)100,100,220	3310
C	3320
C CALCULATE ESTIMATES	3330
C	3340
220 NP3=N+N	3350
DO 230 I=1,N	3360
NP3=NP3+1	3370
P(NP3)=COE(1)	3380
L=I	3390
DO 230 J=1,LA	3400
P(NP3)=P(NP3)+X(L)*COE(J+1)	3410
230 L=L+N	3420

C		3430
C	COPY OBSERVED DATA	3440
C		3450
	N2=N	3460
	L=N*M	3470
	DO 240 I=1,N	3480
	P(I)=X(I)	3490
	N2=N2+1	3500
	L=L+1	3510
	240 P(N2)=X(L)	3520
C		3530
C	PRINT TABLE OF RESIDUALS	3540
C		3550
	WRITE(6,3)PR,PR1	3560
	WRITE(6,5)LA	3570
	WRITE(6,14)	3580
	NP2=N	3590
	NP3=N+N	3600
	DO 250 I=1,N	3610
	NP2=NP2+1	3620
	NP3=NP3+1	3630
	RESID=P(NP2)-P(NP3)	3640
	250 WRITE(6,15)I,P(I),P(NP2),P(NP3),RESID	3650
	GO TO 100	3660
	260 CONTINUE	3670
	RETURN	3680
	END	3690

**B. Computer Program for Propachlor and Diazinon Analysis on the  
Gas Chromatograph**

C		0010
C	-----	0020
C	PROGRAM TO DETERMINE THE AMOUNT AND CONCENTRATION OF PESTICIDE IN A SAMPLE	
C	ANALYZED BY GAS CHROMATOGRAPHY. A CALIBRATION SET IS READ IN AND EITHER A	
C	SIMPLE LINEAR REGRESSION OR A PARABOLIC REGRESSION IS PERFORMED	0050
C		0060
C	1ST DATA CARD OF EACH DATA SET IS AN IDENTIFICATION CARD WITH THE	0070
C	FOLLOWING CODE IN COLUMN 1, READ AS ICARD	0080
C	ICARD=0, END OF DATA	0090
C	ICARD=1, WATER SAMPLES FROM WATERSHED	0100
C	ICARD=2, SEDIMENT SAMPLES FROM WATERSHED	0110
C	ICARD=3, SOIL SAMPLES FROM WATERSHED	0120
C	ICARD=4, SPECIAL TEST	0130
C	ICARD=5, DIFFUSION TEST	
C		0140
C	SECOND DATA CARD GIVES CONDITIONS OF THE DATA	0150
C	FOR WATER OR SEDIMENT SAMPLES FROM WATERSHED	0160
C	COL 5-8..MONTH RAINFALL OCCURRED, A4, MMSAMP	0170
C	9-14..DAY RAINFALL OCCURRED, I6, MDSAMP	0180
C	15-20..YEAR RAINFALL OCCURRED, I6, MYSAMP	0190
C	21-35..DATE OF ANALYSIS, I5A1, DAT	0200
C		0210
C	FOR SOIL SAMPLES FROM WATERSHED	0220
C	COL 1-4..WATERSHED, A4, WAT	0230
C	5-8..DAYS SINCE APPLICATION, I4, MDAYS	0240
C	9-12..MONTH OF SAMPLING, A4, MMSAMP	0250
C	13-18..DAY OF SAMPLING, I6, MDSAMP	0260
C	19-24..YEAR OF SAMPLING, I6, MYSAMP	0270
C	25-39..DATE OF ANALYSIS, I5A1, DAT	0280
C		0290
C	FOR A SPECIAL TEST, TWO CARDS ARE USED TO DESCRIBE THE TEST, THESE CARDS	0300
C	ARE READ IN UNDER THE FORMAT 20A4, ITITLE, ITIT	0310
C		0320
C		
C	IF DATA SET IS A DIFFUSION TEST THE 2ND AND 3RD CARDS DESCRIBE THE	

C	TEST AND ARE READ UNDER THE FORMAT 20A4,ITITLE,TITLE	
C	THE 4TH CARD FOR THE DIFFUSION TEST DESCRIBES THE OPERATING	
C	PARAMETERS OF THE DIFFUSION TEST	
C	COL 1-5 TEMPERATURE,F5.0,TEMP	
C	6-10 SOIL MOISTURE CONTENT,F5.2,ST	
C	11-15 SOIL BULK DENSITY,F5.2,DEN	
C	16-20 LENGTH OF TEST,F5.2,TIME	
C	21-36 DATE TEST PERFORMED,4A4,DATE	
C	37 INDICATES TEST IS A SOIL SAMPLE,IND=2,I1,IND	
C	THE 3RD CARD OF EVERY DATA SET IS AN OPERATING PARAMETER CARD	0330
C	IF THE DATA SET USES THE SAME CALIBRATION CURVE AS THE SET BEFORE,THIS	0340
C	CARD IS BLANK	0350
C	COL 1-5..STANDING CURRENT,I5,CUR	0360
C	16-19..COLUMN TEMPERATURE,A4,COLTEMP	0370
C	20-23..INJECTOR TEMPERATURE,A4,INJTEMP	0380
C	24-27..DETECTOR TEMPERATURE,A4,DETEM	0390
C	28-31..GAS FLOW IN ML/MIN,A4,FLOW	0400
C		0410
C	4TH DATA CARD DESCRIBES THE TYPE OF COLUMN USED	0420
C	COL 1-15..TYPE OF COLUMN,15A1,COL	0430
C	16-35..LIQUID SUPPORT OF COLUMN,20A1,SJP	0440
C	36-60..SOLID SUPPORT OF COLUMN,25A1,SOLID	0450
C		0460
C	NEXT CARDS CONTAIN DATA FOR CALIBRATION CURVE IF CJR IS NOT ZERO	0470
C	IF DATA SET IS A SPECIAL TEST,THE NEXT CARD DETERMINES IF SPECIAL TEST	0480
C	IS A SOIL OR WATER TEST,I1,IND	0490
C	IND = 1,A WATER TEST	0500
C	IND = 2,A SOIL TEST	0510
C		0520
C	NEXT CARDS ARE DATA CARDS	0530
C	IF DATA SET IS WATER SAMPLES,THE DATA CARDS ARE AS FOLLOWS	0540
C	COL 4-15..SAMPLE IDENTIFICATION,3A4,ID(I),C(I),D(I)	0550
C	16-19..PESTICIDE BEING ANALYZED,A4,PEST(I)	0560
C	20-27..SIZE OF WATER SAMPLE EXTRACTED,F8.4,WD(I)	0570

C	28-35..AMOUNT OF SOLVENT USED FOR EXTRACTION,F8.4,EXT(I)	0580
C	36-43..AMOUNT OF SOLVENT CONCENTRATED,F8.4,CONV(I)	0590
C	44-51..FINAL CONCENTRATION OF SOLVENT,F8.4,CONT(I)	0600
C	52-56..ATTENUATION APPLIED TO PEAK HEIGHT,I5,ATTN(I)	0610
C	57-61..PEAK HEIGHT OR AREA,IF EQUAL TO -1 THE PROGRAM WILL PRINT	
C	OUT "TRACE" INSTEAD OF PPM,I5,PKHT(I)	0630
C	62-66..MICROLITERS INJECTED,F5.0,MKLR(I), ALWAYS PUT IN DECIMAL	0640
C	IF IT IS DESIRED TO ENTER A VALUE OF NANOGRAMS INJECTED WHEN POINT	
C	ABOVE LINEAR PART OF CALIBRATION CURVE,ENTER THE VALUE AS TAKEN FROM	
C	THE CALIBRATION IN THE COLUMN RESERVED FOR CONC(I)	0670
C	67-71..NANOGRAMS INJECTED,F5.0,CONC(I),ALWAYS PUT IN DECIMAL	0680
C	80..TELLS PROGRAM WHAT TO DO,I1,IFLAG(I)	0690
C	IFLAG(I) = 1,END OF DATA SET	0700
C	IFLAG(I) = 2,END OF DATA SET AND NANOGRAMS INJECTED ENTERED FOR	0710
C	CONC(I)	0720
C	IFLAG(I) = 3,NANOGRAMS INJECTED ENTERED FOR CONC(I)	0730
C		0740
C	IF DATA SET IS SOIL SAMPLES,DATA CARDS ARE AS FOLLOWS	0750
C	COL 4-15..SAMPLE IDENTIFICATION,3A4,ID(I),C(I),D(I)	0760
C	16-19..PESTICIDE BEING ANALYZED,A4,PEST(I)	0770
C	20-28..GRAMS OF SOIL EXTRACTED,F9.4,WT(I)	0780
C	29-35..MOISTURE CONTENT,F7.4,MC(I)	0790
C	36-43..AMOUNT OF SOLVENT USED FOR EXTRACTION,F8.4,EXT(I)	0800
C	44-51..AMOUNT OF SOLVENT CONCENTRATED,F8.4,CONV(I)	0810
C	52-59..FINAL CONCENTRATION OF SOLVENT,F8.4,CONT(I)	0820
C	60-64..ATTENUATION APPLIED TO PEAK HEIGHT,I5,ATTN(I)	0830
C	65-69..PEAK HEIGHT OR AREA,I5,PKHT(I),IF EQUAL TO -1 PROGRAM WILL	
C	PRINT OUT "TRACE" INSTEAD OF PPM	0850
C	70-74..MICROLITERS INJECTED,F5.0,MCLR(I),ALWAYS PUT IN DECIMAL	0860
C	IF IT IS DESIRED TO ENTER A VALUE OF NANOGRAMS INJECTED WHEN POINT	
C	ABOVE LINEAR PART OF CALIBRATION CURVE,ENTER THE VALUE AS TAKEN FROM	
C	THE CALIBRATION IN THE COLUMN RESERVED FOR CONC(I)	0890
C	75-79..NANOGRAMS INJECTED,F5.0,CONC(I),ALWAYS PUT IN DECIMAL	0900
C	80..TELLS PROGRAM WHAT TO DO,I1,IFLAG(I)	0910
C	IFLAG(I) = 1,END OF DATA SET	0920

C	IFLAG(I) = 2,END OF DATA SET AND NANJGRAMS INJECTED ENTERED FOR	0930
C	CONC(I)	0940
C	IFLAG(I) = 3,NANJGRAMS INJECTED ENTERED FOR CONC(I)	0950
C		0960
C	-----	0970
C		0980
	ODIMENSION ITIT(20),ID(40),C(40),WD(40),EXT(40),CONV(40),CONT(	0990
	140),ATTN(40),PKHT(40),CONC(40),IFLAG(40),WT(40),MC(40),ZN(40),	1000
	2TOTAL(40),PPM(40),MCL(40),MCLR(40),ANS(10),B(10),ITITLE(20),SOLID	1010
	3(25),COL(15),SUP(20),DA(15),PEST(60),D(60),SMT(50),W(50),DIF(50),D	
	4ATE(4)	
	REAL MC,MCL,MCLR	1030
	INTEGER PKHT,CUR,ATTN	1040
	MAX=0	1050
312	FORMAT(3X,4A4,F9.4,F7.4,3F8.4,2I5,2F5.0,I1)	1130
300	FORMAT(I1)	1060
305	FORMAT(4X,A4,2I6,15A1)	1070
306	FORMAT(A4,I4,A4,2I6,15A1)	1080
307	FORMAT(20A4)	1090
308	FORMAT(15,10X,A4,A4,A4,A4)	1100
310	FORMAT(I1)	1110
311	FORMAT (3X,4A4,4F8.4,2I5,2F5.0,8X,I1)	1120
900	READ(5,300) ICARD	1140
	IF(ICARD.EQ.0) GO TO 301	1150
	GO TO (302,302,303,304,309),ICARD	
302	READ(5,305)MMSAMP,MDSAMP,MYSAMP,DA	1170
	GO TO 400	1180
303	READ(5,306)WAT,MDAYS,MMSAMP,MDSAMP,MYSAMP,DA	1190
	GO TO 400	1200
304	READ(5,307) ITITLE	1210
	READ(5,307)ITIT	1220
	GO TO 400	
309	READ(5,307) ITITLE	
	READ(5,307)ITIT	
	READ(5,771)TEMP,ST,DEV,TIME,DATE,IND	



