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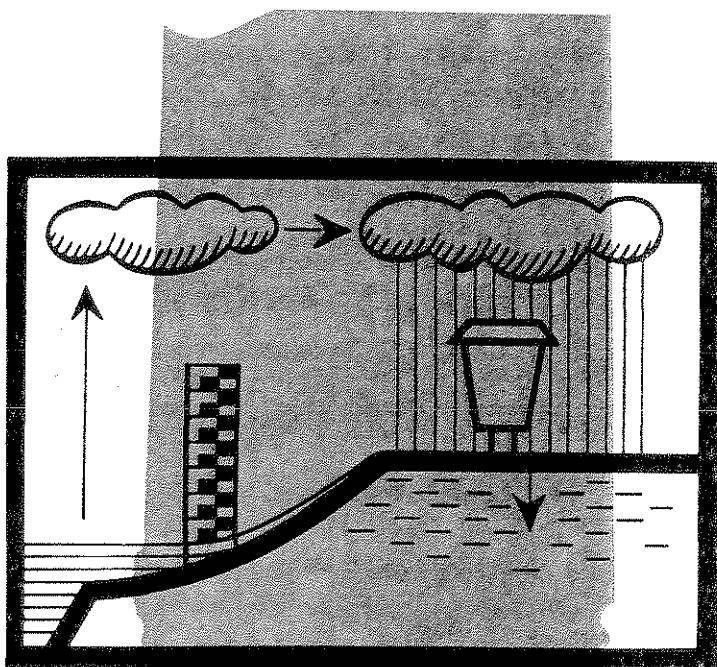
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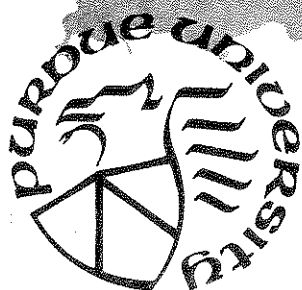**WATER RESOURCES RESEARCH CENTER**
LAFAYETTE, INDIANA

EFFECT OF PESTICIDE RESIDUES AND OTHER ORGANO-TOXICANTS

ON THE QUALITY OF SURFACE AND GROUND WATER RESOURCES

Principal Investigators:

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TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

Modern agricultural and recreational practices require the continued use of large quantities of pesticides and other potentially toxic chemicals. Investors in land whether for farming or recreational interests have learned that they can no longer gamble on practices for effective weed, insect, and plant disease control. Through a judicious application of chemicals, production costs may be lowered and hazards from weeds, insects and disease to man, domestic animals and wildlife will be reduced. An equally important consideration, however, is the health and well-being of people who use organo-toxicant materials and the products protected by their use.

Potentially, organo-toxicant materials may leach through the soil and accumulating in the ground water may reach toxic proportions. These materials may also be carried by surface runoff to pollute reservoirs, ponds, streams, rivers and lakes.

In rural areas, where the small reservoir is often used for domestic water supply and recreational purposes, contamination of the water supply by toxicants applied to the watershed may be a serious problem. The small reservoir, because of the short times of runoff concentration on its watershed, likely presents the ultimate condition for contamination. For this reason, the small reservoir and its associated watershed was studied to determine the fate of potentially toxic substances from their initial application to the watershed through to possible treatment of the reservoir water for domestic purposes. The movement of such materials through the soil profile or over the land, the susceptibility of these materials to microbial decomposition, and the effect of application practices on the pollution of water resources was not well known. The small reservoir and watershed, therefore, offered an excellent opportunity for an evaluation of organo-toxicants under a naturally prevailing environment.

OBJECTIVES

The objectives of Project A-005-IND, Effect of Pesticide Residues and Other Organo-Toxicants on the Quality of Surface and Ground Water Resources, were:

(1) To study the mechanisms by which organo-toxicant materials were held by the mineral and organic fractions in the soil

(2) To determine the fate of organo-toxicant materials in water storage reservoirs

(3) To evaluate effects of organo-toxicants on terrestrial and farm pond invertebrates and vertebrates

(4) To determine the role of microorganisms in the elimination of organo-toxicants from surface and ground waters

(5) To effect control and removal methods for reducing or eliminating organo-toxicant residues from reservoir water supplies

COOPERATION

Initially the project involved four departments from the School of Agriculture at Purdue University located in West Lafayette, Indiana and the Southern Indiana Purdue Agricultural Center (then called the Southern Indiana Forage Farm) located approximately 175 miles south of Purdue University. These departments were Agricultural Engineering, Agronomy, Entomology, and Forestry and Conservation. The Department of Agricultural Engineering was primarily responsible for Objective (5); Agronomy for Objectives (1) and (4); Entomology and Forestry and Conservation for Objective (3); and Agricultural Engineering and Entomology for Objective (2). Research efforts in the laboratories at Purdue University while largely independent functions of each department were guided through planned periodic consultations with the research personnel from the other departments. All of the personnel involved also aided in the design of experiments at the Southern Indiana Purdue Agricultural Center. In addition, the Department of Agricultural Engineering was responsible for the installation of equipment for collecting water samples and recording pertinent micro-climatic conditions at the Southern Indiana Purdue Agricultural Center; and the Department of Entomology was responsible for making chemical analyses of the collected

water, forage, and mud samples. Unfortunately shortly after the project was begun the cooperation of the Department of Forestry and Conservation was terminated because of the loss of key personnel.

PROCEDURE

Field research on the effect of pesticide residues and other organo-toxicants on the quality of water resources were located on three small reservoirs and their watersheds at the Southern Indiana Purdue Agricultural Center. These reservoirs ranging in size from one-third to one surface acres were well constructed and located over soils offering negligible seepage losses. Construction data for each of the reservoirs are shown in Table 1.

Table 1. Construction Data for the Three Reservoirs

	Reservoir		
	A	B	C
Surface area (acres)	0.97	0.67	0.30
Watershed area (acres)	7.0	2.0	3.0
Earth fill (yds)	4600	5500	2100
Maximum depth (ft)	14	14	12
Storage (ac-ft)	7.0	5.5	2.5

The watersheds which drained into the reservoirs were all located in one field consisting of alfalfa and grasses principally fescue. The tap rooted alfalfa was sparce because of severe winter heaving. The watersheds were part of an extensive unglaciated sandstone shale soil region in Southern Indiana. In general, the soils of this region developed under low pH conditions and thin loessial covering. As a result shallow fragipans were formed which severely restrict water movement as well as root penetration. The watersheds were also steep with slopes ranging from 5 to 15 percent. Under these conditions, approximately one-half of the 40 to 46 inches annual rainfall may be expected to occur as runoff.

The organo-toxicants which were used in the field studies were a phorate and a carbaryl. Chlorinated-hydrocarbons were not chosen because they were already being studied intensively and because of the apparent likelihood that this group of pesticides in general would not be approved for use

in the future. The two insecticides chosen were approved and recommended insecticides of some economic importance to the surrounding agricultural and recreational communities. Furthermore, these compounds could be used to control alfalfa weevil which was just beginning to infest this area of Indiana. Watersheds A and B were treated with uniform applications of the insecticides. Watershed C was used as a check area.

The field research at the Southern Indiana Purdue Agricultural Center was spread over a four year span. Starting in July 1965 and continuing into the early part of 1966, equipment for collecting water samples and for monitoring some of the environmental factors surrounding the reservoirs and watersheds were installed. A pretreatment inventory was then made which overlapped most of this same time period extending on throughout all of 1966. The treatment period extended through 1967 and 1968. In 1969, equipment was dismantled and some post-inventory work performed.

Field research and accompanying laboratory research were accomplished by the cooperating departments as follows (numbering refers to objectives):

(1) The effect of the physical-chemical properties of various soil constituents on the nature of sorption reactions and subsequent predictions of the retention characteristics of toxic substances in the soil were determined through study of reactions of toxic substances with well-characterized model soil components. The reactions were characterized according to mechanisms involved, degree of reversibility, environmental effects, and thermodynamic parameters. The naturally occurring soil systems present in the watersheds above the selected small reservoirs were then characterized chemically, mineralogically, physically, and biologically. On the basis of the type and amount of each soil constituent present in the natural soil system, predictions concerning the retention of toxic substances were tested, first under controlled laboratory conditions and finally under monitored field plot conditions on the watershed sites.

(2) Samples of water and bottom materials were taken from selected positions in the small reservoirs and analyzed by chemical, bacteriological and physical techniques for the presence of organo-toxicants. Their

occurrence as free or water-borne molecules and the extent to which they were chelated by organic soil constituents or adsorbed to the surfaces of soil particles were determined. The fate of the organo-toxicant material during the post-treatment period was established from chemical analysis, bio-assay, and physical determinations. Evaluations of the transport of organo-toxicant materials from the watersheds following runoff-producing storms was made in order to estimate their total removal from the land. The degree of pollution of the small reservoirs was related to climatic factors and the rate, time, and method of application.

(3)   Select invertebrates were used primarily as indicator organisms to determine levels of toxic concentrations on the watershed and in the small reservoir. Changes in populations were determined by usual limnological or terrestrial sampling techniques for the particular faunal groups. Samples were obtained periodically throughout the pretreatment, treatment, and post-treatment periods.

     a. Terrestrial invertebrates. A series of pitfall traps were positioned in the watershed areas surrounding the selected reservoirs and operated for 48-hour periods on a biweekly basis. Two insect groups, the spring-tails (Order Collembola) and ants (Order Hymenoptera, Formicoidea), would be observed. All identifications were to the species level.

     b. Aquatic invertebrates. One group, the dragonfly (Order Odonata) at the apex of the food chain of aquatic invertebrates and another group to be selected (Section of Neuropteroids) much lower in the food chain were studied. Samples were taken twice a month to establish seasonal levels.

(4)   Microorganisms, especially bacteria and fungi, capable of decomposing the organo-toxicants chosen for field application were isolated, identified, and systematically classified. The range of organo-toxicants susceptible to decomposition by the strains of microorganisms isolated were determined and attempts made to determine molecular configurations governing the susceptibility of resistance to microbial attack. The

effect of environmental factors such as oxygen, tension and temperature, upon the activity of the various microorganisms in decomposing the organo-toxicants was investigated.

(5) Studies were conducted to determine the feasibility of treating reservoir water with special adsorbing or chelating materials in order to flocculate, precipitate, or otherwise deactivate toxic materials or their residual decomposition products. Model filters were setup for eliminating or reducing organo-toxicant residues in a water supply. Radioisotope tagged materials were used to determine the ultimate effectiveness of the combining process and filtration for producing water suitable for domestic consumption.

Environmental Measurements

During the course of the field research, measurements were made of the stage of each reservoir, the temperature profile of each reservoir, air and soil temperature, humidity, and the water chemistry of each reservoir. All of the environmental measurements were made available to the investigators of any study connected to the project.

Stage measurements were recorded from depth gages and plotted for each reservoir. In general, the reservoir levels tend to stabilize about 1.5 feet below the crests of the vegetated outlets during the summer months. An estimation of the amount of runoff could be made if outflow from the reservoir did not occur. The depth gages, however, provided a good indication of the occurrence of runoff.

Air temperatures and humidities were available from a weather station located at the Southern Indiana Purdue Agricultural Center.

A 24-point temperature recorder provided temperature data for eight locations for each reservoir and watershed combination. Five thermocouple probes were located in each reservoir and three in each watershed. Temperature measurements were taken four times daily at 6:00 a.m., 10:00 a.m., 2:00 p.m. and 8:00 p.m. at all sites. The soil probes were placed about four inches below the soil surface near the pond shoreline, one-half up the slope and at the top of the slope in each watershed. The five probes in each reservoir spanned the distance from the surface to the bottom muds.

An example of the temperature traces for the month of June, 1968 for Pond A is shown in Figure 1. In general, thermoclines were not noticeable, diurnal fluctuations of the surface layer were quite evident in the warmer months and still usually evident but not so pronounced during the colder months, the temperature change of the bottom layer was steady and was neither as hot or as cold as the upper layers, and the bottom layer continued to warm during September while the top layer was getting cooler. The data from the recorder was transferred to punchcard and machine plotted for subsequent use.
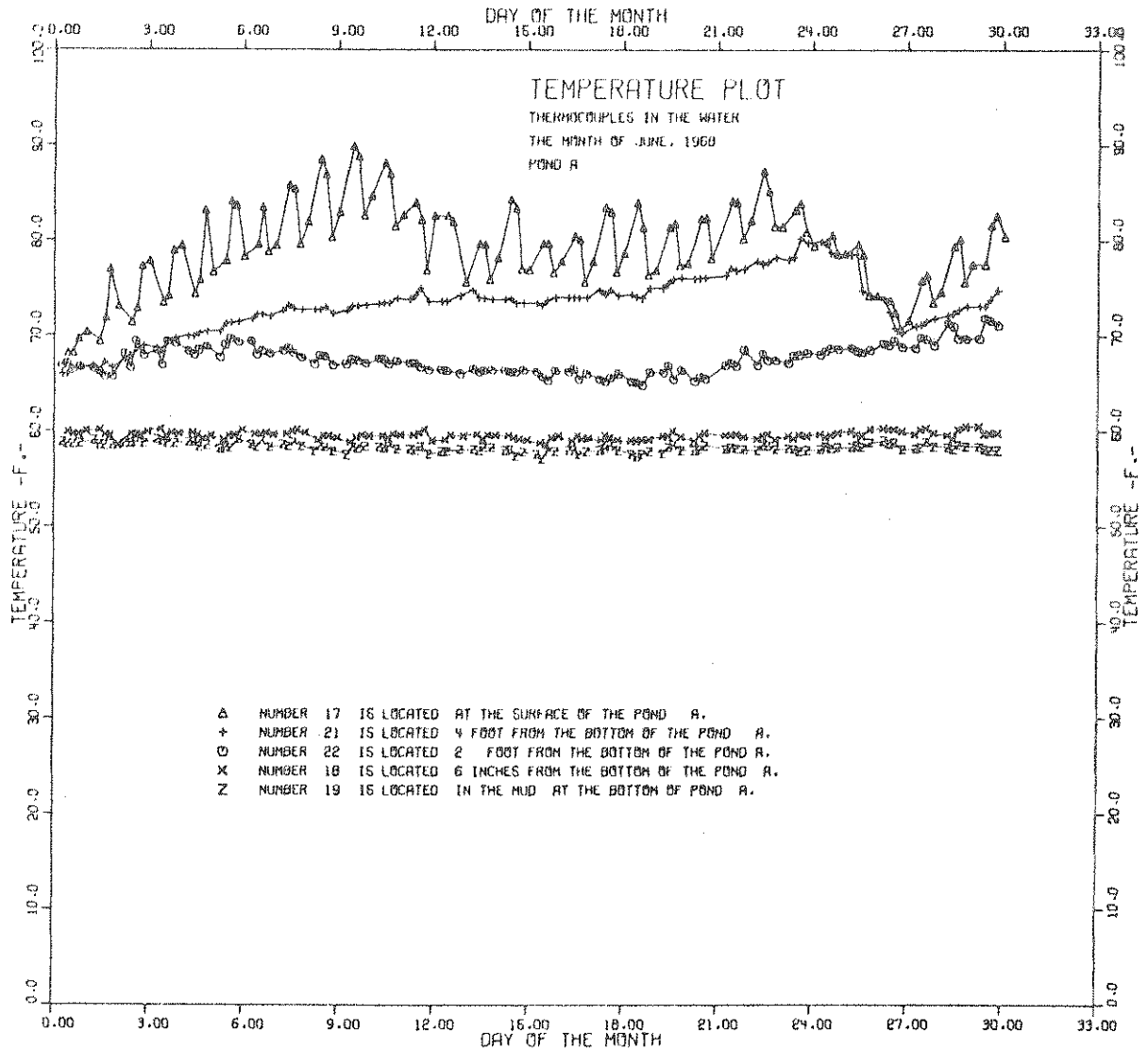
Figure 1.   Temperature Traces for June 1968 for Pond A.

Chemical analyses of water samples from each small reservoir were made three or four times during a year. Included in the analyses were color, sediment, turbidity, pH, hardness as $CaCo_3$, iron, manganese, Mo alkalinity as $CaCo_3$, nitrate as N and silica as SiO_2. A summary of the results is presented in Table 2 for the period May 1966 to November 1968. No attempt was made to average turbidity because of the presence of one or two very high values. Averaging can also be questioned when an inequality sign is present. It was done only to try to reflect differences between reservoirs. All the results are expressed in terms of mg/1 except for sediment and pH.

Table 2. Summary of Chemical Analyses of the Reservoir

	Reservoir	High	Low	Average
Color	A	5	5	5
	B	10	<5	5
	C	20	5	10
Turbidity	A	10	0.1	
	B	15	0.1	
	C	3	0.2	
Sediment	A	slight	very slight	slight
	B	slight	very slight	slight
	C	slight	very slight	slight
pH	A	8.0	6.6	7.2
	B	8.0	6.7	7.5
	C	7.7	6.6	7.2
Hardness	A	65	42	58
	B	82	64	72
	C	109	78	87
Iron	A	0.3	<0.03	0.10
	B	0.2	<0.03	0.09
	C	0.3	0.03	0.16
Manganese	A	0.1	0.03	0.06
	B	0.07	0.03	0.04
	C	0.1	0.02	0.07
Alkalinity	A	48	30	38
	B	46	31	38
	C	68	44	56
Nitrates	A	0.3	<0.1	0.14
	B	0.2	<0.1	0.14
	C	0.3	<0.1	0.18
Silica	A	2	<2	<2
	B	<2	<2	<2
	C	2	<2	<2

CHAPTER II

CONTAMINATION OF FARM PONDS
FOLLOWING TREATMENT OF WATERSHEDS
FOR PEST CONTROL

Jack E. Fahey[*]

The purpose of this study was to obtain information relative to the contamination of farm ponds by pesticides used to control agricultural pests. In 1966 three farm ponds and their respective watersheds were selected for study. The watersheds, located in a single field covered with a mixture of grass and alfalfa, varied from 2 to 7 acres in size, with slopes ranging from 5 to 15 percent. The topsoil was shallow and the subsoil impermeable. Runoff from storms was rapid and complete.

On April 13, 1967, two of the watersheds were treated with insecticides for control of alfalfa weevil. The third pond and watershed was retained as a control for biological observations. At the time of insecticide application there was a 6 to 8 inch stand of forage and the fields were dry. One watershed was treated with 10 percent phorate granules, 6.66 lbs per acre, and the second watershed was treated with a 50% wettable powder suspension of carbaryl, 3 lbs per acre. The insecticides were applied with tractor mounted applicators.

In 1968 the two watersheds treated in 1967 were retreated with the same insecticides but at increased dosage. At the time of the 1968 treatment (April 5) the soil was saturated from recent rains and there was very little growth of the forage crop (less than 2 inches). Granular formulations were applied to both watersheds using hand operated spreaders. A 10 percent phorate granular formulation was applied at the rate of 20 lbs per acre and a 20 percent carbaryl granular formulation was applied at the rate of 25 lbs per acre.

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*Associate Professor, Department of Entomology

SAMPLING PROCEDURE

Twice during the 1966 summer 4 samples of 20 soil cores (1 x 6 inch) were collected from each watershed at the same time two one gallon water samples were collected from each pond.

In 1967 the watersheds were divided into 3 areas for sampling: (1) an area 90 to 140 feet from the high water line at the pond, (2) a similar area 40 to 90 feet from the high water line, and (3) an area 20 feet wide at the high water line of the pond. The area adjacent to the pond was not treated with insecticide. Soil samples consisted of 20 (1 x 6 inch) cores four from each area. Forage samples consisted of 12-6 x 6 inch squares (four from each area). Water samples were taken near the pond inlet and at the overflow.

Soil and water samples were collected on April 13 before treatment and on April 14, 21, 28 and May 12, June 9 and August 9 after treatment. Forage samples were collected on April 13 and 14 only.

On March 26, 1968, before an insecticide treatment was applied 8 soil cores (1 x 6 inch) were collected at the lower edge of the watershed. These cores were divided into 4 inch segments and the segments analyzed separately. Following the application of insecticide on April 5 the watersheds were divided into 4 equal areas by lines running from the high to low level of the treated zone. Forage, soil and water samples were collected on April 6. Water samples were collected on April 16, 18, 24, May 5, August 14, September 12 and 26.

ANALYSIS

All samples were extracted with methylene chloride and dried over sodium sulfate. Aliquots of the extract were analyzed directly by gas liquid chromotography using a flame emission detector in the phosphorus mode for phorate residues. Phorate residues found were principally in the form of phorate sulfone, a small quantity of phorate and phoratoxon were found in the first samples collected in 1967. The phorate residues reported are the sum of all metabolites found. Carbaryl residues were analyzed by the colorimetric method of coupling 1-naphthol with denitro-benzene diazonium fluborate.

RESULTS

Pretreatment samples of soil and water collected in 1966 did not contain phorate or carbaryl residues. Analysis of these samples by G.L.C. using an electron capture detector did not indicate the presence of chlorinated hydrocarbon residues.

Table 1 gives the results of analysis of soil and forage samples collected in 1967. The residues found on forage, April 14, were greater than the residues in soil. This indicates that a large quantity of the insecticide applied did not reach the soil but was held in the forage cover. Residues found in soil on April 21 and 28 were greater than the residues found in soil on April 14. This could be the result of rains washing residue from the forage into the soil. Most of the insecticide residues (both phorate and carbaryl) had disappeared from the treated soil by June 9 and none was detected in soil samples collected on August 9. Samples from the untreated area showed a minimal residue (0.02 ppm) of carbaryl which could have been from spray drift. Phorate residue was found in a single sample collected on May 12.

Table 1. Analysis of Soil and Forage Residue Samples, 1967.

Sample Area	Residue in PPM[1]								
	4-13		4-14		4-21	4-28	5-12	6-9	8-9
	Soil	Forage	Soil	Forage	Soil	Soil	Soil	Soil	Soil
Phorate Residues[2]									
1	ND	ND	.144	6.75	.142	.804	.090	.008	<.005
2	ND	ND	.091	5.64	.211	.270	.042	<.005	ND
3	ND	ND	ND		ND	ND	.010	ND	ND
Carbaryl Residues[3]									
1	.006	.114	0.27	1.75	.70	.29	.15	.02	ND
2	.006	.114	0.12	2.00	.64	.38	.21	<.01	ND
3	.006	.114	.01		.02	.02	.02	ND	ND

[1] Mean of 4 observations

[2] Sum of Phorate, phoratoxon and phorate sulfone found

[3] Sum of carbaryl and 1 - naphthol

Table 2 gives the results of analysis of water samples collected in 1967. Phorate was not found in the pond water until May 12, following a period of heavy rains. The maximum phorate residue, 0.004 ppm, was found in a water sample collected on August 9. Residues of 0.003 and 0.002 ppm of phorate were found on May 12 and September 8, respectively. Carbaryl residues exceeding 0.001 ppm of pond water was found only on April 21. This residue was 0.002 ppm or twice the minimum detectable residue.

Table 2. Analysis of Water Samples, 1967

			Residue in PPM				
4-13	4-14	4-21	4-28	5-12	6-9	8-9	9-8
Phorate Residues							
ND	ND	ND	ND	.003	ND	.004	.002
Carbaryl Residues							
.002	<.001	<.001	<.001	.002	<.001	ND	ND

On April 28 and May 12, 1967 water samples were obtained from four locations in the main water course of each watershed. The results of analysis of these samples are given in Table 3. Sample 4 was obtained near the bottom of the watershed slope and samples 3, 2 and 1 at approximately 20 ft. intervals up the slope. These data show the presence of the two insecticides in the runoff water.

Table 3. Residues in Runoff, 1967

Sample	Phorate Residue		Carbaryl Residue	
	4-28	5-12	4-28	5-12
1	Dry	Dry	.010	Dry
2	.001	.002	.496	Dry
3	.008	.003	.930	.006
4	.019	.004	1.220	.005

The soil samples collected on March 26, 1968 from the two watersheds showed that no residue of carbaryl or phorate remained from the previous seasons treatment.

At the time of application (April 5) of insecticide in 1968 the water-
sheds were near saturation due to heavy rains. Water was standing low in
spots and in wheel tracks. Table 4 gives the results of analysis of soil
and forage on April 6 (24 hours after application). These residues

Table 4. Residues in Soil and Forage, 1968

| Sample | Phorate Residue | | | Carbaryl Residue | |
	Soil PPM	Forage PPM		Soil PPM	Forage PPM
1	.256	34.17		4.71	1.22
2	.261	27.68		4.59	1.17
3	.225	61.33		1.32	1.18
4	.213	66.06		4.17	1.21
Mean	.239	47.31		3.70	1.20

reflect the higher dosage of phorate and carbaryl applied in 1968. Table
5 shows the residues found in water samples from the two ponds fed from

Table 5. Residue in Pond Water, 1968

| Date | PPM Phorate Residue | | PPM Carbaryl Residue[1] | |
	Pond Inlet	Pond Dam	Pond Inlet	Pond Dam
April 5	ND	ND	ND	ND
April 6	ND	ND	ND	ND
April 16	.0007	.0007	ND	ND
April 16	.014	ND	ND	ND
April 24	.174	.117	ND	ND
May 8	.114	.110	ND	ND
August 14	ND	ND	ND	ND
August 19	ND	ND	ND	ND
Sept. 12	ND	ND	ND	ND
Sept. 26	ND	ND	ND	ND

[1] ND-None Detected

the treated watersheds. No carbaryl residue (greater than 0.001 ppm) was found in the pond water. The pond fed by the phorate treated watershed contained a measureable residue (0.0007 ppm) of phorate on April 16, 11 days after treatment. This residue increased to a maximum of 0.174 ppm 19 days after treatment (at pond inlet). By May 8, 33 days after treatment, the residue in the pond had decreased to approximately 0.110 ppm of phorate. Additional samples were not collected until August 14, by which time the phorate residue had disappeared from the pond water.

CHAPTER III

A STUDY OF BACTERIAL POPULATIONS AND
BACTERIAL DECOMPOSITION OF CARBARYL
IN FARM POND WATERS

L. B. Hughes and H. W. Reuszer*

Waters of farm ponds serve many useful purposes, including water for livestock, recreation, fishing, and even water for human consumption and household use. Consequently, the chemical and biological nature of the water is of extreme importance.

