CHLORINATED INSECTICIDE RESIDUES

IN THE SANTA RITA MOUNTAIN AREA

by

James A. Laubscher

A Thesis Submitted to the Faculty of the

DEPARTMENT OF AGRICULTURAL CHEMISTRY AND SOILS

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 6 8

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: James A. Laubscher

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Gordon R. Dutt — July 22, 1968

G. R. DUTT — Date

Associate Professor of
Agriculture Chemistry and Soils

ACKNOWLEDGEMENT

I wish to express my sincere appreciation to Dr. Gordon R. Dutt, Associate Professor of Agriculture Chemistry and Soils, Dr. Thomas H. McIntosh, former Associate Professor of Agricultural Chemistry and Soils and now Associate Professor of Earth Science, University of Wisconsin, Green Bay, and Dr. Clifford C. Roan, Professor of Entomology, under whose direction this study was conducted.

Appreciation is extended to the Community Pesticide Project of the Department of Entomology for supplies, laboratory equipment and stenographic help.

Special gratitude goes to Mrs. Ola Castell for typing this thesis.

Sincere appreciation is extended to my wife, Gerry, for her constant encouragement and our children for their patience during the period of study and during the thesis preparation.

I would also like to thank Dr. D. P. Morgan, Dr. C. R. Hungerford, Dr. R. O. Kuehl, Mr. G. C. Mitchell, and Mr. Bailey Bautiste for their fine cooperation in the accumulation of background information.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

The residual levels of chlorinated insecticides in several chemical and biological systems were studied. The area selected was one in which a diverse ecology existed. The area was predominantly downwind from an agricultural area. The farming operations had included the use of relatively large amounts of extended residual life organochlorine insecticides.

Soil insecticide levels decrease logarithmically with an increase in downwind distance from the application area.

Chlorinated insecticide levels in various animals including deer, quail, mice, rabbits, snakes and rats were studied and related to soil insecticide levels. In each group of animals studied there was a proportional decrease in insecticide residue levels as soil residue levels decreased.

It is apparent from this study that soil insecticide levels may be used to monitor residual concentrations in animals. Conversely, the residue levels in animals may be used to monitor soil residue levels.

The equations for soil - application distance and several animal-soil systems curves have been calculated for this study area.

Based on the above it may possibly be shown that with a single analysis the levels of a contaminant may be predicted within other ecological systems.

INTRODUCTION

In the interceding years since the formulation of synthetic pesticides, tremendous quantities have been applied to agricultural crops.

A major portion of these millions of tons of pesticides are long residual effect organochlorine compounds.

Recently, many people have been concerned with the effects due to the accumulative properties of some pesticides. The effect on wildlife systems which are subjected to some of the pesticides is also under discussion.

The relative levels of pesticides in an ecosystem predominantly downwind from an application area were thought to be of interest. Another aspect would be the relative amounts of drift and accomulation within soil, water and animal species of some of the organochlorine insecticides within the area. A further point of interest was the relationship between the contaminant levels in soil and the contaminant levels within various animal species from the study area.

REVIEW OF LITERATURE

Pesticides are usually applied to crops by spraying. These sprays are subject to drift and may be subsequently deposited downwind.

Following deposition the pesticide residues are subject to the factors of accumulation and degradation within soil, water, plant or animal tissues. All of the above factors determine the ultimate fate of pesticide residues in our environment.

The following discusses the above factors. Pesticide drift from agricultural areas has been studied and documented by many people e.g. (12,26,43).

These papers are typified by that of Gerhardt and Witt (16). These investigators showed that pesticides can and do drift for long distances, and their movements are regulated by particle size, wind velocity and turbulence. For example, a particle 2 microns in diameter will drift up to 21 miles in a three-mile-per-hour wind (3).

Van Middelem (40) in his review of the fate and persistence of pesticides discussed the volatilization of pesticides. By this process it is possible for a pesticide to become airborne again after having been initially precipitated. High temperatures and low humidity tend to increase the amount of insecticide lost through volatilization.

Fleck (14) showed that DDT can be degraded to 4,4'-dichlorobenzophenone in the presence of air and ultraviolet light, under conditions prevalent in Southern Arizona. In all probability much of the DDT transported through the air does not undergo this degradation. Toxaphene can be degraded by prolonged exposure to sunlight (27). Through this mechanism the toxicity and accumulation of toxaphene in an area is probably not of major concern.

Cohen and Pinkerton (10), Abbott, et al. (1), and Wheatly and Hardman (44), have shown widespread distribution of pesticides can be due to translocation of soil particles and subsequent fallout or rainout in far removed areas. Cohen and Pinkerton specifically analyzed a dust storm with a known origin and known deposition location. They found significant quantities of several chlorinated insecticides, with DDT and its metabolites being dominant.

Lichtenstein (21) and Edwards (13) have shown that after accumulation in a given location has taken place, degradation is dependent upon many variables. These variables include chemical and physical properties of the soil, soil biota, organic matter, moisture, temperature, light intensity and formulation of the pesticide. This was in part substantiated by Alexander (4) and others (6,9,20,25). These investigators found that microflora, such as some fungi, and microfauna, such as some bacteria, are partly responsible for decomposition of accumulated chlorinated hydrocarbons.

Water solubility and movement within the soil-water system can also play an important part in the persistence of a chlorinated insecticide before it passes through the soil root area and enters the water table (40). The solubility of DDT has been shown by Biggar, Dutt and Riggs (8) to be in the range of 1.7 ppb.

Most surface waters contain residues of DDD rather than DDT (7). The solubility of DDD is at least 14 ppb (42), much higher than DDT. At the low solubility shown for DDT and DDD, little leaching of these insecticides would be expected. Other chlorinated insecticides, such as toxaphene, are soluble in water up to 50 ppm (18). These soluble insecticides could pose a problem to the environment if allowed to reach the water table. In the water table, the surface factors such as light, biota, and high temperatures could not play their role in the decomposition to non-toxic compounds.

Translocation of some chlorinated insecticides, once in the soil system, have been shown by Lichtenstein (19) and some of his associates (22,23). At the levels at which these authors worked, they noted no significant translocation of pp'-DDT to aerial portions of pea plants. They did note translocation of dieldrin and aldrin. Saha and McDonald (33) from Canada found no relocation of endrin or aldrin in the grain of wheat grown in treated soils, although they did find translocation in the stems and leaves. This is surprising because insecticides are normally more soluble in oils than in water solutions, and the oil content of seeds is about 20 times that of the leaf and stem tissues. Wheeler, et al. (45) noted a two to sixfold increase in dieldrin levels in plants grown in quartz sand over those grown in loam soil. This can be readily explained by the tenacity of adsorption of insecticides by soil clays and organic matter (40).

It can be seen from the preceding that animals would be exposed to pesticides in their environment. Thus, it is not surprising that many investigators such as Turner (35) and others (11,17,32,41) have shown various concentrations of chlorinated insecticides to be present in wildlife and their environment. Within the environment there is a continuous buildup within some species. West (42) reviewed many papers pertaining to concentration of chlorinated insecticides within animals. There is a good possibility that not only is concentration important because of high through-put, but also because of the inability of some species to adequately metabolize chlorinated insecticides.

In summary it has been shown that chlorinated insecticides are transported, deposited and assimilated within the environment. With assimilation, there is also concentration and metabolism to detoxify the insecticides.

OBJECTIVE OF THE STUDY

From the preceding literature review it can be seen that insecticide drift during application has been studied. During the drifting certain chlorinated insecticides may break down into less toxic compounds. Translocation and deposition of adsorbed insecticides on soil particles has been investigated and proven.

Degradation within the soil system is also shown, along with water solubility and plant system translocation of certain chlorinated insecticides.

The levels of chlorinated insecticides have been reported in many different biological systems, among these are mammals, birds, fish, and shellfish.

In all the literature surveyed there has been no indication of any investigators studying an entire ecosystem with respect to the above factors. With this in mind a study ecosystem was chosen that was bordered on the upwind side by intensive agriculture, which in the recent past used large quantities of DDT in its insect control program.

The area selected was the Santa Rita Mountains in Southern Arizona. The area is bounded on the east by State Highway 83, on the south by State Highway 82, on the west by U. S. Highway 89, and on the north by Interstate 10.

Along the western, or upwind, boundary of the area is a narrow zone of intensive agriculture paralleling U. S. Highway 89, almost the entire distance from Tucson to Nogales.

In this ecosystem under surveillance, it was postulated that pesticide drift levels can be predicted by the analysis of representative soil samples. The soil insecticide levels may then be related to different types of mammal, fish, reptile, and bird species, with variations dependent upon their relative abilities to metabolize the pesticides.