400	READ(5,308)CUR,COLTEM,INJTEM,DETEM,FLOW	1230
	IF(CUR.EQ.0) GO TO 401	1240
	READ(5,999)COL,SUP,SOLID	1250
999	FORMAT(15A1,20A1,25A1)	1260
	CALL CALIB(ANS,B,MAX)	1270
	WRITE(6,606)COL,SUP,SOLID,COLTEM,INJTEM,DETEM,FLOW,CJR	1280
401	IF (ICARD.NE.4) GO TO 402	1290
	READ (5,310)IND	1300
	IF(IND.EQ.1) GO TO 403	1310
	IF(IND.EQ.2) GO TO 404	1320
402	IF(ICARD.EQ.1) GO TO 403	1330
	IF(ICARD.EQ.2) GO TO 404	1340
	IF(ICARD.EQ.3) GO TO 404	1350
	IF(ICARD.EQ.5) GO TO 404	
403	M=0	1360
	DO 405 I=1,60	1370
	READ(5,311) ID(I),C(I),D(I),PEST(I),WD(I),EXT(I),CONV(I),CONT(I),	1380
	ATTN(I),PKHT(I),MCLR(I),CONC(I),IFLAG(I)	1390
	M =M+1	1400
	IF(IFLAG(I).EQ.1.OR.IFLAG(I).EQ.3) GO TO 407	1410
405	CONTINUE	1420
404	M =0	1430
	DO 406 I=1,60	1440
	READ(5,312) ID(I),C(I),D(I),PEST(I),WT(I),MC(I),EXT(I),CONV(I),CON	1450
	IT(I),ATTN(I),PKHT(I),MCLR(I),CONC(I),IFLAG(I)	1460
	M =M+1	1470
	IF (IFLAG(I).EQ.1.OR.IFLAG(I).EQ.3) GO TO 408	1480
406	CONTINUE	1490
C		1500
C	CALCULATION OF AMOUNT OF PESTICIDE IN WATER SAMPLE	1510
C		1520
407	DO 500 I= 1,M	1530
	ZN(I)= PKHT(I)*ATTN(I)	1540
	IF(IFLAG(I).EQ.2.OR.IFLAG(I).EQ.3) GO TO 550	1550
	IF(ZN(I))100,100,101	1560

C		1570
C	Z IS NANOGRAMS OF MATERIAL	1580
C		1590
	101 Z = EXP(ANS(1) + B(1)*ALOG(ZN(I)) + B(2)*ALOG(ZN(I))*ALOG(ZN(I)))	1600
	GO TO 551	1610
	550 Z = CONC(I)	1620
	551 TOTAL(I) = (Z*CONT(I)*EXT(I))/(CONV(I)*MCLR(I))	1630
	PPM(I) = TOTAL(I)/WD(I)	1640
	GO TO 500	1650
	100 TOTAL (I) = 0.00	1660
	PPM(I) = 0.00	1670
	500 CONTINUE	1680
	GO TO 799	1690
C		1700
C	CALCULATION OF AMOUNT OF PESTICIDE IN SOIL SAMPLE	1710
C		1720
	408 DO 501 I=1,M	1730
	ZN(I) = PKHT(I)*ATTN(I)	1740
	IF(IFLAG(I).EQ.2.OR.IFLAG(I).EQ.3) GO TO 552	1750
	926 IF(ZN(I))200,200,201	1760
	201 Z = EXP(ANS(1) + B(1)*ALOG(ZN(I)) + B(2)*ALOG(ZN(I))*ALOG(ZN(I)))	1770
	GO TO 553	1780
	552 Z = CONC(I)	1790
	553 TOTAL(I) = (Z*CONT(I)*EXT(I))/(CONV(I)*MCLR(I))	1800
	PPM(I) = TOTAL (I)/(WT(I)/((MC(I)/100.0)+1.0))	1810
	GO TO 501	1820
	200 TOTAL (I) = 0.0	1830
	PPM(I) = 0.0	1840
	501 CONTINUE	1850
	799 IF (ICARD.EQ.1) GO TO 502	1860
	IF (ICARD.EQ.2) GO TO 503	1870
	IF (ICARD.EQ.3) GO TO 504	1880
	IF (ICARD.EQ.4) GO TO 505	1890
	IF (ICARD.EQ.5) GO TO 505	
	502 WRITE(6,610)MMSAMP,MDSAMP,MYSAMP,DA	1900

	GO TO 506	1910
503	WRITE(6,611)MMSAMP,MDSAMP,MYSAMP,DA	1920
	GO TO 507	1930
504	WRITE(6,612)WAT,MMSAMP,MDSAMP,MYSAMP,MDAYS,DA	1940
	GO TO 507	1950
505	WRITE(6,613)ITITLE,ITIT	1960
	IF(IND.EQ.1) GO TO 506	1970
	IF(IND.EQ.2) GO TO 507	1980
506	WRITE(6,614)	1990
C		2000
C	PRINT ONLY 27 LINES OF DATA PER PAGE	2010
C		2020
	DO 700 I=1,M	2030
	0IF(PKHT(I).EQ.-1)WRITE(6,703) ID(I),C(I),D(I),WD(I),PEST(I),MCLR(I	2040
	1),CONV(I),CONT(I)	2050
	IF(PKHT(I).EQ.-1) GO TO 790	2060
	IF(ZN(I).GT.MAX)WRITE(6,702) ID(I),C(I),D(I),WD(I),PEST(I),ZN(I),	2070
	1 MCLR(I),CONV(I),CONT(I),TOTAL(I),PPM(I)	2080
	IF(ZN(I).GT.MAX) GO TO 790	2090
	0WRITE(6,701) ID(I),C(I),D(I),WD(I),PEST(I),ZN(I),MCLR(I),CONV(I),	2100
	1CONT(I),TOTAL(I),PPM(I)	2110
790	IF(I.EQ.27.AND.ICARD.EQ.1)WRITE(6,610)MMSAMP,MDSAMP,MYSAMP,DA	2120
	IF(I.EQ.27.AND.ICARD.EQ.4)WRITE(6,613)ITITLE,ITIT	2130
	IF(I.EQ.27)WRITE(6,614)	2140
	IF(I.EQ.27) GO TO 800	2150
700	CONTINUE	2160
	DO 970 I=1,M	2170
	IF(ZN(I).GT.MAX)WRITE(6,971)	2180
	IF(ZN(I).GT.MAX) GO TO 900	2190
970	CONTINUE	2200
	GO TO 900	2210
800	DO 801 I=28,M	2220
	0IF(PKHT(I).EQ.-1)WRITE(6,703) ID(I),C(I),D(I),WD(I),PEST(I),MCLR(I	2230
	1),CONV(I),CONT(I)	2240
	IF(PKHT(I).EQ.-1) GO TO 801	2250

IF(ZN(I).GT.MAX)WRITE(6,702) ID(I),C(I),D(I),WD(I),PEST(I),ZN(I),	2260
1 MCLR(I),CONV(I),CONT(I),TOTAL(I),PPM(I)	2270
IF(ZN(I).GT.MAX) GO TO 801	2280
OWRITE(6,701) ID(I),C(I),D(I),WD(I),PEST(I),ZN(I),MCLR(I),CONV(I),	2290
1CONT(I),TOTAL(I),PPM(I)	2300
801 CONTINUE	2310
DO 980 I =1,M	2320
IF(ZN(I).GT.MAX) WRITE(6,971)	2330
IF(ZN(I).GT.MAX) GO TO 900	2340
980 CONTINUE	2350
GO TO 900	2360
507 WRITE(6,910)	2370
DO 911 I =1,M	2380
0IF(PKHT(I).EQ.-1) WRITE(6,912) ID(I),C(I),D(I),WT(I),MC(I),PEST(I)	2390
1,MCLR(I),CONT(I)	2400
IF(PKHT(I).EQ.-1) GO TO 915	2410
0IF(ZN(I).GT.MAX) WRITE(6,705) ID(I),C(I),D(I),WT(I),MC(I),PEST(I),	2420
1ZN(I),MCLR(I),CONT(I),TOTAL(I),PPM(I)	2430
0IF(ZN(I).GT.MAX) GO TO 915	2440
WRITE(6,913) ID(I),C(I),D(I),WT(I),MC(I),PEST(I),ZN(I),MCLR(I),CONV	2450
1T(I),TOTAL(I),PPM(I)	2460
9150IF(I.EQ.27.AND.ICARD.EQ.3) WRITE(6,612)WAT,MMSAMP,MDSAMP,MYSAMP,	2470
1MDAYS,DA	2480
0IF(I.EQ.27.AND.ICARD.EQ.2) WRITE(6,611)MMSAMP,MDSAMP,MYSAMP,DA	2490
0IF(I.EQ.27.AND.ICARD.EQ.4) WRITE(6,613)ITITLE,ITIT	2500
IF(I.EQ.27) WRITE(6,910)	2510
IF(I.EQ.27) GO TO 920	2520
911 CONTINUE	2530
DO 921 I =1,M	2540
IF(ZN(I).GT.MAX) WRITE(6,971)	2550
IF(ZN(I).GT.MAX) GO TO 998	
921 CONTINUE	2570
998 CONTINUE	
IF(ICARD.EQ.5) GO TO 772	
GO TO 900	2580

920 DO 923 I =28,M	2590
OIF(PKHT(I).EQ.-1) WRITE(6,912) ID(I),C(I),D(I),WT(I),MC(I),PEST(I)	2600
1,MCLR(I),CONT(I)	2610
IF(PKHT(I).EQ.-1) GO TO 923	2620
OIF(ZN(I).GT.MAX) WRITE(6,705) ID(I),C(I),D(I),WT(I),MC(I),PEST(I),	2630
1ZN(I),MCLR(I),CONT(I),TOTAL(I),PPM(I)	2640
OIF(ZN(I).GT.MAX) GO TO 923	2650
WRITE(6,913) ID(I),C(I),D(I),WT(I),MC(I),PEST(I),ZN(I),MCLR(I),CON	2660
1T(I),TOTAL(I),PPM(I)	2670
923 CONTINUE	2680
DO 933 I =1,M	2690
IF(ZN(I).GT.MAX) WRITE(6,971)	2700
IF(ZN(I).GT.MAX)GO TO 900	2710
933 CONTINUE	2720
GO TO 900	2730
6110FORMAT('1',////////,15X,'PESTICIDE IN SEDIMENT SAMPLES FROM STORM '	2740
1,A4,',',I2,',',I4,',',ON GINGLES WATERSHEDS',/,15X,'DATE OF ANALYSIS	2750
2',1X,15A1)	2760
6120FORMAT('1',////////,15X,'PESTICIDE ON',A4,' WATERSHED,SAMPLED ON ',	2770
1A4,I3,',',I4,',',I4,' DAYS SINCE APPLICATION',/,15X,'DATE OF ANALY	2780
2SIS ',15A1)	2790
613 FORMAT('1',////////,15X,20A4,/,15X,20A4)	2800
6060FORMAT(1H ,16X,'OPERATING CONDITIONS',/,21X,'COLUMN'10X,'--',3X,	2810
115A1,20A1,/,42X,25A1,/,21X,'COLUMN TEMP       -- ',1X,A4,' C',/,21X,	2820
2'INJECTOR TEMP       -- ',1X,A4,' C ',/,21X,'DETECTOR TEMP       -- ',1X,A	2830
34,' C ',/,21X,'FLOW RATE               -- ',1X,A4,' ML/MIN',/,21X,'STANDIN	2840
4G CURRENT--',16,' MM')	2850
6140FORMAT(13X,83(1H-),/,31X,'SAMPLE PEST- ADJ PEAK SAMPLE SOLVENT SO	2860
1LVENT       AMOUNT IN SAMPLE ',/,19X,'REMARKS       SIZE       ICIDE HEIG	2870
2HT       SIZE       CONC.       SIZE       -----',/,32X,'(ML)	2880
3       (MM)       (MCL)       (ML)       (ML)       MICROGRAMS PPM ',/,13X,83(1H-	2890
4))	2900
971 FORMAT(16X,'* ADJUSTED PEAK HEIGHT ABOVE HIGHEST CALIBRATION POINT	2910
1')	2920
7010FORMAT (16X,3A4,1X,F7.2,4X,A4, 2X,F7.1,2X,F4.1,2X,F6.2,2X,F5.2,1X,	2930