Initially, the purpose of this study was to determine the effect of pesticides on bacterial life in farm pond waters and to determine the degradative ability of bacteria on selected insecticides in such pond waters. However, with applications of sevin (carbaryl), a carbamate insecticide, and phorate (Thimet), an organic phosphorus insecticide, to the watersheds of two farm ponds at recommended rates in 1967 and at four times the recommended rates in 1968, no appreciable quantities of either insecticide were found in the pond waters. It was, therefore, not possible to determine any effect of the pesticide upon bacterial populations in the ponds. It was deemed advisable, however, to study bacterial populations over a period of time in the three ponds under actual environmental conditions since so little information is now available. regarding such populations and the factors affecting them. Results of these studies covering a two year period are reported here. Also reported are partial results of a subsequent study on the bacterial decomposition of sevin under laboratory conditions in water from one of the ponds and the effects of sevin on the native bacterial population in the pond water.

LITERATURE REVIEW

Many workers have reported large fluctuations in bacterial numbers in bodies of water. Fred, et al., (1) and Snow and Fred (8) found large fluctuations of bacterial numbers in Lake Mendota (Wis.) in studies covering

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*Graduate Assistant in Research and Associate Professor, respectively, Department of Agronomy.

four years. Extreme fluctuations could not always be explained (1). In a brief study of Flathead Lake (Mont.), Graham and Young (2) found maximum bacterial numbers below 8,000 per ml. Lower numbers of bacteria were found in the surface water than in water below the surface. Stark and McCoy (9) reported striking differences in bacterial numbers in the surface water at different locations on the same lake. Irwin and Claffey (4) found wide variations in numbers of bacteria in the waters of 20 Oklahoma ponds with fewer bacteria found in ponds with higher turbidity. Wilson, et al., (11) reported 5,000 to 30,000 bacteria per ml in six West Virginia ponds. Little differences in bacterial numbers were detected at different depths. Water temperature and pH showed no correlation to the bacterial numbers.

Menzie (7), in a comprehensive review of the degradation of many pesticides, indicated that carbaryl is very short-lived in both soils and water. Karinen, et al., (5) found that carbaryl applied to estuarine water under natural conditions was rapidly removed from the water by adsorption by the bottom mud. However, carbaryl did persist in the mud for 2-6 weeks. Kaufman (6) reported that carbamates were lost from soils mainly by volatilization and microbial decomposition.

METHODS AND PROCEDURES

Bacterial Populations Study

Three ponds (A, B, and C) on the Southern Indiana Purdue Agricultural Center were studied. These ponds and their watersheds are described in the introductory chapter of this comprehensive report. Ponds A and C had densely growing aquatic plants in the edge of the water, while little such growth occurred in pond B. Substantial algal growth was also noted in ponds A and C in late spring and early summer, but little algal growth was noted in pond B.

Samples of water were taken from a raft at the surface and six inches from the bottom at four different locations on each pond approximately once per month over a two year period (April, 1967 to March, 1969). The water samples were immediately placed in ice and transported back to the laboratory, stored overnight at 5° C and plated the following day on an agar medium containing 1.0 gm glucose, 1.0 gm peptone, 0.5 gm yeast extract,

0.25 gm K_2HPO_4, 12 gm agar and 1,000 ml deionized water. Bacterial numbers were determined by colony counts made after 14 days incubation in the dark.

Water temperatures were obtained by E. J. Monke and P. R. Goodrich of the Purdue University Agricultural Engineering Department with water temperatures recorded four times daily. Data used in this paper were the means of the four temperatures recorded on the day of sampling.

Aliquots of water were evaporated and organic carbon was determined using the manometric procedures described by Van Slyke and Folch (10).

Data on pH, nitrate concentration, and turbidity were obtained from the Indiana State Board of Health.

Bacterial Decomposition of Carbaryl

Five milligrams of recrystallized carbaryl were added aseptically to 9 sterilized 2-liter Erlenmeyer flasks, stoppered with cotton plugs. These flasks (1-9) constituted 3 treatments of 3 replicates each. In treatment 1 (flasks 1-3), 250 ml of pond water (from pond A) were added. On Day 29, 0.05 ml of water from pond A, in which the native bacteria had been incubated with 30 ppm carbaryl for 12 months, was added. For treatment 2 (flasks 4-6) 250 ml of pond water were also added but with no other additions. In treatment 3 (flasks 7-9), 250 ml of sterilized pond water were added. This treatment served as a control with respect to the possible decomposition of carbaryl in the absence of microorganisms. In treatment 4, 250 ml of pond water were added to flasks 10-12 which contained no carbaryl. This treatment served as a control with respect to the effect of carbaryl upon the native bacteria. All 12 flasks were placed on an Eberbach rotary shaker and shaken at "high" speed.

Bacterial numbers were determined in the same manner as in the bacterial populations study. Bacterial numbers were determined on day 0, day 5, and once per week thereafter for 9 weeks.

Carbaryl and its immediate degradative products were analyzed by observing spectral changes in the UV wavelength range, using a DK-2 recording spectrophotometer. Extractions for these analyses were made using redistilled methylene chloride.

RESULTS AND DISCUSSION

Bacterial Populations Study

The factors possibly influencing the bacterial numbers in the pond waters that were studied included organic matter content, water temperature and to a lesser extent, pH, nitrate concentration, and turbidity of the water.

Nitrate concentration, pH and water turbidity of the three ponds are shown in Table 1. Highest average pH was found in pond B which would seem to be farther from potimum pH for maximum bacterial growth than the pH in either ponds A or C. Water turbidity was also found to be highest in pond B. Only small quantities of nitrate were found in the pond waters and the small variations would not be expected to have a significant effect on the number of bacteria.

Water temperature of the three ponds for a nine month period are shown in Figure 1. Surface water temperatures were quite similar in all three ponds reaching a maximum near 80° F in June. The minimum temperature of the surface water in the ponds was near 40° F in December. The temperature of the water near the bottom of ponds A and B reached a maximum slightly above 70° F in August while cooling began one month earlier in pond C. Lowest temperature of the bottom water in the ponds occurred in December and was about equal to the temperature of the surface water at that time.

Seasonal variations of organic carbon content occurred in both depths of water in each of the ponds as shown in Figure 2. Generally highest organic carbon content occurred in late spring or early summer in both years of the study. Pond B showed smallest seasonal variations of organic matter content ranging from 7.1 to 14.8 mg of organic carbon per liter of water with similar quantities of organic carbon in the surface water and in the water near the bottom. Pond A showed larger seasonal variations of organic matter at both depths with organic carbon quantities ranging from 8.0 to 24.0 mg per liter. Higher organic matter content was generally prevalent in the water near the bottom than in the surface water of pond A. The waters at both depths of pond C contained even higher organic matter content and largest seasonal variations ranging from 11.1
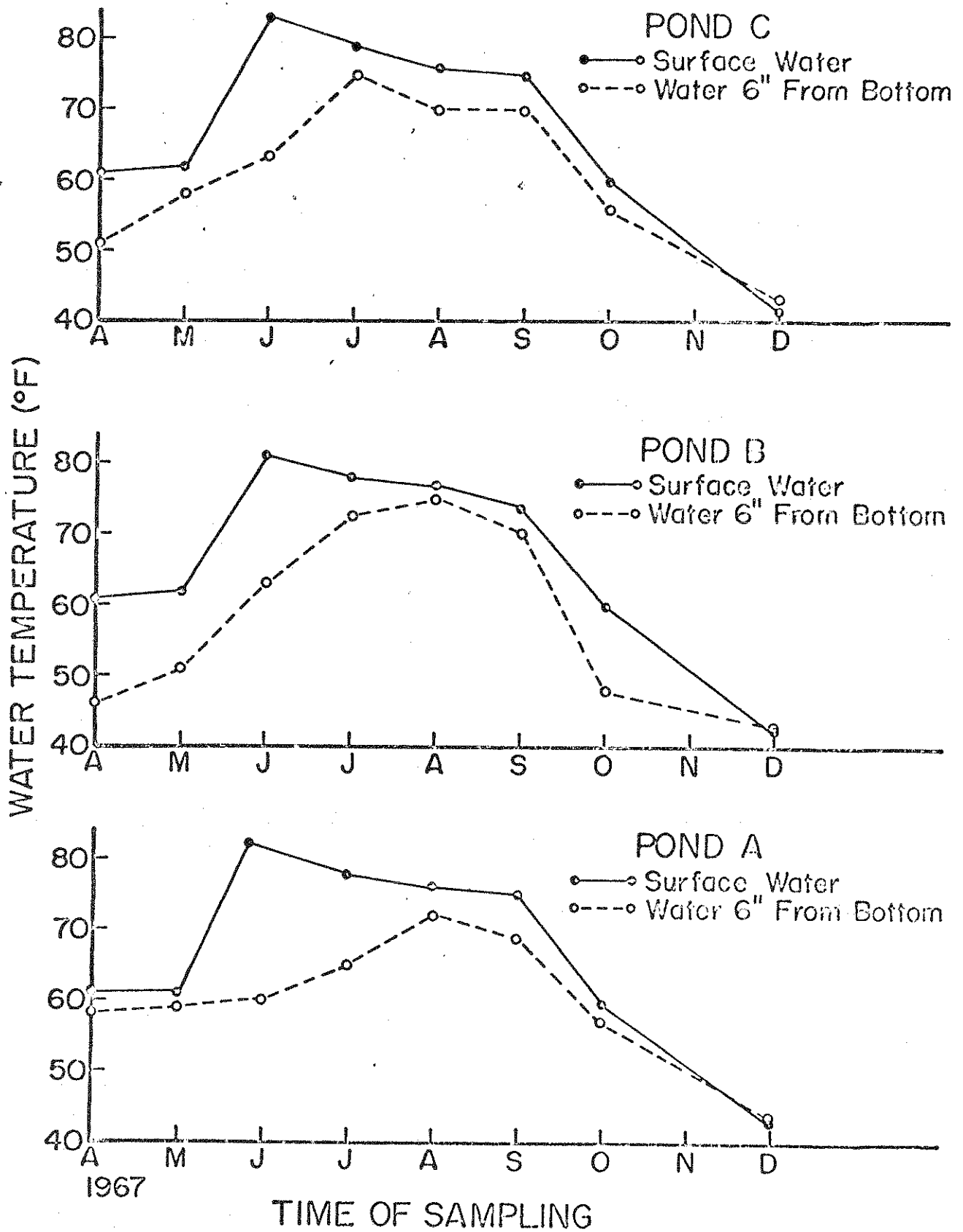
Figure 1. Seasonal variations in water temperatures in 3 Indiana farm ponds for a nine month period.
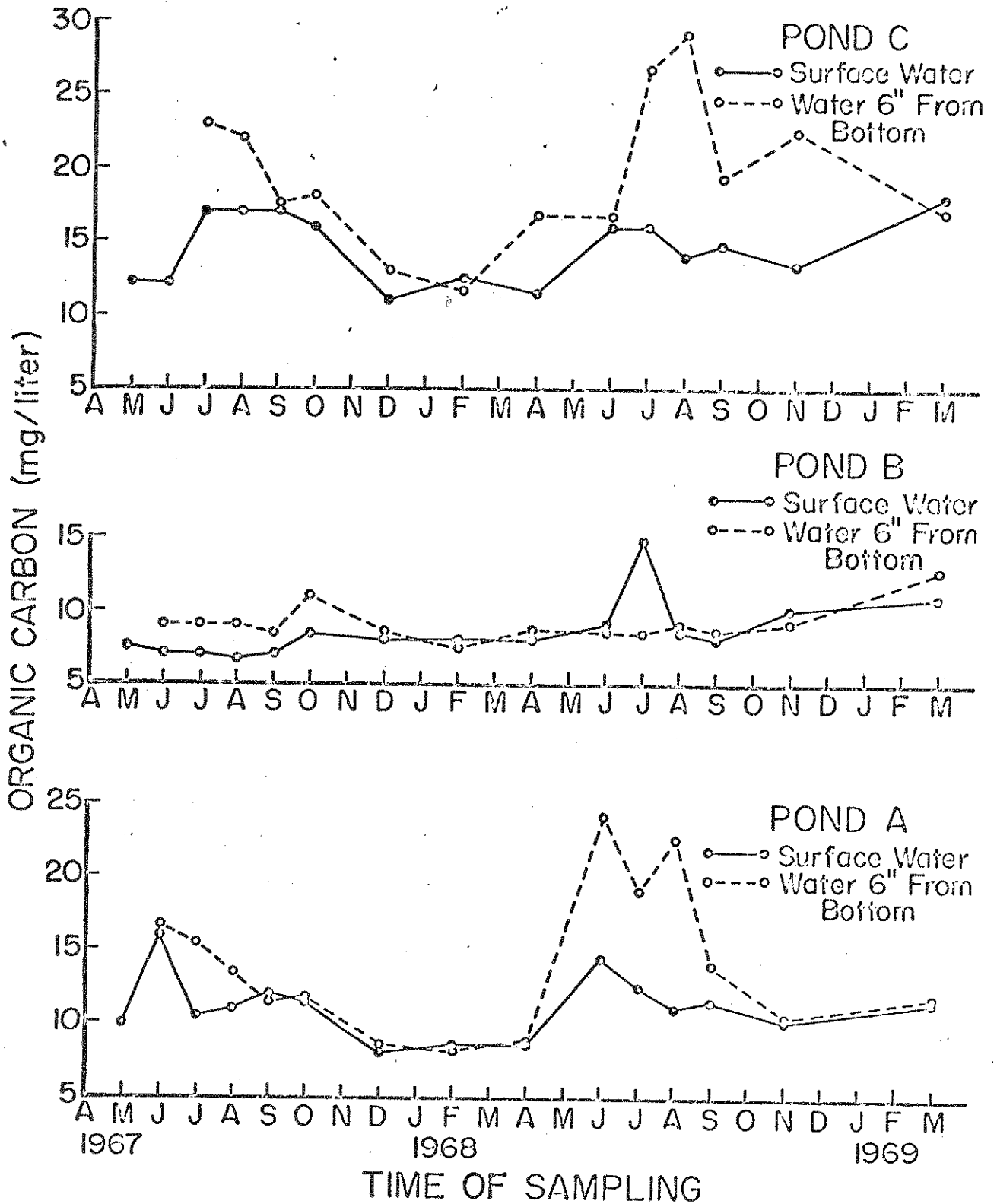
Figure 2. Seasonal variations in organic carbon content in 3 Indiana farm pond waters for a two year period.

Figure 3. Seasonal variations in bacterial numbers in 3 Indiana farm pond waters for a two year period.

Table 1. Turbidity, pH and nitrate concentration of the pond waters at different times.

	April 1967	August 1967	December 1967	April 1968	July 1968	Avg.
			pH			
Pond A	7.4	6.8	8.0	7.1	7.0	7.3
Pond B	7.4	8.0	7.4	7.7	7.8	7.7
Pond C	7.3	7.1	7.4	7.6	7.3	7.3
		Nitrate Concentration (ppm)				
Pond A	0.1	0.1	0.3	0.1	0.1	0.14
Pond B	0.1	0.2	0.2	0.1	0.1	0.14
Pond C	0.1	0.2	0.3	0.1	0.2	0.18
			Turbidity			
Pond A	0.3	0.1	10	2	0.3	2.5
Pond B	15	0.1	3	15	3	7.2
Pond C	0.7	0.2	3	1	0.6	1.1

Table 2. Effect of carbaryl (sevin) on the numbers of bacteria in pond water. (Thousands per ml)

| Days After the addition of Carbaryl	Treatment 1	Treatment 2	Treatment 4
0	24	24	24
5	214	219	125
13	188	205	82
22	123	198	67
28	84	41	83
36	1129	282	129
43	1767	219	75
49	2157	230	142
56	2533	283	230
63	3427	304	126

to 29.2 mg of organic carbon per liter of water.

The numbers of bacteria and the seasonal variations of bacteria have been reported by Hughes and Reuszer (3) and are shown in Figure 3. Highest numbers of bacteria were generally present in each of the pond waters in late spring or early summer in both years of the study. Highest numbers of bacteria seemed associated with the active growth period of aquatic plants rather than the period of their death and decay in autumn while the role of algae with respect to numbers of bacteria was not clear. The waters of pond A had very distinct increases in bacterial numbers with maximum numbers occurring at the same time each year with the surface water usually having fewer numbers of bacteria than the bottom water. Numbers of bacteria in pond A ranged from 4,400 to 102,000 per ml in the surface water and from 5,100 to 118,000 in the bottom water. The waters of pond B had only small variations of bacterial numbers with similar numbers of bacteria at both depths throughout the two year period. Numbers of bacteria in this pond ranged from 4,200 to 48,000 per ml in the surface water and from 3,400 to 28,300 per ml in the water near the bottom. The waters of pond C had the highest numbers of bacteria and the largest seasonal variations of bacterial numbers of the ponds studied. In pond C, the numbers of bacteria ranged from 7,700 to 160,000 per ml in the surface water and from 3,200 to 121,00 per ml in the bottom water.

Many chromogenic bacterial colonies appeared on the plates including red, pink, shades of yellow and orange, in addition to white and cream colored.

A statistical analysis of variance of the bacterial numbers with respect to time of sampling, location of sampling, and depth of sampling was determined. The numbers of bacteria varied significantly with each in all three ponds. Correlation coefficients between water temperature and bacterial numbers were non-significant in ponds A and B but were highly significant in pond C. The correlation coefficients between organic carbon and bacterial numbers were highly significant in both ponds A and B while a negative correlation was significant at the 5% level in pond C. All statistical data were reported by Hughes and Reuszer (3).

<u>Bacterial Decomposition of Carbaryl</u>

At this time, the complete pathway of the bacterial decomposition of carbaryl in pond water under laboratory conditions has not been elucidated. But several interesting facts have been found with many more equally interesting questions posed.

With all treatments in which carbaryl was present, a spectral change occurred within two days after the experiment had begun. The spectral change was the appearance of a peak at 322 mµ, corresponding to the spectrum of 1-naphthol. This indicated the following hydrolysis reaction:

Carbaryl   1-Naphthol
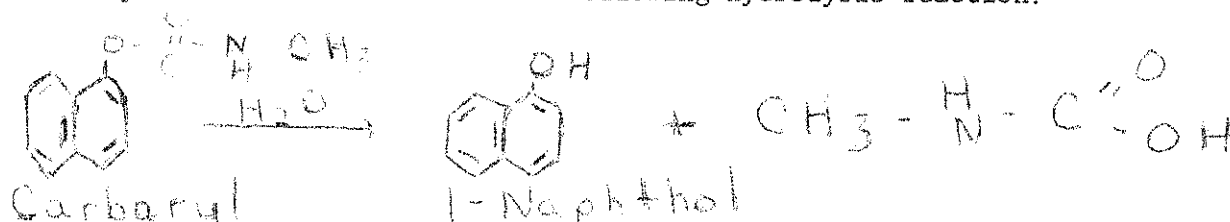
Even under sterile conditions, the rate of hydrolysis and formation of 1-naphthol was identical to the rate of hydrolysis with the native micro-organisms of the water present. This suggested that under the given conditions of the experiment, the reaction was merely a chemical reaction and not a biological reaction. However, an additional experiment has shown that under sterile conditions and without shaking, carbaryl did not hydrolyze to an appreciable extent. Thus, even though the hydrolysis seemed to be a chemical reaction, aeration appeared to be necessary.

Maximum hydrolysis and formation of 1-naphthol was attained in 21-28 days. During this time, the numbers of bacteria increased about two-fold relative to the control. Although it is not known at this time, it seems probable that the relatively simple N-methyl-carbamic acid molecule may be serving as a source of carbon and nitrogen.

On day 29, 0.05 ml of pond water, in which the native bacteria had been incubated with 30 ppm carbaryl for 12 months and in which the bacteria could have become somewhat adapted to the carbaryl environment, was added to each of the three replicate flasks of treatment 1. A total of approximately 4,000 bacteria was added to each ml of the pond water in the flasks. Within one week or by day 36, a dramatic decrease in the 1-naphthol peak at 322 mµ had occurred. Within 14 days or by day 43, no trace of 1-naphthol remained. In treatment 2 (and 3), the peak remained.

This indicated that the specific organism(s) added had the ability to degrade the aromatic ring structure of 1-napthol. At the same time, two other facts were noted. The numbers of bacteria in Treatment 1 (Table 2) increased more than ten-fold between Day 28 and 36 and continued increasing until there was a 30-fold increase by Day 63 with over 3.4 million per ml. In addition, while a dramatic increase in total bacterial cells occurred, there was an equally noticeable decrease in types of bacterial colonies appearing on the agar plates. A yellow pigmented colony was the predominate colony type, almost to the exclusion of all others. This culture was isolated and is currently being checked to determine if it can, in pure culture, degrade carbaryl or 1-napthol.

On Day 43 of the experiment, a small decrease in the 1-napthol peak was noticed in Treatment 2. This decrease continued very slowly and by Day 63, only a tiny blip was left at 322 mu. At this same time, the bacterial numbers were steadily increasing, but to a much smaller extent than the increase in Treatment 1. Also, no single colony type seemed to predominate. This data from Treatment 2 indicated that some period of time is needed before the bacteria can degrade the carbaryl molecule. Perhaps this time is the time necessary for enzyme inducement. Further work will, hopefully, lead to the complete metabolic pathway involved in the bacterial degradation of carbaryl in water.

SUMMARY

A two year study of the bacterial populations in three Indiana farm pond waters showed large seasonal variations in bacterial numbers. Data showed significant variation of numbers of bacteria in each pond with time of sampling, location of sampling, and depth of sampling. In addition correlation coefficients for water temperature with bacterial numbers were significant in pond C and non-significant in ponds A and B. Correlation coefficients for organic matter content with bacterial numbers were significant in ponds A and B, but a significant negative correlation coefficient was found in pond C.

Results of an incomplete study of the bacterial decomposition of carbaryl (sevin) indicated that indigenous bacteria could degrade the compound by breaking the ring structure after 1-naphthol was formed.

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CHAPTER IV

ADSORPTION OF INSECTICIDES ON POND
SEDIMENTS AND WATERSHED SOILS

N. L. Meyers, J. L. Ahlrichs and J. L. White*

The pollution of water resources by pesticides and other organo-toxicants has received much attention since contamination of the Tennessee River by toxaphene in 1951 as reported by Young and Nicholson (7). Entrance of a pollutant into water from use on agricultural land is regulated by the factors controlling the fate of pesticides in the soil. Removal of the pesticide from the soil might occur through leaching, volatization, or runoff while adsorption of pesticides tends to retard or prevent removal. In addition, pesticides may undergo alterations in the soil as the result of chemical, biological, or photochemical processes. The ultimate fate of a pesticide depends on a combination of these parameters. However, adsorption on colloidal surfaces of the soil appears to determine to a greater extent than any other single factor the ultimate fate of pesticides. The nature and extent of adsorption has been discussed by Bailey and White (2) and Meyers (4).

This study deals with the adsorption of three insecticides on watershed soils and their corresponding pond sediments. Generally, adsorption of a pesticide to a significant degree will greatly reduce, if not eliminate, movement into surface waters. To facilitate the study, three small farm ponds were selected on the Purdue University Southern Indiana Forage Farm in Dubois County. The watershed soil types were Zanesville (6-18% slope) and Welston (12-18% slope) silt loams which have developed from sandstone and shale. The soils are similar except for the fragipan formation in the Zanesville soil. Each of the watersheds was devoted to alfalfa production. Prior to the application of insecticides, soil samples were collected from the

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watersheds and sediment samples were collected from the pond bottoms. The mineralogical characterizations and the adsorption studies described below were conducted using these materials. Since the mineralogical and physical properties of the three ponds were similar, only results from one of the ponds are reported.

RESULTS

Mineralogical Characterization

The mineralogical composition of the clay fraction of pond sediment in relation to its watershed soil has not previously been reported in Indiana. Therefore, the mineralogical composition of both soil and sediment was determined to provide information on this relationship as well as to provide a basis for meaningful interpretation of the adsorption studies. The mineralogical composition was determined by x-ray diffraction and infrared techniques. The x-ray diffractograms of the soil and sediment clay fraction ($<2.0\mu$) from the pond are shown in Figure 1. The positions of intensities of the peaks show the mineralogical composition of the soil and sediment to be essentially identical. The 14Å peak present on Mg saturation, glycerol solvation, and mild heating was interpreted to indicate the presence of vermiculite. The 10Å peak is characteristic of micaeous minerals and is greatly enhanced by collapse of the 14Å material on strong heating (550°C). The presence of kaolinite is confirmed by the 7Å peak remaining on K saturation and mild heating and by the disappearance of the 7Å peak on heating to 550°C which destroys the kaolinite structure. Detailed procedures for the identification of clay minerals are given by Whittig (6).

The infrared patterns of the clay fractions are shown in Figure 2. The presence of kaolinite is confirmed by the weak band at 3690 cm^{-1} and a strong band at 3620 cm^{-1}. Montmorillonite or vermiculite would also exhibit a strong band at 3620 cm^{-1} in addition to a broad band in the 3400 cm^{-1} region. Details concerning the application of infrared spectroscopy to clay mineral systems has been given by Ahlrichs et. al. (1).