EXPERIMENTAL DESIGN

The study ecosystem in the Santa Rita Mountains covers an area of 670 square miles.

Thirteen soil samples were selected, each to represent about 50 square miles (Table 1 and Fig. 1). It was thought that this sampling frequency would give an indication of the relative distribution of chlorinated insecticides present in the area. The samples were taken with a sampling hoe at the soil surface to a depth of 1 cm and covering an area of 0.1 square meters.

Within the area are three streams that flow continuously. Six water grab samples were taken, their locations are shown in Table 1 and Fig. 1. Three samples of water from the flowing streams were collected (sites 5,9,12). Two samples of flood water were also taken (sites 6,11), these were waters that had originated within the study area. The final water sample collected was accumulated runoff (site 13).

Deer fat samples were collected at a local frozen food locker during the past hunting season. The locations from which the animals had been taken were established by telephone conversation with the hunters (Table 1 and Fig. 1). Due to the feeding range of deer, the locations are probably ± six miles (10 km).

Rodents, with the use of museum snap traps, were collected around the periphery of the study area (Table 1 and Fig. 1). Collection sites in the southern portion of the area were washed out by a flood

Table 1. Location and identification of samples.

Site No.	Sample Composition	Location	Soil Type	Tissue Type
1	Soil	NW 1/4 Sec 33 T 15S R14E	Sand	
	Cottonrat	"		Liver
2	Soil	SW 1/4 Sec 8 T 17S R14E	Loam	
	Snake	NW 1/4 Sec 18 T 17S R14E		Liver & Fat
	Cottonrat	NE 1/4 Sec 23 T 18S R13E		Liver & Fat
	Rabbit	"		Liver
	Quail	"		Liver
3	Soil	Sec 34 T 17S R14E	Silt loam	
4	Soil	Sec 4 T 19S R14E	Sand	
	Pack rat	"		Liver
	Quail	Sec 29 T 19S R14E		Liver
	Mule deer	"		Fat
5	Soil	NE 1/4 Sec 11 T 20S R14E	Silt loam	
	Water	"		
6	Soil	NW 1/4 Sec 7 T 20S R13E	Sand	
	Water	"		
	Quail	"		Liver
	Mouse	"		Liver
7	Soil	NE 1/4 Sec 21 T 22S R13E	Sandy loam	
8	Soil	NW 1/4 Sec 2 T 24S R14E	Sandy loam	
9	Soil	SE cor Sec 15 T 22S R15E	Sandy loam	
	Water	"		
	Fish	"		Whole Fish
10	Soil	NW cor Sec 21 T 21S R16E	Sandy loam	
11	Soil	Cent. Sec 36 T 19S R16E	Sandy loam	
	Water	"		
	Deer	T 20S R15E		Fat
	Quail	Sec 10 T 19S R16E		Liver
	Mice	Sec 22 T 19S R16E		Liver
12	Soil	Sec 14 T 18S R16E	Sandy loam	
	Water	"		
	Mice	"		Liver
	Rabbit	"		Fat
	Deer	"		Fat
13	Soil	Sec 7 T 17S R16E	Sand	
	Water	"		
	Mice	"		Liver
14	Whitetail deer	Sec 15 T 19S R15E		Fat
15	Whitetail deer	Sec 27 T 20S R14E		Fat
16	Mule deer	Sec 18 T 20S R14E		Fat
17	Mule deer	Sec 35 T 21S R13E		Fat
18	Whitetail deer	Sec 33 T 20S R15E		Fat

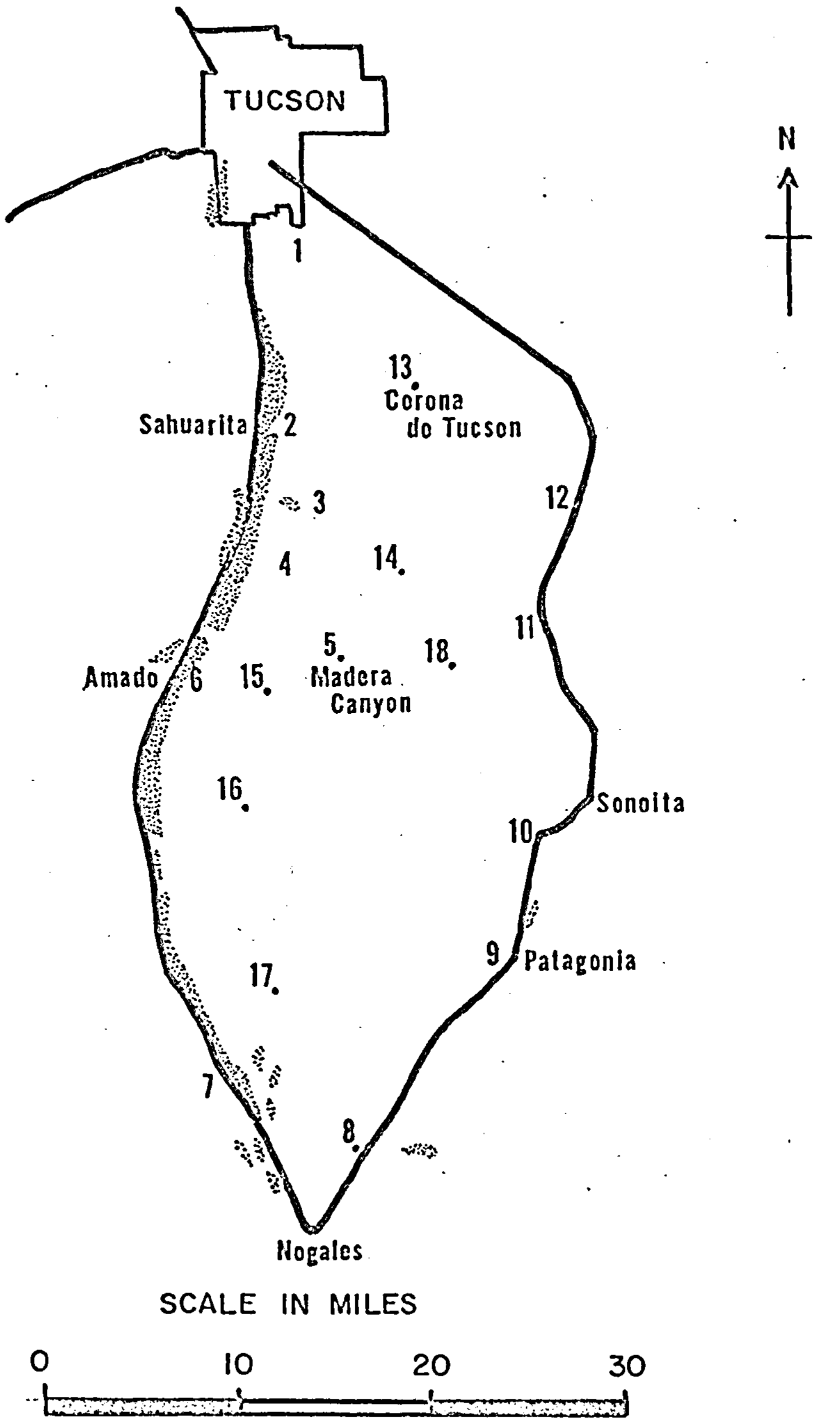

Figure 1. Map of Study Area.

during the sampling program. Many species of rodents hibernate during the winter when the samples were collected.

Quail and rabbit samples were collected by the usual hunting technique during the quail season at the locations given in Table 1 and Fig. 1. The road to the southermost end of the area was washed out and hampered collection of quail and rabbits at that time.

There is only one stream in the area that supports small native fish (Table 1 and Fig. 1). Two different species of fish were collected at the site with the use of an aquatic insect net.

Flood waters forced some hibernating snakes from their nests and two were collected in the agricultural area, site 2 (Table 1 and Fig. 1).

ANALYTICAL PROCEDURES

Sampling, Extraction and Cleanup of Extracts

Soil samples. The soil samples were air dried in the laboratory and passed through a 2 mm sieve. The chemical and physical properties of the soils were determined by the Soil and Water Testing Laboratory, University of Arizona (Table 2). One hundred gm of the less than 2 mm fraction was placed in a 43 x 123 mm preextracted Soxhlet thimble, and refluxed for 24 hours with 300 ml of 1:1 (V/V) hexane and acetone (39). The extract was transferred to a 2 l separatory funnel and washed three times with distilled water to remove the acetone and any polar contaminants. The hexane extract was placed in a 250 ml beaker under a dry air jet on a warm water bath (35 - 40° C) and reduced to about 5 ml (36). The concentrated extract was poured onto 20 gm of n-hexane prewetted (30) 60/100 mesh florisil in a 25 mm I.D. column that had been partially deactivated by the addition of 2 ml of water. The pesticides were then eluted with 200 ml of 0.6:29.4:170 ethanol:ether:hexane. The eluate was concentrated by evaporation to approximately 1 ml, in a 250 ml beaker as described previously. The concentrated eluate was transferred quantitatively to a known volume in a 5 ml graduated centrifuge tube. A measured volume of microliters was injected into the gas chromatograph, described later, for qualitative and quantitative identification.