1F10.3,2X,F8.4)	2940
7020FORMAT (16X,3A4,1X,F7.2,4X,A4, 2X,F6.1,3X,F3.1,3X,F5.2,3X,F5.2,1X,	2950
1F10.3,2X,F8.4,'*')	2960
7030FORMAT (16X,3A4,1X,F7.2,4X,A4, 12X,F3.1,3X,F5.2,3X,F5.2,15X,'TRACE	2970
1')	2980
6100FORMAT('1',////////,15X,'PESTICIDE IN WATER SAMPLES FROM STORM ',A4	2990
1,',',I2,',',I4,',',ON GINGLES WATERSHEDS',/,15X,'DATE OF ANALYSIS',1	3000
2X,15A1)	3010
9100FORMAT(13X,83(1H-),/,36X,'WET MOIST PEST- ADJ PEAK SAMPLE SOLVE	3020
1NT AMOUNT IN SAMPLE',/,19X,'REMARKS WEIGHT -URE ICIDE H	3030
2EIGHT SIZE SIZE -----',/,35X,'(GMS) (%)	3040
3 (MM) (MCL) (ML) MICROGRAMS PPM',/,13X,83(1H-))	3050
913 FORMAT (1H,15X,3A4,F12.4,F6.2,2X,A4,F9.1,F7.1,F8.1,F12.3,F7.2)	3060
705 FORMAT (1H,15X,3A4,F12.4,F6.2,2X,A4,F9.1,F7.2,F8.1,F12.3,F7.2,'*')	3070
912 FORMAT (1H,15X,3A4,F12.4,F6.2,2X,A4,9X,F7.1,F8.1,14X,'TRACE')	3080
772 DO 977 I=1,M	
977 SMT(I)=TOTAL(I)	
WRITE(6,414)ITITLE,ITIT,DATE,TEMP,ST,DEN,TIME	
DO 411 I=2,M,2	
411 W(I)=(TOTAL(I)+TOTAL(I-1))	
DO 413 I =2,M,2	
413 DIF(I)=SMT(I)/W(I)	
DO 415 I=2,M,2	
K=I/2	
415 WRITE(6,416) K,DIF(I)	
771 FORMAT(F5.0,3F5.2,4A4,I1)	
416 FORMAT(16X,'REP',I2,2X,F10.4)	
4140FORMAT('1',////////,15X,20A4,/,15X,20A4,/,15X,'DATE OF ANALYSIS ',4	
1A4,/,13X,80(1H-),/,15X,'EXPERIMENTAL VARIABLES',/,17X,'TEMPERATU	
2RE',F5.0,' DEG F',/,17X,'INITIAL SOIL MOISTURE ',F5.1,' %',/,17X,'	
3BULK DENSITY ',F5.2,' GM/CC',/,16X,' LENGTH OF DIFFUSION ',F4.1,'	
4DAYS',/,15X,'DIFFUSION COEFFICIENTS',/,13X,29(1H-),/,15X,'REMARKS	
5 COEFFICIENT',/,13X,29(1H-))	
925 GO TO 900	3090
301 STOP	3100

END	3110
-----	3120
C	3130
C SUBROUTINE CALIB	3140
C	3150
C PURPOSE	3160
C THIS SUBROUTINE COMPUTES THE LEAST SQUARES REGRESSION EQUATION WITH	3170
C HEIGHT AS DEPENDENT VARIABLE	3180
C	3190
C 1ST DATA CARD HAS FOLLOWING INFORMATION	3200
C COL 1-6..PR AND PR1..,PROBLEM IDENTIFICATION (MAY BE ALP+AMERIC),A4	3210
C 7-11..NUMBER OF OBSERVATIONS,I5,N	3220
C 12-13..HIGHEST DEGREE POLYNOMIAL SPECIFIED,I2,M	3230
C 14...NPLOT OPTION CODE,I1	3240
C 0...RESIDUALS NOT WANTED	3250
C 1...RESIDUALS PRINTED	3260
C 15-18...PESTICIDE BEING ANALYZED,4A1,PES	3270
C 19-33...DATE OF ANALYSIS,15A1,DAT	3280
C DATA CARDS ARE	3290
C COL 1-5..ATTENUATION APPLIED TO PEAK HEIGHT,I5,ATTN(I)	3300
C 6-10..PEAK HEIGHT OR AREA,I5,PKHT(I)	3310
C 11-15..MICROLITERS INJECTED,F5.0,MCL(I),ALWAYS PUT IN DECIMAL	3320
C 16-22..CONCENTRATION OF STANDARD,F7.0,CN(I),ALWAYS PUT IN DECIMAL	3330
C LAST DATA CARD IS ALWAYS BLANK	3340
C	3350
-----	3360
C	3370
C SUBROUTINE CALIB(ANS,B,MAX)	3380
C ODIMENSION ATTN(40),PKHT(40),MCL(40),CN(40),APK(40),NG(40),COL(15)	3390
C 1,SOLID(20),X(500),DI(100),D(50),B(10),E(10),SB(10),T(10),XBAR(11),	3400
C 2STD(11),COE(11),SUMSQ(11),ISAVE(11),ANS(10),LL(10),MM(10),P(101),	3410
C 3Y(60),SUP(25),PES(4),DAT(15)	3420
C INTEGER PKHT,ATTN	3430
C REAL MCL,NG	3440
C 100 READ(5,1)PR,PR1,N,M,NPLOT,PES,DAT	3450

	IF(N)260,260,270	3460
270	WRITE(6,3)PR,PR1	3470
	WRITE(6,4)N	3480
	DO 130 I=1,N	3490
130	READ(5,2)ATTN(I),PKHT(I),MCL(I),CN(I)	3500
	L=M*N	3510
	DO 110 I=1,N	3520
	APK(I)= ATTN(I)*PKHT(I)	3530
	NG(I) = MCL(I)*CN(I)	3540
C		3550
C	TRANSFORM THE VARIABLE TO LOGS BASE E	3560
	Y(I)= ALOG(NG(I))	3570
	X(I)= ALOG(APK(I))	3580
	J=L+I	3590
110	X(J)=Y(I)	3600
	IF(M.EQ.1)B(2)=0.000	3610
C		3620
C	FIND MAXIMUM CALIBRATION POINT	3630
	MAX = 0	3640
	DO 700 I=1,N	3650
	IF (APK(I).GT.MAX) MAX = APK(I)	3660
700	CONTINUE	3670
	3 FORMAT (27H1POLYNOMIAL REGRESSION.....,A4,A2/)	3680
	4 FORMAT (23H0NUMBER OF OBSERVATIONS,I6//)	3690
	5 FORMAT (32H0POLYNOMIAL REGRESSION OF DEGREE,I3)	3700
	6 FORMAT (12H0 INTERCEPT,F15.5)	3710
	7 FORMAT (26H0 REGRESSION COEFFICIENTS/(10F15.8))	3720
	8 FORMAT (1H0/24X,24HANALYSIS OF VARIANCE FOR,I4,19H DEGREE POLYNOMIAL/)	3730
	9 FORMAT (1H0,5X,19HSOURCE OF VARIATION,7X,9HDEGREE OF,7X,6HSUM OF,9	3740
	1X,4HMEAN,10X,1HF,9X,20HIMPROVEMENT IN TERMS/33X,6HFREDDM,8X,7HSQUA	3750
	2RES,7X,6HSQUARE,7X,5HVALUE,8X,17HOF SUM OF SQUARES)	3760
10	FORMAT (20H0 DUE TO REGRESSION,12X,I6,F17.5,F14.5,F13.5,F20.5)	3770
11	FORMAT (32H DEVIATION ABOUT REGRESSION ,I6,F17.5,F14.5)	3780
12	FORMAT (8X,5HTOTAL,19X,I6,F17.5//)	3790
		3800



13	FORMAT (17H0 NO IMPROVEMENT)	3810
14	FORMAT(1H0,/,/,27X,18HTABLE OF RESIDUALS,/,/,16H OBSERVATION NO.,	3820
	15X,7HX VALUE,7X,7HY VALUE,7X,10HY ESTIMATE,7X,8HRESIDUAL,/) )	3830
15	FORMAT(1H0,3X,16,F18.5,F14.5,F17.5,F15.5)	3840
	CALL GDATA(N,M,X,XBAR,STD,D,SUMSQ)	3850
	MM=M+1	3860
	SUM=0.0	3870
	NT=N-1	3880
	DO 200 I=1,M	3890
	ISAVE(I)=I	3900
	CALL ORDER (MM,D,MM,I,ISAVE,DI,E)	3910
	CALL UMINV (DI,I,I,DET,LL,MMM)	3920
	CALL MULTR (N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,S3,T,ANS)	3930
	WRITE (6,5)I	3940
	SUMIP=ANS(4)-SUM	3950
	IF (SUMIP)140,140,150	3960
140	WRITE (6,13)	3970
	GO TO 210	3980
150	WRITE (6,6)ANS(1)	3990
	WRITE(6,7)(B(J),J=1,I)	4000
	WRITE(6,8)I	4010
	WRITE(6,9)	4020
	SUM=ANS(4)	4030
	WRITE (6,10)I,ANS(4),ANS(6),ANS(10),SUMIP	4040
	NI=ANS(8)	4050
	WRITE(6,11)NI,ANS(7),ANS(9)	4060
	WRITE(6,12)NT,SUMSQ(MM)	4070
	COE(1)=ANS(1)	4080
	DO160 J=1,I	4090
160	COE(J+1)=B(J)	4100
	LA=I	4110
200	CONTINUE	4120
C		4130
C	TEST IF PLOT AND RESIDUALS ARE REQUIRED	4140
C		4150

210	IF(NPLOT)100,100,220	4160
C		4170
C	CALCULATE ESTIMATES	4180
C		4190
220	NP3=N+N	4200
	DO 230 I=1,N	4210
	NP3=NP3+1	4220
	P(NP3)=COE(1)	4230
	L=I	4240
	DO 230 J=1,LA	4250
	P(NP3)=P(NP3)+X(L)*COE(J+1)	4260
230	L=L+N	4270
C		4280
C	COPY OBSERVED DATA	4290
C		4300
	N2=N	4310
	L=N*M	4320
	DO 240 I=1,N	4330
	P(I)=X(I)	4340
	N2=N2+1	4350
	L=L+1	4360
240	P(N2)=X(L)	4370
C		4380
C	PRINT TABLE OF RESIDUALS	4390
C		4400
	WRITE(6,3)PR,PR1	4410
	WRITE(6,5)LA	4420
	WRITE(6,14)	4430
	NP2=N	4440
	NP3=N+N	4450
	DO 250 I=1,N	4460
	NP2=NP2+1	4470
	NP3=NP3+1	4480
	RESID=P(NP2)-P(NP3)	4490
250	WRITE(6,15)I,P(I),P(NP2),P(NP3),RESID	4500

WRITE(6,600)DAT	4510
WRITE(6,601)PES	4520
DO 610 I=1,N	4530
610 WRITE(6,602)CN(I),MCL(I),PKHT(I),ATTN(I),NG(I),APK(I)	4540
IF(M.EQ.1)WRITE(6,604)ANS(1),B(1)	4550
IF(M.EQ.2)WRITE(6,605)ANS(1),B(1),B(2)	4560
1 FORMAT(A4,A2,I5,I2,I1,4A1,15A1)	4570
2 FORMAT(2I5,F5.0,F7.0)	4580
6000 FORMAT('1',////////,22X,' CALIBRATION DATA FOR ',15A1,/,13X,63(1H-)	4590
1,/,16X,'CONCENTRATION SAMPLE PEAK ATTEN WEIGHT ADJ PEA	4600
2K',/,16X,'OF STANDARD SIZE HEIGHT',18X,'HEIGHT',/,19X,	4610
3'(PPM) (MICROLITERS) (MM)',11X,'(NG) (MM)',/,13X,63(1H-	4620
4))	4630
601 FORMAT (1H ,27X,' DATA FOR ',4A1,/,28X,20(1H-))	4640
6040 FORMAT(1H ,18X,'EQUATION IS LN(WEIGHT) =',F7.3,' + ',F6.3,'LN(ADJ	4650
1PK HT)',/,13X,63(1H-))	4660
6050 FORMAT(1H ,12X,'LN(NG) =',F8.3,' + ',F6.3,'LN(ADJ PK HT) +',F6.3,	4670
1'LN(ADJ PK HT)**2',/,13X,63(1H-))	4680
602 FORMAT(1H ,18X,F5.2,F12.1,I13,I6,F9.2,F10.1)	4690
GO TO 100	4700
260 CONTINUE	4710
RETURN	4720
END	4730

**XI. APPENDIX B. EXPERIMENTAL DATA**

Table 27. Surface runoff (inches)  
from Gingles Watersheds for  
surface contoured planted  
corn during 1967 crop year