Although the mineralogical composition of the clays appears to be identical, the quantity of clay is much higher in the sediment than in the soil (Table 1). This is in agreement with the work of Kohnke (3) and is in the order expected. Thus, clay and silt are preferentially eroded into the pond at the expense of sand but no differential erosion of clay types occurs.
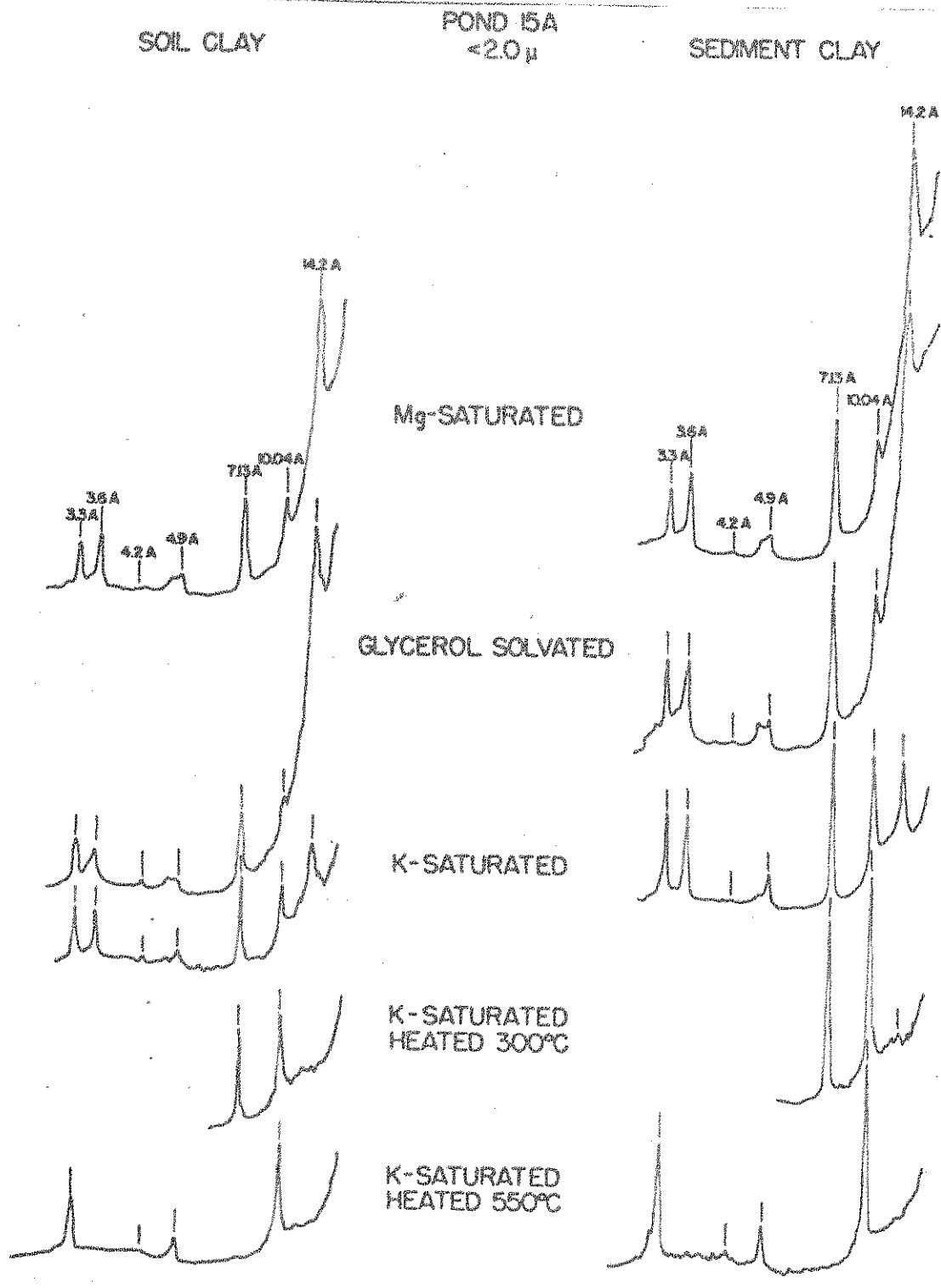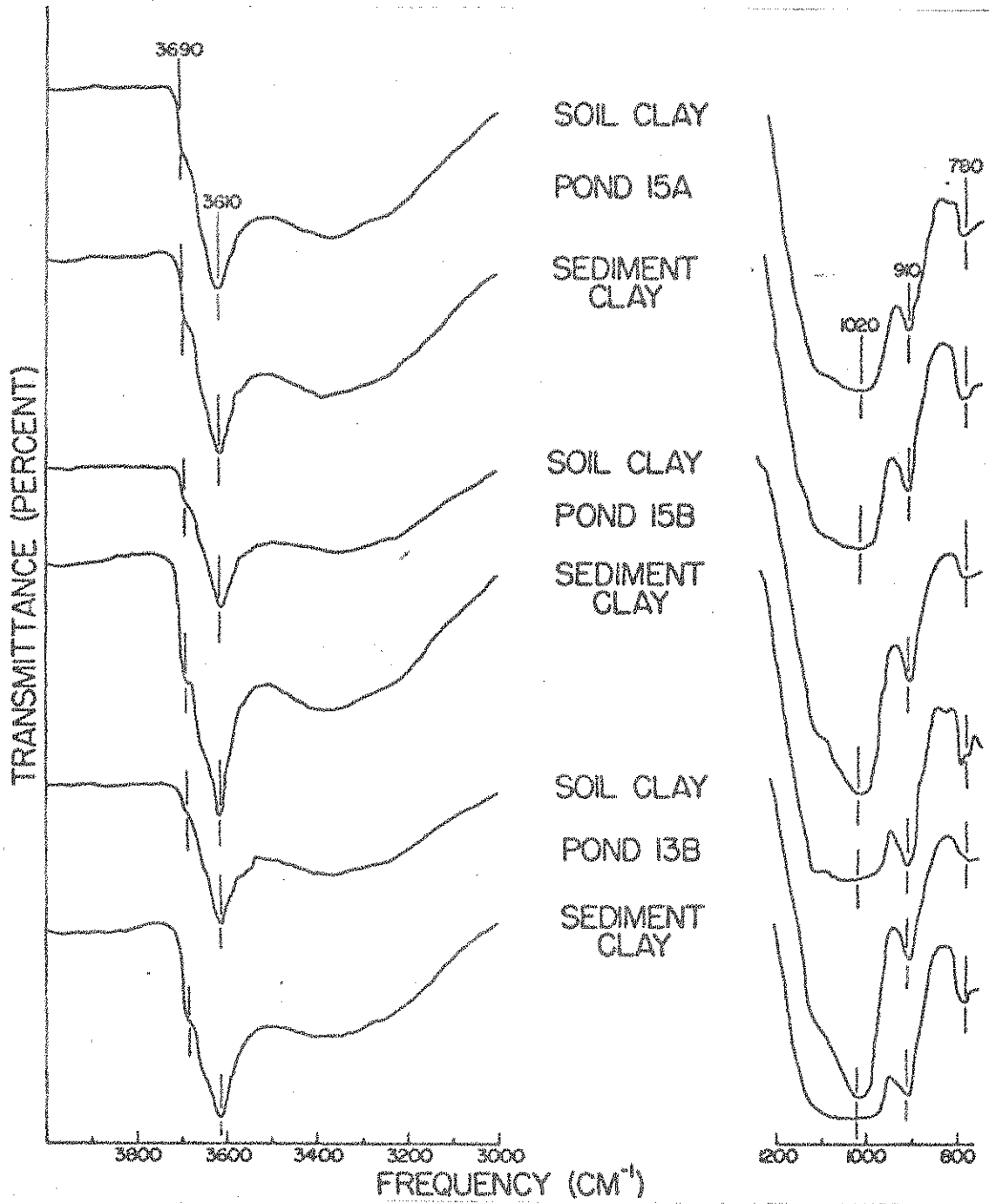
Figure 1. Diffractograms of soil and sediment clay.

Figure 2. Infrared absorption spectra for soil and sediment clay.

Table 1. Texture of the watershed soil and pond sediment.

% sand	% silt	% clay	Coarse clay % of total	Fine clay % of total
15.6	68.4	16.0	63.1	36.9
4.6	70.4	25.0	58.7	41.3

Adsorption Studies

Adsorption of malathion, phorate, and carbaryl was studied using water-shed soils and the pond sediments as adsorbents. Selection of these materials was based largely on their current use on alfalfa for weevil and spittlebug control. Adsorption of the insecticides is represented as Fruendlich iso-therms in Figure 3. It can be noted that malathion is strongly adsorbed followed by carbaryl, with phorate showing limited adsorption.

Comparison of adsorption on soil with adsorption on sediment showed little difference for malathion and phorate while carbaryl adsorption was greater on the sediment. Examination of Table 1 would lead one to expect greater adsorption on the sediment due to the increased clay content. However, the expected increase occurred only with carbaryl.

Absolute interpretation of adsorption data is of limited value but comparison of the relative extent of adsorption is worthwhile. If a pesticide is adsorbed it would be less likely to enter a pond as compared to a non-adsorbed counterpart. We might expect then that the degree of pollution for these insecticides following application to the soil would be in the order phorate $>$ carbaryl $>>$ malathion. In addition, adsorption in the soil under field conditions should be more complete since concentrations used in laboratory studies represent an application of 10-300 times the normal rates of application.
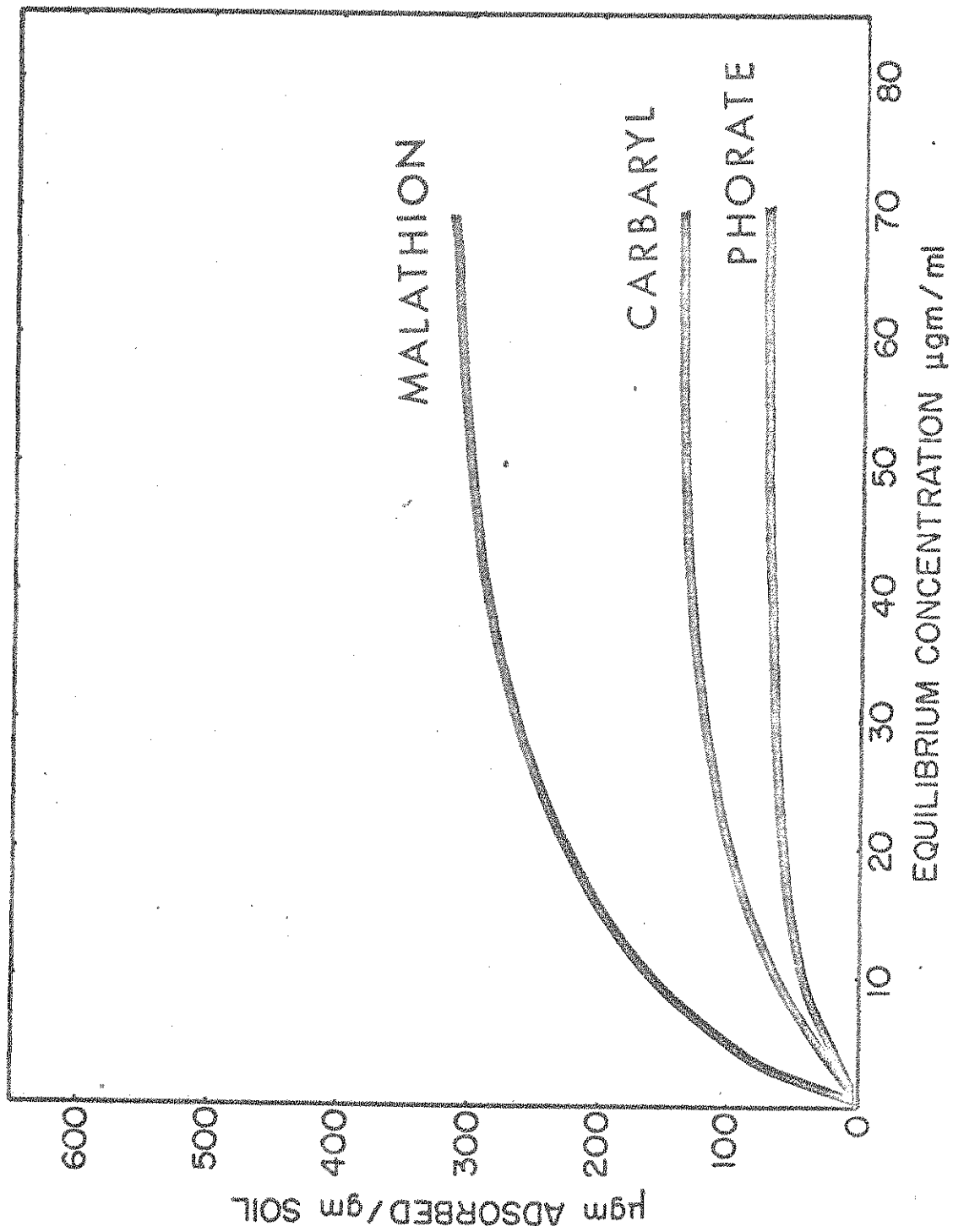
Figure 3. Relative adsorption of malathion, carbaryl, and phorate.

CONCLUSIONS

Little difference was found between the clay mineralogy of a pond sediment and the soil from which it is derived. The soils and sediments used in this study contain kaolinite, micaeous minerals, and vermiculite.

Adsorption studies showed that malathion is adsorbed to the largest extent followed by carbaryl and then phorate with significant adsorption by the soil of all three. If a pesticide is adsorbed, it should not be subject to movement into a pond by leaching or runoff, thus, we would conclude that contamination of a farm pond probably would not occur following application of malathion, carbaryl or phorate to the watershed, and that phorate would probably be the first to reach the pond if contamination did occur. These conclusions are based on the assumption that pesticide applications are made according to the manufacturers suggestion and applied at the recommended rate.

Further support of these observations is given by the work of other cooperators on the project (5). Continuous monitoring of the pond water for 8 months following application of phorate and carbaryl at levels four times their recommended dosage showed no trace of carbaryl at anytime in the water and only a slight temporary trace of phorate. When recommended rates were applied, no trace of either insecticide was found in the pond.

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CHAPTER V

A KINETIC AND EQUILIBRIUM STUDY OF THE ADSORPTION
OF THE ORGANIC INSECTICIDES CARBARYL AND PARATHION
UPON SOME SOIL ORGANIC MATTER SURFACES

J. A. Leenheer and J. L. Ahlrichs*

In most soil systems, the most active constituent relating to pesticide adsorption is the soil organic matter present in the system. In order to evaluate the potential certain pesticides applied to the watershed hold for water pollution, and to estimate the extent to which pesticides are deactivated by the soil through adsorption, a knowledge of the mechanisms involving ion exchange for organic bases (1), and hydrogen bonding for organic acids (5) have been fairly well elucidated for these classes of pesticides, but adsorption mechanisms of neutral non-ionic pesticides such as the carbamates and organic phosphates are much more obscure and have not been investigated to a large extent. Insight into the mechanisms of adsorption of the insecticides carbaryl and parathion upon some characterized organic matter surfaces was obtained by a two fold kinetic and equilibrium study of adsorption from dilute aqueous solutions of the insecticides.

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*Respectively, N.D.E.A. Fellow and Professor, Department of Agronomy.

MATERIALS AND METHODS

Soil organic matter adsorbents were obtained from the Zanes-
ville silt loam which is a light colored soil developed under forest
Romney silty clay loam which is a dark colored soil developed under
prairie, and Carlisle muck soil. The Zanesville silt loam was
characteristic of the soils of the watershed studied in this general
project. Soil organic matter was obtained as an organic residue after
the sand and silt fractions had been removed from a soil-water suspension
by sedimentation, and the clay removed by HCl-HF acid dissolution
treatments (4). The Romney and Zanesville soils were pretreated with
H_2SiF_6 to remove the biotite and vermiculite resistant to HCl-HF dissolu-
tion (2). From organic matter contents of 1.4% for the Zanesville soil,
7.0% for the Romney soil, and 58% for the Carlisle muck, the inorganic
material remaining in the organic matter preparations was reduced to
about 35% for the Zanesville soil, 10% for the Romney soil, and 1.5%
for the Carlisle muck. X-ray diffraction of the inorganic constituents
of these organic matter preparations indicated that most of the material
was composed of the titanium oxides, rutile and anatase, which were
found to have little effect in the adsorption studies. The organic matter
adsorbents were characterized by functional group analysis of the
carboxyl, aliphatic hydroxyl, phenolic hydroxyl, and carbonyl functional
groups (4).

Adsorption studies were conducted in 90 ml centrifuge tubes immersed
in a constant temperature water bath. Agitation of the organic matter
adsorbent in aqueous suspension was maintained by a small magnetic stirrer
in the bottom of each tube. Samples of the organic matter adsorbent
were weighed into the centrifuge tubes, and 25 ml of water were added
and agitated for 24 hours to allow complete adsorption of water on the
organic matter. At the time the adsorption study was to begin, 25 ml of
10-12 ppm solution of the insecticide was added to give a 5-6 ppm
solution for the initial concentration of the insecticide. For equilibrium
studies, adsorption was considered complete after 24 hours, and the
organic matter adsorbent was removed from suspension through centri-

fugation. Two 20 ml portions of the supernatant solution were carefully pipetted from the centrifuge tubes into two 125 ml separatory funnels, and 20 ml of methylene chloride added to each funnel. Vigorous shaking of the funnel for two minutes extracted better than 97% of the carbaryl or parathion into the methylene chloride. The water and methylene chloride phases were allowed to separate for two minutes, and the lower methylene chloride solution was placed in five centimeter quartz UV absorption cells. Slight heating of the methylene chloride solutions in the absorption cells was sometimes necessary to clear up the cloudiness of the water not in solution. The UV spectra of carbaryl and parathion in methylene chloride were taken from 340 mμ to 240 mμ which is the cut off point for the methylene chloride solvent. For carbaryl, the wavelength of maximum absorbance is 281 mμ with molar absorptivity of 5,890 liter/mole-cm, and the maximum absorbance of parathion is at 276 mμ with molar absorptivity of 10,837 liter/mole-cm. A small amount of organic matter in water solution may be extracted by the methylene chloride and cause significant absorbance in the UV spectrum and this absorbance must be subtracted from the spectrum before a quantitatitive determination of the insecticide concentration can be made from the standard curve. With each set of adsorption samples, two blank samples were run without any organic matter in suspension. The blank samples were buffered to the same pH which existed in the organic matter suspensions, and duplicate determinations were made on each blank. The amount of insecticide adsorbed was determined as the difference in concentrations between the blank samples and the organic matter suspensions. Desorption of the carbaryl and parathion was determined by measuring concentration increases in 50 ml aqueous suspensions of organic matter previously saturated with the insecticides . These procedures of insecticide analysis with organic matter suspensions were also found applicable to synthetic resins used as adsorbents.

Adsorption of water vapor upon organic adsorbents was used to determine the hydrophobic-hydrophilic nature of the adsorbent. After the adsorbent had been completely dried over P_2O_5, 250 mg were weighed on a microbalance into previously tared weighing bottles, and placed in desiccators whose relative humidities were controlled at 22, 53, 75 and 93 percent by the respective saturated salt solutions of KAc, $Na_2Cr_2O_7$, NaCl, and $NH_4H_2PO_4$. Adsorption was allowed to proceed for one week
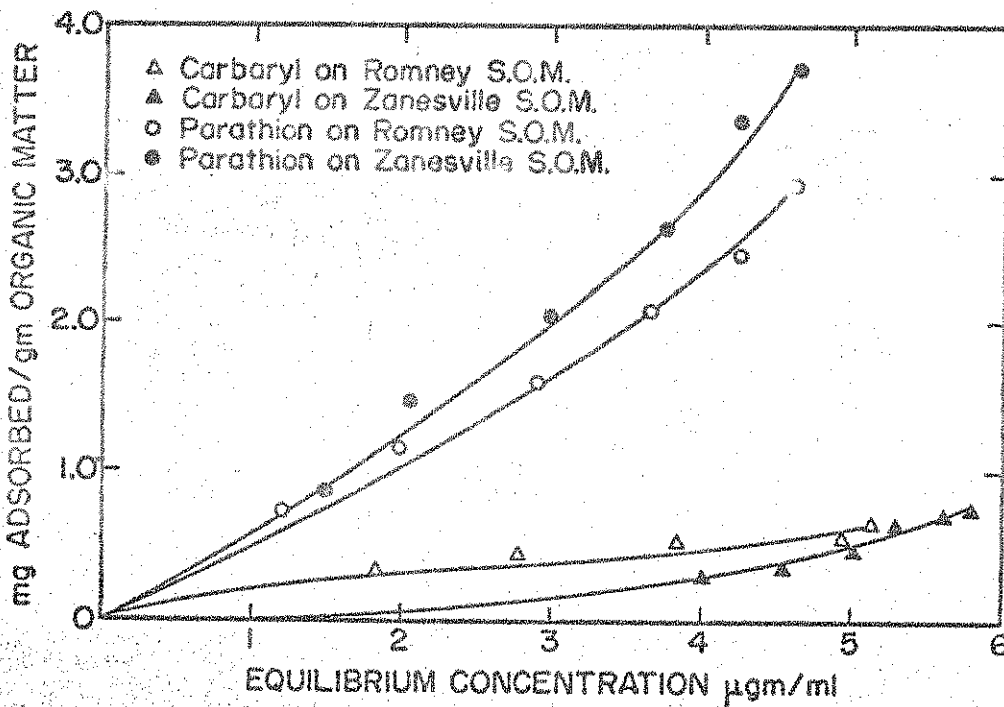
after which the samples were again weighed on the microbalance to determine the amount water absorbed. A few crystals of thymol were placed in each desiccator to prevent microbial growth on the organic adsorbents. The weighing bottles were immediately capped after being taken from the desiccators to prevent adsorption or desorption of water from the adsorbent.

RESULTS AND DISCUSSION

The adsorptive capacities of carbaryl and parathion upon various organic matter adsorbents were compared by determining adsorption isotherms for aqueous insecticide concentrations up to six parts per million. The adsorption isotherms for calcium saturated Romney and Zanesville organic matter, and for hydrogen saturated Romney organic matter are given in Figure 1. For each adsorbent, the adsorptive capacities of parathion were two to three times the adsorptive capacities of carbaryl on a weight basis. Romney organic matter with hydrogen on the exchange sites adsorbs significantly larger amounts of carbaryl and parathion than with calcium on the exchange sites. The water vapor adsorption isotherms of Figure 2 show the hydrogen saturated organic matter to have a greater hydrophobic nature than the calcium saturated organic matter. A similar direct relationship between the hydrophobic nature of the adsorbent surface, and extent of adsorption was found for a carboxyl cation exchange resin with calcium and hydrogen saturation. The solvent water competes much more effectively with the insecticides for adsorption sites on the organic matter surface when the exchangeable ion is calcium rather than hydrogen. It is a general observation that acid soils adsorb much larger amounts of organic pesticides than do neutral or alkaline soils, and varying competition between solvent and solute for adsorption sites at different pH levels is a definite possible explanation for this effect.

Differences in the adsorptive capacities between the organic matter adsorbents derived from different soils were relatively slight. Although functional group analysis showed that the Romney organic matter existed in a higher degree of humification (oxidation) than did the Zanesville organic matter, the total number of oxygen containing functional groups is

Ca Saturated Soil Organic Matter

Legend:
- △ Carbaryl on Romney S.O.M.
- ▲ Carbaryl on Zanesville S.O.M.
- ○ Parathion on Romney S.O.M.
- ● Parathion on Zanesville S.O.M.

Y-axis: mg ADSORBED/gm ORGANIC MATTER

X-axis: EQUILIBRIUM CONCENTRATION µgm/ml

H - Saturated Romney Soil Organic Matter

Legend:
- △ CARBARYL
- ○ PARATHION

Y-axis: mg ADSORBED/gm ORGANIC MATTER
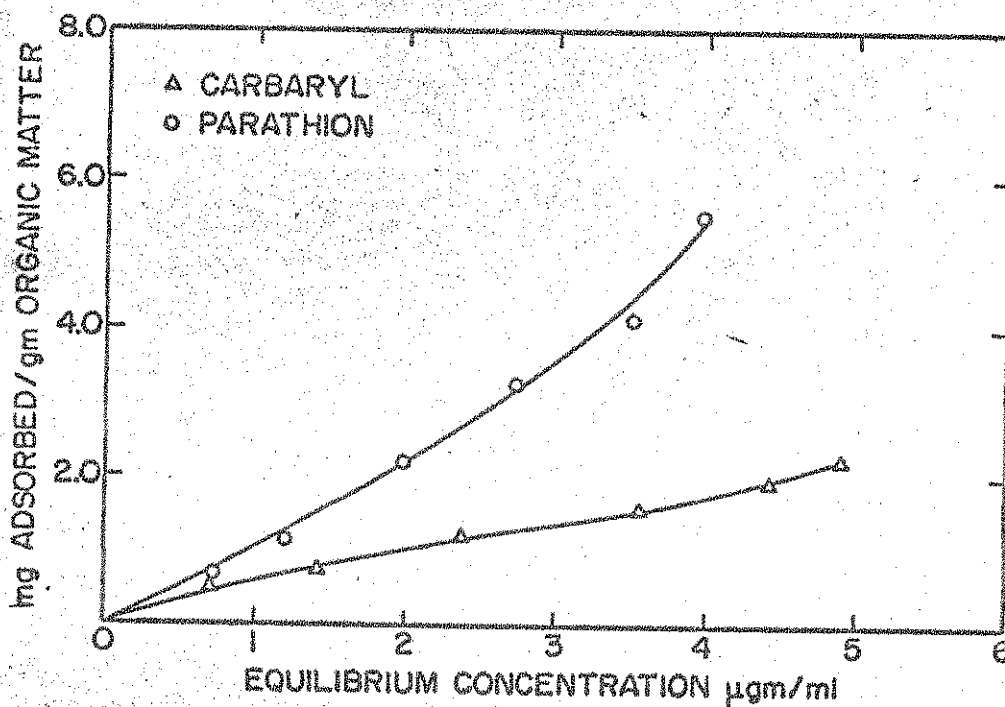
X-axis: EQUILIBRIUM CONCENTRATION µgm/ml

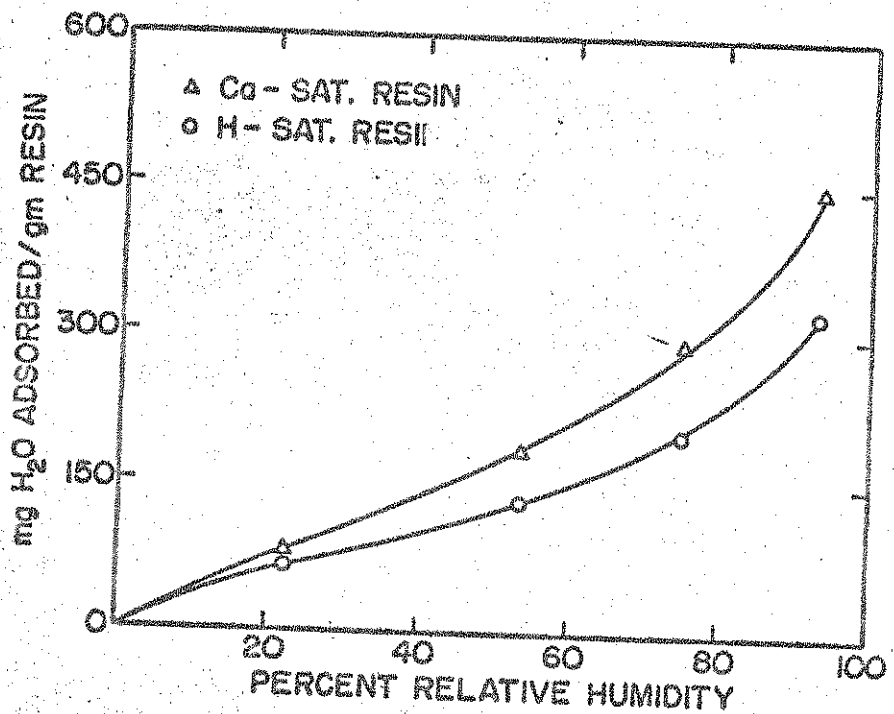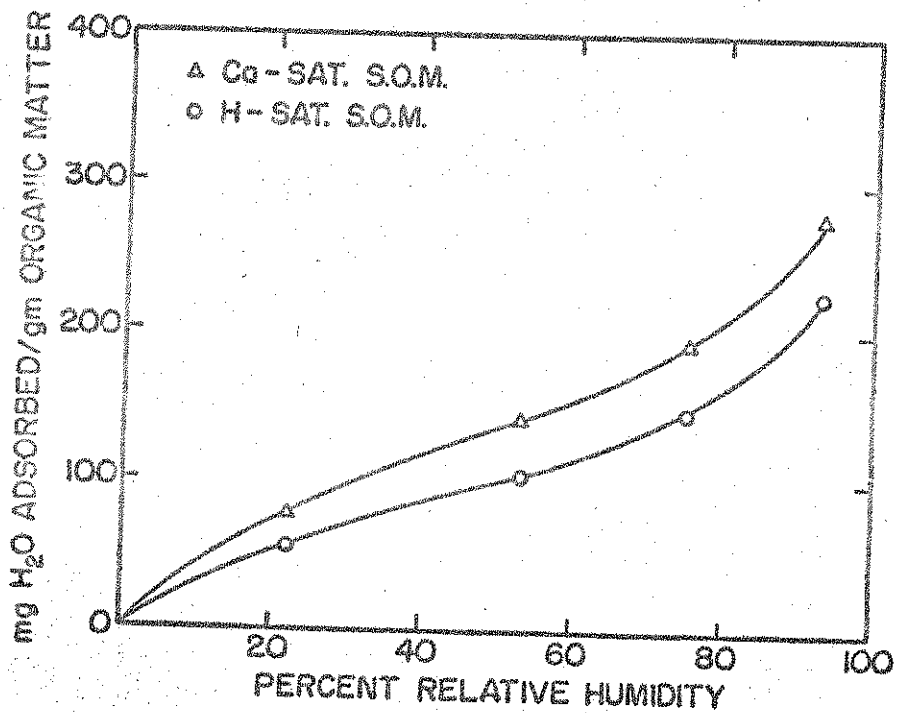Figure 1.   Insecticide adsorption isotherms

Figure 2. Water adsorption isotherms.

the same on both types of organic matter which gives them similar hydrophobic natures. The organic matter derived from the muck soil gave adsorptive capacities similar to the organic matter derived from the two mineral soils; so it is unlikely that the extended treatments removing mineral material from the organic matter preparations had much effect on the adsorptive nature of the organic matter other than making more surface area available for adsorption.