Water samples. Chemical analysis of the water was done by the Soil and Water Testing Laboratory (Table 3). Two liters of sample

Table 2. Chemical and physical properties of soils.

					Soluble Salts in Sat. Ext.						
Site No.	Soil Type	pH Paste	O.M. (1) %	mm hos/cm $EC_e \times 10^3$	Total salts meq	Na meq	Ca meq	Mg meq	Sand %	Silt %	Clay %
1	Sand	7.8	4.70	.77	.92	.2	.44	.28	90	9	1
2	Loam	7.4	1.25	2.7	7.16	4.8	1.76	.6	36	45	19
3	Silt Loam	6.6	.36	.14	.28	.2	.06	.02	25	61	14
4	Sand	6.6	.60	.2	.28	.1	.08	.1	98	1	1
5	Silt Loam	8.1	5.02	.54	1.14	.6	.36	.18	17	72	11
6	Sand	7.7	.50	.31	.32	.1	.14	.08	97	2	1
7	Sandy Loam	7.5	4.92	1.75	2.20	.3	1.58	.32	60	35	5
8	Loamy Sand	6.9	5.98	.23	.68	.5	.06	.12	77	16	7
9	Sandy Loam	7.8	5.43	.45	.60	.2	.24	.16	61	32	7
10	Sandy Loam	7.4	6.63	.56	.40	.1	.26	.04	64	28	8
11	Sandy Loam	7.5	2.85	.93	1.16	.4	.54	.22	70	25	5
12	Loamy Sand	7.9	1.01	.68	.84	.2	.52	.12	84	15	1
13	Sand	8.0	1.11	.47	.68	.4	.24	.04	96	3	1

(1) O.M. - organic matter
(2) meq - milliequivalents

Table 3. Water chemical analysis.

Site Number	5	6	9	11	12	13
	ppm					
Soluble Salts	397	170	754	132	542	350
Calcium	88	25	136	16	94	37
Magnesium	12	4	28	6	15	2
Sodium	10	15	60	11	30	NA(2)
Chloride	12	8	16	12	24	NA
Sulfate	134	28	266	4	104	NA
Carbonate	24	0	0	0	7	NA
Bicarbonate	117	88	244	83	268	NA
Nitrate	0	2	3.8	0.5	0	NA
$Ecx10^3$ (1)	0.5	0.19	0.82	0.13	0.62	0.39
pH	8.8	7.9	7.3	7.2	8.1	8.8
% Solids (3)		0.8		0.3		

(1) Electrical conductivity - mhos/cm.
(2) Not analyzed.
(3) Residue remaining following filtration.

water, and 100 ml each of methanol and n-hexane were poured into a 2 l separatory funnel. The funnel was vigorously shaken for two minutes after which the phases were allowed to separate. The water phase was discarded, and the hexane phase washed twice with distilled water, concentrated as previously described. The extract was transferred quantitatively to a 5 ml centrifuge tube for further concentration to 0.2 ml. Samples containing suspended solids and coloring components were subjected to the same column chromatography procedure as soil samples except only one-tenth the amount of florisil and eluent were used in an 8 mm I.D. column.

Deer samples. The fat (5 gm) was extracted in a Lourdes omnimixer with a 50 ml microcup containing 35 ml of 1:1 n-hexane and ethanol (28). The extract was transferred to a 250 ml separatory funnel and washed three times with distilled water, discarding each time the water phase. The separatory funnel containing the extract was chilled and the saturated fats removed by quantitative filtration through prerinsed Whatman #1 paper (5). The extract was next concentrated by evaporation on a water bath to approximately 10 ml and partitioned four times with 10 ml of hexane-saturated acetonitrile in a 125 ml separatory funnel (37). After each partitioning, the lower acetonitrile layer was added to a 250 ml separatory funnel containing 10 ml n-hexane and 150 ml distilled water. On completion of the partitioning, the acetonitrile water phase was discarded and the hexane phase rewashed with two additional portions of water. The hexane layer was then subjected to column chromatography exactly as described for the soil samples. The lipid content was determined by The Folch Method (15), by placing 200 mg deer fat tissue in a Duall "B" tissue grinder with 1:1 (V/V) chloroform:methanol, with subsequent solvent evaporation being done in a 50° C oven overnight. The tared weighing vessel was then reweighed and the percent lipid calculated.

Other animal samples. These samples were extracted with the same technique as the deer samples, except 1:1:1 (V/V/V) hexane-diethyl ether-ethanol was used. The chilled filtration step was deleted as was the acetonitrile partitioning on non-fat samples.

An aliquot of the hexane-ether-alcohol extract was evaporated in a tared vessel and the remaining lipid determined gravimetrically (2).

Analysis

Equipment and operating parameters. All the analyses were made using a MicroTek 220 Gas Chromatograph. Operating parameters were as follows:

Column Packing: 5% QF-1 on 80/100 mesh Gas Chrom Q

Pyrex Glass U-tube - 1/4" O.D. x 6'

Temperatures:

Inlet - 230° C

Column - 180° C

Transfer - 238° C

Detector - 203° C

Gas Flow:

Column - 100 ml/min N_2

	Tritium source detector at 23 volts DC polarizing voltage
Recorder:	Honeywell, 0-1 mv single channel

Several confirmatory analyses were made using a MicroTek 220 with a Dohrmann C-200 microcoulometer attached to the column exit to measure halogen specifically. The operating parameters for the work done on the microcoulometer were as follows:

Column Packing:	10% Dow 11 (see reference 31) + 15% QF-1 on 60/80 mesh Chromasorb W Pyrex Glass U-tube - 1/4" I.D. x 7'
Temperatures:	
	Inlet - 230° C
	Oven - 222° C
	Transfer - 230° C
	C-200 inlet - 215° C
	C-200 furnace - 825° C
Gas Flow:	
	Column - 225 ml/min N_2
	Sweep - 20 ml/min N_2
	Oxygen - 20 ml/min O_2
Splitter:	500 parts to microcoulometer, 1 part to tritium source electron capture detector
Bias Read:	120 mv
Titrating cell:	T-300 (silver acetate solution)
Recorder:	Dohrmann, Dual channel 0-1 mv response

Pesticide Identification and Quantitation. A mixed known standard containing α, β, and γ hexachlorocyclohexane, op' and pp' DDE, DDD, DDT, and Dieldrin was injected and the resulting output peaks measured for both retention time and peak height between standard and unknown was used for identification and quantitation respectively.

All solvents used, except ethanol, were redistilled in glass prior to use. The 200-proof ethanol was used as received from U. S. Industrial Chemicals.

Recovery standards and reagent blanks coinciding with each group of samples were simultaneously processed.

Insecticides mentioned in this Thesis and their accepted chemical name:

Dieldrin	- 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonapthalene
α, β, γ BHC	- 1,2,3,4,5,6-hexachlorocyclohexane isomers
DDD	- 2,2-bis(p-chlorophenyl)-1,1-dichloroethane
DDT	- 2,2-bis(p-chlorophenyl)-1,1,1-trichlorethane
DDE	- 2,2-bis(p-chlorophenyl)-1,1-dichloroethylene
Toxaphene	- Octachloro camphene
DDA	- 2,2-bis(p-chlorophenyl)-acetic acid
Aldrin	- 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonapthalene
Endrin	- 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonapthalene

RESULTS AND DISCUSSION

Soil Insecticide Levels. As can be seen in Table 4 and Fig. 2, the proximity to agriculture affects the level of chlorinated insecticide residues present in the soil. The farther downwind a sample site is from an area of agricultural application, the lower the level of residue. The equation of best fit for the points shown is $y = 62680\ x^{-0.844}$ with y being the soil residue level variable and x the downwind distance variable. The correlation coefficient for the points with respect to the calculated curve is 0.325. The standard deviation of y given x is 7.255 ppb.

Since the samples represent only the 0 to 1 cm depth from each site, any removal by leaching of the insecticide cannot be estimated. DDT and its metabolites DDD and DDE are nearly insoluble in water, i.e., 1-15 parts per billion. Leaching therefore should not be important in the loss of these insecticides from the soil surface. Insecticides that are more soluble in water, such as toxaphene (up to 50 ppb) would be affected to a much greater extent. The amount of precipitation penetrating the soil would control the residual levels of the more soluble compounds at the surface.