Storm Date	NM	SW	SM	NE
June 4	0.06	0.03	0.07	0.14
5	0.09	0.09	0.09	0.20
7	0.27	0.25	0.25	0.34
	0.21	0.19	0.20	0.18
	0.07	0.09	0.06	0.07 <sup>a</sup>
9	0.38 <sup>a</sup>	0.32	0.50	0.31
	0.17 <sup>a</sup>	0.13	0.22	0.16
	0.05	0.66	0.03	0.05 <sup>a</sup>
11	0.07	0.08	0.04	0.08
	0.53	0.20	0.40	0.49
13	0.05	0.03	0.01	0.04
	0.57	0.32	0.48	0.58
14	0.56	0.45	0.50	0.58
	0.15	0.15	0.14	0.16
15	0.03	0.01	0.01	0.01
19	0.61	0.39	0.54	0.51 <sup>a</sup>
24	0.54	0.20	0.35	0.33
27	0.09	0.05	0.06	0.07 <sup>a</sup>
TOTALS	4.50	3.04	3.95	4.30

<sup>a</sup>Estimated Data

Table 28. Surface runoff (inches)  
from Gingles Watersheds for  
ridge planted corn and  
surface contoured planted  
corn during 1968 crop year

Storm Date		Corn			
		Ridge		Surface	
		NM	SW	SM	NE
June	23	0.01	T <sup>b</sup>	0.01	T
	23	0.01	0.00	0.01	T
	24	0.18	0.03	0.28	0.24
	25	0.23	0.07	0.38	0.33
	25	0.02	T	0.04	0.05
	29	0.08	0.01	0.10	0.12
July	17	T	0.00	0.01	0.02
Aug.	8	0.20 <sup>a</sup>	0.05 <sup>a</sup>	0.30 <sup>a</sup>	0.27
	27	0.10	0.05 <sup>a</sup>	0.20 <sup>a</sup>	0.15 <sup>a</sup>
Sept.	3	0.07	T	0.20	0.14
	6	T	0.00	0.01	T
	22	0.01	0.00	0.03	0.00
Oct.	16	0.02 <sup>a</sup>	0.01 <sup>a</sup>	0.05 <sup>a</sup>	0.10 <sup>a</sup>
TOTALS		0.93	0.22	1.62	1.42

<sup>a</sup>Estimated Data  
<sup>b</sup>Trace

Table 29. Surface runoff (inches)  
from Gingles Watersheds for  
ridge planted corn and  
surface contoured planted  
corn during 1969 crop year

Storm Date	Corn			
	Ridge		Surface	
	NM	SW	SM	NE
May 16	0.06	0.01	0.01	T <sup>b</sup>
21	T	0.00	0.00	0.00
June 11	0.29	0.05	0.51	0.41
11	0.16	0.02 <sup>a</sup>	0.38	0.20
22	0.06	0.01 <sup>a</sup>	0.04	0.03
28	0.23	0.03	0.39	0.16
July 7	0.35 <sup>a</sup>	0.20 <sup>a</sup>	0.59	0.30 <sup>a</sup>
Aug. 6	0.40	0.08	0.73	0.35
8	0.30	0.06 <sup>a</sup>	0.42	0.26
TOTALS	1.85	0.46	3.07	1.71

<sup>a</sup>Estimated Data

<sup>b</sup>Trace

Table 30. Surface runoff (inches)  
from Gingles Watersheds for  
ridge planted corn and  
surface contoured planted  
corn during 1970 crop year

Storm Date		Corn			
		Ridge		Surface	
		NM	SW	SM	NE
May	12	T <sup>b</sup>	T	0.07	0.03
	13	0.16	0.01	0.58 <sup>a</sup>	0.40
	29	0.00	0.00	0.01	T
	30	0.11	T	0.28	0.26
	31	0.01	0.00	0.00	0.01
June	10	0.00	0.00	0.01	0.00
	11	0.06	0.00	0.24	0.24
	12	0.03	0.00	0.01	0.03
Sept.	14	T	T	T	0.00
	15	0.01	0.01	0.03	0.00
Oct.	8	0.01	T	0.03	0.00
TOTALS		0.39	0.02	1.26	0.97

<sup>a</sup>Estimated Data

<sup>b</sup>Trace



Table 31. Concentration of atrazine in water samples from the southmiddle watershed, 1967-1970

Storm Date	Sample Number						B-1	B-2	Avg
	1	2	3	4	5	6			
	Concentration (ppm)								
5-13-70	4.91	4.38	2.45	1.44	1.17				2.87
5-30-70	0.49	0.16	0.29						0.31
6-11-70	0.10	0.20							0.15
5-16-69							0.97		0.97
6-11-69	0.10	0.35	0.30	0.80	0.80		0.29	0.35	0.43
6-22-69	0.23	0.19							0.21
6-28-69	0.12	0.16	0.17	0.15	0.07				0.13
7- 7-69	0.11	0.12	0.12	0.15		0.15	0.17		0.14
8- 6-69	0.05	0.04			0.05	0.00	0.00	T <sup>a</sup>	0.02
8- 8-69		T	0.00	0.06	0.00		0.00	0.00	0.01
6-25-68							0.07		0.07
8- 8-68							0.03		0.03
6-11-67							0.07		0.07
6-13-67				0.04					0.04
6-14-67	0.05	0.06					0.05		0.05
6-15-67	0.07						0.17		0.12
6-19-67	0.06	0.08							0.07
6-24-67	0.08	0.12							0.10
6-27-67	0.03	0.00					0.03	0.02	0.02

<sup>a</sup>Trace

Table 32. Concentration of atrazine in water samples from the northmiddle watershed, 1967-1970

Storm Date	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
5-13-70	1.68				1.68
5-30-70	0.23	0.47			0.35
6-11-70	0.39				0.39
6-11-69	0.53	0.53	0.59		0.55
6-22-69	0.10	0.28			0.19
6-28-69	0.16	0.17	0.00		0.11
7- 7-69	0.09	0.09	0.15		0.11
8- 6-69	0.00	0.04	0.00	0.00	0.01
8- 8-69	0.02	0.02	T <sup>a</sup>	0.00	0.01
6-25-68		0.02			0.02
6-29-68	0.03	0.03			0.03
6-13-67		0.10			0.10
6-14-67	0.05			0.06	0.06
6-15-67	0.06	0.06			0.06
6-24-67	0.05	0.06			0.06
6-27-67	0.03				0.03

<sup>a</sup>Trace

Table 33. Concentration of atrazine in sediment samples from the southmiddle watershed, 1967-1970

Storm Date	Sample Number						Avg	
	1	2	3	4	5	6		B
	Concentration (ppm)							
5-13-70	7.25	7.35	4.66	3.39	1.77	2.38		4.47
5-30-70	0.41	0.04	0.18					0.21
6-11-70		0.18						0.18
6-11-69				0.55			0.97	0.76
6-22-69	0.30	0.40					0.22	0.31
6-28-69	0.11	0.18	0.58	0.18				0.26
7- 7-69	0.22	0.25	0.23	0.42		0.25	0.00	0.23
8- 6-69	0.35				0.00		T <sup>a</sup>	0.12
8- 8-69	T				T		0.00	T
6-25-68							0.28	0.28
6-11-67							0.45	0.45
6-13-67			0.34					0.34
6-14-67	1.32						T	0.66
6-15-67							0.49	0.49
6-19-67	0.27							0.27
6-24-67	0.33	0.30						0.31
6-27-67	0.00	0.00					0.01	T

<sup>a</sup>Trace

Table 34. Concentration of atrazine in sediment samples from the northmiddle watershed, 1967-1970

Storm Date	Sample Number			Avg
	1	2	3	
	Concentration (ppm)			
5-13-70	8.55			8.55
5-30-70	2.00	1.73		1.87
6-22-69	1.20	1.18		1.19
6-28-69	0.27	0.32	0.00	0.20
7- 7-69	0.32	0.00	0.22	0.18
6-25-68	0.19			0.19
6-13-67		0.51		0.51
6-14-67	0.47		0.43	0.45
6-15-67	0.41	0.91		0.66
6-19-67		0.41	0.37	0.39
6-24-67	0.29	0.64		0.47

Table 35. Concentration of propachlor in water samples from the northeast watershed, 1970

Date of Storm	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
5-13-70	2.52	0.71	0.78	1.12	1.28
5-30-70	0.45	0.29	0.41	0.00	0.29
6-11-70	0.34	0.13			0.23

Table 36. Concentration of propachlor in sediment samples from the northeast watershed, 1970

Date of Storm	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
5-13-70	9.33	0.19	2.53	T <sup>a</sup>	3.01
5-30-70	0.00	0.00	0.00	T	0.00
6-11-70	0.00	0.00			0.00

<sup>a</sup>Trace

Table 37. Concentration of diazinon in water samples from the northeast watershed, 1968-1969

Date of Storm	Sample Number					Avg
	1	2	3	4	5	
	Concentration (ppm)					
6-28-69	.062	.047				.054
7- 7-69		.028	.041	.042	.035	.037
8- 6-69	.014	.011	.018			.014
8- 8-69	T <sup>a</sup>	.000	.000	.000		.000
6-25-68	.021	.027	.026			.025
6-29-68	.000	.000				.000
7-17-68	.000					.000
8- 8-68		.000				.000
8-27-68	.000	.000				.000

<sup>a</sup>Trace

Table 38. Concentration of diazinon in water samples from the southmiddle watershed, 1968-1969

Date of Storm	Sample Number							Avg
	1	2	3	4	5	6	B	
	Concentration (ppm)							
6-22-69	.068						.082	.075
6-28-69	.008	T <sup>a</sup>	.000	.016				.006
7- 7-69	.000		.000	.000				.000
8- 6-69	.000	.000	.000		.000	.000		.000
6-29-68							.000	.000
7-17-68							.000	.000
8- 8-68							.000	.000

<sup>a</sup>Trace

Table 39. Concentration of diazinon in water samples from the northmiddle watershed, 1968-1969

Date of Storm	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
6-22-69	.020	.000			.010
6-28-69	.000	.000	.000		.000
7- 7-69	.000	.000	.000		.000
8- 6-69	.000	.000	.000	.000	.000
6-25-68		.000			.000
6-29-68	.000	.000			.000
8- 6-68	.000				.000

Table 40. Concentration of diazinon in water samples from the southwest watershed, 1968-1969

Date of Storm	Sample Number				Avg
	1	2	3	B	
	Concentration (ppm)				
6-28-69	.000				.000
7- 7-69	.000	.000	.000	.000	.000
8- 6-69	.000	.000		.000	.000
8- 8-69	.000	.000			.000
8- 8-68				.000	.000

Table 41. Concentration of diazinon in sediment samples from the southmiddle watershed, 1969

Date of Storm	Sample Number					Avg
	1	2	3	4	5	
	Concentration (ppm)					
7- 7-69	T <sup>a</sup>	0.02	T	T	0.01	T
8- 6-69			0.00			0.00
6-25-68	0.17	0.02	0.02			0.07
6-29-68	0.00	0.00				0.00

<sup>a</sup>Trace

Table 42. Concentration of diazinon in sediment samples from the northeast watershed, 1968-1969

Date of Storm	Sample Number		Avg
	B-1	B-2	
	Concentration (ppm)		
6-22-69	0.00		0.00
7- 7-69	0.00	0.00	0.00
8- 6-69	0.00	0.00	0.00
8- 8-69	0.00	0.00	0.00



Table 43. Concentration of atrazine in the soil for the southmiddle watershed, 1967

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			3	39	40	41	42		Max	Min
			Concentration (ppm)							
June 13	22	0-4	0.62	0.54	0.60	0.15	1.77	0.74	1.77	0.15
		4-8	0.19	0.22	0.30	0.60	4.09	1.08	4.09	0.19
July 6	45	0-4	0.49		0.42	0.39	0.82	0.53	0.82	0.39
		4-8	0.39	0.32	0.48	0.60	0.99	0.56	0.99	0.32
July 21	60	0-4	0.64	0.44	0.30	0.27	0.64	0.46	0.64	0.27
		4-8	0.38	0.31	0.35	0.12	1.15	0.46	1.15	0.12
Aug. 4	74	0-4	0.49	0.43	0.32	0.28	0.52	0.41	0.52	0.28
		4-8	0.37	0.45	0.54	0.26	1.17	0.56	1.17	0.26
Aug. 24	94	0-4	0.38	0.15	0.25	0.11	0.49	0.28	0.49	0.11
		4-8	0.33	0.28	0.43	0.20	0.93	0.43	0.93	0.20
Oct. 23	154	0-4	0.27	0.34	0.23	0.35	0.41	0.32	0.41	0.23
		4-8	0.21	0.22	0.16	0.15	0.44	0.24	0.44	0.16

Table 44. Concentration of atrazine in the soil for the southmiddle watershed, 1968