Kinetic studies of carbaryl and parathion adsorption on organic matter adsorbents were conducted at 5, 25 and 40°C. The change of carbaryl and parathion concentrations with time is shown in Figure 3 for the calcium saturated Romney organic matter adsorbent. The shortest time at which adsorption measurements could be obtained was around one minute at which time significant amounts of adsorption had already occurred. Figure 3 shows that the amount of adsorption decreases as temperature increases, but this effect is much more pronounced for carbaryl than for parathion. The differential heat of adsorption calculated from maximum levels of adsorption at the three temperatures by the van't Hoff equation ranges from around 400 cal/g-mole for parathion to about 2,000 cal/g-mole for carbaryl. The greater heat of adsorption for carbaryl may be due to its greater solubility change with temperature change than for parathion.

Since adsorption and desorption are taking place simultaneously in the nonflow system used in this experiment, the rate of adsorption is proportional to the distance of the system from equilibrium. The following equation takes into account both adsorption and desorption in obtaining a rate constant for adsorption (3): $d\phi/dt = 2k(1-\phi) \sinh b(1-\phi)$ where ϕ is the distance from equilibrium as a fraction of initial distance from equilibrium, b is a constant, and k is the rate constant for adsorption when $\phi = 0$. A plot of ϕ vs. time is given in Figure 4 for carbaryl and parathion adsorption on calcium saturated Romney organic matter. The differential $d\phi/dt$ for various values of ϕ from one to fifteen minutes was measured as the slope of the tangent to the plot at certain values of ϕ and t. A computer program was prepared which solved the rate equation
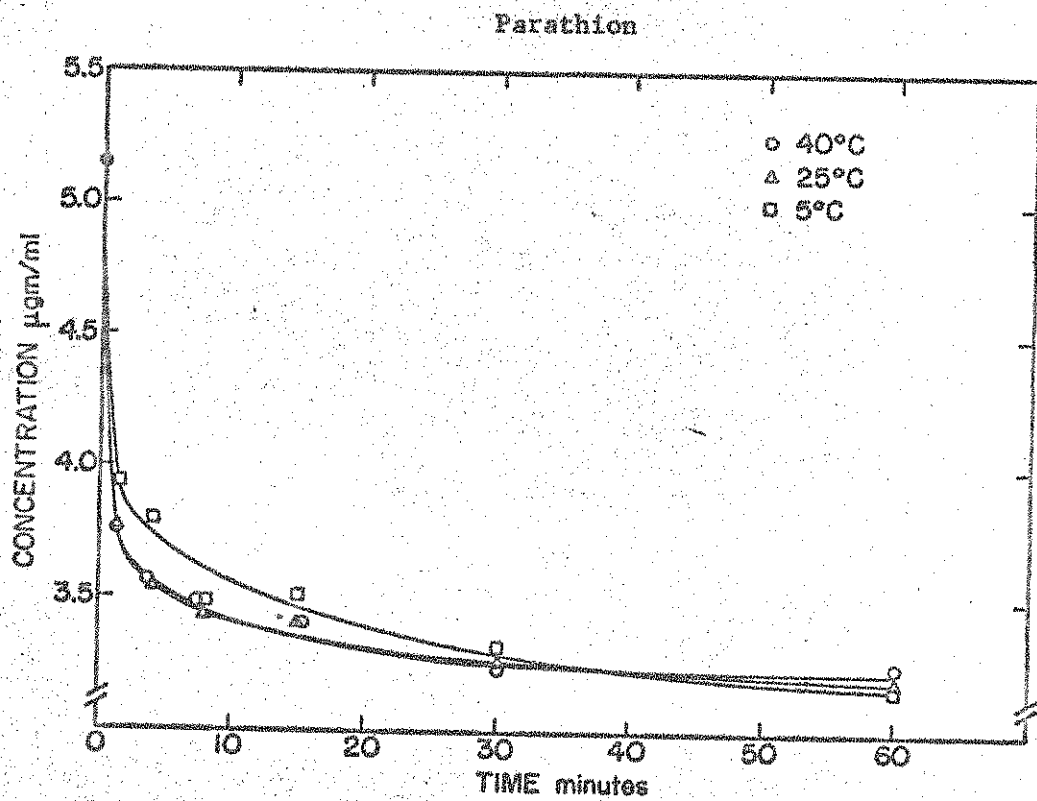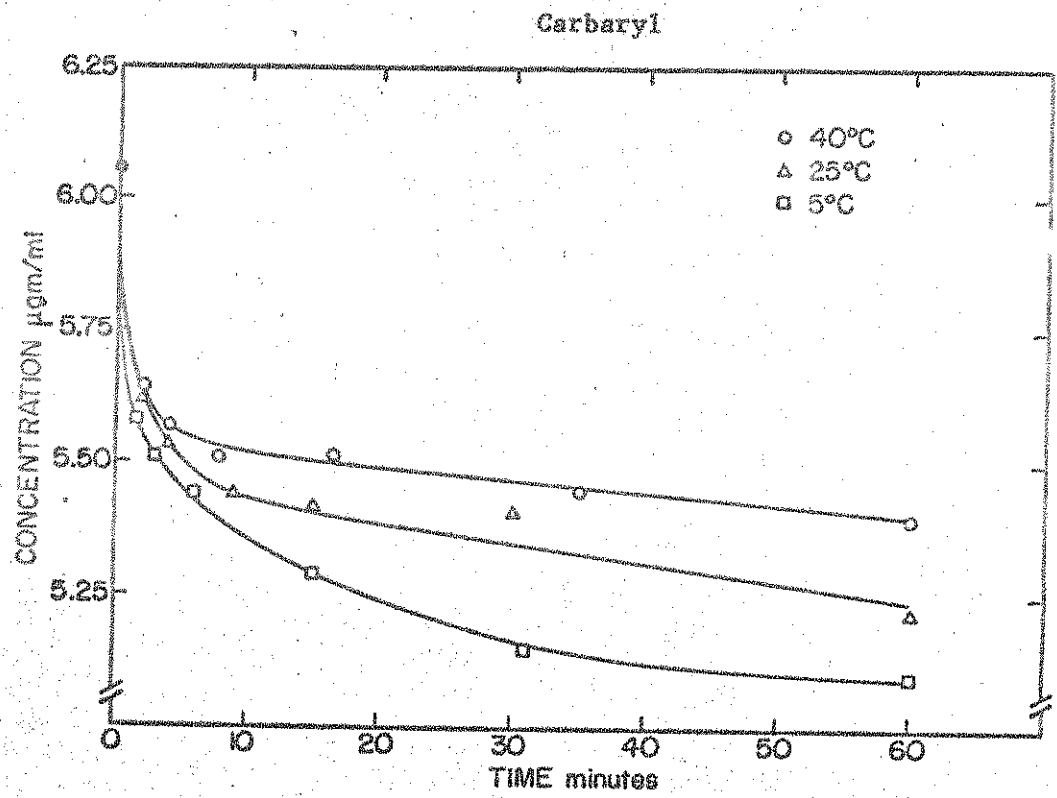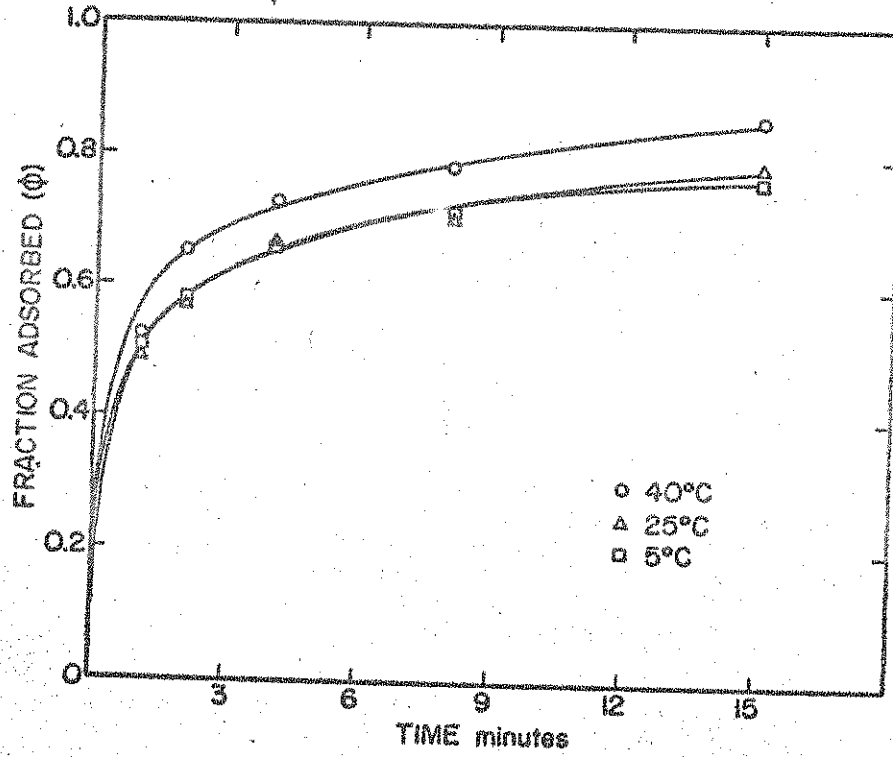
Carbaryl

Parathion

Figure 3. Adsorption as a function of time on Ca saturated Romney soil organic matter.
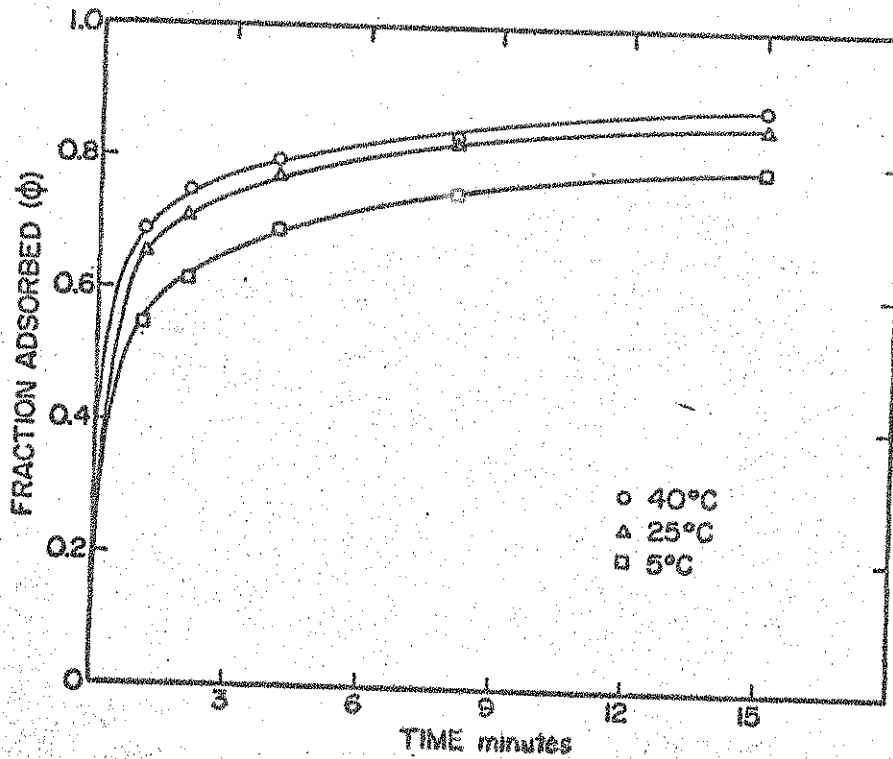
Carbaryl

Parathion

Figure 4. Adsorption as a function of equilibrium versus time on Ca saturated Romney soil organic matter.

for the rate constant k for a series of substituted b values raised in increments of 0.1 from 1 to 10. The variance of k for six known values of $d\phi/dt$ and $1-\phi$ was determined for each b value. The solution of the rate equation was obtained when the ratio of the variance of k over the mean of k reaches a minimum for a certain value of b. For all the soil organic matter adsorbents tested, the order of magnitude of the rate constant was 10^{-4} sec^{-1}, and the rate increased with increases in temperature. The activation energy of adsorption averaged about 4 kcal/mole for soil organic matter adsorbents as determined by the Arrhenius equation. The fastest rates were obtained for organic matter adsorbents which adsorbed the largest amounts of insecticides. The fast adsorption rates and the adsorption activation energy are on the order one would expect from a process where the rate limiting step is diffusion of the adsorbate in solution to the surface of the adsorbent, and adsorption is physical in nature with formation of Van der Waals bonds between hydrophobic portions of the adsorbate molecules and the adsorbent surface in aqueous systems.

For times greater than 10 minutes, adsorption rates were found to depart from a dependence on the concentration of the insecticides in solution. The rate limiting step for the removal of a series of organic pesticides from dilute aqueous solution by porous active charcoal was found to involve intraparticle transport of the solute from exterior adsorption sites into the pores and capillaries of the adsorbent (6). For systems in which intraparticle transport is the rate limiting step, data for uptake of solute from solution should give a linear plot as a function of the square root of time. Figure 5 does indeed show that the adsorption of carbaryl and parathion on calcium saturated Romney organic matter is linear with the square root of time for times greater than 10 minutes. Thus it is reasonable to assume that the rate limiting step in the adsorption process at initial times is diffusion of the solute to the surface of the adsorbent with intraparticle transport of the adsorbate into the interior of the adsorbent becoming the dominant process after 10 minutes. Determinations of adsorption rates on organic matter adsorbents can at best be

Carbaryl
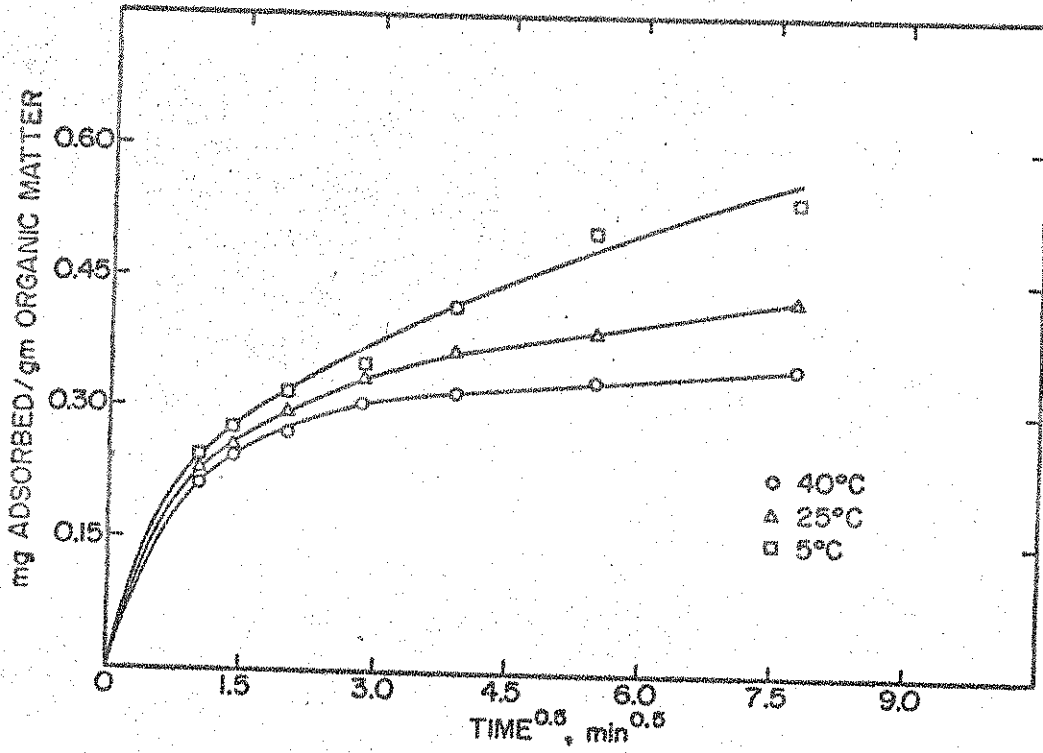
Parathion
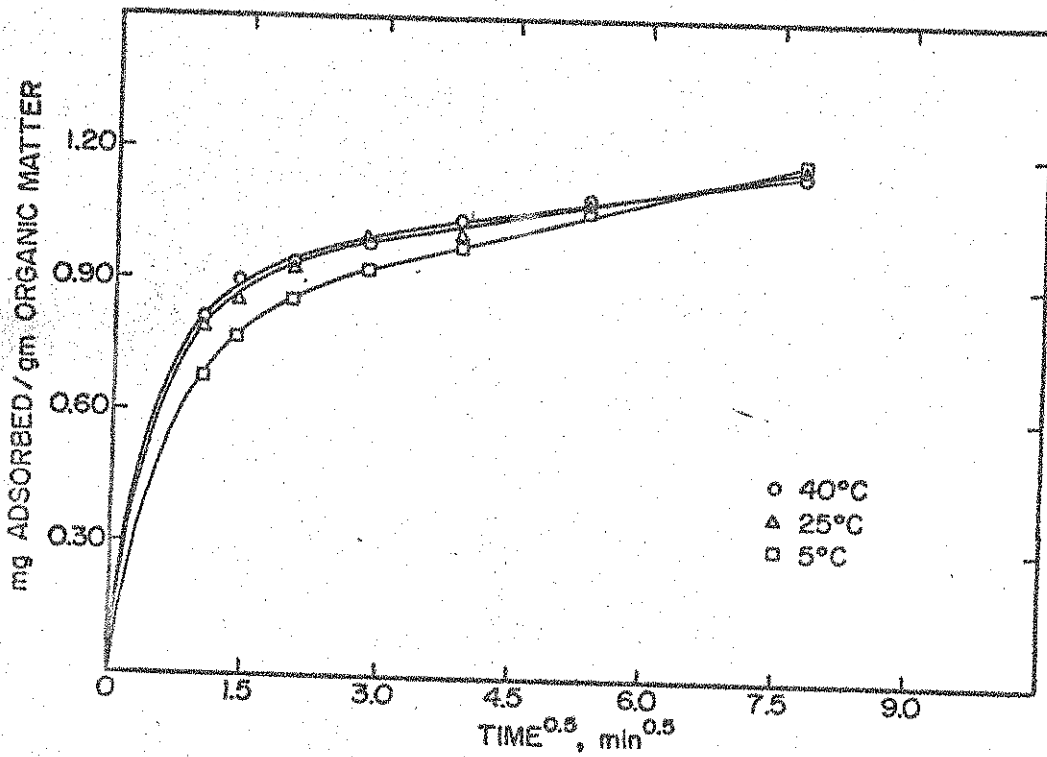
Figure 5. Adsorption as a function of the square root of time on
Ca saturated Romney soil organic matter.

only fair approximations of the actual rates due to the heterogeneous nature
of the organic matter surface where some adsorption sites are more active
than others, the rate limiting step changes with time, and the high
adsorption rates along with interferences by the organic matter adsorbents
causes difficulty in pesticide analysis.

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CHAPTER VI

ACTIVITY AND LOCAL DISTRIBUTION OF SURFACE-ACTIVE
COLLEMBOLA (INSECTA):II. POND-SHORE POPULATIONS

Larry P. Pedigo[*]

Collembola, as a group, are generally limited to environments with
high moisture content. Christiansen (4) stated that near saturated
atmospheres are probably required for most species. The land area
bordering bodies of water often satisfies this requirement and may support
a varied collembolan fauna.

This study, part of a cooperative water resources project, was
initiated to determine the seasonal activity and local distribution of
surface-active collembolan fauna inhabiting a pond shore and to assess
the seasonal activity of these. Information obtained from this research
will be used for future studies of pesticide residues and watershed
relationships.

Previous studies dealing exclusively with shore-inhabiting Collembola
are few. Davenport (6) studied the Collembola of Cold Spring Beach,
located on the north shore of Long Island, and reported three species
present. He described intertidal activity of one, Xenylla humicola
(Fabricius), and discussed reaction of this species to various environ-
mental factors. Haarlov (9) sampled the microarthropod fauna of several
habitats, including a pond and lake shore in Denmark. Fifteen collembolan
species were reported from pond-shore samples, and six species from
lake-shore samples. Based on quotients of similarity, Haarlov indicated
that the pond and lake shores were substantially different in fauna from
other habitats sampled.

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MATERIALS AND METHODS

Characterization of the Study Area

Three ponds located at the Purdue University Southern Indiana
Forage Farm, Dubois County, Indiana, were selected for study. The ponds
were constructed following the establishment of the farm in 1953 and
were bordered, primarily, by unglaciated sandstone-shale soil types.
Pond-peripheral topography was rolling to very steep in some areas, and
each pond was located at the base of a cultivated watershed. Although
ponds were in close proximity to one another (maximum distance approxi-
mately 1000 ft.), they were separated by high ridges at the apex of their
respective watersheds.

The intended watershed crop was alfalfa, Medicago sativa L., but red
clover, Trifolium pratense L., alta fescue, Festuca arundinacea Schreb.,
and buckhorn plantain, Plantago lanceolata L., were also common. Each
pond was separated from its cultivated watershed by a wire fence, inside
of which grasses predominated, almost to the water's edge.

Collembola Sampling

Three sites were selected at each pond for sampling. Selection was
based on watershed drainage intensity and proximity to the pond's edge.
Four stations were established at each pond; two near a trough of
intense watershed drainage, one from a site at the watershed base lacking
intense drainage, and one outside the watershed perimeter. Because of
fluctuating pond levels, all stations were flooded during the first
spring season, which required adding new stations further inland from
the original sites.

Stations were located at the three ponds as follows: Pond A--
stations 1,2,2a,3,4,4a, and 4b; Pond B--stations 5,5a,6,7,7a,7b, and 8;
Pond C--stations 9,10,10a,11,11a, and 12. Stations without a letter
designation were original establishments, located about 9 ft. from the
water's edge with pond at lowest level. Stations with letter designations
were located at greater distances inland (a=stations 15 ft. and b=stations
30 ft. further inland from originals).

Pitfall traps similar to Fichter's (8) were placed at each station
to sample surface-active Collembola. Original pitfalls were operated

where: IV = importance value

      RDI = relative density index

= $\dfrac{\text{number individuals of species captured at station}}{\Sigma \text{ Collembola captured at station}}$

      RF = relative frequency

= $\dfrac{\text{number of sampling periods species was captured}}{\Sigma \text{ periods of capture for all collembolan species}}$

      RD = relative dominance

= $\dfrac{\text{dominance index of species}}{\Sigma \text{ dominance indices for all collembolan species}}$

Dominance index was calculated by computing mean body volume of five of the largest individuals collected and multiplying this by the number collected.

Relative importance values (RIV) were used directly in constellation construction and were calculated for each collembolan species at each station as follows:

$$RIV = \dfrac{\text{IV of species at station}}{\Sigma \text{ IV for all collembolan species at station}}.$$

For constellation construction, the method of Beals (1) was used with the following modifications: (1) AZ axis was constructed using Y axis methodology and (2) the selection of second reference points for Y and Z axes were stations most dissimilar to first reference points, occurring within a 10 percent distance along the X axis of the first Y or Z reference point.

Interpoint distances between stations in the constellation were calculated as: $d = {}^2 + {}^2 + z^2$, where: d = interpoint distance, x, y, z = respective distances between compared stations along the X, Y, and Z axes.