The average level of total DDT, excluding agricultural areas, is approximately 50 ppb. This level would represent about 45,000 kg (100,000 lbs) of DDT over the entire 1735 sq km (670 sq mi).

Table 4. Chlorinated insecticide levels in soil samples from study area.

Site No.	Km (1)	parts per billion op'-DDE	pp'-DDE	Diel.	op'-DDT	pp'-DDD	pp'-DDT	Total* DDT	pH	Clay %	O.M. %
1	6.6	0.8	26	0.6	3.7	0.9	20	55.4	7.8	1	4.7
2	.01	200	1300		600	500	3800	6700	7.4	19	1.3
3	5	0.3	6		0.7	0.6	8.8	17.4	6.6	14	0.4
4	8	0.7	11.5		1.3	0.4	27	42.6	6.6	1	0.6
5	16		0.5	0.3	0.7	0.1	6.4	7.8	8.1	11	5.0
6	5	0.3	13	0.2	3.7	0.9	20	39.7	7.7	1	0.5
7	2	7	180		21	7	100	341	7.5	5	4.9
8	13	1.5	7	1.3	6	0.9	13	29.8	6.9	7	6.0
9	24		2.6	0.6	3.2		9.6	15.8	7.8	7	5.4
10	29	0.4	7.5	1.1	5	0.6	11	25.7	7.4	8	6.6
11	40	0.3	1.1	0.3	1.0		2.6	5.2	7.5	5	2.9
12	30		0.8	0.2	0.5	0.2	2.0	3.6	7.9	1	1.0
13	19		3.4	0.1	4.5	0.5	15	23.9	8.0	1	1.1

(1) Km - distance upwind to cotton field.
*Total DDT = DDT + 1.114 (DDE + DDD).

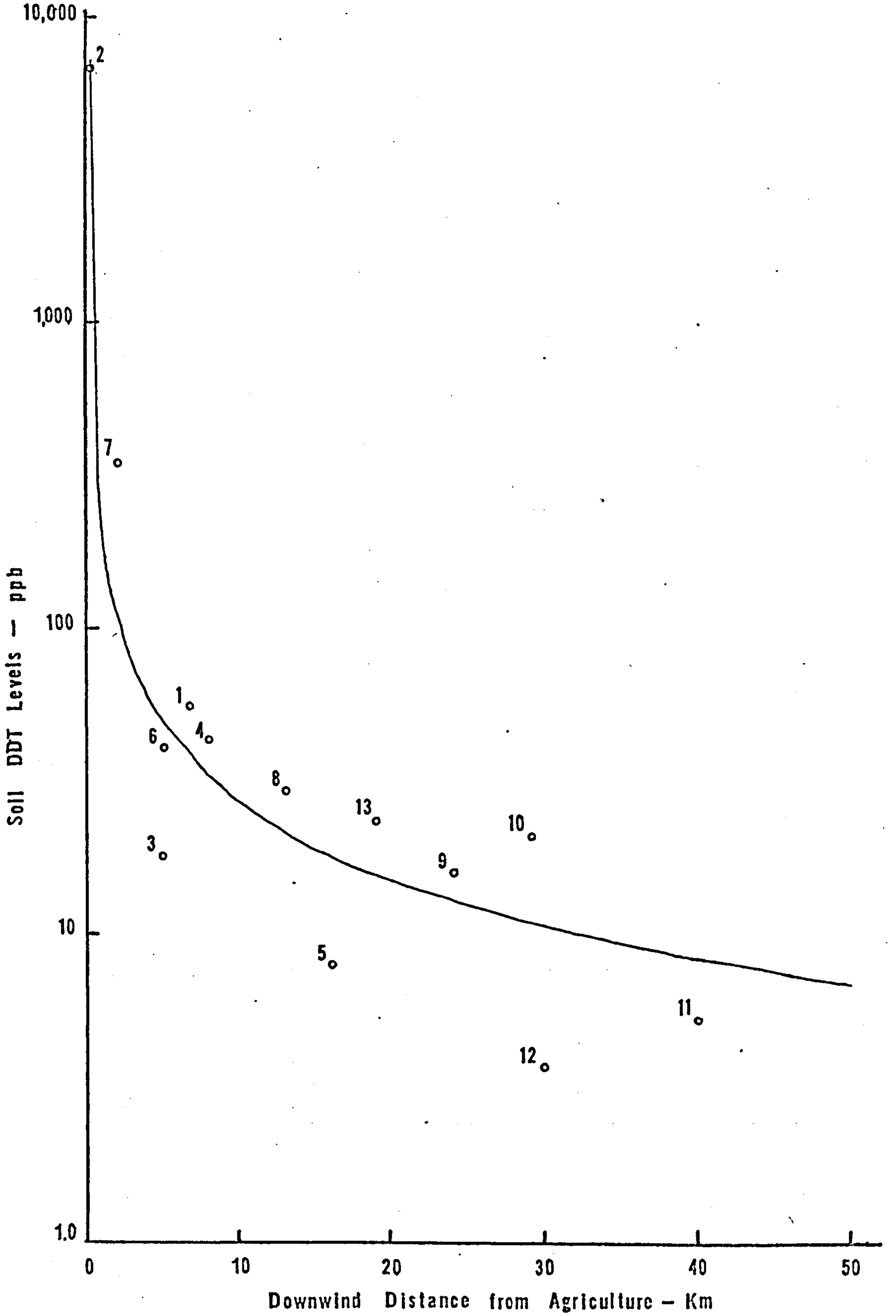

Figure 2. Soil DDT Levels vs Downwind Distance from Agriculture.

There are approximately 9,000 to 13,600 kg (20,000 to 30,000 lbs) of insecticide applied annually on the western edge of the area, predominantly DDT and toxaphene. Therefore, there is either an annual accumulation from drift or a deposition during rainfall and duststorms from other areas. It is likely that both are contributors to the general soil residual levels.

The bulk of insecticides are applied in the months of July and August. In the morning application hours the wind velocity averages 5 to 8 km/hour (3 to 5 mi/hour) from the south, but in the afternoon the wind direction is primarily from the northwest at a rate of 19 to 21 km/hour (12 to 13 mi/hour). Spray drift would therefore tend to go north in the morning and southeast in the afternoon. Due to the increased velocity in the afternoon, the net result would be drift to the southeast from the application area.

A silt loam sample from site number three appeared to have a lower level of insecticide than a sandy soil sample (site No. 4) taken 8 km (five miles) south and both about equidistant from cotton fields. The best explanation seems to be due to the level of soil clay. Some chlorinated insecticides are known to be irreversibly bound to the soil clay fraction and not extractable with the mixed hexane-acetone system (40).

The bulk of the soils represented was quite sandy with little clay and would probably indicate near actual levels. In Arizona in 1967, an average of 2.3 kg of DDT was applied per hectare of cotton (2 lbs/acre). When calculated to the sample size collected for this thesis, it would represent about 8.5 ppm total DDT. In the soil sample from site two, in the center of a cottonfield, a level of 6.7 ppm was reported. The difference between 8.5 ppm applied and 6.7 ppm analyzed is well within reasonable experimental error.

Toxaphene is difficult to analyze due to its multiple component composition, and low response to detection by electron capture. In most of the soil samples analyzed, a peak that corresponds to a major peak in toxaphene appeared in the chromatogram but positive identification was not made.

In several soils dieldrin was reported as being present. Dieldrin is normally not applied to agricultural crops in Arizona, but the retention time and peak characteristic did correspond to dieldrin. It is possible that a degradation product of toxaphene could correspond to dieldrin under the particular column parameters used for this analysis. Figs. 3 and 4 show typical results obtained when both microcoulometric and electron capture detection were employed simultaneously on the same soil sample.

Microcoulometric detection is a means of automatically titrating halogen ions specifically. After silver ions are precipitated by halogens, the amount of current necessary to regenerate the solution is amplified and recorded.

Electron capture detection uses a tritium source for Beta particle radiation. The relative number of Beta particles absorbed by a compound is reflected in a standing current reduction which is amplified and recorded.