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			3	39	40	41	42		Max	Min
			Concentration (ppm)							
May 1	1	0-1	3.60	5.37	6.75	3.46	0.76	3.99	6.75	0.76
		1-3	0.57	1.55	6.84	2.49	1.21	2.53	6.84	0.57
May 14	14	0-1	4.38	2.42	1.00	1.58	1.21	2.12	4.38	1.00
		1-3	3.44		0.69	1.03	0.85	1.50	3.44	0.69
May 23	23	0-1	3.61	2.65	2.96	5.71	1.82	3.35	5.71	1.82
		1-3	0.75	1.59	1.83	1.62	0.68	1.29	1.83	0.68
		3-5			1.03		5.15	3.09	5.15	1.03
June 20	51	0-2	1.73	1.18	1.52	1.73	1.09	1.45	1.73	1.18
		2-4	0.56	0.48	0.69	1.04	0.67	0.69	1.04	0.48
June 27	58	0-2	0.96	0.70	0.60	0.67	0.60	0.71	0.96	0.60
		2-4	1.27	1.56	1.43	0.76	0.89	1.18	1.56	0.76
July 12	73	0-2	0.72	0.55	0.64	0.51	0.49	0.58	0.72	0.49
		2-4	0.76	1.23	0.91	0.49	0.79	0.84	1.23	0.49
July 30	91	0-2	0.97	0.31	0.38	0.35	0.31	0.46	0.97	0.31
		2-4	0.89	0.83	0.63	0.50	0.30	0.63	0.89	0.30

Table 44 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			3	39	40	41	42		Max	Min
			Concentration (ppm)							
Aug. 15	107	0-2	0.71	0.52	0.44	0.27	0.41	0.47	0.71	0.27
		2-4	1.17	0.71	0.64	0.43	0.37	0.66	1.17	0.37
		4-6	0.79	0.56	0.69	0.35	0.44	0.57	0.79	0.35
		6-8	0.34	0.22	0.34	0.18	0.28	0.27	0.34	0.18
Sept. 28	151	0-2	0.34	0.25	0.24	0.19	0.19	0.24	0.34	0.19
		2-4	0.49	0.42	0.12	0.30	0.21	0.31	0.49	0.12
		4-6	0.61	0.50	0.30	0.22	0.31	0.39	0.61	0.22
Oct. 29	182	0-2			0.12		0.18	0.15	0.18	0.12
		2-4		0.39	0.16		0.30	0.28	0.39	0.16
		4-6		0.44	0.20		0.34	0.33	0.44	0.20
		6-8		0.32	0.20		0.33	0.28	0.33	0.20
		8-10		0.08	0.07		0.08	0.08	0.08	0.07

Table 45. Concentration of atrazine in the soil for the southmiddle watershed, 1969

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			25	26	27	28	29		Max	Min
			Concentration (ppm)							
May 8	0	0-1	6.90	8.18	3.34	3.30	3.17	4.98	8.18	3.17
		1-3	0.64	0.29	0.58	1.87	0.42	0.76	1.87	0.29
May 14	6	0-1	3.07	2.54	1.09	2.88	1.24	2.16	3.07	1.09
		1-3	0.27	0.47	0.51	0.12	0.38	0.35	0.51	0.12
		3-5			0.37			0.37	0.37	0.37
May 20	12	0-1	1.95	1.49	5.05	2.44	3.07	2.80	5.05	1.49
		1-3	2.25	0.98	2.10	1.10	0.70	1.43	2.25	0.70
		3-5			0.50	0.31		0.40	0.50	0.31
May 28	20	0-1	3.72	2.69	2.14	2.70	2.86	2.82	3.72	2.14
		1-3	2.13	1.36	0.59	0.97	0.62	1.13	2.13	0.59
		3-5			0.34	0.42		0.38	0.42	0.34
June 13	36	0-1	1.63	1.53	1.27	0.60	1.56	1.32	1.63	0.60
		1-3	0.64	0.90	0.83	0.91	0.35	0.73	0.91	0.35
		3-5	0.18	0.44	0.45	0.50	0.27	0.37	0.50	0.18
June 27	50	0-2	1.74	1.72	1.77	1.34	2.14	1.74	2.14	1.34
		2-4	1.92	1.21	1.73	0.86	0.67	1.28	1.92	0.67
		4-6	0.71	0.56	0.41	0.32	0.38	0.48	0.71	0.32

Table 45 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			25	26	27	28	29		Max	Min
			Concentration (ppm)							
July 10	63	0-2	1.45	1.20	1.95	2.13	1.59	1.66	2.13	1.20
		2-4	1.47	1.48	1.32	0.65	0.67	1.12	1.48	0.65
		4-6	0.52	0.40	0.34	1.34	0.39	0.60	1.34	0.34
July 28	81	0-2	0.94	1.02	1.47	1.81	1.34	1.32	1.81	0.94
		2-4	0.93	0.86	0.79	1.08	0.53	0.84	1.08	0.53
		4-6	0.40	0.38	0.23	0.50	0.27	0.36	0.50	0.23
		6-8				0.57		0.57	0.57	0.57
Aug. 18	102	0-2	0.56	0.63	0.70	0.66	0.86	0.68	0.86	0.56
		2-4	0.91	0.73	0.62	0.56	0.53	0.67	0.91	0.53
		4-6	0.51	0.46	0.61	0.26	0.35	0.44	0.61	0.26
		6-8		0.18		0.21		0.20	0.21	0.18
Sept. 25	140	0-2	0.22	0.25	0.29	0.35	0.52	0.33	0.52	0.22
		2-4	0.64	0.40	0.47	0.51	0.48	0.50	0.64	0.40
		4-6	0.40	0.26	0.41	0.33	0.28	0.34	0.41	0.28
		6-8	0.39	0.35	0.17	0.21	0.20	0.26	0.39	0.17
Nov. 5	181	0-2	0.34	0.23	0.36	0.32	0.61	0.37	0.61	0.23
		2-4	0.30	0.29	0.51	0.53	0.49	0.42	0.53	0.29
		4-6	0.32	0.25	0.35	0.06	0.21	0.24	0.32	0.06
		6-8	0.23	0.31	0.23	0.20	0.22	0.24	0.31	0.20
		8-10	0.17	0.19	0.20	0.17	0.39	0.22	0.39	0.17

Table 46. Concentration of atrazine in the soil for the southmiddle watershed, 1970

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			7	8	9	10	11		Max	Min
			Concentration (ppm)							
May 6	0	0-1	10.37	4.32	7.48	8.22	3.36	6.75	10.37	3.36
		1-3	2.00	0.80	1.47	1.65	0.83	1.35	2.00	0.80
May 12	6	0-1	7.35	1.90	1.42	7.38	2.03	4.02	7.38	1.42
		1-3	0.87	0.00	0.50	0.58	0.23	0.44	0.87	0.00
May 19	13	0-1	10.24	3.20	2.03	8.03	3.19	5.34	10.24	2.03
		1-3	1.51	0.42	0.32	0.70	0.64	0.72	1.51	0.32
		3-5	0.61	0.00	0.23	0.68	0.74	0.45	0.74	0.00
May 25	19	0-1	9.81	1.99	2.75	12.10	4.21	6.17	12.10	1.99
		1-3	4.35	0.57	0.26	2.46	0.36	1.60	4.35	0.26
		3-5	3.14	0.00	0.22	0.00	0.26	0.72	3.14	0.00
June 2	27	0-1	2.01	3.29	2.38	1.59	3.35	2.52	3.35	1.59*
		1-3	4.82	0.26	2.35	1.60	0.55	1.92	4.82	0.26
		3-5	1.32	0.29	0.00	T	0.41	0.40	1.32	0.00
June 15	40	0-2	5.95	1.61	1.95	3.08	1.35	2.79	5.95	1.35
		2-4	2.14	0.00	0.45	0.34	0.70	0.73	2.14	0.00
		4-6	1.61	T	0.33	0.33	0.58	0.57	1.61	T

Table 46 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location					Avg	Extremes	
			7	8	9	10	11		Max	Min
			Concentration (ppm)							
July 6	61	0-2	4.96	1.35	1.66	3.30	2.65	2.78	4.96	1.35
		2-4	1.36	0.41	0.28	1.63	0.88	0.91	1.63	0.28
		4-6	0.64	0.51	0.15	0.69	0.40	0.51	0.69	0.15
July 21	76	0-2	0.91	1.43	1.54	2.13	1.92	1.59	2.13	0.91
		2-4	1.06	0.41	1.02	0.80	0.86	0.83	1.06	0.41
		4-6	0.91	0.52	0.35	0.93	0.60	0.66	0.93	0.35
Aug. 11	97	0-2	4.42	1.10	1.28	2.70	1.58	2.22	4.42	1.10
		2-4	0.90	0.33	0.39	1.49	0.41	0.70	1.49	0.33
		4-6	1.37	0.59	0.86	0.16	0.34	0.66	1.37	0.16
		6-8	0.07	0.16	0.42	0.37	0.44	0.29	0.44	0.07
Sept. 23	140	0-2	2.34	0.18	0.56	1.24	1.93	1.25	2.34	0.18
		2-4	3.62	1.66	0.38	1.83	2.14	1.93	3.62	0.38
		4-6	1.04	0.19	0.23	3.51	0.89	1.17	3.51	0.19
		6-8	1.06	0.43	0.69	0.88	0.71	0.75	1.06	0.43
Oct. 28	175	0-2	1.31	0.20	0.36	0.42	1.43	0.74	1.31	0.20
		2-4	1.49	0.51	0.49	1.80	0.76	1.01	1.80	0.49
		4-6	0.96	0.69	0.60	1.60	0.67	0.90	1.60	0.60
		6-8	0.69	0.07	0.39	1.38	0.38	0.58	1.38	0.07

Table 47. Concentration of atrazine in the soil for the northmiddle watershed, 1967

Date of Sampling	Days from Application	Depth (inches)	Location									
			1	2	11	12	18	19	20	26	27	28
			Concentration (ppm)									
June 13	22	0-4	0.49	1.15	0.14	0.38	1.04	1.40	0.81	0.90	0.48	0.56
		4-8	0.52	1.31	0.46	0.30	0.69	0.41	0.42	0.24	0.38	0.70
July 6	45	0-4	0.42	1.05	0.35	0.28	0.53	0.51	0.81	0.82	0.46	
		4-8	0.58	0.87	0.30	0.53	0.68	0.30	0.53	0.63	0.26	
July 20	59	0-4	0.30	0.32	0.37	0.38	0.28	0.22	0.73	0.24	0.32	0.37
		4-8	0.30	0.35	0.58	0.58	0.30	0.25	0.78	0.43	0.47	0.70
Aug. 24	94	0-4	0.16	0.40	0.27	0.16	0.16	0.31	0.60	0.52	0.16	0.69
		4-8	0.37	0.36	0.22	0.24	0.19	0.20	0.33	0.31	0.17	0.25
Oct. 23	154	0-4	0.19	0.41	0.25	0.28	0.15	0.22	0.57	0.48	0.15	0.22
			0.20	0.12	0.21	0.20	0.19	0.21	0.27	0.26	0.16	0.41



Table 47 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location		Avg	Extremes	
			29	44		Max	Min
			Concentration				
			(ppm)				
June 13	22	0-4	0.55	0.36	0.69	1.40	0.14
		4-8	0.27	0.29	0.50	1.31	0.24
July 6	45	0-4		0.44	0.57	1.05	0.28
		4-8		0.46	0.51	0.87	0.26
July 20	59	0-4	1.14	0.52	0.43	1.14	0.22
		4-8	0.46	0.52	0.48	0.78	0.25
Aug. 24	94	0-4	0.30	0.41	0.35	0.69	0.16
		4-8	0.32	0.32	0.27	0.37	0.17
Oct. 23	154	0-4	0.30	0.37	0.30	0.57	0.15
		4-8	0.27	0.27	0.23	0.41	0.12

Table 48. Concentration of atrazine in the soil for the northmiddle watershed, 1968