Stations based on plant species sampled were ordinated using the same method as Collembola ordination. Plant population statistics were calculated for each species at each station as follows: density index = Σ points along sampler frame where species was struck (maximum value = 12), frequency = number of frame positions where species was struck at least once $\div$ 4 (maximum value = 1.00), dominance = Σ

species strikes. Relative values were calculated for each statistic by dividing each species valued by the statistic sum for all species at the station.

RESULTS AND DISCUSSION

Collembola Collected

Twenty-seven collembolan species were collected (Table 1). Using Salmon's (14) classification, the species represent all collembolan suborders and the families Hypogastruridae, Tomoceridae, Isotomidae, Entomobryidae, Neanuridae, Poduridae, and Sminthuridae. Two species were previously undescribed. These, B. millsi and P. chandleri, were described and named (12).

The RIV of each species at the stations (Table 1) indicates species prominence. RIV calculations were made from collection data obtained between May 26, 1966, to March 2, 1967 (all 20 pitfalls had been established at the beginning of this period). Species with largest RIV's were: P. flavescens (ΣRIV = 484.74), L.paradoxus (ΣRIV = 230.42), L.near pallidus (ΣRIV = 221.77), I. palustris (ΣRIV = 214.24), H.armata (ΣRIV = 171.77), and H. matura (ΣRIV = 148.22). Four species, D. sp., O. ainsliei, P. unicolor, and P. chandleri had ΣRIV's below 3.00. O. ainsliei and P. unicolor are, most typically, woodland species (11), which accounts for their low values.

Distribution at the stations varied widely among the species (Table 1). O. ainsliei and P. unicolor occurred at only one station. H. armata was restricted to stations at Pond A only, in spite of supposed broad habitational limits (11). Most species had extensive distributions, with the following eight being collected at all stations: I. palustris, L. near pallidus, L. paradoxus, P. flavescens, S. malmgreni, S. aureus, and S. pumilis.

Collembolan Activity and Seasonal Aspection.

Drift (7) concluded that pitfall traps yield information on seasonal activity and local density of surface-active fauna. Collection data obtained in this study were used to assess local distribution, seasonal activity, and relative levels of abundance.

The activity of many species was seasonally restricted, but for other species it was not. The greatest number of species, 25, was active during summer, but surprisingly, 14 species (51.9 percent) were active during winter. Nearly half (48.1 percent) of the species was collected year round.

Five categories of seasonal-activity could be distinguished. Categories, percentage of species, and member species were as follows:

A. Species Active All Season (48.1%)

1. B. millsi
2. E. nivalis
3. H. armata
4. H. matura
5. I. trispinata
6. I. palustris
7. L. near pallidus
8. L. paradoxus
9. P. flavescens
10. P. minuta
11. S. aurcus
12. X. humicola
13. P. aquatica

B. Species Active Spring-Summer-Autumn (25.9%)

1. E. marginata
2. E. purpurascens
3. P. saxatilis
4. P. unicolor
5. S. hyogramme
6. S. pseudassimilis
7. S. trilineatus

C. Species Active Autumn-Winter-Spring (3.7%)

1. S. malmgreni

D. Species Active Spring-Summer (3.7%)

1. O. ainsliei

E. Species Active Summer-Autumn (11.1%)

1. Brachystomella stachi
2. P. petterseni
3. S. pumilis

Species assigned to the seasonal-activity categories were collected in numbers great enough to assure their position within a category. The sporadic collection of small numbers of P. chandleri and D. sp. prevented their assignment.

Mean number of all Collembola collected is shown in Figure 1. The
highest activity peak occurred on June 9, 1966, with a mean of 923 Collembola
per pitfall. Other peaks of less than 400 but more than 200 were recorded
for November 20, 1966, March 12, 1966, July 7, 1966, September 30, 1966,
and February 16, 1967. Greatest depressions occurred on January 28, 1966,
December 8, 1966, and January 19, 1967. These were associated with weekly
mean minimum temperatures of -17.2°C, -12.2°C, and -16.7°C, respectively.
Summer peaks and depressions were not closely associated with precipitation
amounts as in the case of woodland Collembola (13).

Six species, H. armata, H. matura, L. near pallidus, S. aurcus, P.
flavescens, and I. palustris were captured during at least 75 percent of
the collecting periods and contributed substantially to the mean-number
trends of all Collembola collected. Activity trends of the six species
are shown in Figures 1 and 2. Activity of H. armata and H. matura (Fig. 1)
were quite similar with major activity peaks occurring nearly every
season. Peaks of L. near pallidus (Fig. 1) occurred only during late
spring and summer, with activity relatively low during the remainder of
the year.

S. aurcus reached major activity peaks during autumn, winter, and
early spring, with little activity during summer months (Fig. 2).
Activity peaks for P. flavescens occurred in June and October (Fig. 2).
An October peak of I. palustris coincided with that of S. aurcus and P.
flavescens.

Edge-Distance Effect

The yearly wet-dry pond cycle which produced variations in edge
distance as much as 12 feet, caused complete submergence of many lower-
level pitfalls during several months of the year. The pond cycle included
increasing pond levels in December, highest levels in February, decreasing
levels in April, and lowest levels in August.

Although the effects of edge distance on numbers of each major
species was considered, a meaningful pattern only occurred with H. armata.
This species was observed in large numbers on the Pond A water surface
and was collected as far as 35 feet from the water's edge. Numbers of
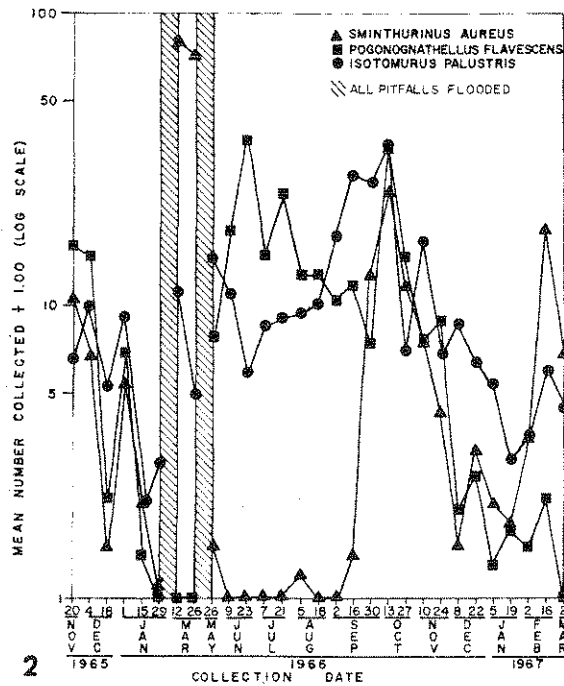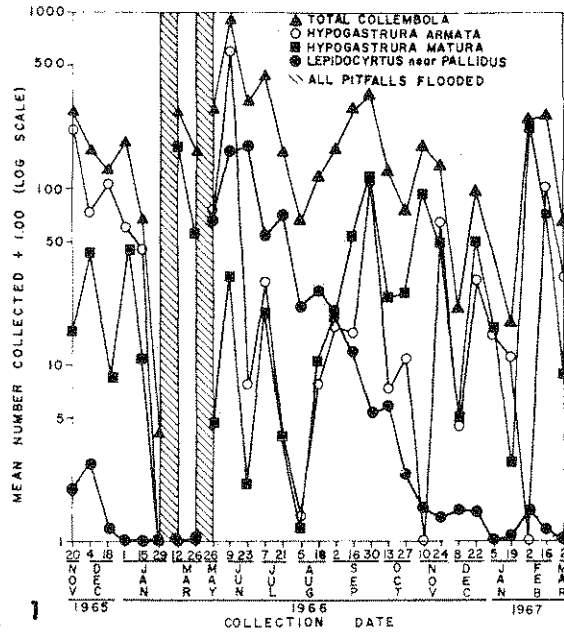H. armata collected at stations 2, 2a, and 3, and distance are shown in

FIG. 1.—Mean numbers of all Collembola, *H. armata*, and *L.* sp., near *pallidus* collected per pitfall during the study.

FIG. 2.—Mean numbers of *S. aureus*, *P. flavescens*, and *I. palustris* collected per pitfall during the study.
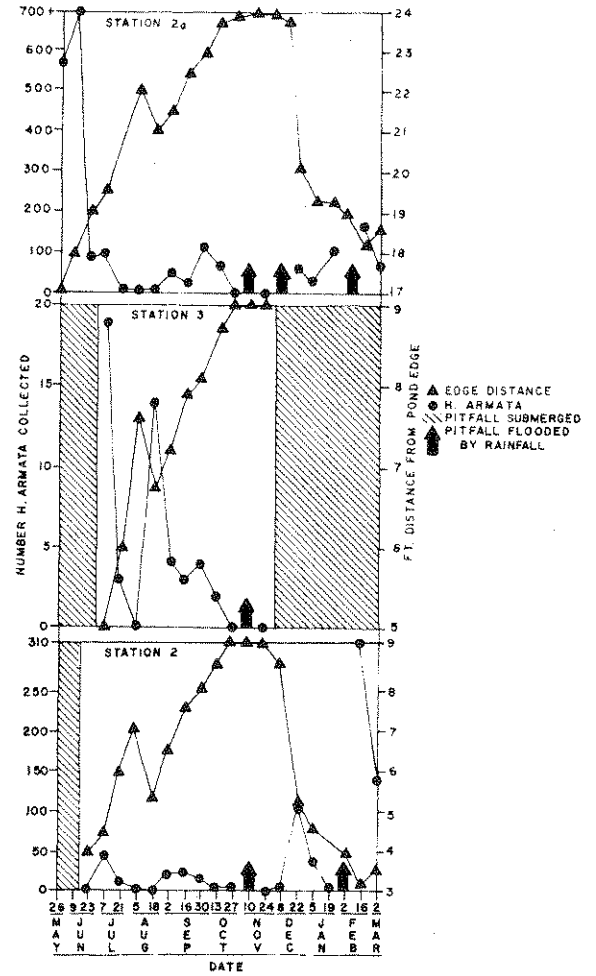
FIG. 3.—Numbers of *H. armata* collected at stations 2a, 3, and 2 with coinciding edge-distance measures.

Figure 3. Although the number of individuals collected varied greatly among the stations, the relationship of numbers to edge distance was similar at each station, i.e. the number collected was inversely related to edge distance.

It is believed that H. armata either moved freely from water surface to shore during normal activities or was accidentally washed ashore. In either case, lesser edge distances provided greater chance of capture. Factors other than edge distance were involved, however, because of the large differential in numbers collected at these stations. This effect did not occur at stations 4, 4a, and 4b, since these were located on a relatively steep slope, introducing an additional variable. Edge-distance effects on station 1 could not be determined because of continued submergence in the pond and flooding of the pitfall by rain.

Collembola Ordination

The collembolan ordination constellation is shown in Figure 4 as three two-dimensional views. Axes represent relative units of station dissimilarity based on RIV of each species (Table 1), and planes present different aspects of the constellation (Y to X plane = front aspect, Z to X plane = top aspect, Y to Z plane = side aspect).

In the constellation, a notable distribution is shown by stations of Pond A. All stations at Ponds B and C are clustered in the upper right corner in each of the planes, indicating considerable homogeneity in fauna. However, stations of Pond A are dispersed, with station 1, the most dissimilar, having an interpoint distance of 100.38 units from the closest station of another pond.

The Z axis to X axis plane shows the dispersed distribution of Pond A stations best. Notable, station 3 is the only Pond A station to occur within the Pond B-Pond C cluster, and a diagonal gradient, terminating at station 1, is present. An inspection of species RIV at the Pond A stations offers an explanation of station distribution.

At three Pond A stations, 1, 2a, and 4, H. armata had the largest RIV of the species collected at those stations (Table 1). H. armata RIV was substantially less at the remaining Pond A stations, and as mentioned previously, the species was not collected at Pond B or C stations.

By superimposing various size dots, representing H. armata RIV, on the Z to X plane of the Collembola constellation, a definite pattern was observed (Fig. 5). In Figure 5, larger dots, indicating greater RIV, are located in the lower left corner, and dot size decreases when moving up the gradient (open circles represent no occurrence). Kendall's tau coefficient was computed between rankings of stations based on H. armata RIV and position along the gradient (same ranking is obtained using either X or Z axis positions). Results showed a correlation of +0.81 (P<.01). It was thus believed that H. armata was most responsible for the distribution of Pond A stations in the constellation.

The reason for the restricted occurrence of H. armata is unknown. It is hypothesized that the species reached the pond from adjacent woodlands, and movement to other ponds was prevented by moisture barriers created by high ridges surrounding the pond. Ponds B and C were not near wooded areas.

Analysis of Vegetational Relationship

Plant species sampled and their RIV at the stations are listed in Table 2. F. arundinacea a cultured species growing inside the wire fence at each pond, was most prominent. Many species had a low ΣRIV, being less than 5.00 for L. serriola and O. europaea.

Three planes of the plant ordination constellation are shown in Figure 6. The Y to X and Z to X planes show a cluster to the left, a space, and a cluster to the right. Stations to the left had more floral variety, were generally closest to the pond edge, and were submerged part of the year. Most of the stations in the right cluster were less varied in flora and were further from the pond edge. In the Z to Y plane, side aspect, the space between clusters is obscured.

When comparing the plant constellation (Fig. 6) with the Collembola constellation (Fig. 4), a great difference is seen. The pond clustering shown with the Collembola is replaced by a general site clustering with the plants. This indicated that the plants were more restricted to a given location, while Collembola, as mobile organisms, could move to areas of favored environment with brief temporal changes. Thus, T. latifolia, an emergent, was never found on a dry slope, whereas H. armata, a species observed on the pond surface, was also captured at drier locations,
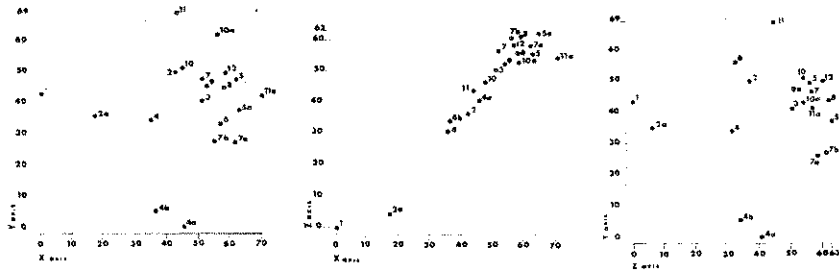
FIG. 4.—Planes of the Collembola ordination constellation.
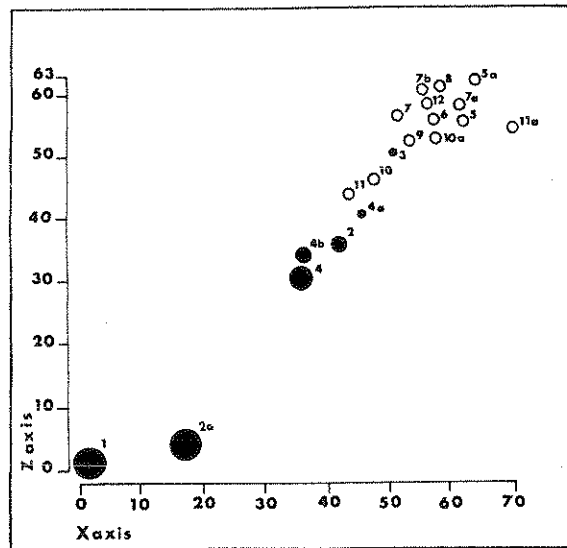
FIG. 5.—Top aspect of the Collembola ordination constellation with black dot size representing magnitude of *H. armata* relative importance values.
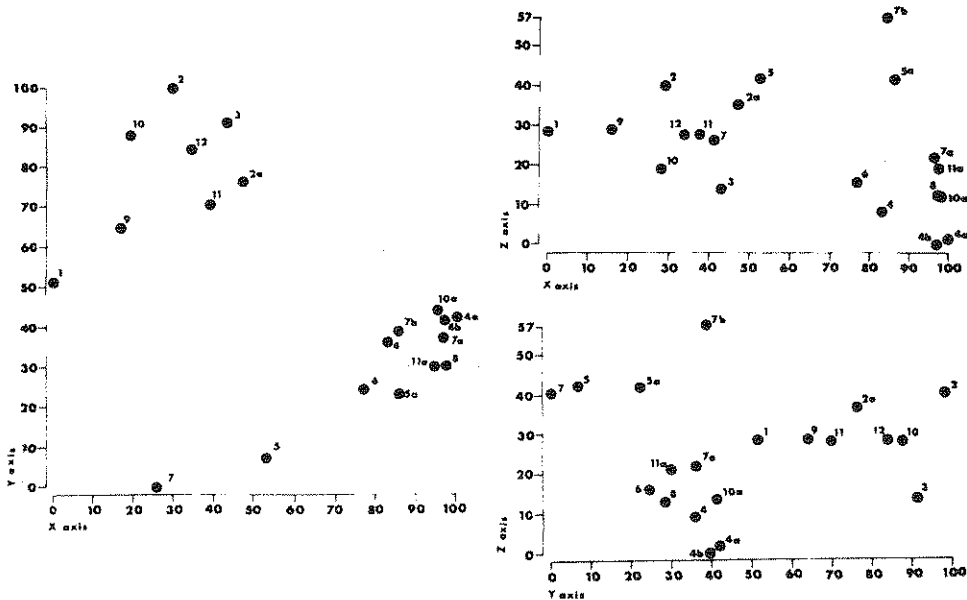
FIG. 6.—Planes of the plant ordination constellation.

especially following rains. When drier conditions resumed at these stations, it was possible for this species to move nearer the pond's edge. Thus, since most Collembola were collected in a variety of vegetational types, the particular species composition of the plant communities had little influence on numbers or activity of surface-active Collembola.

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Table 1. Relative importance values (RIV) of Collembola.

SPECIES	STATION			
	1	2	2a	3
Bourletiella millsi Pedigo	0.80	0.72	0.69	--
Brachystomella stachi Mills	2.62	--	--	--
Deuterosminthurus sp.	0.83			
Entomobrya griseo-olivata (Packard)	--	--	0.37	--
E. nivalis (Linne)	--	--	0.64	--
Entomobryoides purpurascens (Packard)	--	--	0.32	--
Hypogastrura armata (Nicolet)	50.99	16.76	50.90	6.39
H. matura (Folsom)	1.76	1.25	2.39	--
Isotoma trispinata MacGillivray	--	12.04	1.62	7.83
Isotomurus palustris (Muller)	15.24	8.91	3.82	11.47
Lepidocyrtus near pallidus (Reuter)	4.52	6.03	5.70	15.53
L. paradoxus Uzel	1.76	7.33	7.69	11.30
Orchesella ainsliei Folsom	--	--	--	--
Podura aquatica Linne	--	0.58	0.32	2.35
Pogonognathellus flavescens (Tullberg)	8.40	27.90	16.51	33.22
Proisotoma minuta (Tullberg)	--	0.31	--	--
Pseudachorutes saxatilis MacNamara	--	0.31	0.39	--
Pseudobourletiella chandleri Pedigo	--	--	--	--
Pseudosinella violenta (Folsom)	--	0.94	--	--
Ptenothrix unicolor (Harvey)	--	--	1.86	--
Sminthurides hyogramme Pedigo	--	2.68	0.31	--
S. malmgreni (Tullberg)	3.62	2.34	1.16	2.43
S. pseudassimilis Stach	5.21	2.84	0.62	2.92
Sminthurinus aureus (Lubbock)	2.59	4.10	1.33	1.78
Sminthurus trilineatus (Banks)	--	1.48	1.46	0.65
Sphaeridia pumilis (Krausbauer)	1.63	3.51	0.62	4.13
Xenylla humicola (Fabricius)	--	--	1.25	--

Table 1. Relative importance values (RIV) of Collembola.

SPECIES	STATION			
	4	4a	4b	5
Bourletiella millsi Pedigo	0.31	3.80	0.90	2.04
Brachystomella stachi Mills	1.20	0.60	--	0.31
Deuterosminthurus sp.	0.30	0.60	0.27	--
Entomobrya griseo-olivata (Parkard)	--	--	--	0.30
E. nivalis (Linne)	--	0.62	--	--
Entomobryoides purpurascens (Packard)	1.27	2.57	4.14	--
Hypogastrura armata (Nicolet)	25.19	5.59	15.95	--
H. matura (Folsom)	5.65	2.87	5.30	7.50
Isotoma trispinata MacGillivray	0.30	--	0.27	2.61
Isotomurus palustris (Muller)	7.40	5.43	6.07	8.16
Lepidocyrtus near pallidus (Reuter)	12.39	29.16	23.76	5.71
L. paradoxus Uzel	10.40	30.19	22.02	8.79
Orchesella ainsliei Folsom	--	2.93	--	--
Podura aquatica Linne	0.66	--	--	3.97
Pogonognathellus flavescena (Tullberg)	19.90	7.53	7.94	38.02
Proisotoma minuta (Tullberg)	--	1.14	2.71	4.54
Pseudachorutes saxatilis MacNamara	0.34	1.21	1.15	2.17
Pseudobourletiella chandleri Pedigo	--	0.64	0.30	--
Pseudosinella violenta (Folsom)	0.93	--	0.58	1.65
Ptenothrix unicolor (Harvey)	--	--	--	--
Sminthurides hyogramme Pedigo	2.23	--	--	0.27
S. malmgreni (Tullberg)	1.82	1.11	1.40	3.15
S. pseudassimilis Stach	2.46	0.56	--	3.09
Sminthurinus aureus (Lubbock)	1.69	0.66	2.76	4.00
Sminthurus trilineatus (Banks)	2.78	1.62	3.81	1.02
Sphaeridia pumilis (Krausbauer)	2.78	0.56	0.66	2.44
Xenylla humicola (Fabricius)	--	0.60	--	0.27

Table 1. Relative importance values (RIV) of Collembola.

SPECIES	STATION			
	5a	6	7	7a
Bourletiella millsi Pedigo	4.03	1.17	0.47	2.02
Brachystomella stachi Mills	0.32	--	1.83	1.52
Deuterosminthurus sp.	--	--	--	--
Entomobrya griseo-olivata (Packard)	1.50	--	0.56	0.55
E. nivalis (Linne)	--	--	--	--
Entomobryoides purpurascens (Packard)	--	--	1.65	5.52
Hypogastrura armata (Nicolet)	--	--	--	--
H. matura (Folsom)	18.26	5.37	8.54	16.01
Isotoma trispinata MacGillivray	0.73	2.53	--	0.56
Isotomurus palustris (Muller)	8.48	9.72	14.20	4.89
Lepidocyrtus near pallidus (Reuter)	13.26	12.31	9.17	23.53
L. paradoxus Uzel	7.45	21.68	9.98	12.67
Orchesella ainsliei Folsom	--	--	--	--
Podura aquatica Linne	--	--	0.51	--
Pogonognathellus flavescens (Tullberg)	31.31	27.45	29.16	18.77
Proisotoma minuta (Tullberg)	0.28	0.61	0.47	0.25
Pseudachorutes saxatilis MacNamara	3.30	1.76	1.09	2.54
Pseudobourletiella chandleri Pedigo	--	--	--	--
Pseudosinella violenta (Folsom)	0.84	0.56	0.99	1.34
Ptenothrix unicolor (Harvey)	--	--	--	--
Sminthurides hyogramme Pedigo	0.56	--	3.30	0.52
S. malmgreni (Tullberg)	2.15	0.62	2.53	2.84
S. pseudassimilis Stach	--	3.84	6.96	--
Sminthurinus aureus (Lubbock)	4.50	2.46	1.90	2.55
Sminthurus trilineatus (Banks)	0.90	1.54	--	--
Sphaeridia pumilis (Krausbauer)	1.58	8.37	6.03	1.75
Xenylla humicola (Fabricius)	0.55	--	0.94	2.16

Table 1.   Relative importance values (RIV) of Collembola.

SPECIES	STATION			
	7b	8	9	10
Bourletiella millsi Pedigo	2.59	3.10	--	1.16
Brachystomella stachi Mills	0.41	0.93	--	--
Deuterosminthurus sp.	--	0.80	--	--
Entomobrya griseo-olivata (Packard)	2.92	0.28	--	1.53
E. nivalis (Linne)	--	2.98	--	--
Entomobryoides purpurascens (Packard)	3.07	0.29	--	--
Hypogastrura armata (Nicolet)	--	--	--	--
H. matura (Folsom)	12.72	34.96	0.71	1.51
Isotoma trispinata MacGillivray	0.30	--	2.98	2.79
Isotomurus palustris (Muller)	11.87	7.58	15.05	26.38
Lepidocyrtus near pallidus (Reuter)	15.20	6.78	7.15	8.71
L. paradoxus Uzel	13.75	4.31	14.16	8.38
Orchesella ainsliei Folsom	--	--	--	--
Podura aquatica Linne	0.30	0.49	0.71	--
Pogonognathellus flavescens (Tullberg)	9.14	25.46	35.85	29.31
Proisotoma minuta (Tullberg)	0.92	1.19	--	--
Pseudachorutes saxatilis MacNamara	4.19	0.85	--	0.73
Pseudobourletiella chandleri Pedigo	0.33	--	--	--
Pseudosinella violenta (Folsom)	0.92	0.27	--	--
Ptenothrix unicolor (Harvey)	--	--	--	--
Sminthurides hyogramme Pedigo	--	--	--	--
S. malmgreni (Tullberg)	2.84	1.08	2.92	3.53
S. pseudassimilis Stach	--	2.17	11.25	8.73
Sminthurinus aureus (Lubbock)	3.19	4.80	0.71	0.72
Sminthurus trilineatus (Banks)	--	--	0.82	--
Sphaeridia pumilis (Krausbauer)	2.61	1.68	7.69	6.40
Xenylla humicola (Fabricius)	12.71	--	--	--

Table 1. Relative importance values (RIV) of Collembola.