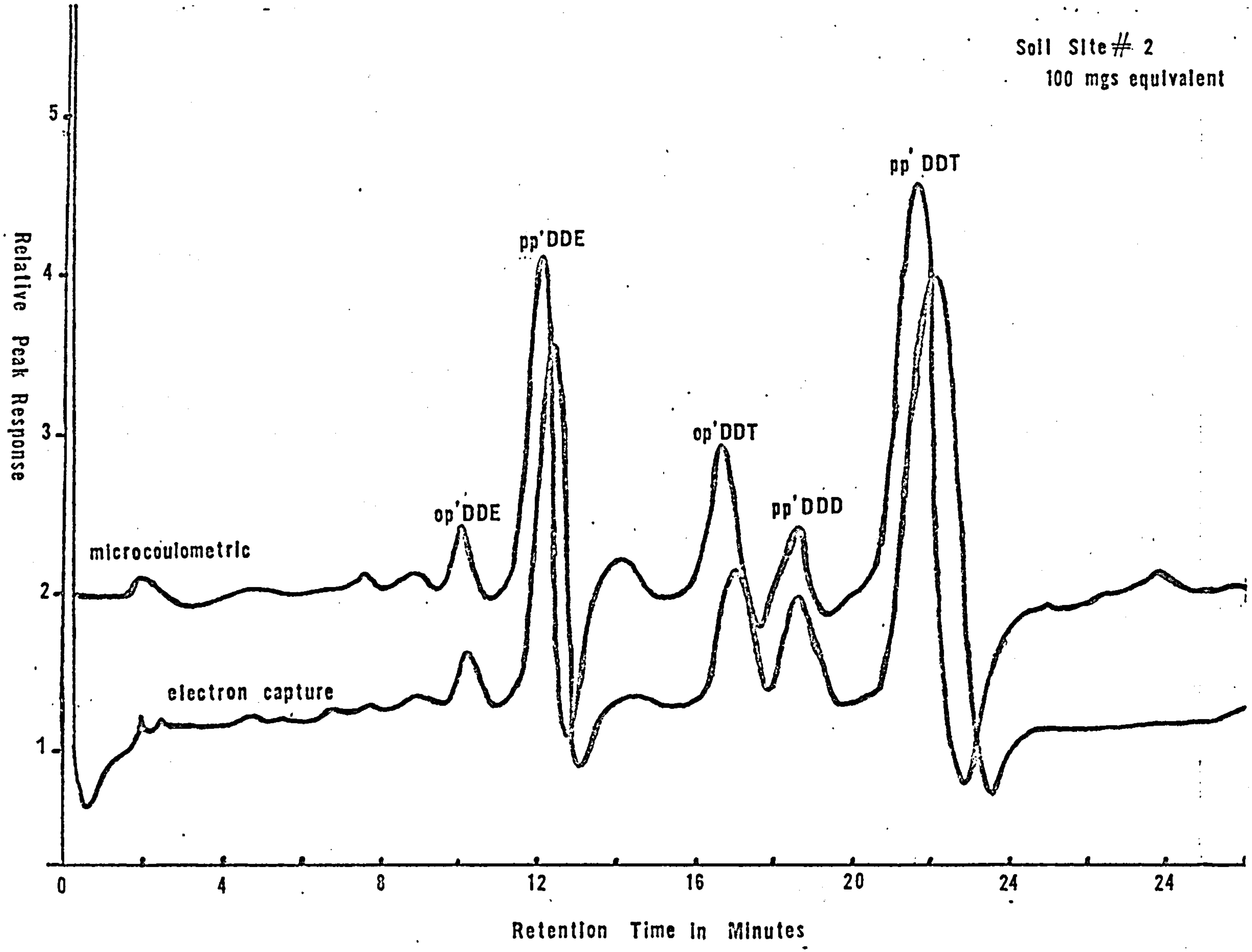

Figure 3. Results of Microcoulometric and Electron Capture Detection, Site No. 2.

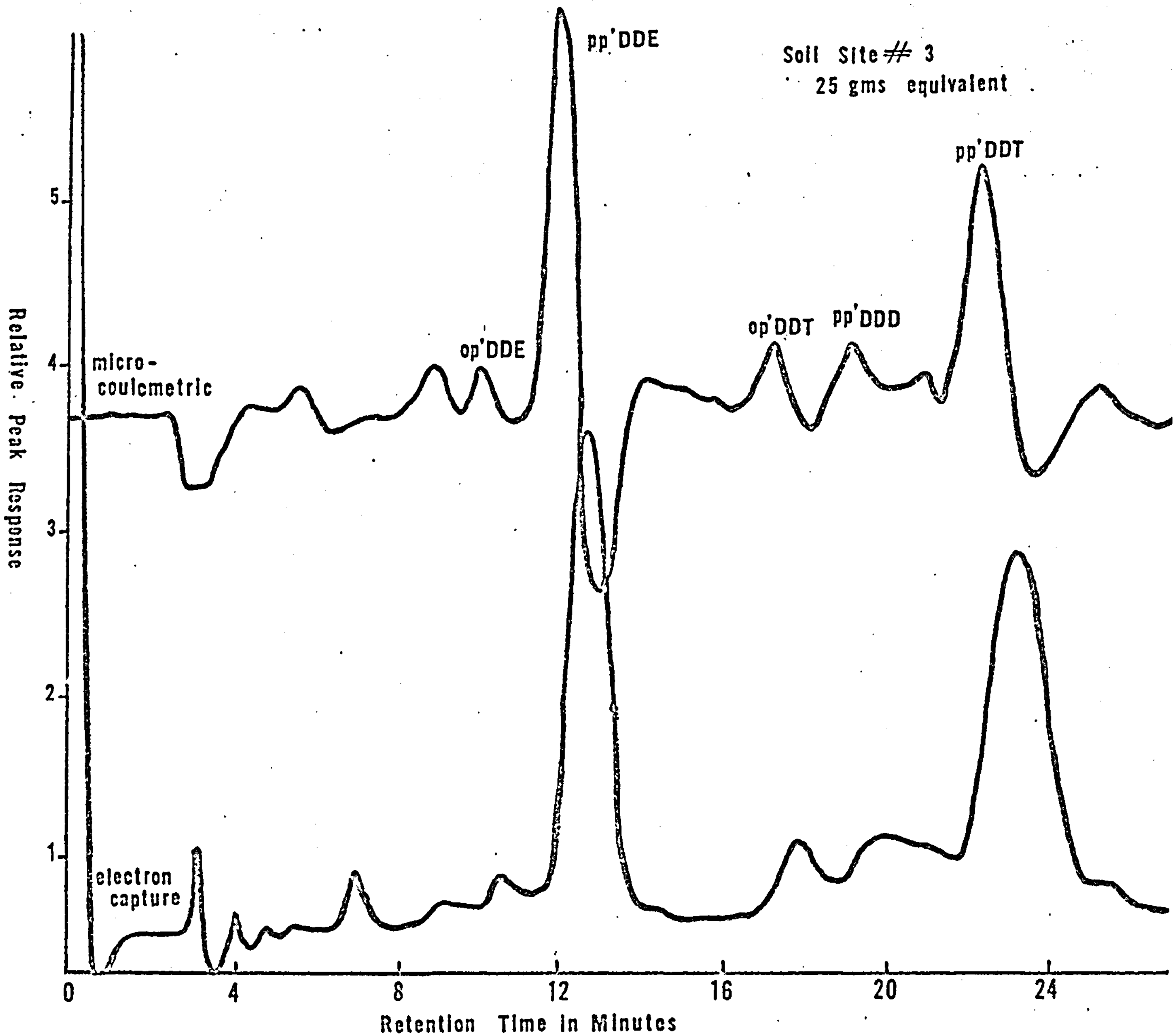

Figure 4. Results of Microcoulometric and Electron Capture Detection, Site No. 3.

Deer peri-renal fat. Seven deer fat samples were analyzed from the area and tabulated in Table 5. Three from desert mule deer (*Odocoileus hemionus crooki*) and four from whitetail deer (*Odocoileus virginianus cousei*).

Table 5. Deer peri-renal fat chlorinated insecticide levels from study area.

Species	Site No.	% Lipid	parts per billion lipid pp' DDE	op' DDT	pp' DDD	pp' DDT	Diel.	Total* DDT	Soil Levels Total DDT ppb
Mule	4	88	22	7	9	80	6	122	39
	16	72	18	7	13	61	6	103	28
	17	91	17	6	8	28	3	62	10
Whitetail	11	100	2	1	4	22	3	29	5.5
	14	93	4	4	12	41	4	63	14
	15	99	7	3	9	68	3	89	25
	18	99	3	4	6	29	2	43	7.4

*Total DDT = DDT + 1.114 (DDE + DDD).

Fig. 5 shows the level of contained total DDT in deer fat plotted against the soil total DDT levels determined from the theoretical curve found in Fig. 2. The equation for the curve is $y = 2.5997\ x + 25.128$, with y representing the deer fat residue levels and x representing the soil residue levels. The linear correlation coefficient between deer fat DDT residues and DDT residues in the soil is 0.9787. The mean residue level is 73.0 ppb and the standard deviation from the mean 30.74 ppb.