Date of Sampling	Days from Application	Depth (inches)	Location									
			1	2	11	12	18	19	20	26	27	28
			Concentration (ppm)									
May 1	1	0-1	2.49	2.29	5.26	1.73	1.37	4.99	1.93	5.07	2.75	5.65
		1-3	2.33	4.63	7.20	2.43	1.79	7.33	2.54	6.15	6.76	6.25
May 14	14	0-1	2.09	6.64	2.26	3.05	3.31	5.37	2.02	3.84	3.70	3.35
		1-3	0.67	1.32	0.54	1.61	1.73	2.76	0.62	1.55	1.95	1.48
		3-5			0.33							
May 24	24	0-1	3.24	6.01	4.47	3.21	3.64	3.51	2.93	5.97	9.15	2.89
		1-3	1.03	1.37	2.00	0.90	1.53	1.34	0.88	1.74	1.73	1.14
		3-5	0.70									
June 18	49	0-2	0.80	2.10		1.13	1.22	1.71	1.32	1.64	1.29	1.59
		2-4	0.69	0.73	1.56	0.34	0.47	0.52	0.45	0.55	0.65	0.92
June 27	58	0-2	0.49	0.56	0.51	0.44	0.57	1.34	0.71	1.51	0.37	0.63
		2-4	0.63	1.04	1.30	0.70	1.16	2.31	0.66	1.29	0.93	1.61
July 12	73	0-2	0.31	0.31	0.43	0.32	0.69	1.00	0.61	0.72	0.52	0.30
		2-4	0.62	0.59	0.71	0.63	1.13	1.30	0.79	0.82	0.97	0.50

Table 48 (Continued)

Date of Sampling	Days from Application	Depth (inches)	<u>Location</u>		Avg	<u>Extremes</u>	
			29	44		Max	Min
			Concentration (ppm)				
May 1	1	0-1	1.24	1.76	3.04	5.65	1.24
		1-3	3.57	7.67	4.89	7.67	1.79
May 14	14	0-1	2.09	7.16	3.74	7.16	2.02
		1-3	1.37	2.35	1.50	2.76	0.54
		3-5			0.33	0.33	0.33
May 24	24	0-1	2.61	3.61	4.27	9.15	2.89
		1-3	1.03	0.97	1.31	2.00	0.88
		3-5			0.70	0.70	0.70
June 18	49	0-2	1.28		1.41	2.10	0.80
		2-4	0.38		0.66	1.56	0.34
June 27	58	0-2	0.74		0.72	1.51	0.37
		2-4	1.17		1.16	2.31	0.63
July 12	73	0-2	0.43	0.41	0.50	1.00	0.30
		2-4	0.96	0.91	0.83	1.30	0.50

Table 48 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location									
			1	2	11	12	18	19	20	26	27	28
			Concentration (ppm)									
July 30	91	0-2	0.36	0.48	0.42	0.18	0.46	0.49	0.26	0.87	0.38	0.21
		2-4	0.35	0.47	0.46	0.56	1.37	0.77	0.61	0.81	0.56	0.40
Aug. 15	107	0-2	0.14	0.20	0.21	0.25	0.22	0.48	0.37	0.72	0.18	0.21
		2-4	0.22	0.59	0.33	0.27	0.49	0.73	0.41	1.06	0.46	0.32
		4-6					0.41	0.45	0.66			
		6-8					0.20	0.24	0.26			
Sept. 28	151	0-2	0.10	0.16	0.14	0.14	0.16	0.26	0.23	0.55	0.17	0.09
		2-4	0.13	0.24	0.23	0.07	0.28	0.40	0.32	0.41	0.21	0.16
		4-6	0.13	0.66	0.21	0.24	0.36	0.29	0.15	0.29	0.36	0.16

Table 48 (Continued)

Date of Sampling	Days from Application	Depth (inches)	<u>Location</u>		Avg	<u>Extremes</u>	
			29	44		Max	Min
			Concentration (ppm)				
July 30	91	0-2	0.44	0.57	0.43	0.87	0.21
		2-4	0.61	0.85	0.65	1.37	0.35
Aug. 15	107	0-2	0.82	0.39	0.35	0.82	0.14
		2-4	0.49	0.55	0.49	1.06	0.22
		4-6			0.51	0.66	0.41
		6-8			0.23	0.26	0.20
Sept. 28	151	0-2	0.11	0.09	0.18	0.55	0.09
		2-4	0.15	0.36	0.25	0.41	0.07
		4-6	0.18	0.22	0.27	0.66	0.13

Table 49. Concentration of atrazine in the soil for the northmiddle watershed, 1969

Date of Sampling	Days from Application	Depth (inches)	Location									
			14	15	16	17	18	19	20	21	22	23
			Concentration (ppm)									
May 8	0	0-1	5.46	3.01	5.83	5.19	3.64	6.36	3.52	4.63	3.26	1.13
		1-3	1.12	0.52	0.74	0.58	1.27	0.75	0.89	0.54	1.08	0.31
May 14	6	0-1	2.28	1.28	1.88	1.59	0.90	2.35	1.76	1.26	3.97	0.57
		1-3	0.30	0.47	0.32	0.47	0.32	0.61	0.25	0.50	0.55	0.27
		3-5		0.41					0.28			
May 20	12	0-1	1.76	1.73	1.39	1.65	2.18	2.22	1.96	3.28	2.38	0.87
		1-3	1.06	0.68	0.56	1.23	0.99	0.57	0.72	1.25	0.99	0.74
		3-5		0.85					0.45		0.36	
May 28	20	0-1	1.06	2.64	1.74	2.25	2.52	3.33	1.97	2.27	1.51	0.78
		1-3	1.74	0.85	1.56	0.98	0.88	0.96	0.56	0.76	0.76	0.30
		3-5		0.36					0.43		0.26	
June 13	36	0-1	1.32	0.93	1.15	1.60	1.47	1.30	1.87	1.76	0.93	0.57
		1-3	0.70	0.39		1.89	0.75	1.36	0.58	0.99	0.90	0.25
		3-5	0.23	0.29	0.35	0.54	0.32	0.65	0.37	0.25	0.23	0.22
June 27	50	0-2	0.72	1.44	1.45	2.06	2.02	1.65	1.49	1.75	1.65	1.02
		2-4	0.24	0.52	0.59	1.14	0.20	0.98	0.47	1.00	0.79	0.00
		4-6	0.00	0.00	0.00	0.36	0.00	0.16	0.21	0.00	0.26	0.00

Table 49 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location		Avg.	Extremes	
			24	30		Max.	Min.
			Concentration (ppm)				
May 8	0	0-1 1-3		5.06 0.69	4.28 0.77	6.36 1.27	1.13 0.31
May 14	6	0-1 1-3 3-5	1.69 0.87	2.21 0.49	1.81 0.45 0.35	3.97 0.87 0.41	0.57 0.25 0.28
May 20	12	0-1 1-3 3-5	4.10 1.17	2.63 1.43	2.18 0.95 0.55	4.10 1.43 0.85	0.87 0.68 0.36
May 28	20	0-1 1-3 3-5	4.28 0.90	2.09 0.47	2.20 0.89 0.35	4.28 1.74 0.43	0.78 0.30 0.26
June 13	36	0-1 1-3 3-5	2.72 0.59 0.50	1.09 0.32 0.37	1.39 0.79 0.36	1.87 1.89 0.65	0.57 0.25 0.22
June 27	50	0-2 2-4 4-6	3.21 0.58 0.00	1.67 0.22 0.14	1.68 0.56 0.09	3.21 1.14 0.36	0.72 0.00 0.00

Table 49 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location									
			14	15	16	17	18	19	20	21	22	23
			Concentration (ppm)									
July 10	63	0-2	0.45	1.15	1.25	0.48	1.90	1.34	1.88	1.69	1.54	0.42
		2-4	0.69	0.63	0.90	1.71	0.43	1.31	0.63		1.30	0.24
		4-6		0.39	0.48	1.80	0.30	0.35	T <sup>a</sup>	T	0.32	0.15
July 28	81	0-2	0.64	0.96	0.95	0.90	0.63	0.95	1.02	0.68	0.86	0.47
		2-4	0.59	0.11	0.92	1.02	0.50	1.09	0.71	0.74	0.69	
		4-6	0.12	0.29	0.49	0.29	0.25	0.39	0.63	0.39	0.32	0.12
		6-8		0.30			0.18		0.07			0.09
Aug. 18	102	0-2	0.39	0.84	0.73	0.53	0.61	0.62	0.78	0.54	0.29	0.26
		2-4	0.46	0.55	0.67	0.83	0.44	0.42	0.59	0.80	0.37	0.18
		4-6	0.27	0.20	0.27	0.54	0.16	0.40	1.07	0.57	0.47	0.28
		6-8		0.27				0.37	0.79		0.19	
Sept. 25	140	0-2	0.27	0.45	0.28	0.24	0.26		0.41	0.22	0.31	
		2-4	0.41	0.37	0.28	0.32	0.33		0.37	0.39	0.23	
		4-6	0.28	0.21	0.26	0.29	0.21		0.27	0.30	0.26	
		6-8		0.61	0.21	0.15	0.19		0.25	0.50	0.27	
Nov. 5	181	0-2	0.25	0.34	0.20		0.20		0.15	0.23		
		2-4	0.28	0.37	0.26		0.32		0.29	0.17		
		4-6	0.38	0.25	0.22		0.25		0.32	0.28		
		6-8	0.19	0.22	0.19		0.18		0.30	0.19		
		8-10	0.15	0.19	0.14		0.18		0.27	0.19		

<sup>a</sup>Trace



Table 49 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location		Avg	Extremes	
			24	30		Max	Min
			Concentration (ppm)				
July 10	63	0-2	1.49	1.51	1.26	1.38	0.42
		2-4	0.54	0.32	0.79	1.71	0.24
		4-6	0.22	0.25	0.39	1.80	T
July 28	81	0-2	0.78	1.34	0.77	1.34	0.47
		2-4	0.51	0.59	0.69	1.09	0.11
		4-6	0.33	0.26	0.32	0.63	0.12
		6-8			0.16	0.30	0.07
Aug. 18	102	0-2	0.88	0.93	0.62	0.93	0.26
		2-4	0.61	0.61	0.54	0.83	0.18
		4-6	0.44	0.41	0.42	1.07	0.16
		6-8			0.41	0.79	0.19
Sept. 25	140	0-2	0.54	0.71	0.37	0.71	0.22
		2-4	0.58	0.17	0.35	0.58	0.17
		4-6	0.38	0.40	0.29	0.40	0.21
		6-8	0.19	0.29	0.30	0.50	0.15
Nov. 5	181	0-2			0.23	0.34	0.15
		2-4			0.28	0.37	0.17
		4-6			0.28	0.38	0.18
		6-8			0.21	0.30	0.18
		8-10			0.19	0.27	0.14

Table 50. Concentration of atrazine in the soil for the northmiddle watershed, 1970

Date of Sampling	Days from Application	Depth (inches)	Location									
			19	20	21	22	23	24	25	26	27	28
			Concentration (ppm)									
May 6	0	0-1	3.55	2.30	1.46	2.73	3.47	1.84	1.82	4.15	1.39	3.10
		1-3	0.33	0.82	0.54	0.35	0.66	0.65	0.88	0.62	1.07	0.25
May 12	6	0-1	1.79	3.10	1.71	2.31	1.20	2.49	2.19	2.94	1.18	2.35
		1-3	0.00	0.59	0.38	0.20	0.97	0.55	0.31	0.27	0.00	0.22
May 19	13	0-1	2.68	3.88	2.40	2.67	2.36	3.75	4.23	2.74	2.19	3.05
		1-3	0.35	1.00	0.00	0.00	0.68	2.54	0.23	1.30	0.21	2.94
May 25	19	0-1	2.20	1.85	3.13	3.59	3.65	2.91	4.49	6.00	3.19	4.33
		1-3	0.00	0.00	0.45	0.20	0.59	0.65	0.58	0.80	0.00	0.85
		3-5	0.34	T <sup>a</sup>	0.00	0.00	0.20	0.23	0.00	T	0.25	0.00
June 2	27	0-1	2.19	4.03	2.01	1.82	3.49	3.06	3.52	3.25	2.66	3.15
		1-3	0.47	1.07	1.22	0.44	0.84	1.49	2.29	2.13	1.01	3.42
		3-5	0.00	0.19	0.40	0.00	0.41	0.82	0.00	0.21	0.00	0.56
June 15	40	0-2	1.82	2.07	1.77	1.76	2.62	1.95	2.50	2.21	1.44	0.86
		2-4	0.69	1.71	0.42	0.68	0.64	0.44	0.51	0.39	0.84	1.48
		4-6	0.35	0.18	0.38	0.38	0.30	0.23	0.00	0.28	0.00	0.46