SPECIES	STATION			
	10a	11	11a	12
Bourletiella millsi Pedigo	5.26	0.30	3.04	--
Brachystomella stachi Mills	--	1.01	--	1.58
Deuterosminthurus sp.	--	--	--	--
Entomobrya griseo-olivata (Packard)	2.21	0.62	2.32	0.85
E. nivalis (Linne)	0.27	0.31	2.37	--
Entomobryoides purpurascens (Packard)	0.88	0.67	1.58	--
Hypogastrura armata (Nicolet)	--	--	--	--
H. matura (Folsom)	5.55	3.48	11.38	13.01
Isotoma trispinata MacGillivray	1.44	9.95	2.91	1.30
Isotomurus palustris (Muller)	15.01	13.87	6.75	13.94
Lepidocyrtus near pallidus (Reuter)	6.39	4.23	3.50	8.74
L. paradoxus Uzel	12.25	4.89	12.21	9.21
Orchesella ainsliei Folsom	--	--	--	--
Podura aquatica Linne	0.28	28.11	0.90	2.61
Pogonognathellus flavescens (Tullberg)	27.64	19.30	34.81	37.09
Proisotoma minuta (Tullberg)	2.02	--	0.25	--
Pseudachorutes saxatilis MacNamara	1.51	0.93	0.47	2.43
Pseudobourletiella chandleri Pedigo	0.28	--	--	--
Pseudosinella violenta (Folsom)	0.27	1.52	0.45	2.15
Ptenothrix unicolor (Harvey)	--	--	--	--
Sminthurides hyogramme Pedigo	0.28	--	0.93	--
S. malmgreni (Tullberg)	5.69	3.00	1.40	2.36
S. pseudassimilis Stach	1.15	3.35	1.15	0.65
Sminthurinus aureus (Lubbock)	4.82	1.55	3.78	1.31
Sminthurus trilineatus (Banks)	2.17	--	1.00	--
Sphaeridia pumilis (Krausbauer)	2.74	2.00	1.92	2.12
Xenylla humicola (Fabricius)	1.87	0.91	6.82	0.65

Table 2. Relative importance values (RIV) of plant species.

SPECIES	STATION			
	1	2	2a	3
Achillea millefolium L.	--	--	--	--
Agrostis alba L.	--	--	--	8.51
Ambrosia trifida L.	--	--	--	--
Asclepias syriaca L.	--	--	4.71	--
Dactylis glomerata L.	--	--	--	--
Daucus carota L.	--	--	--	--
Diospyros virginana L.	--	--	9.42	--
Eleocharis obtusa Willd.	33.30	--	--	--
Eupatorium perfoliatum L.	9.17	--	--	--
Festuca arundinacea Schreb.	--	--	12.75	--
Lactuca serriola L.	--	--	--	--
Medicago sativa L.	--	--	--	--
Oxalis europaea Jord.	--	--	4.85	--
Phalaris arundinacea L.	16.30	71.97	44.39	82.40
Phleum pratense L.	--	--	--	--
Plantago cordata Lam	--	--	--	--
P. lanceolata L.	--	--	--	--
Poa. sp.	--	--	--	--
Rubus flagellaris L.	--	7.01	4.85	--
Rumex crispus L.	--	--	--	--
Salix sp.	--	--	--	9.09
Scirpus atrovirens Willd.	33.04	--	--	--
Solanum carolinense L.	--	7.01	--	--
Solidago sp.	--	--	14.13	--
Trifolium pratense L.	--	--	--	--
Typha latifolia L.	8.19	7.01	--	--
Vernonia altissima Nutt.	--	7.01	5.19	--

Table 2. Relative importance values (RIV) of plant species.

SPECIES	STATION			
	4	4a	4b	5
Achillea millefolium L.	--	--	--	--
Agrostis alba L.	7.04	24.87	29.12	--
Ambrosia trifida L.	--	--	--	--
Asclepias syriaca L.	--	--	--	4.24
Dactylis glomerata L.	--	--	--	--
Daucus carota L.	14.15	--	--	5.08
Diospyros virginana L.	--	--	--	--
Eleocharis obtusa Willd.	7.04	--	--	--
Eupatorium perfoliatum L.	--	--	--	--
Festuca arundinacea Schreb.	64.81	74.13	61.40	12.14
Lactuca serriola L.	--	--	--	4.24
Medicago sativa L.	--	--	9.48	--
Oxalis europaea Jord.	--	--	--	--
Phalaris arundinacea L.	--	--	--	--
Phleum pratense L.	--	--	--	21.98
Plantago cordata Lam.	--	--	--	--
P. lanceolata L.	--	--	--	--
Poa. sp.	--	--	--	8.49
Rubus flagellaris L.	--	--	--	--
Rumex crispus L.	--	--	--	--
Salix sp.	--	--	--	--
Scirpus atrovirens Willd.	--	--	--	8.49
Solanum carolinense L.	--	--	--	--
Solidago sp.	--	--	--	19.80
Trifolium pratense L.	--	--	--	15.55
Typha latifolia L.	7.04	--	--	--
Vernonia altissima Nutt.	--	--	--	--

Table 2. Relative importance values (RIV) of plant species.

SPECIES	STATION			
	5a	6	7	7a
Achillea millefolium L.	--	--	5.81	--
Agrostis alba L.	7.23	--	--	--
Ambrosia trifida L.	--	--	--	--
Asclepias syriaca L.	--	--	--	--
Dactylis glomerata L.	--	--	--	--
Daucus carota L.	--	--	--	--
Diospyros virginana L.	--	--	--	--
Eleocharis obtusa Willd.	--	--	5.81	--
Eupatorium perfoliatum L.	--	--	--	--
Festuca arundinacea Schreb.	40.39	57.28	7.09	71.07
Lactuca serriola L.	--	--	--	--
Medicago sativa L.	--	--	--	--
Oxalis europaea Jord.	--	--	--	--
Phalaris arundinacea L.	14.16	--	8.37	--
Phleum pratense L.	--	--	--	--
Plantago cordata Lam.	--	--	--	--
P. lanceolata L.	--	--	--	9.65
Poa. sp.	--	5.17	9.05	--
Rubus flagellaris L.	18.36	--	--	9.65
Rumex crispus L.	--	5.17	--	--
Salix sp.	--	--	12.89	--
Scirpus atrovirens Willd.	--	14.63	36.80	--
Solanum carolinense L.	--	--	--	--
Solidago sp.	7.25	12.57	--	--
Trifolium pratense L.	12.64	5.17	14.17	9.65
Typha latifolia L.	--	--	--	--
Vernonia altissima Nutt.	--	--	--	--

Table 2. Relative importance values (RIV) of plant species.

SPECIES	STATION			
	7b	8	9	10
Achillea millefolium L.	--	--	--	--
Agrostis alba L.	--	--	--	--
Ambrosia trifida L.	--	--	--	--
Asclepias syriaca L.	--	--	--	--
Dactylis glomerata L.	31.82	--	--	--
Daucus carota L.	--	--	--	--
Diospyros virginana L.	--	--	--	--
Eleocharis obtusa Willd.	--	--	--	31.78
Eupatorium perfoliatum L.	--	--	--	--
Festuca arundinacea Schreb.	43.31	88.75	5.72	5.85
Lactuca serriola L.	--	--	--	--
Medicago sativa L.	--	--	--	--
Oxalis europaea Jord.	--	--	--	--
Phalaris arundinacea L.	--	--	35.92	55.85
Phleum pratense L.	8.96	--	--	--
Plantago cordata Lam.	--	--	--	6.52
P. lanceolata L.	--	--	--	--
Poa. sp.	--	--	5.13	--
Rubus flagellaris L.	15.91	--	--	--
Rumex crispus L.	--	--	--	--
Salix sp.	--	--	5.13	--
Scirpus atrovirens Willd.	--	--	42.97	--
Solanum carolinense L.	--	--	--	--
Solidago sp.	--	--	--	--
Trifolium pratense L.	--	11.25	--	--
Typha latifolia L.	--	--	5.13	--
Vernonia altissima Nutt.	--	--	--	--

Table 2. Relative importance values (RIV) of plant species.

SPECIES	STATION			
	10a	11	11a	12
Achillea millefolium L.	--	--	--	--
Agrostis alba L.	--	--	--	--
Ambrosia trifida L.	11.90	7.44	--	--
Asclepias syriaca L.	--	--	--	--
Dactylis glomerata L.	--	--	--	--
Daucus carota L.	--	--	--	--
Diospyros virginana L.	--	--	--	--
Eleocharis obtusa Willd.	--	31.11	--	7.90
Eupatorium perfoliatum L.	--	--	--	--
Festuca arundinacea Schreb.	88.10	28.33	89.19	11.71
Lactuca serriola L.	--	--	--	--
Medicago sativa L.	--	--	--	--
Oxalis europaea Jord.	--	--	--	--
Phalaris arundinacea L.	--	25.67	--	64.60
Phleum pratense L.	--	--	10.81	--
Plantago cordata Lam.	--	--	--	--
P. lanceolata L.	--	--	--	--
Poa. sp.	--	--	--	--
Rubus flagellaris L.	--	--	--	--
Rumex crispus L.	--	--	--	--
Salix sp.	--	7.44	--	7.90
Scirpus atrovirens Willd.	--	--	--	--
Solanum carolinense L.	--	--	--	--
Solidago sp.	--	--	--	--
Trifolium pratense L.	--	--	--	--
Typha latifolia L.	--	--	--	7.90
Vernonia altissima Nutt.	--	--	--	--

CHAPTER VII

COMPOSITION AND DYNAMICS OF ODONATA POPULATIONS IN FARM POND ECOSYSTEMS

Vinnedge M. Lawrence[*]

Although Odonata are a major factor in preserving the balance of insect life in ponds (11) many aspects of their aquatic-stage biology are not known. Few studies have been conducted on a year-around basis and most have not employed effective sampling techniques. In analyzing techniques of benthic sampling Cummins (2) stressed the relationship between benthic invertebrate distribution and the nature of the substrate. The influence of this relationship on the evolution of Odonata naiads was recognized by Wright (14) when he separated them into five groups according to the type of substrate inhabited, and characterized each group morphologically. Superimposed upon these substrate adaptations are differences in feeding behavior which Pritchard (10) associated with the microhabitats occupied by various genera. Corbet (1) cited changes in corresponding brain centers between stream-dwelling and pond-dwelling naiads and even between surface-dwelling and bottom-dwelling pond species, and correlated these with differences observed in feeding behavior.

Substrate relationships are complicated by the tendency of naiads of a given species to occupy different microhabitats during their development. Lieftinck (7) reported that young Procordulia artemis naiads displayed active behavior with restless wanderings whereas later instars became more sluggish with older individuals remaining stationary under debris for many days. Kormondy (4) found Tetragoneuria cynosura naiads rather lethargic, living in shallow water near shore throughout their development, but noted decreasing activity and a tendency to burrow in later instars. In temperate regions older naiads of several species move to deeper and more sheltered situations during winter (1).

This study was designed to sample the Odonata populations of three southern Indiana farm ponds intensively enough to determine their species compositions and dynamics through an annual cycle.

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SURVEY SITES AND PROCEDURES

Study Ponds

Three ponds were selected for study on the Purdue University Southern
Indiana Forage Farm, a 1016-acre agricultural field laboratory in
Columbia Township, Dubois County, Indiana. The ponds bordered a 40-acre
field used in the production of forage for a dairy herd and were identified
as A, B, and C according to decreasing surface area. The sampling period
extended from June 1966 through October 1967.

Pond A was constructed in September 1955, is located on the north-
westerly perimeter of the field area, has a surface area of approximately
0.97 acres and a maximum depth of 3.5 meters. The pond has steep sides
only along its earth dam and over 80% of its area is less than three meters
in depth. Dominant in the emergent vegetation are the common cattail
(Typha latifolia) and narrow-leaved cattail (T. angustifolia). The pond
has been stocked with bluegill (Lepomis macrochirus) and largemouth bass
(Micropterus salmoides).

Pond B was constructed in June 1956, is on the southeastern margin
of the field area, and reaches five meters in depth. Its embankments are
steep and over one-third of its area exceeds three meters in depth. The
common cattail is the dominant emergent plant species. Bluegill and
crappie (Pomoxis sp.) occur in the pond but no bass have been stocked.

Pond C was constructed in 1954, is near the northeastern boundary
of the field area, and reaches 3.6 meters in depth although over 80% of
its area is less than three meters deep. It has few shallow areas as
its depth increases rapidly up to two meters. A heavy growth of common
cattail nearly surrounds the pond, and pondweed and algae cover large
areas of its surface in spring and summer. Bluegill and largemouth bass
have been stocked.

Catamarans

Three catamarans were constructed for use in sampling the ponds
through the modification of plans for a craft described by Laun (5,6).
The deck of each raft was 6' x 10' and featured a 2' x 3' opening placed
two feet from one end. A flange was anchored near the center of the deck,
one foot from the edge of the opening. An inverted "V"-shaped upright

was mounted at the end farthest from the opening, and along each side were placed rails rising eight inches from the surface. Each deck was supported by two pontoons of Dow Styrofoam BB buoyancy billets, each 10" x 20" x 10', enclosed on the sides by pine sheeting and above and below by pine slats. The buoyancy rating thus obtained was over 1530 pounds.

Each catamaran was equipped with two sieves, each consisting of a metal screen and wooden frame. In operation the sieve with 1/8"-mesh hardware cloth was placed over that with 16-mesh screen and the combination was placed over the deck opening. Samples were deposited on the hardware cloth and rinsed with pails of water until the organisms were separated from the substrate and debris. The location of the opening between the pontoons precluded any obstruction to the discarding of substrate materials.

The low displacement of water by the pontoons enabled the catamarans to penetrate well into emergent vegetation and facilitated sampling the shallow peripheries of the ponds.

Sampling Devices

Dredges

A Foerst-Petersen dredge and a 9" Ekman dredge were employed in sampling the pond bottoms at various depths. The Petersen dredge was operated through the opening in the raft deck with the aid of a Foerst boat crane mounted in the flange and connected to hooks on the deck by a chain to counterbalance the weight of the dredge. The Ekman dredge was operated manually both through the opening and over the sides and ends of the deck. Samples obtained with both dredges were processed through the sieves.

Twenty-nine Petersen samples were taken from June through November 1966 of which 11 were from pond A, 10 from pond B, and eight from pond C. During this period 21 Ekman samples were taken, including 12 from pond A, four from pond B, and five from pond C.

Artificial substrates

The sampling device used most extensively in the study was an artificial substrate type similar to the multiplate sampler described by Hester and Dendy (3). Each unit was constructed of 20 square plates of 1/8" length of 1/4" threaded brass rod, and separated from each other by 1/8" brass washers. The plates and washers were firmly held by two wing nuts placed near the ends of the rod. A polyethylene line was attached

to the sampler and to a Styrofoam block which served as a buoy while the
sampler was submerged.

Fifteen samplers, each consisting of 20 four-inch plates separated
by alternate spacings of 1/4" and 3/8", were in operation from June 1966
through October 1967. Six were submerged in pond A, five in pond B,
and four in pond C. In March 1967 three additional, similar samplers were
placed in each pond. These nine samplers were constructed of six-inch
plates separated by alternate spacings of 3/8" and 1/2". A fourth sampler
was added to those in pond C and differed in being partially enclosed
in a screening wire bucket which fitted over one side of the sampler and
surrounded half of each plate. Instead of resting on the pond bottom,
this sampler was suspended two feet below the water surface in dense
vegetation and anchored by a line attached to a rock on the bottom.

One sampler was stationed in the deepest part of each pond through-
out the study. The others were placed in emergent vegetation around the
pond margins or at intermediate depths beyond the emergent vegetation.
Collection of naiads from the samplers originally involved disassembly
and inspection of individual plates. Equally satisfactory results were
obtained, however, by placing the sampler on the sieves with the plates
positioned vertically and systematically rinsing each side by pouring water
through the spaces between the plates. Samplers were examined at two-week
intervals.

Nets

Aerial nets were employed to aid in the determination of species
present at the ponds as adults. They were not used in any standard
method, but in random sweeps through vegetation and in concentrated efforts
to capture selected individuals.

Systematic sampling with aquatic nets extended from October 1966
through August 1967. Most of the samples were taken at depths of one
meter or less at two-week intervals; a few samples were taken at depths
of up to 1.5 meters.

Two devices to sample emerging Odonata were employed during portions
of the sampling period. Emergence cages were maintained at each pond in
June and July 1966. As correlations between naiads and adults were
especially desired at this time, cages were used to restrict emerging
adults to the area near which they had left their exuviae. Each cage
consisted of five wooden frames covered with clear plastic screening and
sampled an area of approximately one square meter. One lower edge was
placed at the shoreline and the others were buoyed just below the water
surface by small blocks of Styrofoam grooved to accommodate them. Thus
the cage was open underwater on three sides allowing naiads to enter and
leave the sampling area unobstructed. Four cages were operated at pond A,
four at pond B, and three at pond C. The cages were examined daily and
were repositioned occasionally to conform to changing water levels.

In June 1967 an emergence support similar to that described by
Trottier (12) was erected at each pond. Each support consisted of
three metal posts driven into the bottom mud at two-meter intervals so as
to extend from shoreline to about four meters into the pond and connected
by a strand of polyethylene line over which bolts of cheesecloth were
suspended from about one meter above the water surface. The cloth
extended well below the surface, and the vegetation immediately
surrounding the supports was clipped below the water surface. Each
support met the shoreline at a slight angle from the perpendicular. The
supports were examined for exuviae at two-week intervals.

Preservation and Identification

Adult specimens were killed with cyanide and papered. Naiads were
collected from the sieves with forceps, placed in vials of 95% ethanol
for killing, then transferred to vials of 70% ethanol for preservation.
Exuviae were preserved in vials of 70% ethanol. All preserved specimens
sufficiently intact were determined to species.

Live naiads frequently were brought into the laboratory for rearing
under procedures developed by Dr. B. Elwood Montgomery. Successful
rearings provided specimens of exuviae and adults which made possible the
correlation of certain previously undetermined naiads with their adult
stages.

Measurement of Environmental Factors

Environmental factors investigated during the study were fluctuations in pond levels, water temperatures, conductivity, resistivity, bacterial content, color, turbidity, alkalinity, hardness, dissolved oxygen, free carbon dioxide, pH, sulfate, choloride, sodium chloride, and orthophosphate. Measurement of pond levels, water temperatures, and dissolved oxygen concentrations was emphasized because these factors were suspected of exerting the greatest influence on the distribution of naiads within the ponds.

Pond levels

Pond level readings were taken from a gauge installed on the dam of each pond. An initial reading from each was standardized with the maximum pond depth and subsequent readings were converted accordingly. The gauges were read at two-week intervals.

Water temperatures

Five thermocouples were installed in each pond and were located in bottom sediment, 15 cm from bottom, 60 cm from bottom, 120 cm from bottom, and at the surface. Measurements were recorded automatically in $^{\circ}F$ by a remote recorder at 0600 hours, 1000 hours, 1400 hours, and 2000 hours daily. Surface temperatures were measured manually at two-week intervals as a check on the automatic equipment.

Dissolved oxygen concentrations

Dissolved oxygen concentrations were determined in parts per million at four levels from the surface to the bottom of each pond by the Winkler method using Hach chemical powder pillows and titrating with phenylarsene oxide. Measurements were made in September 1966 and at two-week intervals from March through October 1967.

RESULTS AND DISCUSSION

Species Composition

Thirty-four species of Odonata were collected from the three ponds. Twenty-eight species were taken at pond A, 27 at pond B, and 23 at pond C. Evidence based on collections and observations suggests that the ponds share at least 22 species in common. Table 1 shows the total numbers of adults collected from each pond and the numbers of naiads taken by each sampling device. Larger numbers for adults reflect

Table 1. Odonata collected by all sampling devices

Species	Adults			Naiads & Exuviae																	
Sampling device:	(Totals)			Ekman			Petersen			Multiplate			Aquatic Net			Cage			Support		
Pond:	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Lestes inaequalis Walsh	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lestes unguiculatus Hagen	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Argia sedula (Hagen)	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Argia violacea (Hagen)	0	53	0	0	0	0	0	6	0	4	350	0	2	25	0	0	51	0	0	0	0
Anomalagrion hastatum (Say)	4	2	0	0	0	0	0	0	0	0	0	0	0	0	0	4	2	0	0	0	0
Enallagma antennatum (Say)	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0
Enallagma aspersum (Hagen)	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
Enallagma basidens Calvert	62	44	0	1	0	1	1	9	0	76	139	52	103	52	15	70	43	0	2	1	0
Enallagma civile (Hagen)	1	0	0	0	1	0	0	0	0	1	2	1	1	0	1	0	0	0	0	0	0
Enallagma exsulans (Hagen)	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
Enallagma signatum (Hagen)	2	2	0	0	0	0	0	0	0	18	1	5	11	1	0	1	2	0	0	0	0
Enallagma traviatum (Selys)	3	5	0	0	0	0	1	0	0	11	24	8	5	13	8	1	2	0	0	0	0
Enallagma vesperum Calvert	0	0	0	0	0	0	1	0	0	4	0	3	2	0	0	0	0	0	0	0	0
Ischnura posita (Hagen)	1	2	4	0	0	1	1	1	2	26	30	104	1	7	17	1	2	4	0	0	0
Ischnura verticalis (Say)	22	34	16	0	0	0	0	0	10	76	108	97	12	34	35	23	35	16	0	0	0

emergence cage yields, as adults were collected by net only to the extent necessary to determine species diversity. Totals for naiads, however, reflect the relative abundance of the various species in the three ponds to the extent possible with the sampling procedures employed.

The species compositions of ponds A and C resemble each other more than that of pond B. The former are at more advanced successional stages and exhibit greater physical-factor similarities than the latter.

Comparison of Sampling Devices

Dredges

Although dredges are the devices most frequently used in population studies of benthic organisms, they are inefficient and provide low quantitative estimates as compared with other techniques, particularly in the case of dominant species. Of 55 naiads taken in the 29 Petersen dredge samples, 25 were found in two samples. These results suggest a clumped distribution and indicate that numerous dredge samples are required to obtain an accurate estimate of population density. The Petersen dredge recovered 15 species as compared with 11 species taken by the Ekman dredge. Twenty-one Ekman dredge samples produced 31 naiads. The species taken by the dredges were also obtained by other sampling devices.

Artificial substrates

Multiplate samples yielded 18 species and nearly 95% of the Pachydiplax longipennis naiads collected. The dominant position of this species in each pond was reflected by only the multiplate yields. High population density does not seem to be a criterion for recovery by this device, however, as the samplers took Enallagma civile and E. vesperum naiads although these species apparently are not abundant in the ponds. Since the multiplates did not restrain naiads, some may have abandoned the samplers during retrieval. Such losses could have been significant in deep water where fewer naiads were taken. An attached restraining device might have reduced losses during retrieval, but the partially enclosed sampler did not produce results superior to those of a conventional unit operated nearby. Multiplate samplers exhibited remarkable

specificity in attracting Odonata naiads. Numerous Trichoptera larvae were present on some samplers from January through March 1967, but only in these instances did organisms other than Odonata actually colonize the samplers. The multiplates proved ineffective in recovering burrowing, semi-burrowing, and large climbing naiads. Other types of artificial substrate devices probably could be designed to sample species having these substrate requirements.

Nets

Five of the 23 species taken as adults by aerial netting were obtained by no other method; these were Lestes unguiculatus, Argia sedula, Anax longipes, Sympetrum vicinum, and Pantala hymenaea.

Aquatic netting produced more species than any other sampling method. Of the 27 species recovered, Enallagma exsulans and Libellula pulchella were taken by no other method. The aquatic net also collected more burrowing naiads (Gomphus) and semiburrowers (Libellula and Ladona) than did any other device used. Despite its value in obtaining a wide variety of species, the aquatic net is limited to sampling shallow water where vegetation makes uniform sampling virtually impossible and introduces a sampling bias. Samples obtained by different individuals using the net in the same area differed substantially in content.

Emergence samplers

Of the 21 species which emerged in cages, seven were represented by at least 25 individuals each. Since emerging Odonata are known to avoid any object casting a shadow (9), these seven species were analyzed for possible differences in emergence behavior in the three ponds. Comparison of the number of individuals of each species taken in emergence cages with the number of naiads and exuviae of that species taken by all methods revealed statistically significant differences in five species (Table 2). The comparatively low numbers of Libellula luctuosa, Celithemis elisa, and C. fasciata which emerged in cages in pond B may represent an avoidance response to the reduced light intensity within those cages. The water of pond B was usually very clear and registered less color than that of the other ponds. Shadows cast by cages in pond B, therefore, could have presented greater contrast to emerging naiads.

Table 2. Chi square analysis of emergence behavior

Species	Pond	A vs. B	A vs. C	B vs. C
E. basidens		4.5*	14.5**	8.1**
L. luctuosa		12.6**		12.4**
P. tenera			8.0**	
C. elisa		35.9**		
C. fasciata		8.5**		5.1*

**Significant at 1% level *significant at 5% level

The exuviae of only seven species were found on emergence supports, but C. eponina and P. longipennis emerged in greater numbers on supports than in cages. The failure of C. eponina to emerge in cages and the behavior exhibited by C. elisa and C. fasciata in the three ponds suggest a varying response to shadows by emerging naiads of different species within the genus Celithemis. Such a behavioral pattern illustrates a distinct advantage of supports over cages in sampling emergence in Odonata where exuviae can provide the required data. Daily examination of the supports would have yielded much more information than was obtained from this source

Environmental Factors

Pond levels

From June 1966 through October 1967 the maximum and minimum values at the gauge in pond A differed by 78.6 cm, those of pond B by 60.4 cm, and those of pond C by 88.1 cm. The minimum depth reached at the deepest point of each pond during this period was 2.76 m in pond A, 4.41 m in pond B, and 2.73 m in pond C. Levels were slightly higher in the summer of 1967 than in the corresponding period of 1966.