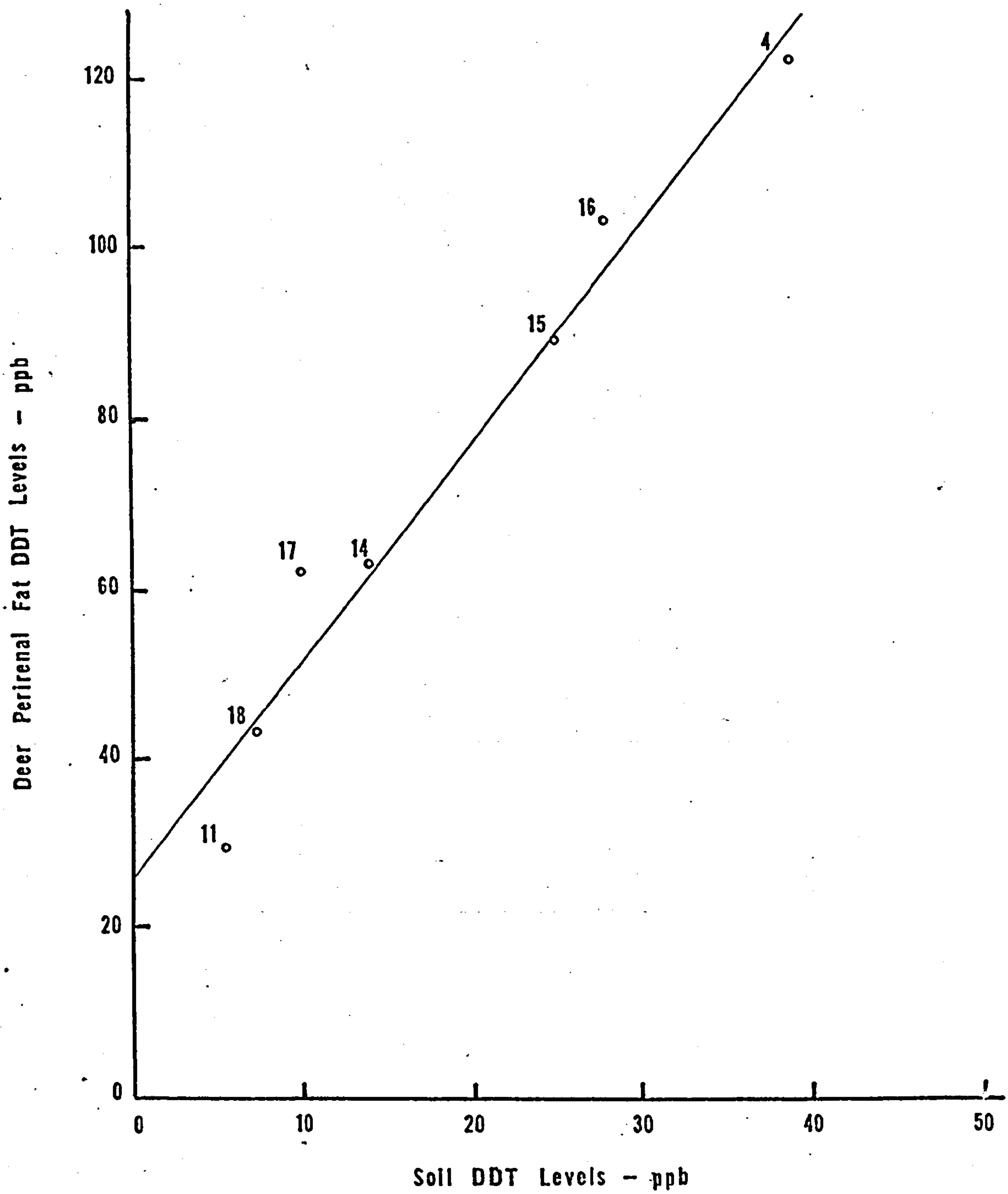

Figure 5. Total DDT in Deer Peri-renal Fat Levels vs Soil Levels.

In this study only male animals were included as the metabolic differences due to sex are not known.

The correlation between deer fat levels and soil levels of insecticide residues is quite good even though the range of the animals may be several kilometers.

The two species sampled eat browse and grass, and apparently little concentration of insecticides occurs. The mule deer reside on the side of the area closest to agriculture and the whitetail are primarily on the side farthest from crop lands.

Quail Liver. The majority of the 14 quail were collected in two non-agricultural areas (Table 6). Arizona quail are non-migratory, having a total range of only one km (0.6 mi) (29). With such a limited range, they should be representative of the local area.

Two Gambel quail (*Lophortyx gambelii gambel*) collected in agricultural areas (sites 2 and 6) had the highest chlorinated insecticide residue levels of any of the animals collected. Their current diet as determined from the contents of their crops consisted mostly of weed seeds common to the site. The Gambel quail collected at site 4 had been eating primarily catclaw (*Acacia greggii*) seed.

The Mearn quail (*Cyrtonym montezumae*) from site 11 had been eating mostly roots and bulbs from the proximity, and had slightly higher levels of chlorinated insecticide residues than would be expected from the soil level analyses. This could be explained by the fact that their diet of roots and bulbs would have soil particles adhering to the surface.

Table 6. Study area. Quail liver pesticide levels.

Site No.	% Lipid	ppm lipid basis pp'-DDE	pp'-DDD	Total DDT*	Soil levels Total DDT ppb
2	4.2	57	0.9	65	6700
4	3.5	18		20	23
	3.5	14		16	"
	3.5	14		16	"
	3.9	17		19	"
	3.4	20		22	"
	3.8	16		18	"
	4.0	12.5		14	"
6	5.3	47	0.6	53	87
11	2.4	28		31	7.6
	5.0	9		10	"
	3.9	15		17	"
	3.8	13		14	"
	4.2	18		20	"

*Total DDT = DDT + 1.114 (DDE + DDD)

As previously noted, DDT probably does not concentrate into seed oils which constitute the Gambel quails' primary food source.

Fig. 6 shows the curve plotting liver lipid DDT levels in quail against soil DDT levels. The equation for the curve is $y = 0.4261x + 11.391$ with y being the liver residue levels and x the soil residue levels.

In spite of the difference in species and diets, the quail liver levels had a correlation coefficient of 0.7588. The mean level was 21.3 and the standard deviation 13.3 from the mean. Quail apparently are not as metabolically active on chlorinated hydrocarbons as other animals and tend to store larger quantities in their livers.

Whitefooted Mice Liver. Whitefooted mice (*Peromyscus sp.*) occur in most all geographical areas of the world and are plentiful in the Santa Rita area.

Twelve mice, (*P. eremicus* and *P. miniculatus*) were collected by trapping. The DDE content of their liver tissue is tabulated in Table 7.

Fig. 7 shows a plot of the liver DDT residue levels against soil DDT residue levels. The equation for the curve is $y = 0.2403x + 0.461$ with y representing the liver residue levels and x representing the soil residue levels. The linear correlation coefficient for the curve is 0.9937 with a mean of 3.10 ppm and a standard deviation of 5.30.

The diet of whitefooted mice is varied and includes seeds and grasses as staples. The total range of the animals is usually less than 100 m (328 ft) radius (29), and the mice are therefore good indicators of insecticide residue levels.