<sup>a</sup>Trace

Table 50 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location		Avg	Extremes	
			29 Concentration (ppm)	30 Concentration (ppm)		Max	Min
May 6	0	0-1	0.21	1.83	2.32	4.15	0.21
		1-3	0.00	0.63	0.57	1.07	0.00
May 12	6	0-1	0.00	1.72	1.92	3.10	0.00
		1-3	0.00	0.49	0.33	0.97	0.00
May 19	13	0-1	0.28	3.08	2.78	4.23	0.28
		1-3	0.00	0.59	0.82	2.94	0.00
May 25	19	0-1	0.26	2.12	3.14	6.00	0.26
		1-3	0.17	0.29	0.38	0.85	0.00
		3-5	T	0.00	0.09	0.34	0.00
June 2	27	0-1	0.45	2.94	2.71	4.03	0.45
		1-3	0.00	0.58	1.25	3.42	0.00
		3-5	0.00	0.00	0.22	0.82	0.00
June 15	40	0-2	0.38	2.06	1.79	2.62	0.38
		2-4	0.00	0.53	0.69	1.71	0.00
		4-6	0.00	0.32	0.24	0.46	0.00

Table 50 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location									
			19	20	21	22	23	24	25	26	27	28
			Concentration (ppm)									
July 6	61	0-2	1.50	2.15	2.06	1.69	1.21	1.26	1.12	1.96	1.13	1.51
		2-4	0.71	0.54	0.42	0.32	0.45	0.30	0.27	0.60	0.55	1.02
		4-6	0.15	0.23	T <sup>a</sup>	0.22	0.26	0.51	0.20	0.36	1.03	0.30
July 21	76	0-2	2.05	1.59	1.68	1.38	1.53	1.81	2.09	2.00	1.41	1.42
		2-4	0.44	0.69	0.34	1.13	0.41	0.59	0.49	0.71	0.29	0.76
		4-6	T	0.18	0.48	0.40	1.09	T	0.11	0.27	T	0.20
Aug. 11	97	0-2	0.88	1.22	1.04	1.01	0.39	2.12	1.61	1.50	0.73	1.23
		2-4	0.00	0.33	0.00	0.44	0.14	0.76	0.94	0.62	0.84	0.75
		4-6	0.22	1.23	0.00	0.00	0.00	0.41	0.56	0.16	0.10	0.48
		6-8	0.00	0.11	T	0.00	T	0.25	0.19	0.26	T	0.00
Sept. 23	140	0-2	0.89	0.61	0.74	1.30	1.03	1.04	0.95	1.02	3.24	0.69
		2-4	0.44	1.09	1.37	1.32	2.59	0.57	0.89	0.59	0.44	0.58
		4-6	0.00	0.47	0.46	0.84	1.29	0.25	0.53	1.70	0.12	0.71
		6-8	0.00	0.76	0.85	1.13	0.30	0.36	0.81	0.96	0.00	0.63
Oct. 28	175	0-2	0.52	0.17	0.42	1.19	0.38	0.12	0.35	0.81	0.51	0.46
		2-4	0.75	0.55	0.72	0.47	0.98	0.21	0.92	0.15	0.26	0.33
		4-6	0.66	1.05	0.80	0.83	0.18	0.13	0.41	0.12	0.81	0.39
		6-8	0.60	0.15	0.82	0.46	0.28	0.68	0.00	0.55	1.05	0.30

<sup>a</sup>Trace

Table 50 (Continued)

Date of Sampling	Days from Application	Depth (inches)	Location		Avg	Extremes	
			29 Concentration (ppm)	30 Concentration (ppm)		Max	Min
July 6	61	0-2	0.27	1.39	1.44	2.15	0.27
		2-4	0.38	0.31	0.49	1.02	0.27
		4-6	0.20	0.63	0.34	1.03	T
July 21	76	0-2	0.21	1.35	1.54	2.05	0.21
		2-4	T	0.42	0.52	1.13	T
		4-6	0.00	0.37	0.26	1.09	0.00
Aug. 11	97	0-2	0.09	0.66	1.04	2.12	0.09
		2-4	0.13	1.42	0.53	1.42	0.00
		4-6	0.47	0.00	0.30	1.23	0.00
		6-8	0.24	0.00	0.09	0.26	0.00
Sept. 23	140	0-2	0.46	0.89	1.07	3.24	0.46
		2-4	0.18	1.44	0.96	2.59	0.18
		4-6	0.94	0.20	0.63	1.70	0.00
		6-8	0.00	0.31	0.51	1.13	0.00
Oct. 28	175	0-2	0.33	0.58	0.49	1.19	0.12
		2-4	0.18	0.36	0.49	0.98	0.15
		4-6	0.08	0.54	0.50	1.05	0.12
		6-8	0.00	0.43	0.44	1.05	0.00

Table 51. Concentration of propachlor in the soil on the northeast watershed, 1969

Date of Sampling	Days from Application	Depth (inches)	Location								Avg.	Extremes	
			7	8	9	10	11	12	13	Max.		Min.	
			Concentration (ppm)										
May 7	1	0-1	14.60	12.67	11.83	6.35	17.96	13.65	6.61	11.91	17.96	6.35	
		1-3	0.00	0.00	T <sup>a</sup>	0.00	3.57	3.82	0.00	1.06	3.82	0.00	
May 14	8	0-1	12.96	6.26	4.17	10.55	7.19	3.55	2.62	6.76	12.96	2.62	
		1-3	0.00	0.00	0.92	0.00	0.00	0.00	0.00	0.13	0.92	0.00	
		3-5	0.00	0.00		0.00				0.00	0.00	0.00	
May 20	14	0-1	7.13	6.99	2.52	5.12	2.91	3.76	2.54	4.40	7.13	2.52	
		1-3	6.10	1.03	1.48	2.49	1.18	5.45	4.10	3.22	6.10	1.03	
		3-5	0.00	1.03		0.00				0.34	1.03	0.00	
May 28	22	0-1	3.14	6.30	T	7.75	2.24	3.69	1.24	3.48	7.75	T	
		1-3	0.00	0.00	0.52	0.00	4.22	2.06	T	0.97	4.22	0.00	
		3-5	0.00	0.00		0.00				0.00	0.00	0.00	

<sup>a</sup>Trace

Table 52. Concentration of propachlor in the soil for the northeast watershed, 1970

Date of Sampling	Days From Application	Depth (inches)	Location								Avg.	Extremes	
			12	13	14	15	16	17	18	Max.		Min.	
			Concentration (ppm)										
May 5	0	0-1	10.62	9.71	6.20	12.34	20.02	6.41	18.20	11.93	20.02	6.20	
		1-3	0.00	0.00	0.00	0.00	0.74	0.00	1.04	0.25	1.04	0.00	
May 12	7	0-1	3.87	15.87	2.00	4.32	10.73	5.16	11.59	7.65	15.87	2.00	
		1-3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
May 19	14	0-1	8.46	5.52	4.94	11.41	8.28	10.17	4.58	7.62	11.41	4.58	
		1-3	0.00	0.00	0.00	0.00	0.50	0.00	0.27	0.04	0.50	0.00	
		3-5	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	
May 25	20	0-1	1.29	3.49	2.33	5.47	3.16	4.92	1.04	3.10	5.47	1.04	
		1-3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
		3-5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
June 2	28	0-1	1.21	1.93	2.41	2.38	3.68	3.72	1.67	2.43	3.72	1.21	
		1-3	0.00	0.44	0.00	1.14	0.31	0.00	0.00	0.27	1.14	0.00	
		3-5	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.04	0.27	0.00	

Table 53. Concentration of propachlor in the soil for the southwest watershed, 1969

Date of Sampling	Days from Application	Depth (inches)	Location						Avg.	Extremes	
			1	2	3	4	5	6		Max.	Min.
			Concentration (ppm)								
May 7	1	0-3	4.14	4.73	2.64	2.33	8.59	6.73	4.86	8.59	2.33
		1-3	0.00	T <sup>a</sup>	T	0.00	0.00	0.00	0.00	T	0.00
May 14	8	0-1	3.19	3.56	3.11	0.64	3.82	6.47	3.47	6.47	0.64
		1-3	T	0.00	0.00	0.00	0.00	0.00	0.00	T	0.00
		3-5	T					0.00	0.00	T	0.00
May 20	14	0-1	1.08	1.16	2.76	2.04	1.73	3.52	2.05	3.52	1.08
		1-3	0.00	2.38	0.00	0.93	0.49	0.00	0.63	2.38	0.00
		3-5	0.00		0.00			0.00	0.00	0.00	0.00
May 28	22	0-1	2.31	4.29	0.00	0.61	0.38	1.27	1.48	4.29	0.38
		1-3	0.00	1.99	0.00	0.00	0.00	0.82	0.47	1.99	0.00
		3-5	0.00		0.00			0.00	0.00	0.00	0.00

<sup>a</sup>Trace



Table 54. Concentration of propachlor in the soil for the southwest watershed, 1970

Date of Sampling	Days From Application	Depth (inches)	Location						Avg.	Extremes	
			1	2	3	4	5	6		Max.	Min.
			Concentration (ppm)								
May 5	0	0-1	7.37	5.52	0.00	16.97	0.00	0.00	4.98	16.97	0.00
		1-3	0.00	0.00	0.00	2.49	0.00	0.00	0.62	2.49	0.00
May 12	7	0-1	3.57	7.26	0.00	10.12	3.61	0.00	4.09	10.12	0.00
		1-3	0.00	0.00	0.00	T <sup>a</sup>	0.00	0.00	0.00	T	0.00
May 19	14	0-1	2.42	2.25	0.00	10.83	0.94	0.00	2.74	10.83	0.00
		1-3	1.50	0.00	0.00	0.00	0.00	0.00	0.25	1.50	0.00
		3-5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
May 25	20	0-1	0.00	0.00	0.00	7.56	0.00	0.00	1.26	7.56	0.00
		1-3	0.33	0.00	0.00	0.00	0.00	0.00	0.05	0.33	0.00

<sup>a</sup>Trace

Table 55. Diffusion coefficients for atrazine

Amount Added (ppm)	Temperature (°F)	Bulk Density (g/cm <sup>3</sup> )	Moisture Content (%)	Diffusion Coefficient (mm <sup>2</sup> /day)
10	80	0.90	8	1.36
10	80	0.90	8	1.08
10	80	0.90	8	1.21
10	80	0.90	15	1.28
10	80	0.90	15	1.83
10	80	0.90	15	0.65
10	80	0.90	23	1.13
10	80	0.90	23	2.72
10	80	0.90	23	1.42
10	80	1.30	8	0.71
10	80	1.30	8	0.36
10	80	1.30	8	1.06
10	80	1.30	15	3.21
10	80	1.30	15	1.64
10	80	1.30	15	1.83
10	80	1.30	23	1.15
10	80	1.30	23	0.68
10	80	1.30	23	1.10
10	50	0.90	8	0.25
10	50	0.90	8	0.26
10	50	0.90	8	0.73
10	50	0.90	15	0.23
10	50	0.90	15	0.19
10	50	0.90	15	0.74
10	50	0.90	23	0.55
10	50	0.90	23	1.33
10	50	0.90	23	0.99
10	50	1.30	8	0.00
10	50	1.30	8	0.00
10	50	1.30	8	0.00
10	50	1.30	15	0.03
10	50	1.30	15	0.09
10	50	1.30	15	0.14
10	50	1.30	23	0.13
10	50	1.30	23	0.99
10	50	1.30	23	0.49
10	110	0.90	8	2.08
10	110	0.90	8	1.81
10	110	0.90	8	2.86

Table 55 (Continued)

Amount Added (ppm)	Temperature (°F)	Bulk Density (g/cm <sup>3</sup> )	Moisture Content (%)	Diffusion Coefficient (mm <sup>2</sup> /day)
10	110	0.90	15	2.60
10	110	0.90	15	2.77
10	110	0.90	15	4.57
10	110	0.90	23	5.76
10	110	0.90	23	3.55
10	110	0.90	23	5.62
10	110	1.30	8	1.33
10	110	1.30	8	2.15
10	110	1.30	8	1.00
10	110	1.30	15	2.36
10	110	1.30	15	3.12
10	110	1.30	15	2.38
10	110	1.30	23	4.61
10	110	1.30	23	2.85
10	110	1.30	23	2.60