Water temperatures

Although the maximum temperatures reached in 1967 were 4° to 7° below those of 1966, similar annual cycles were observed in both years. During winter, water temperatures were nearly uniform at all depths. In mid-March surface waters became heated 10°F above the temperature of the deepest water in each pond. The temperature differences between surface and
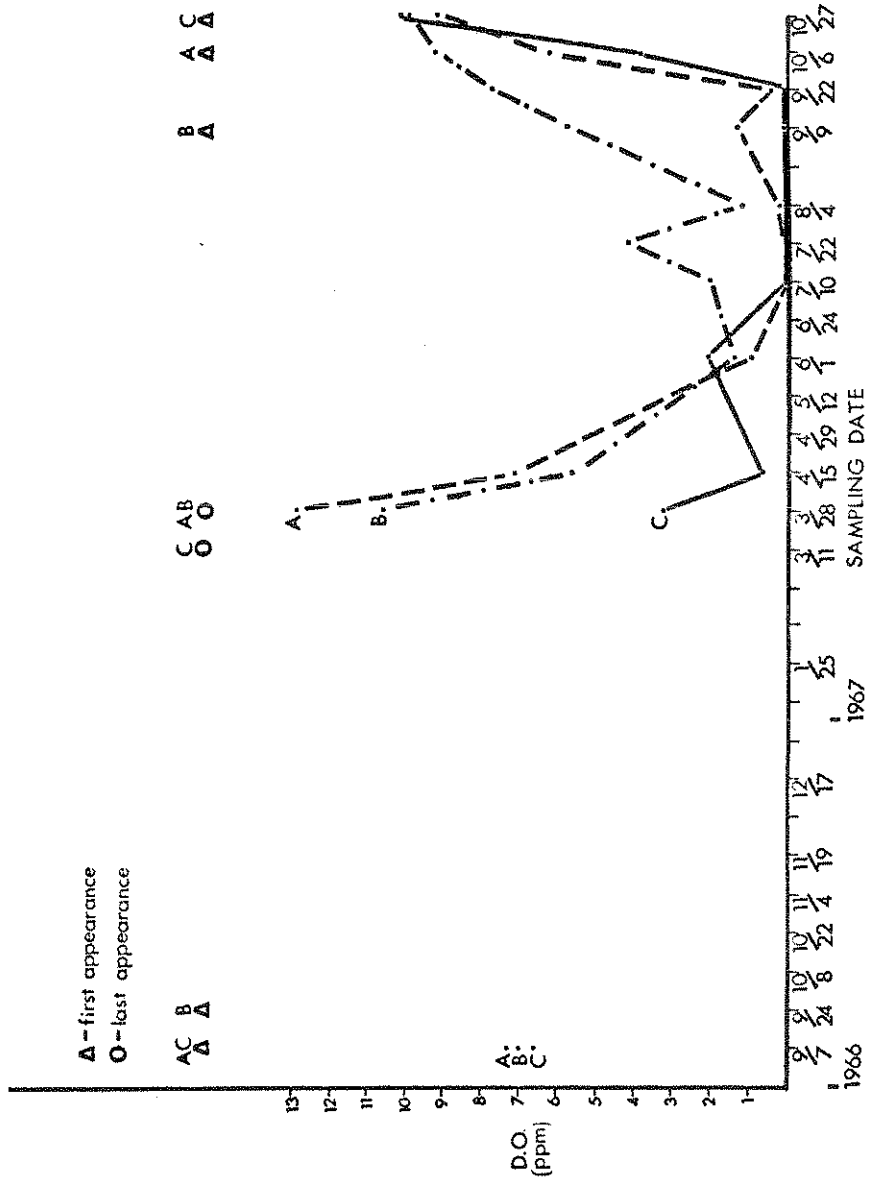
Figure 1. Relationship between seasonal occurrence of naiads and concentration of dissolved oxygen in deep water. Triangles indicate first appearance of naiads on deep samples in fall; circles indicate last occurrence in spring.

deep waters increased to a maximum of 20°F by the end of June. During
the period of surface warming a gradual decrease in temperature was
found from surface to bottom with no evidence of a thermocline.
Temperature uniformity was restored in ponds A and C in early October,
but not until mid-October in pond B in which the deeper waters warmed
more slowly. The ponds then cooled uniformly until minimum temperatures
were reached in mid-January.

Dissolved oxygen concentrations

On September 7, 1966, dissolved oxygen concentrations of over 6 ppm
were found at all depths in each pond. On March 28, 1967, a concentration
of only 3.3 ppm was found at the bottom of pond C, a depth of 3.35 m.
By April 15 the concentration at this site had decreased to 0.8 ppm and
the concentrations at the bottoms of ponds A and B also were declining
markedly. In June the concentration at the bottom of each pond dropped
below 2 ppm. During July ponds A and C indicated no dissolved oxygen
below 2 m. Concentrations exceeding 5 pmm were restored at the bottom of
pond B by September 9, pond A by October 6, and pond C by October 27
(Figure 1).

Population Dynamics

Seasonal Trends

Data provided by dredge and, particularly, multiplate samples
indicate that portions of the naiad populations of certain species migrate
annually between shallow water and deeper parts of the ponds. From
September through March naiads of Enallagma basidens, E. signatum, Ischnura
verticalis, Epicordulia princeps, Tetragoneuria cynosura, L. luctuosa, and
P. longipennis were found at depths up to 5 m, but from April through
August naiads were recovered only from shallower water in or near emergent
vegetation. Naiads of these species were present throughout the year in
samples from shallow water, indicating that only portions of the populations
migrate.

Multiplate samples revealed naiad population peaks in shallow water
in spring prior to emergence and again in fall near the time of dispersal
into deeper water. The spring maximum probably reflects the return of
naiads which have overwintered in deeper water. The fall maximum is more
pronounced and, with the occurrence of naiads in shallow water throughout

the winter, suggests that the fall dispersal to deeper water of a portion of population may enhance species survival by reducing population density in shallow water during a critical period rather than by removing the migrants from exposure to the climatic rigors of shallow water. Such a mechanism would support Moore's analysis (8) of the naiad stage as the most critical in the life cycle of Odonata because of high population densities, limited food resources, and competition in the absence of territorial behavior exhibited as adults. Multiplate data from pond A did not reflect the population peaks so distinctly as did data from ponds B and C in which zones of shallow water with emergent vegetation were compressed into narrow bands by steep banks, thus providing smaller areas of suitable summer habitat.

<div align="center">Environmental interactions</div>

The initial appearance of naiads on multiplate samplers in deep water at nearly the same time in 1966 and 1967 (Figure 1) suggests that the disperasal response may be photoperiodically induced. In 1966 naiads were found on the deep samplers in all three ponds by September 24. In 1967, however, naiads did not appear on the deep sampler in pond A until October 6 nor on that in pond C until October 27. Differences in pond levels did not appear critical. The lower water temperatures in 1967 should have favored earlier dispersal. In 1966 the dissolved oxygen concentration in the deepest water of each pond was greater than 6 ppm when naiads were first found there. In 1967 naiads appeared on the deep sampler in pond B on September 9 when the dissolved oxygen concentration at that site was measured at 5.8 ppm. On October 6 when naiads appeared on the deepest sampler in pond A the concentration was 6.3 ppm, but at another deep sampler which yielded no naiads on that date the concentration was only 4.3 ppm. Thus, the replenishment of dissolved oxygen and dispersal of naiads over the pond bottom were not temporally uniform. The critical level of dissolved oxygen concentration appeared to be around 5 ppm for the species involved in the fall dispersal. In pond C the presence of naiads on the deep sampler again coincided with the restoration of a dissolved oxygen concentration above 5 ppm. These data indicate that the duration of the fall population peak and the time of disperal to deeper water are at least partially determined by prevailing dissolved

oxygen concentrations. In the fall of 1967 the stimulus which triggered the dispersal apparently was offset by low dissolved oxygen concentrations in ponds A and C (Figure 1).

In addition to seasonal dispersal movements, naiads of all species taken regularly on multiplate samplers seem to move about more or less constantly, actively seeking and relocating in protective microhabitats which are probably in the proximity of available food. Naiads found on the samplers obviously moved onto them during the two-week interval between examinations. T. cynosura was collected at 23 of 26 multiplate sites and was the only species found at the deepest site in each of the three ponds. This is particularly interesting in view of Kormondy's description of the behavior of these naiads in Michigan (4). In southern Indiana naiads of this species do not remain in shallow water throughout their development, nor can they be characterized as lethargic. Similar wandering behavior appears to occur in Epicordulia princeps, which Walker (13) believes to be congeneric. Multiplate sampler data indicate a more active behavior in naiads of most of the species sampled than is frequently reported in the literature.

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CHAPTER VIII

REMOVAL OF THE INSECTICIDE, DIELDRIN, FROM WATER BY ACTIVATED CARBON FILTRATION

P. R. Goodrich and E. J. Monke*

Possible contamination of farm ponds by agricultural insect-icides is of concern both to farmers using these ponds for farm-stead water supplies and to the public who ultimately may consume food products coming in contact with these water supplies. Some insecticides persist in measurable quantities as long as one year in water solutions (1). Normal filtration using sand filter beds will not usually remove these materials (6).

Even small amounts of the persistent insecticides in farm-stead water supplies pose a potential hazard because animals tend to concentrate some of these insecticides from food and water into their body and milk fats (7). Although the potential danger to humans from small quantities of insecticides is not fully under-stood, studies on lower-order mammals have shown that care should be exercised to limit intake of insecticides by humans whenever possible (2).

The Food and Drug Administration has set a low tolerance for insecticide residues in milk since it comprises a large pro-portion of the diet of babies, the sick, and the invalid. Government condemnation of milk from herds has occurred where cattle were fed contaminated forage. As yet, milk has not been condemned where insecticide residues have been traced to drinking water. In the future, the detection of insecticides in quantities heretofore undetected will be possible and condemnation of milk and other farm products may become a common occurrence, if caution is not practiced. Farmers frequently rely on surface water from ponds or streams for livestock and domestic use in areas without good ground water sources. Depending on the amount and occurrence

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of rainfall, runoff from watersheds to which insecticides have
been applied can carry detectable quantities of the applied insect-
icide. A simple and inexpensive method for removing trace
amounts of organic material from water has been activated carbon
filtration. In this study, activated carbon was also selected
to remove trace amounts of the chlorinated hydrocarbon Dieldrin*
from water. For experimental advantages, the insecticide was also
radioactive, with the C_{12} atoms in the molecular structure re-
placed by C_{14} atoms. The resulting molecule emitted beta particles
of energy 0.156 million electron volts (mev.) and had a specific
activity of 19.5 microcuries per milligram.

Specific objectives of the study as previously reported (3,4)
were (a) to determine the effectiveness of granular activated
carbon to filter out an insecticide, Dieldrin, from water supplies, (b)
to determine the optimum granular size and length of carbon filter
for efficient removal of the insecticide, and (c) to evaluate the
suitability of radio-tracer techniques for low level insecticide
research.

PROCEDURE

The radioactive-labeled Dieldrin was first diluted with benzene
so that a 0.5 microliter aliquot contained 65 nanograms Dieldrin.
After the benzene evaporated, the Dieldrin was diluted with one liter
of deionized water. The contaminated water was then split into two
500 ml volumes; one volume was saved as the unfiltered sample, and the
second was passed through an activated carbon column.

The column was contained in a Pyrex chromatographic cylinder,
400 mm long with a 20 mm inside diameter. A coarse-porosity fritted
disc was sealed into the cylinder and a small amount of Pyrex glass
wool was placed above the disc to keep it from clogging.

The activated carbon used as the filter medium was sold as a
commercial Grade ACC, size 6/14 mesh derived from petroleum residue.
The size ranges of granules used in the tests corresponded to
standard sieve sizes 6 to 8, 8 to 10, 10 to 12, and 12 to 14.

*From Shell Chemical Company. The mention of specific products
involves no endorsement by the author or the research sponsors.

Activated carbon from a tared container was packed into the cylinder in small amounts. When the desired depth of activated carbon was reached, an additional glass wool plug was inserted to keep the activated carbon granules from floating during an experiment.

Column lengths of 70, 140, 210, and 280 ml were used. An assembled column was placed into the top of a 1000 ml vacuum flask as shown in Figure 1. Then a suction of 20 cm Hg was applied to the flask and 1000 ml of deionized water more-or-less was flushed through the column. A clean 1000 ml vacuum flask was now attached to the bottom of the column and tests were begun. The entire experimental apparatus under a safety hood is shown in Figure 2.

The 500 ml solution was filtered through an activated carbon column under a suction of 3 to 5 cm Hg. After the contaminated solution was filtered, rinses of deionized water were used to assure that all the Dieldrin possible had been removed from a column. When flow had stopped, the vacuum flask was removed from the base of the column and the filtered solution transfered to a 1000 ml separatory funnel.

The Dieldrin in both the filtered and unfiltered solution was separated out using chloroform extraction procedures through 5 successive extractions. Chloroform was added to separatory funnels containing both solutions, and after vigorous shaking and periodic venting to release pressure buildup, the phases were allowed to separate. The lower layer, the chloroform layer, was drawn into erlenmeyer flasks and the remaining water solution was extracted again. After the fifth extraction, the water left in the separatory funnels was discarded into a plastic carboy used to store radioactive wastes.

Each chloroform extract was evaporated under a dry air manifold, first in the erlenmeyer flask and then in a centrifuge tube, until a volume of approximately one-half ml remained. Several small rinsings of chloroform brought the volume up to about one ml in total. Five microliters of ethylene glycol was then added to retard vaporization. A 0.5 ml sample now was pipetted onto an aluminum planchet and allowed to dry slowly in a chemical hood.
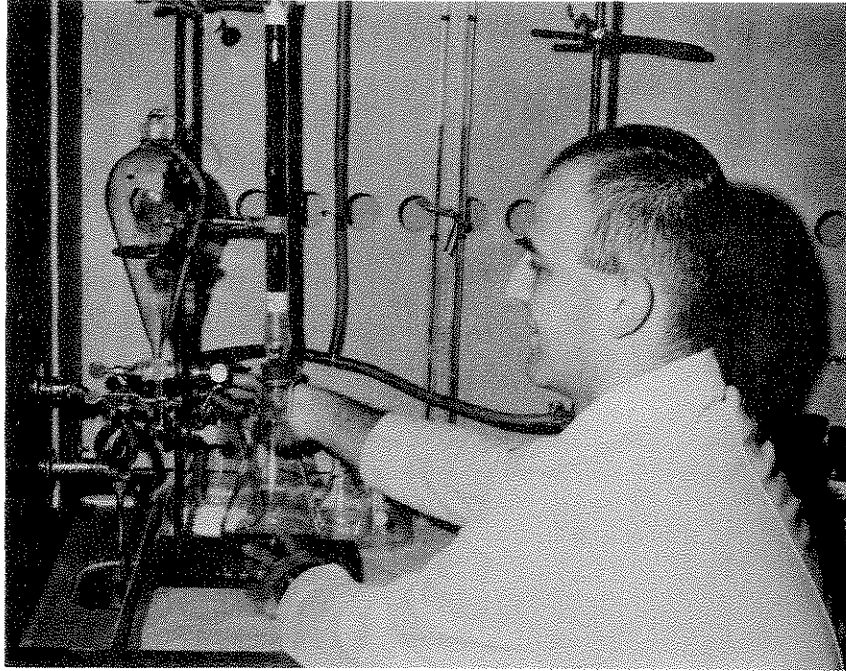
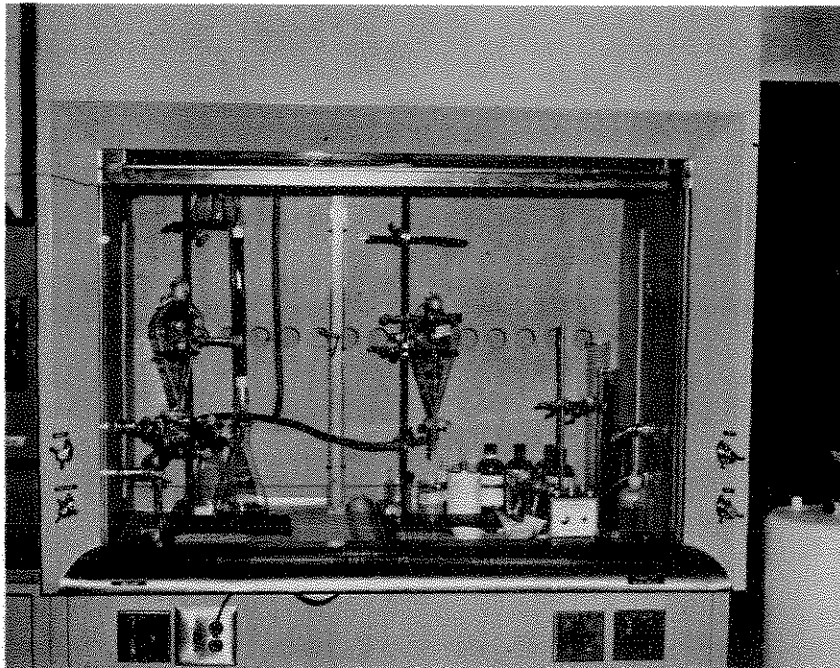Figure 1. Filtering the Dieldrin Contaminated Water

Figure 2. Experimental Apparatus in the Safety Hood

Samples on the planchets were analyzed by radioactive counting of the decay rate of the C_{14} isotope. Two systems were used for counting; one, the RIDL (Radiation Instrument Development Laboratory) system sensed the quanta of energy emitted with an ultra-thin window Geiger-Muller gas flow tube, and the other, the Beckman Low Beta Counting System sensed emissions with a thin window gas flow proportional tube.

The RIDL System

The RIDL system as shown in Figure 3 consisted of a gas flow detector operating in the Geiger region and associated electronics to run the detector, scaler, and ratemeter. The gas flow detector (Nuclear-Chicago Model 470) was operated with a 2-inch diameter ultra-thin window having a density less than 150 micrograms per sq. cm.

For count periods up to one hour, an x-ray type timer was used to control the decade counter which accumulated the pulses from the detector. For the longer counting periods, an on-line control system was developed using a small hybrid computer. The hybrid computer, an Electronics Associates Incorporated (EAI) Digital Logic System, DES-30, was programmed to act as a high precision timer and as a control system for the scaler. A block diagram of the computer -- RIDL system is shown in Figure 4. The DES-30 performed the following operations in sequence for the experimental work: (1) When the scaler was set to zero, the DES-30 began to accumulate on its memory system the sixty pulses per second from the line source, (2) after the DES-30 had accumulated the preset number of seconds equal to the desired counting time, the scaler was stopped, and (3) one second later a solenoid attached to the cable release of a Canon automatic camera was energized. The number of accumulated counts on the scaler and the clock time, the sample number, duration of counting and the date which were placed on a board in front of the camera were all recorded on film.
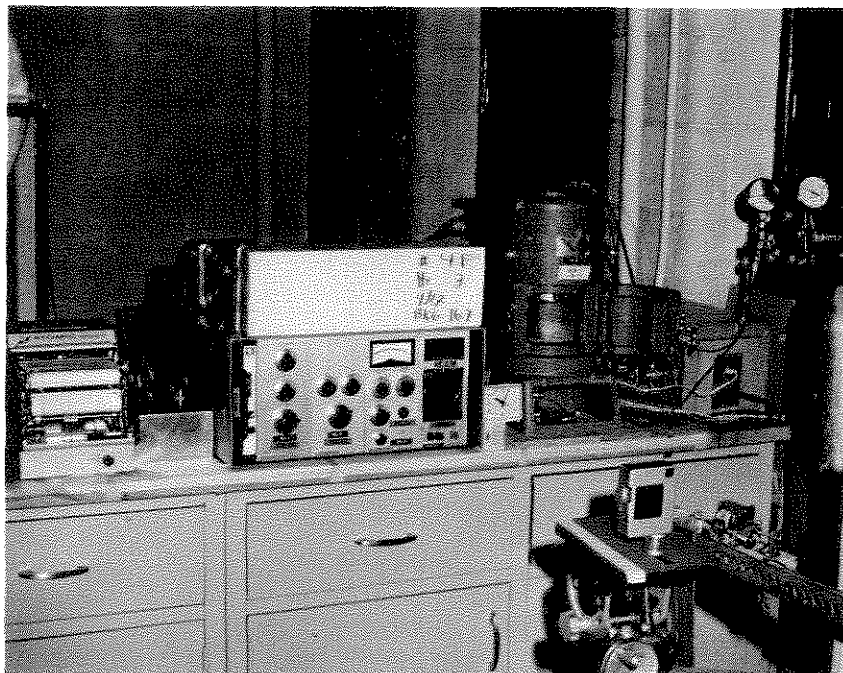
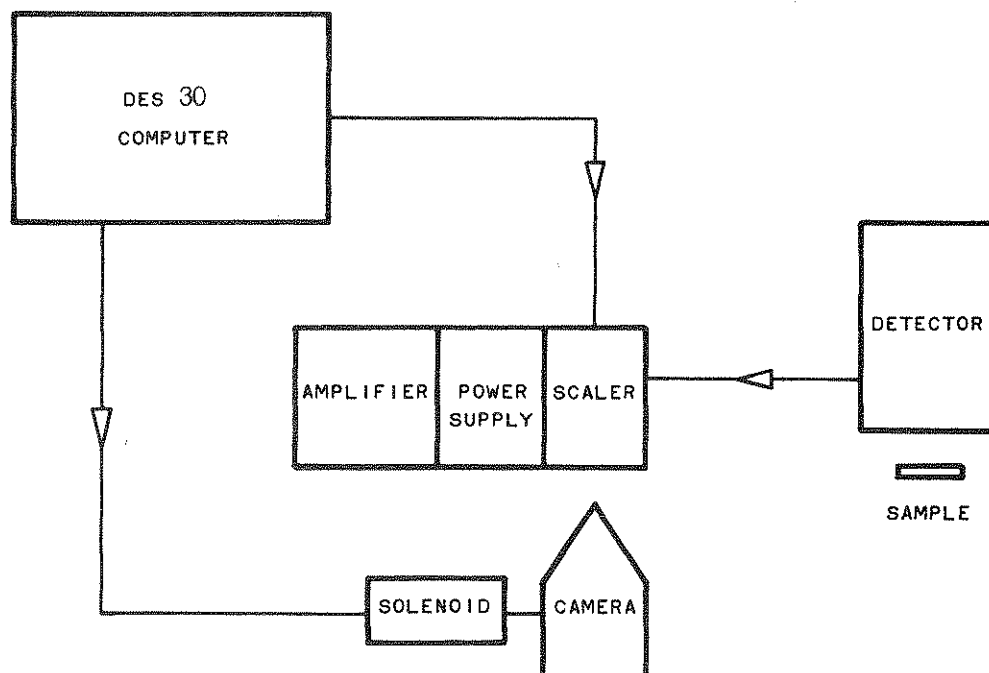Figure 3.   RIDL Radioactive Counting System

Figure 4.   Block Diagram of Computer-RIDL System

Beckman Low Beta Counting System.

The Low Beta System is a low background automatic counting system with all of its functions internally programmed. This instrument was used to count all samples on the planchets. Working in the proportional range at a potential of 1825 volts, the thin window detector uses a gas mixture of 90 percent argon and 10 percent methane at a flow rate of 0.12 cfm. This instrument has capabilities for up to 100 planchets to be loaded and counted with no further attendance by an operator. The output is then printed on paper tape.

PRESENTATION AND DISCUSSION OF RESULTS

Tests were conducted on activated carbon columns using radioactive Dieldrin in a deionized water solution. A slight negative pressure was maintained at the outlet of the columns for all tests.

Contaminated water was first passed through the empty glass cylinders. The effluent then was extracted following the procedure presented previously. The results of these "blank tests" showed that more than 98 percent of the insecticide placed in the column was recovered in the sample when analyzed by radioactive counting.

Dieldrin contaminated water was filtered through each activated carbon column. Both the unfiltered portion and the filtered effluent were extracted and the solvents evaporated separately. Planchets holding the residues were placed in the detectors and radioactive emissions counted for given time periods. The quantity of Dieldrin retained (removed) on the activated carbon column was calculated from the count rate of the unfiltered sample minus the count rate of the filtered effluent. The fraction of the insecticide removed by the filter was that difference in count rate between filtered and unfiltered samples divided by the count rate for the unfiltered sample. .

All samples were counted with the same geometrical relationship to the detectors. The sample thickness on the planchet was assumed to be infinitely thin for all samples and only a minute

amount of ethylene glycol was needed to hold the insecticide in a nonvolatile state. A correction for radioactive decay was not needed because of the long half-life of C_{14} (5730 years). Background corrections were applied to all sample counts. The experimental results giving the percent removal of the insecticide, Dieldrin, are presented in Table 1.

Table 1. Percent Insecticide Removed

Carbon Filter Length (mm)	System and Block Identification*	Size of Carbon Granules U.S. Standard Sieve Size Range			
		6-8	8-10	10-12	12-14
70	LB-1	87.4	89.9	92.6	94.1
70	LB-2	89.2	94.5	92.7	96.0
70	R-1	90.6	87.9	94.6	83.2
140	LB-1	89.7	98.9	93.8	88.3
140	LB-2	97.4	98.9	95.5	97.8
140	R-1	96.9	97.1	95.4	78.1
210	LB-1	97.1	96.5	99.8	99.4
210	LB-2	99.4	97.4	99.1	99.6
210	R-1	96.1	84.5	97.8	71.4
280	LB-1	94.0	97.7	99.4	99.2
280	LB-2	99.9	98.7	99.6	99.0
280	R-1	98.4	94.7	89.4	94.2

*LB and R denote the Beckman Low Beta Counting System and RIDL System, respectively.

The removal efficiency for the various column lengths and activated carbon size ranges were analyzed statistically using a randomized complete block design. Each block included sixteen treatment combinations of four sizes of carbon and four column lengths. When the requirements of normality and homogeneity of variances were satisfied according to Ostie (5), an analysis of variance was made on the transformed data. The results are presented in Table 2 where calculated F values are compared with tabulated F values at a one percent confidence level.

Table 2. Analysis of Variance

Source	Degrees of Freedom	Sum of Squares	Mean Square	F Value
Blocks	1	0.01436	0.01436	not tested
Treatments	(15)			
Length	3	0.15897	0.05299	18.53*
Size	3	0.00410	0.00137	0.48
Length x Size	9	0.06374	0.00708	2.48
Error	15	0.04272	0.00286	
Total	31	0.28389		

*Significant at 1 percent level

The results of the analysis of variance show that the length
of the carbon filter was an important parameter in the design of
an efficient filter to remove small concentrations of the insecti-
cide, Dieldrin. The size of carbon granules within the size ranges
tested, however, had no significant effect on the efficiency of the
activated carbon filter. The interaction of size and length also
did not have a significant effect on the removal of Dieldrin from
the contaminated water supply.

When the activated carbon column was deep, insecticide-laden
water had a long contact time with the working surfaces of the
activated carbon. Also with a given granule size, the potential
adsorption sites were much more numerous with the deeper rather
than the shorter columns. However, with the very small amount of
insecticide used in this study, the surface area available to adsorb
the insecticide was apparently always more than needed. Although
the surface area would increase as the size of granules decreased,
granule size was not a significant factor within the somewhat
narrow size range used in this test. More area was not needed
to trap the small amounts of insecticide, but a longer period of
opportunity for the insecticide molecule to be in close contact

with the granules was beneficial. The deeper columns provided
that longer contact time for the process of adsorption to occur.