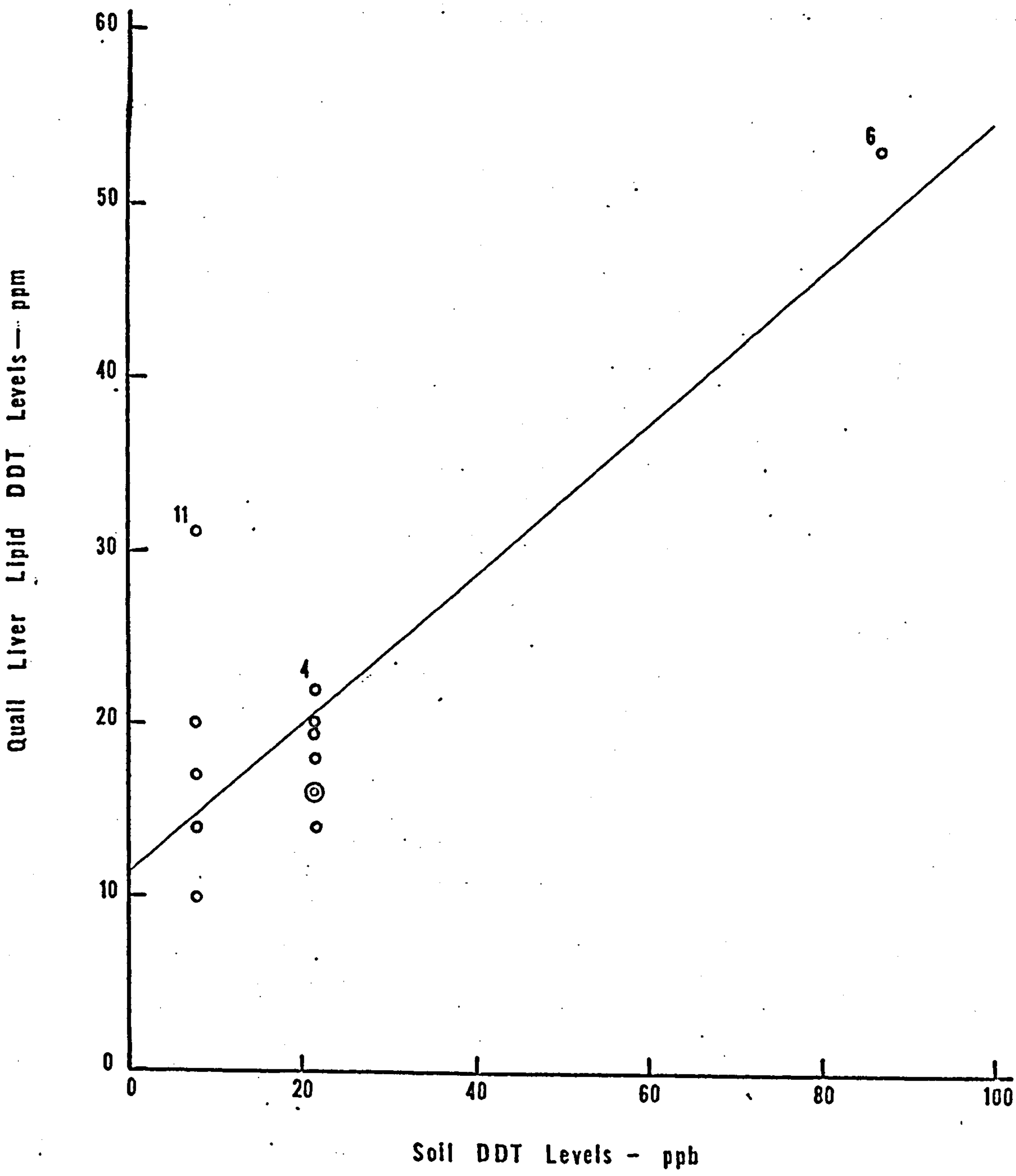

Figure 6. Total DDT in Quail Liver Lipid Levels vs Soil Levels.

Table 7. Study area. Whitefooted mice liver chlorinated insecticide levels.

Site No.	Sex	% Lipid	ppm lipid basis DDE	DDD	Soil levels Total DDT ppb
6	F	4.5	20.5	0.2	39.7
11	F	3.6	0.8		5.2
	M	3.4	0.4		"
	M	4.2	0.14		"
12	M	2.9	1.7		3.6
	F	3.2	1.6		"
	M	3.1	1.1		"
	F	3.0	2.3		"
13	F	2.7	2.0		23.9
	M	4.1	2.9		"
	F	4.1	1.6		"
	M	5.5	2.2		"

Total DDT = DDT + 1.114 (DDE + DDD)

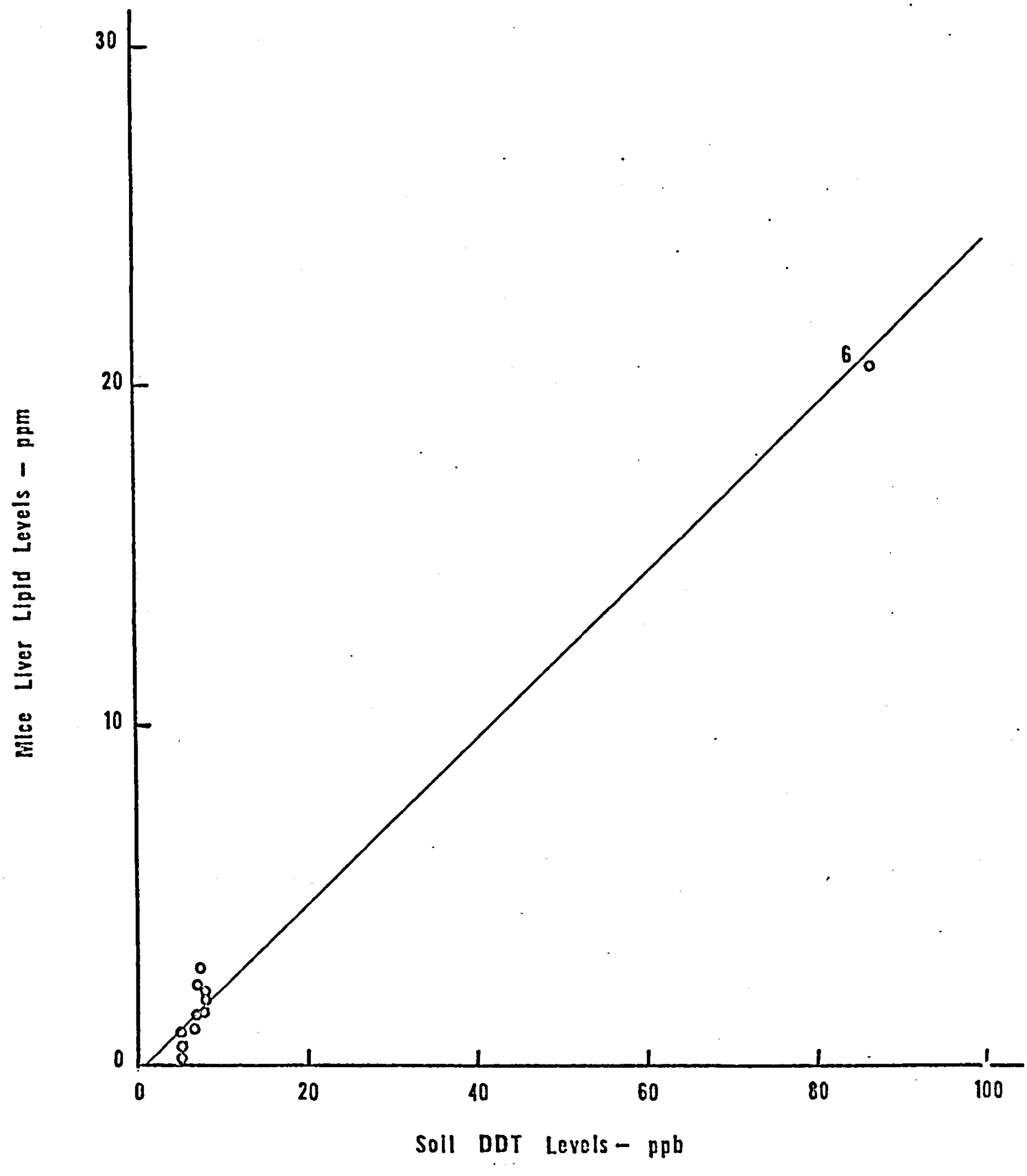

Figure 7. Total DDT in Mice Liver Lipid Levels vs Soil Levels.

Other Animals Represented. Two cotton rats (*Sigmodon hispidus*) were collected (Table 8). One was found drowned the morning after a flood, and the other was trapped. The animal from site No. 2 was much higher in total pesticides than the animal from site No. 1, as expected from the soil levels. The cotton rat diet consists primarily of grass, weed leaves and seeds. The levels were similar to those found in rabbits from like areas listed in the next paragraph. The difference in levels between ppm lipid in liver and fat samples in rats is not known at this time. In human adipose and liver samples, the liver levels are about 80% of adipose expressed on a ppm lipid basis (34).

Two cottontail rabbits (*Sylvilagus auduboni*) were collected from vastly different areas. The animal collected near site No. 12 had levels similar to the deer of the entire area. The animal collected near site No. 2 was as high as the cotton rat from site No. 2 previously mentioned. Originating in an agricultural area, the animal most probably ate plants that had been sprayed directly for insect control.

Two bull snakes (*Pituophis melanoleucus*) were collected and analyzed. It was expected that the levels in these reptiles would be extremely high; however, this was not the case. In the only snake liver analyzed there was an unexpectedly high level of dieldrin. An explanation for this may be that dieldrin has been used around the farm buildings for rodent control, and the snake had ingested a rodent with high levels of dieldrin. Most reptile food would contain epoxides such as dieldrin and metabolized DDT such as DDD or DDE rather than primary products.