Table 56. Diffusion coefficients for propachlor

Amount Added (ppm)	Temperature (°F)	Bulk Density (g/cm <sup>3</sup> )	Moisture Content (%)	Diffusion Coefficient (mm <sup>2</sup> /day)
10	80	0.90	8	2.33
10	80	0.90	8	4.46
10	80	0.90	8	4.62
10	80	0.90	15	2.91
10	80	0.90	15	2.94
10	80	0.90	15	1.64
10	80	0.90	23	4.63
10	80	0.90	23	2.62
10	80	0.90	23	4.99
10	80	1.30	8	1.11
10	80	1.30	8	1.90
10	80	1.30	8	1.91
10	80	1.30	15	0.59
10	80	1.30	15	0.50
10	80	1.30	15	0.46
10	80	1.30	23	0.35
10	80	1.30	23	0.58
10	80	1.30	23	0.51
10	50	0.90	8	0.64
10	50	0.90	8	0.74
10	50	0.90	8	0.81
10	50	0.90	15	0.38
10	50	0.90	15	1.18
10	50	0.90	15	2.07
10	50	0.90	23	2.70
10	50	0.90	23	1.99
10	50	0.90	23	1.32
10	50	1.30	8	2.52
10	50	1.30	8	1.44
10	50	1.30	8	0.71
10	50	1.30	15	1.86
10	50	1.30	15	2.09
10	50	1.30	15	1.26
10	50	1.30	23	1.76
10	50	1.30	23	1.36
10	50	1.30	23	1.48
10	110	0.90	8	5.87
10	110	0.90	8	2.95
10	110	0.90	8	4.33

Table 56 (Continued)

Amount Added (ppm)	Temperature (°F)	Bulk Density (g/cm <sup>3</sup> )	Moisture Content (%)	Diffusion Coefficient (mm <sup>2</sup> /day)
10	110	0.90	15	7.68
10	110	0.90	15	6.23
10	110	0.90	15	8.84
10	110	0.90	23	8.92
10	110	0.90	23	8.54
10	110	0.90	23	8.72
10	110	1.30	8	2.26
10	110	1.30	8	9.31
10	110	1.30	8	7.60
10	110	1.30	15	6.16
10	110	1.30	15	4.55
10	110	1.30	15	4.47
10	110	1.30	23	9.28
10	110	1.30	23	8.78
10	110	1.30	23	11.26

Table 57. Diffusion coefficients for diazinon

Amount Added (ppm)	Temperature (°F)	Bulk Density (g/cm <sup>3</sup> )	Moisture Content (%)	Diffusion Coefficient (mm <sup>2</sup> /day)
10	80	0.90	8	0.28
10	80	0.90	8	1.44
10	80	0.90	8	1.71
10	80	0.90	15	0.45
10	80	0.90	15	0.67
10	80	0.90	15	1.04
10	80	0.90	23	0.06
10	80	0.90	23	0.25
10	80	0.90	23	0.15
10	80	1.30	8	0.19
10	80	1.30	8	0.47
10	80	1.30	8	0.17
10	80	1.30	15	0.86
10	80	1.30	15	0.78
10	80	1.30	15	0.53
10	80	1.30	23	0.68
10	80	1.30	23	0.80
10	80	1.30	23	0.93
10	50	0.90	8	0.21
10	50	0.90	8	0.11
10	50	0.90	8	0.75
10	50	0.90	15	0.00
10	50	0.90	15	0.00
10	50	0.90	15	0.00
10	50	0.90	23	0.00
10	50	0.90	23	0.00
10	50	0.90	23	0.00
10	50	1.30	8	0.00
10	50	1.30	8	0.00
10	50	1.30	15	0.00
10	50	1.30	15	0.00
10	50	1.30	15	0.06
10	50	1.30	23	0.00
10	50	1.30	23	0.00
10	50	1.30	23	0.00

Table 58. Analysis of variance for atrazine diffusion tests

Source of Variation	Degrees of Freedom	Mean Square
A (replication)	2	0.0564
B (moisture content)	2	5.2915**
C (temperature)	2	31.2267**
BC	4	2.0303**
D (density)	1	3.4051**
BD	2	0.9932
CD	2	1.0045
BCD	4	0.3767
Error	34	0.4285
Total	53	

\*\* = Significant at the 1 percent level

Table 59. Analysis of variance for propachlor diffusion tests

Source of Variation	Degrees of Freedom	Mean Square
A (replication)	2	0.4534
B (moisture content)	2	10.7838**
C (temperature)	2	162.6616**
BC	4	8.2234**
D (density)	1	6.6781*
BD	2	3.0118
CD	2	11.9160**
BCD	4	3.7034
Error	34	1.5222
Total	53	

\*\* = Significant at the 1 percent level

\* = Significant at the 5 percent level

Table 60. Analysis of variance for diazinon diffusion tests

Source of Variation	Degrees of Freedom	Mean Square
A (replication)	2	0.1428
B (moisture content)	2	0.1275
C (temperature)	1	2.9987**
BC	2	0.0491
D (density)	1	0.0812
BD	2	0.6790**
CD	1	0.0051
BCD	2	0.2534*
Error	22	0.0658
Total	35	

\*\* = Significant at the 1 percent level

\* = Significant at the 5 percent level

Table 61. Analysis of variance for diazinon degradation

Source of Variation	Degrees of Freedom	Mean Square
A (replication)	2	165.13
B (moisture content)	2	1621.32**
C (temperature)	2	3799.97**
BC	4	306.73**
D (density)	1	44.83
BD	2	322.04*
CD	2	57.97
BCD	4	174.58
Error	34	61.02
Total	53	

\*\* = Significant at the 1 percent level

\* = Significant at the 5 percent level



Table 62. Analysis of variance for propachlor degradation

Source of Variation	Degrees of Freedom	Mean Square
A (replication)	2	41.83
B (moisture content)	2	996.13**
C (temperature)	2	21348.16**
BC	4	129.41
D (density)	1	123.00
BD	2	265.75
CD	2	802.89**
BCD	4	370.49*
Error	34	80.90
Total	53	

\*\* = Significant at the 1 percent level

\* = Significant at the 5 percent level

XII. APPENDIX C. DATA FOR 1971 FROM GINGLES WATERSHEDS

The concentrations of atrazine and alachlor measured in runoff and sediment samples collected in 1971 from the Gingles Watersheds are presented in Tables 63 to 72. In 1971 the southeast and northwest watersheds were also planted in corn. At planting time 2 lb/A of atrazine and 2 lb/A of alachlor were applied broadcast to all six watersheds. Carbofuran was applied in a band application at planting time at 1 lb/A to the south-middle, northmiddle, southwest, and northeast watersheds. Atrazine and alachlor were applied on May 1, 1971 and Carbofuran was applied April 30, 1971.

Alachlor sediment samples (20 grams) were extracted with methanol (50 ml) and the water samples (300 ml) were extracted with three 25 ml portions of benzene. Alachlor was analyzed on a Microtek 220 gas chromatograph with a Michel-63 electron capture detector. A 6 foot by 1/4 inch diameter glass column was used with a 5 percent Carbowax 20 M liquid support on acid-washed 60/80 Chromosorb W. Operating conditions were: detector temperature 280°C, injection port temperature 270°C, and column temperature 190°C. Nitrogen was used as a carrier gas at a flow rate of 90 to 100 ml per minute.

The average amount of alachlor recovered from soil and water samples fortified with alachlor was 84 and 97 percent, respectively. The minimum detection limit for the water samples was 0.010 ppm and 0.10 ppm for the sediment samples.

Table 63. Concentrations of atrazine and alachlor in sediment samples from the northmiddle watershed, 1971

Storm Date	Sample Number				Avg
	1	2	3	4	
Concentration (ppm)					
Atrazine					
6 -7-71	1.74		1.45	1.06	1.42
6-30-71	T <sup>a</sup>	T	T		T
7-10-71				T	T
7-28-71	0.00				0.00
8- 4-71	0.00				0.00
Alachlor					
6- 7-71	1.50		0.76	0.36	0.87
6-10-71	3.98				3.98

<sup>a</sup>Trace

Table 64. Concentrations of atrazine and alachlor in water samples from the northmiddle watershed, 1971

Storm Date	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
Atrazine					
6- 7-71	0.44		0.42	0.57	0.48
6-10-71	0.06				0.06
7-10-71		T <sup>a</sup>	T		T
7-28-71	0.00	0.00			0.00
8- 4-71	0.00				0.00
Alachlor					
6- 7-71			0.013	0.000	0.006
6-10-71	0.000				0.000

<sup>a</sup>Trace

Table 65. Concentrations of atrazine and alachlor in sediment samples from the southeast watershed, 1971

Storm Date	Sample Number				Avg
	1	2	3	4	
Concentration (ppm)					
Atrazine					
6 -7-71	0.84	1.20	0.82	0.76	0.91
6-10-71	T <sup>a</sup>				T
6-30-71	0.49	T			0.25
7-10-71	T				T
7-28-71	0.00				0.00
Alachlor					
6- 7-71	0.46	0.57	0.41	0.25	0.42
6-10-71	1.81				1.81

<sup>a</sup>Trace

Table 66. Concentrations of atrazine and alachlor in water samples from the southeast watershed, 1971

Storm Date	Sample Number				Avg
	1	2	3	4	
Concentration (ppm)					
Atrazine					
6- 7-71	0.54	0.55	0.49	0.35	0.48
6-10-71	0.05				0.05
6-30-71	0.06	0.10			0.08
7-10-71	T <sup>a</sup>	T			T
7-28-71	T	0.00			0.00
Alachlor					
6- 7-71	0.054	0.000	0.000		0.014
6-10-71	0.000				0.000

<sup>a</sup>Trace

Table 67. Concentrations of atrazine and alachlor in sediment samples from the northwest watershed, 1971

Storm Date	Sample Number					Avg
	1	2	3	4	5	
	Concentration (ppm)					
Atrazine						
6- 7-71	1.20	0.80	0.64	0.62	0.60	0.77
6-10-71	0.40	T <sup>a</sup>	T			0.14
7-10-71		0.49				0.49
Alachlor						
6- 7-71	0.72	0.30	0.30	0.21	0.42	0.39
6-10-71	1.18	0.44				0.81

<sup>a</sup>Trace

Table 68. Concentrations of atrazine and alachlor in water samples from the northwest watershed, 1971

Storm Date	Sample Number					Avg
	1	2	3	4	5	
Concentration (ppm)						
Atrazine						
6- 7-71	0.25	0.38	0.30	0.43	0.43	0.36
6-10-71	0.10	0.07	0.05			0.07
6-30-71	T <sup>a</sup>	0.05				0.03
7-10-71	T	T				T
Alachlor						
6- 7-71	0.032	0.032	0.058	0.046	0.00	0.034
6-10-71	0.000	0.014				0.007

<sup>a</sup>Trace

Table 69. Concentrations of atrazine and alachlor in sediment samples from the southmiddle watershed, 1971

Storm Date	Sample Number						Avg
	1	2	3	4	5	6	
	Concentration (ppm)						
Atrazine							
6- 7-71	0.48	0.50	0.31	0.00	0.35	0.48	0.35
6-10-71		0.21					0.21
6-30-71	T <sup>a</sup>	T					T
Alachlor							
6- 7-71	0.28	1.22	0.54	0.67	0.54	0.61	0.64
6-10-71	1.63	1.96					1.80

<sup>a</sup>Trace

Table 70. Concentrations of atrazine and alachlor in water samples from the southmiddle watershed, 1971

Storm Date	Sample Number						Avg
	1	2	3	4	5	6	
	Concentration (ppm)						
Atrazine							
6- 7-71	0.36	0.50	0.44	0.58	0.61	0.57	0.51
6-10-71	0.35	0.04					0.19
6-30-71	0.03	0.04					0.04
7-10-71	T <sup>a</sup>	T					T
7-28-71	0.00						0.00
8- 4-71	0.00						0.00
Alachlor							
6- 7-71	0.061	0.046	0.058		0.102	0.044	0.062
6-10-71		0.022					0.022

<sup>a</sup>Trace

Table 71. Concentrations of atrazine and alachlor in sediment samples from the northeast watershed, 1971

Storm Date	Sample Number				Avg
	1	2	3	4	
	Concentration (ppm)				
Atrazine					
6- 7-71	0.68	0.61	0.71	0.53	0.63
6-10-71	0.37	T <sup>a</sup>			0.19
6-30-71	0.00				0.00
7-28-71	T				T
Alachlor					
6- 7-71	5.34	0.56	0.92		2.27
6-10-71	0.77	1.14			0.96

<sup>a</sup>Trace

Table 72. Concentrations of atrazine and alachlor in water samples from the northeast watershed, 1971

Storm Date	<u>Sample Number</u>				Avg
	1	2	3	4	
	Concentration (ppm)				
Atrazine					
6- 7-71	0.43	0.50	0.47	0.39	0.45
6-10-71	0.09	0.08			0.09
6-30-70	0.05				0.05
7-10-71	T <sup>a</sup>				T
7-28-71	0.00	0.00			0.00
Alachor					
6- 7-71	0.037		0.076	0.038	0.050
6-10-71		0.000			0.000

<sup>a</sup>Trace