The porous glass plate as part of the experimental apparatus
had the effect of reducing the permeability differences due to
sizes of granules. However, the resistance of the porous glass
plate to the laboratory filter system is not unlike the base
resistance found in plumbing systems in a household or farmstead.
If a filter is placed in a plumbing system, contact time can be
increased normally only by increasing filter length.

The radio-tracer technique was quite sensitive in detecting
small quantities of the insecticide. Impurities in the samples
did not interfere with the determinations as they would with
other analytical techniques. Moreover, the clean up procedures
were not as difficult as might be expected.

SUMMARY AND CONCLUSIONS

A radioactive labeled insecticide, Dieldrin, was mixed into
deionized water, 500 ml volumes of which were passed through
granular activated carbon filters. The effluent water was extracted
with chloroform and the chloroform solvent evaporated on small
aluminum planchets. The residue on the planchet was then analyzed
using two radioactive counting detectors. The amount of insecti-
cide retained on the activated carbon in the filter columns was
calculated and presented as a percent of the influent quantity.
Four lengths of activated carbon columns and four size ranges of
activated carbon granules were analyzed using a randomized complete
block statistical model. Radio-tracer techniques were evaluated
to determine their capabilities for analyzing low level insecticide
amounts.

The conclusions reached were:

1. The granular activated carbon used was very efficient
   in removing minute quantities of Dieldrin from a water
   solution. Up to 99 percent of the pesticide applied
   to the filter was removed.

2. The size of carbon granules within the range of those tested was not significant in the removal of the insecticide.

3. The longest column gave more than 99 percent removal of Dieldrin. This degree of removal normally could provide ample protection for individuals and products from water supplies contaminated with Dieldrin. Most other insecticides, at least the chlorinated-hydrocarbons, would be expected to react in a similar manner.

4. Radio-tracer techniques can give very sensitive measurments of low insecticide levels. The processes were much more simple than those required by other sensitive analytical techniques such as gas chromatography.

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CHAPTER IX

MOVEMENT OF PHOSPHORUS IN POLLUTION
CONCENTRATIONS IN SATURATED SOIL

E. J. Monke and P. R. Goodrich*

Irrigation of liquid wastes onto land is gaining favor as a means for disposing of farm wastes, cannery waste water and the effluent from sewage treatment plants. This report deals with the adsorption of phosphorus applied in pollution strengths onto sand and sandy loam soils (2, 3).

Phosphorus is readily adsorbed by soils. The application of low concentrations of phosphorus through fertilization or the application of phosphorus-based organo-toxicants likely will not cause pollution of our water resources if the soil particles to which the phosphorus ions are attached remaining in place and do not erode (6). With the application of phosphorus in pollution concentrations, however, perhaps a closer look should be taken to see if any special problems exist with movement through soil.

Many studies have been made on the movement, uptake, and decomposition of chemicals which are applied to soil (1, 4, 7). The qualitative nature of most of this work, while giving an understanding of the processes involved, does not lend itself readily to procedures for the design of soil disposal systems. Detailed analyses of movement of chemicals in saturated, porous models can also be found in chromatograph and ion-exchange resin studies (5, 8).

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OBJECTIVES

A laboratory experiment concerning phosphorus movement in saturated soil was carried out using uniform soil columns and radioactive tracer solutions. The objectives were: (a) to develop means for monitoring continuously the dynamic movement of the pollutant phosphorus inside a soil column without removal of any solution or soil material; (b) to construct and evaluate an electronic data acquisition system to continuously monitor long term studies with little operator attention, and (c) to obtain results useful in predicting the movement of phosphorus under waste irrigation conditions without field trials at each disposal site.

EXPERIMENTAL APPARATUS

Detectors which would allow minitoring of a radioactive tracer inside the soil matrix during dynamic flow conditions were investigated. Miniature Geiger-Mueller tubes, semiconductor detectors, and anthracene crystals were judged not workable. Plastic scintillator filaments, making a grid across the flow path, were also investigated; but they were not readily available in the size needed. The detector finally selected was a 1/4 inch diameter plastic scintillator rod of Pilot Y (Pilot Chemicals Division, New England Nuclear Corp.)

The material in the plastic scintillator rod had good light transmission properties and a peak fluorescence wave length of 434 millimicrons. A portion of the energy of any incident ionizing radiation (Beta particle) would be transferred to fluor molecules in the plastic. The adsorbed energy would then cause excitation of orbital electrons in the fluor and de-excitation would give rise to the emission of the adsorbed energy as electro-magnetic radiation (scintillations) in the visible or near ultraviolet region. These photons could then be detected by a photomultiplier tube.

Measurement of phosphorus movement in the soil column was made inside a totally dark chamber to prevent extraneous light from impinging on the photomultiplier tube. The soil column was supported by a vertical lathe bed as shown in Figure 1. A rack fixed to the lathe carriage in place of the cutting head supported the photomultiplier tube in a horizontal position. By driving the carriage lead screw, the photomultiplier tube was positioned under clock control at one of several detectors.

The phosphorus solution was placed in a glass carboy on a rack out-
side the chamber. Flow to the soil column was controlled by a constant
head device.

The container for the soil column was made of Lucite plate and tubing.
A 4-inch inside diameter tube, 24 inches long, was placed on a base with
an outlet port. The top of the container consisted of a capped tube which
was sealed with O-rings bearing against the outer periphery of the tube.
Ports in the capped tube provided an inlet for the phosphorus solution
and a standpipe for escaping air.

Plastic scintillator rod detectors, 4.7 inches long and 1/4 inch
diameter, were inserted through holes in the tube. The detectors were
placed horizontally at positions 2, 4, 8, 14 and 20 inches from the top of
the tube. With the soil packed into the tube, the detectors were then
perpendicular to the Darcian flow direction.

The data acquisition system shown schematically in Figure 2 consisted
of (a) a nuclear detection instrument, (b) counter-timer electronics, and
(c) a Teletype output terminal. A Radiation-Instruments Design Laboratory
(RIDL) nuclear counting instrument was used to count light scintillations
from the rod-shaped detectors. The pulse output from the instrument was
then fed into the high speed digital counter, buffer and digitizer. Out-
put was on punch paper tape using the Teletype machine.

PROCEDURE

Two soils, a sand and a sandy loam, were used in the study. Both soils
were obtained from natural sites but were subsequently disturbed during the
experimentation. A predetermined weight of soil was placed into the plastic
tube and a 6-inch extension. A small vibrator was then moved up and down
the tube to obtain uniform density. The density distribution was checked
using gamma ray attenuation. After the column was wetted to approximately
field capacity with deionized water, the plastic scintillator rods were
inserted through the soil column and sealed. The soil column was then
placed in the chamber and correctly aligned with respect to the photo-
multiplier tube on the lathe carriage.

An anhydrous potassium dihydrogen phosphate (KH_2PO_4) solution of the
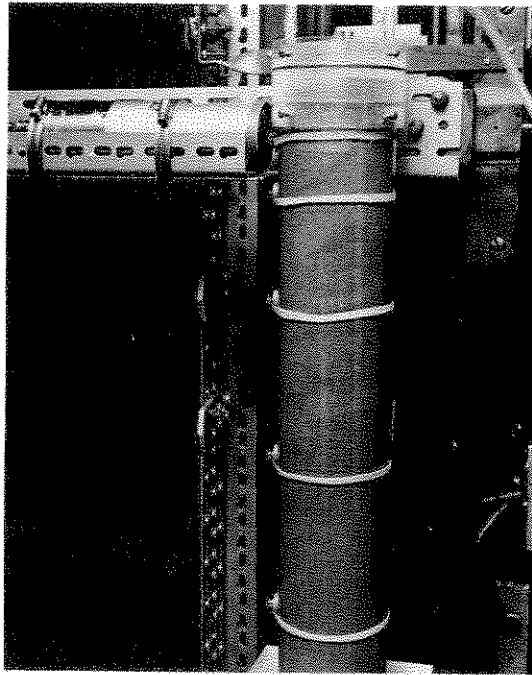desired phosphate concentration containing carrier-free radioactive ortho-

Figure 1.   Soil Column Supported on Vertical Lathe Bed Showing
Photomultiplier Tube in Position to Receive Light
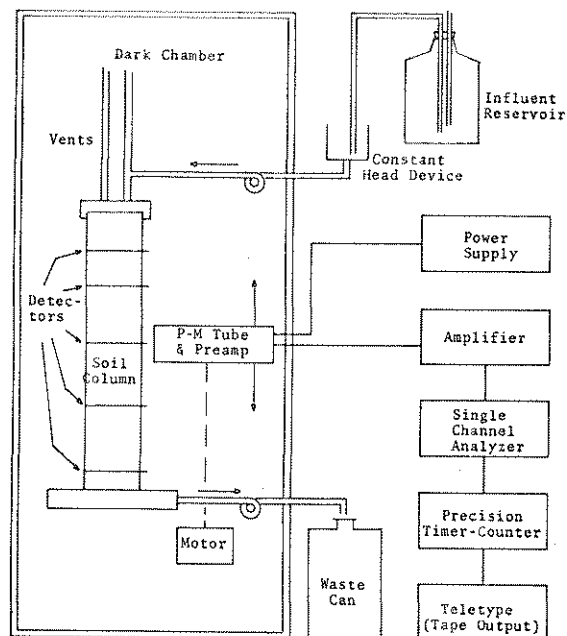Emmissions from a Plastic Scintillator Rod

Figure 2.   Block Diagram of Experimental Apparatus Showing the Flow
System and the Detection and Recording Equipment

phosphate of known specific activity was prepared in 20 liters of deionized water. Deionized water was introduced through the constant head tank to saturate the column and to evaluate the flow rate.

At time zero, the prepared phosphorus solution was introduced onto the soil column and a run was begun. The nuclear detection instrument and associated data equipment were cycled for 10 one-minute readings starting at position 1. The overflow rate was measured volumetrically. When necessary, the head device was adjusted to maintain a nearly constant flow rate. A test was continued until the required degree of adsorption was achieved. The punched paper tape output from the Teletype was then processed through the Purdue CDC 6500 computer.

To obtain the adsorption isotherms, 5 grams samples of a soil were placed into Erlenmeyer flasks to which 100 ml of standard phosphate solution of the desired concentration were added. The stoppered flasks were placed on a horizontal shaker operation at 120 cycles per minute in the climate-controlled chamber. After shaking for 12 or 24 hrs, 10 ml of 5 normal NaCl was added to each flask. The supernatant was centrifuged at 4000 rpm. A phosphate test according to Standard Methods (1968) was then performed to determine the residual phosphate in solution. Subtraction of the amount of phosphate still in solution from the amount placed in the flask yielded the amount of phosphate adsorbed on the 5 grams of soil.

PRESENTATION AND DISCUSSION OF RESULTS

Results were obtained in form of adsorption isotherms, arrival times of the chemical front, and breakthrough curves. The data for breakthrough curves consisted of scintillation counts from each of the five internal positions in the soil columns. As such these counts represented both adsorbed phosphorus ions as well as ions still in solution. An attempt was made to divide the total counts into its adsorbed and solution components using isotherm data. The results were not highly satisfactory because the isotherm data were obtained for equilibrium times while the scintillation counting represented a transient flow condition.

Adsorption Isotherms

The amount of phosphate adsorbed on a soil was determined for equilibrium times of 12 and 24 hr for each soil. The sandy loam, as expected, exhibited a much higher adsorptive capacity than the sand largely because of the differences in clay content.

The isotherms for the sandy loam, however, were not linear as often assumed in modeling the adsorption process. Also, the data from the sand adsorption tests showed very poor correlation with accepted isotherm theory. When the data were fitted to the Freundlich isotherm by a nonlinear regression program, the R^2 values for 12 and 24 hr were 0.12 and 0.73, respectively. Part of the variation was undoubtedly caused by difference in clay content of the samples. Even so, only small amounts of phosphorus were adsorbed per 100 grams of sand. While sandy soils have high infiltration rates and in this respect are often chosen for land disposal systems, these soils may also lack capacity to adsorb troublesome nutrient chemicals from high loadings of waste water effluent.

Arrival of the Phosphorus Front

The arrival times of the phosphorus front at the five detector locations are plotted in Figure 3. The data points are the average of two replications of 300, 500 and 700 mg per liter concentrations for each of the two soils. Comparing the 700 mg per liter results, 17 hr were needed for the phosphate to reach the 20 inch depth in the sand soil while 67 hr were needed to reach the same depth in the sandy loam soil.

The phosphorus front in the sand soil advanced at a fairly constant rate as shown by the nearly straight line relationship between depth and time. The breakthrough curves also were very steep and well defined.

The curves for the sandy loam soil tended to concave downward, however. This shows that the advance of the front speeded up with depth. Less time was needed to reach a position farther down in the column because the soil above the front was not being saturated to its maximum phosphate adsorption capacity. This occurred because of dead end pores and entrapped air. The phosphate ion would have to diffuse into the stagnant water of a dead end pore to reach the soil surfaces surrounding the pore. And the entrapped

air would have to be flushed out by the solution before adsorption could take place. As a result, the sandy loam soil had a smaller percentage of the total soil mass directly exposed to the initial solution stream than the sand. The breakthrough curves were less steep than those for the sand soil and also tended to be more dispersed at greater depths.

Breakthrough Curves

An example of the breakthrough curves is given in Figure 4 for a 700 mg per liter phosphate concentration onto the sandy loam soil. At the end of 72 hours the breakthrough curve at the 2 inch depth was more-or-less complete and a curve was just beginning at the 20 inch depth. The breakthrough curves for the sand soil were steeper than for the sandy loam soil but the sand was able to adsorb only about one-fourth that of the sandy loam soil. A plateau of maximum counts (meaning maximum adsorption) was not reached with any of the tests. The count rate continued to increase even after the breakthrough was essentially completed.

The soil column as under natural soil conditions contained entrapped air even through, in the case of the soil column, provisions were taken to more completely saturate the column before a test was begun. Additionally, ion diffusion caused slow contamination of water in dead end pores and channels which were not directly carrying the flow of phosphate-laden water. The sand soil had channels which were easier flushed and filled with the phosphate solution. In contrast, the sandy loam soil had many more intricate and smaller channels which resulted in a more gentle concentration gradient after the initial period of rapid adsorption.

The effect of the entrapped air and dead end pores was the long, slow rise in count rate after the breakthrough was completed. Practically, this would result in the faster arrival of phosphorus at any depth than would occur if the soil could react totally in the adsorption of phosphorus ions.

SUMMARY AND CONCLUSIONS

The dynamic tracing of a radioisotope-tagged pollutant within a soil column was accomplished through the use of an internal solid scintillator and automatic data collection equipment. The detectors were highly successful in detecting the radioactive pollutant at various depth.
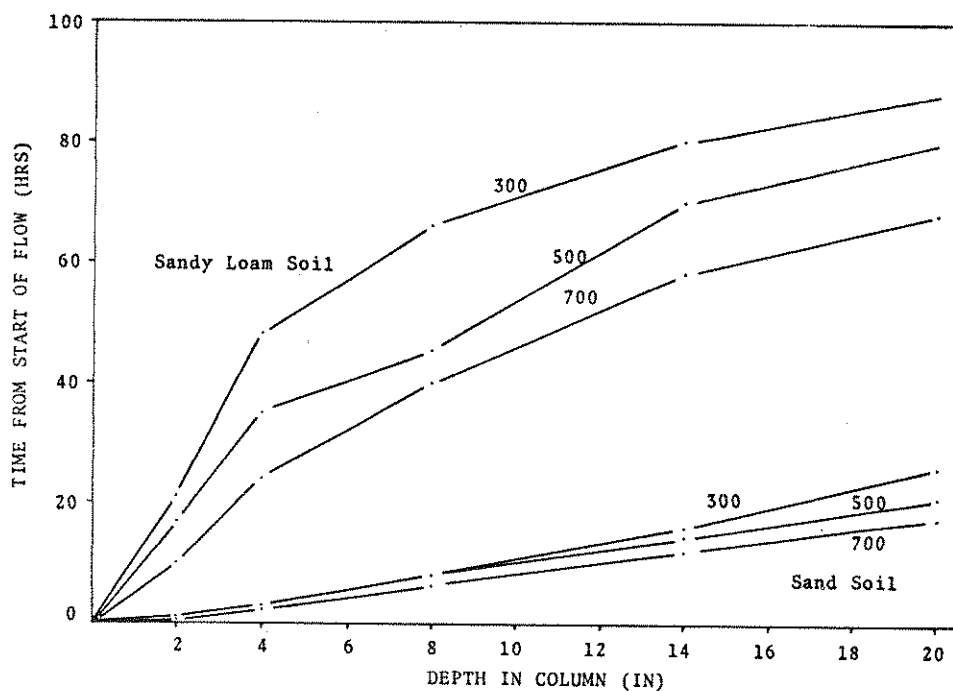
Figure 3.   Arrival Times of the Phosphorus Front in Sand and Sandy Loam Soils Using 300, 500, and 700 Mg per Liter Phosphate Solutions
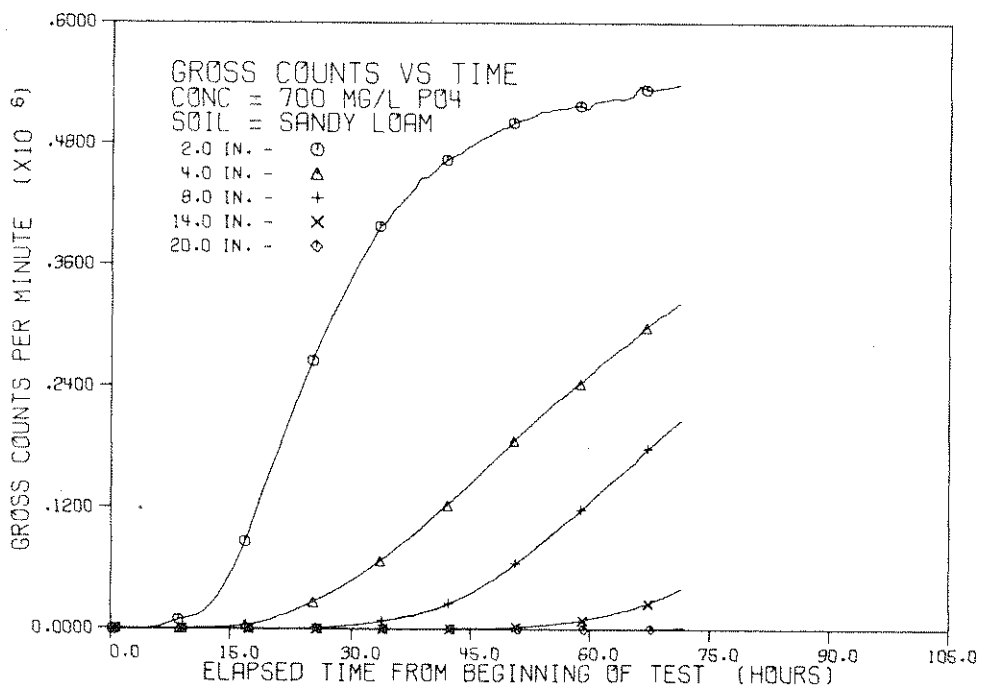

Figure 4.   Breakthrough Curves at the Five Scintillator Positions for a 700 Mg per Liter Phosphate Solution in a Sandy Loam Soil

The arrival time information provides a simple prediction of the time for contaminated water to reach various depths. In lieu of other means, this information could provide some approximate estimates, at least for these or similar soils, on which to base suggested treatment facilities.

The sandy loam with its higher clay content adsorbed up to four times as much phosphate as did the sand used in this study, emphasizing the importance of clay minerals in the adsorption of phosphate by soils.

It is common knowledge that phosphate ions are quickly attached to soil particles. The study, however, brought out at least two considerations regarding the movement of phosphorus in soil. First, if the phosphate ion does not come into ready contact with soil particles its downward penetration is more rapid than would normally be predicted. Rapid irrigation of waste water on dry, well-structured soil may allow phosphorus movement say into shallow subsurface drains. Second, the application of high rates of waste water effluent can fairly rapidly saturate some soils with phosphate ions. A critical situation could presumably exist with the longtime irrigation of waste water on coarse soil underlain with relatively shallow interceptor drains. Based on our study, some phosphorus might be expected to flow into a 3-foot deep drain in a sandy loam soil on the order of a week if the surface was ponded with waste water containing 300 mg per liter phosphate. Application of large quantities of municipal waste water is being accomplished on relatively coarse soil with a high water table at Muskingum, Michigan under an Environmental Protection Agency grant and the discharge of waste water from Chicago onto similar lands in Indiana has been proposed by the Corps of Engineers. In both systems a saving feature is that return flow collections have been or will be installed. Monitoring of the return flow could then give an early indication of trouble hopefully before excessive pollution of water supplies could occur.

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CHAPTER X

SUMMARY

The objectives of the project were all fairly well met. The mechanisms
by which organo-toxicants are held by the mineral and organic fractions
in the soil are discussed by Meyers and Ahlrichs in Chapter IV and by
Leenheer and Ahlrichs in Chapter V. The fate of organo-toxicant materials
in water storage reservoirs was determined for a carbaryl and a phorate
as reported by Fahey in Chapter II. The work performed on the effects of
organo-toxicants on terrestrial and farm pond invertebrates and verte-
brates was only partially completed, however. Studies with vertebrates
were discontinued in the early part of the project because of the loss
of key personnel. The watersheds upon which the carbaryl and phorate
were applied were very open and singularly devoid of most higher forms of
vertebrates. An initial census of the bluegill population in the reser-
voirs below the treated watersheds showed that individuals in this species
were severely stunted in growth. Although not specifically studied, the
effects of the carbaryl and phorate applications were noted as not par-
ticularly harmful to the vertebrates especially the fish populations.
The effects of organo-toxicants on terrestrial and farm pond invertebrates,
however, were studied in more detail as reported by Pedigo in Chapter VI
and Lawrence in Chapter VII. The role of microorganisms in the elimina-
tion of organo-toxicants from surface and ground waters is discussed by
Hughes and Reuszer in Chapter III. And finally, some control and removal
methods for reducing or eliminating organo-toxicant residues from reser-
voir water supplies are reported by Goodrich and Monke in Chapter VIII
and by Monke and Goodrich in Chapter IX. While Chapter IX concerns the
movement of phosphorus in pollution concentrations in soil, hopefully the
results can be applied to the phosphorus-based pesticides also.

The cooperation between the personnel from the Department of Agri-
cultural Engineering, the Department of Agronomy, the Department of Entom-
ology and the Southern Indiana Purdue Agricultural Center was excellent.
Although the studies were quite diverse, the selection of a problem site

at the Southern Indiana Purdue Agricultural Center had a unifying effect. Most of the studies were based upon the environmental model provided by the three small reservoirs and their respective watersheds at the Center. In total the project resulted in five M.S. theses, five Ph.D. theses and approximately fifteen technical articles.

The small reservoirs, because of their proximity to the application sites and because of the short times of runoff concentrations, presented a ready condition for contamination of their water supplies. However, only trace amounts of phorate and carbaryl residues were ever found in the water samples taken from the reservoirs. The results between years are difficult to compare because of the variation in climatological and agronomic conditions and because of the small amounts of pesticide run-off involved. The amount of pesticide lost from an application site would depend on the occurrence of runoff-producing storms shortly after application and on the availability of the pesticide material to the runoff water. The pesticides used in this project including thimet (phorate), sevin (carbaryl), malathion, parathion and dieldrin were all shown to be highly adsorptive on soil. These pesticides would be largely unavailable to runoff provided the compounds are in contact with soil particles and the particles are not susceptible to erosion. At times, however, an appreciable amount of the pesticide material may be deposited on vegetative material and in this position might be more readily available to runoff.

Adsorption studies on a representative soil of the experimental watersheds and on a Central Indiana soil showed that malathion was very readily adsorbed followed by carbaryl and then phorate. This conclusion was substantiated by the field studies in which continuous monitoring of reservoir water for eight months following applications of phorate and carbaryl at levels four times their recommended dosage showed no trace of carbaryl at anytime in the water and only a slight temporary trace of phorate. The absorptive capacities of carbaryl and parathion upon various organic matter absorbents from the two soils were also studied. Adsorption isotherms for aqueous pesticide concentrations up to six parts per million were determined for calcium and hydrogen saturated organic matter. It is a general observation that acid soils absorb much larger amounts of

organic pesticide than do neutral or alkaline soils, and varying comple-
tion between solvent and solute for adsorption sites at different pH levels
is a definite possible explanation for this effect. Differences in the
adsorptive capacities between the organic matter adsorbents derived from
the two soils were relatively slight.

If for some reason a water supply should become contaminated with a
pesticide, another study showed that a granular activated carbon filter
was very effective in removing minute quantities of dieldrin insecticide
from a water solution. Up to 99 percent of the insecticide was removed.

A study of the decomposition of carbaryl indicated that indigenous
bacteria could degrade the compound by breaking the ring structure after
1-naphthol was formed. Data concerning the role of microorganisms in
the elimination of organo-toxicants from surface waters showed a signi-
ficant variation in numbers of bacteria in each reservoir with time and
location of sampling. Correlation coefficients for water temperature and
organic matter with bacteria were also determined. These data collected
over a significant length of pretreatment time provided baseline informa-
tion for assessing the effect of pesticides on the reservoirs. An effect,
if any, was not apparent from changes in bacterial patterns and behavior.

The establishment of a faunistic baseline based on studies conducted
mostly during a pretreatment period was the singularly most important
criterion for evaluating the effects of organo-toxicants on both terrestrial
and aquatic non-target groups. Comparative data were routinely available
to assess pesticide impact. The objective of this phase of the project
was thus fulfilled by direct comparison analyses. Likewise, the avail-
ability of environmental monitoring equipment provided a bank of data util-
ized in multiple regression analysis to relate population fluctuations
to physical factors, resulting in species models in which the interaction
of temperature and rainfall accounted for from 74.2 to 95.5 percent of
the variation.

While both the Collembola and Odonata work were confirmatory in
their conclusions that no environmental side effects were created by pesti-
cide usage, the multiple collection methods used in the Odonata studies

were particularly instructive because of the diverse and unique data
which could be derived depending upon the sampling method. It would seem
an appropriate conclusion that, in addition to the selection of dissimilar
groups, a series of complementary sampling methods be adopted in future
studies, and that apparent sampling discrepancies should be studied to in-
terrelate their biological significance.