Table 8. Other animal sample chlorinated insecticide levels.

Site No.	Genus	Tissue	% Lipid	ppm lipid basis DDE	Diel.	DDD	DDT	Total DDT	Soil levels total DDT ppb
1	Sigmodon	Liver	3.0	1.2		0.9	1.0	3.4	55.4
2	Sigmodon	Liver	6.9	0.49		2.9	10.0	13.9	6700
		Fat	77	0.07			3.5	3.6	6700
2	Sylvilagus	Liver	2.2	9.1	1.8	0.5		10.7	6700
12	Sylvilagus	Fat	65	0.082	0.008		0.034	0.13	6.9
2	Pituophis	Liver	2.4	5.5	7.1			6.3	6700
		Fat	96	7.8	0.02	0.05	1.2	10.0	
	Pituophis	Fat	95	9.0	0.06	0.05	1.7	11.7	
4	Neotoma	Liver	2.2	0.11				0.13	42.6
9	Rhinicthyus	Whole Fish	7.5	5.4				5.8	
	Pautosteus	Whole Fish	3.0	0.25				0.29	

Total DDT = DDT + 1.114 (DDE + DDD)

A packrat (<u>Neotoma albigula</u>) collected from site No. 4 had insecticide levels approximately the same as deer. This is readily explained by the fact that packrats eat mostly succulent cactus and grass, a very similar diet to deer. They have a very limited travel range of about 30 m (100 ft) or less in their lifespan.

Two adult fish, speckled dace (<u>Rhinicthyus osculus</u>) and Gila sucker (<u>Pantosteus clarki</u>) were netted in Sonoita Creek, site No. 9. The insecticide levels in the two fish were quite different. The speckled dace is omnivorous and feeds on insects and algae. The Gila sucker is a bottom-feeding fish and subsists mostly on dead and decomposing organic matter (24). The site was downstream from the Patagonia sewage treatment plant, but the levels in the water and fish do not indicate significant quantities of insecticides in the water from widespread local use.

<u>Water Pesticide Levels</u>. The levels of pesticides in the water samples as shown in Table 9 were extremely low.

The quantity of chlorinated insecticides was not sufficiently large in any case to be confirmed on the microcoulometer. The peaks that were obtained by electron capture detection corresponded exactly to the standards, but there may be some doubt as to the actual identity. There were many unidentified peaks in each water sample. Many of these peaks could be attributed to hydrocarbons deposited by rainfall from volatile products present in the atmosphere.

Table 9. Water sample analyses from study area.

Site No.	pH	% solids	parts per trillion op'-DDE	pp'-DDE	pp'DDT	Total DDT
5	8.8		0.3	1.8		2.4
6	7.9	0.8		0.1	1.2	1.3
9	7.3				0.8	0.8
11	7.2	0.3	0.05	0.8	1.7	2.7
12	8.1				0.8	0.8
13				0.2	2.4	2.6

Total DDT = DDT + 1.114 (DDE + DDD)

SUMMARY AND CONCLUSIONS

Chlorinated insecticide residue levels in soils downwind from an application area decrease logarithmically as the distance from the area of application increases. Levels of organochlorine residues in the agricultural area studied are about 7 ppm. The levels decreased as the distance increased to about 8 ppb at 40 km. As expected the net wind direction influences the ultimate deposition area with regard to particle settling.

Chlorinated insecticide residue levels in animals within the area vary widely, but all are directly proportional to the soil residue levels. The residue levels within deer fat averaged 73 ppb, with a range of 29 to 122 ppb. The mean residue levels in quail livers were 21.3 ppm (lipid basis) with a range of 10 to 65 ppm. Whitefooted mice livers contained an average of 3.10 ppm chlorinated insecticides, with a range of 0.14 to 20.5 ppm, also on a lipid basis.

The high residue levels present in quail and mice are either due to inability of the animal to efficiently metabolize the insecticides or due to good liver storage capabilities for chlorinated insecticides.

Water analyses for insecticide residues would require large samples to effectively quantitate residue levels. A further point to investigate would be the residue levels of the suspended materials with regard to solubility within the water and extraction efficiency from the mixed system.

Other animal species tissues within the area may follow the same trend of linearity with respect to soil levels as do the largest groups of animals sampled. This would depend upon the relative storage or metabolic capabilities and the dietary habits of the individuals.

From this study it is apparent that soil insecticide residue levels are directly proportional to insecticide residue levels in various animals.

Representative analyses should be made to further extend the analytical levels. Analytical manipulation may vary the slope of the curves, but a linear relationship could still exist for most soil-animal systems.

Further study on the proportionality of insecticide residues in soil-animal systems should be conducted.

It is highly likely that with a single representative sample, whether it is an animal or a soil from a given area, the contained contaminating residue levels in other ecological systems from the same area could be predicted with reasonable accuracy. It is also possible that residual levels in other areas may be calculated, knowing the amounts of contaminants being applied and the meteorological conditions pertinent to that area.

SELECTED BIBLIOGRAPHY

1. Abbott, D. C., Harrison, R. B., Tatton, J. O. G., and J. Thomson. Organochlorine Pesticides in the Atmosphere Environment. Nature. 208:1317 (1965).

2. Adams, G. Personal Communication. The University of Arizona (1967).

3. Akeeson, N. B. and W. E. Yates. Problems Relating to Application of Agricultural Chemicals and Resulting Drift Residues. Ann. Rev. Entomol. 9:285 (1964).

4. Alexander, M. The Breakdown of Pesticides in Soils. Paper presented at AAAS Meeting, Washington, D. C. (1966).

5. Anglin, C. and W. P. McKinley. Procedure for Cleanup of Plant Extracts Prior to Analysis for DDT and Related Pesticides. J. Agr. Food Chem. 8:186 (1960).

6. Baily, G. W. and S. L. White. Soil Pesticide Relationships. Agr. Food Chem. 12:324-332 (1965).

7. Barthel, W. Personal Communication. National Communicable Disease Center, Atlanta, Ga. (1968).

8. Biggar, J. W., Dutt, G. R. and R. L. Riggs. Predicting and Measuring the Solubility of pp'-DDT in Water. Bull. Environ. Contamin. Toxicol. 2(2):90-100 (1967).

9. Chacko, C. I., Lockwood, J. L. and M. Zabik. Chlorinated Hydrocarbon Pesticides. Degradation by Microbes. Science. 154(3750):893-895 (1966).

10. Cohen, J. M. and Cecil Pinkerton. Widespread Translocation of Pesticides by Air Transport and Rainout. Amer. Chem. Soc. Series 60:163-176 (1966).

11. Cole, H., Barry, D., Frear, D. E. H. and A. Bradford. DDT Levels in Fish, Streams, Stream Sediments, and Soil Before and After DDT Aerial Spray Application for Fall Cankerworm in Northern Pennsylvania. Bull. Environ. Contamin. Toxicol. 2(3):127-146 (1967).

12. Dean, H. A., Editor
Pesticide drift report. Texas Agr. Exp. Sta. Misc. Publ. MP-620 (1962).

13. Edwards, C. A.
Factors Affecting the Persistence of Insecticides in Soil. Soils and Fert. 27:451-454 (1964).

14. Fleck, E. E.
The Action of Ultraviolet Light on DDT. J. Amer. Chem. Soc. 71:1034 (1949).

15. Folch, J., Lees, M. and G. H. S. Stanley.
A Simple Method for the Isolation and Purification of Total Lipids from Animal Tissues. J. Biol. Chem. 226:497-509 (1957).

16. Gerhardt, P. D. and J. M. Witt.
Summary of Downwind Drift Limits, Comparison of Dust vs. Spray. Pesticide Residue Study, Univ. of Ariz., Sept. (1963).

17. Greenwood, R. J., Greichus, Y. A. and E. J. Hugghins.
Insecticide Residues in Big Game Mammals of South Dakota. J. of Wildlife Mgmt. 31(2):288-292 (1967).

18. Johnson, W. C.
Toxaphene Treatment of Big Bear Lake, California. Cal. Fish Game. 52(3):173-179 (1966).

19. Lichtenstein, E. P.
Absorption of Some Chlorinated Hydrocarbon Insecticides from Soils into Crops. J. Agr. Food Chem. 7:430-433 (1959).

20. Lichtenstein, E. P.
Persistence and Behavior of Pesticidal Residues in Soils. Arch. Env. Health. 10:825-826 (1965).

21. Lichtenstein, E. P.
Research in Pesticides. Academic Press, New York and London. Part V, p 199 (1965).

22. Lichtenstein, E. P. and K. R. Schulz.
Translocation of Insecticides into Aerial Parts of Peas Under Greenhouse Conditions. J. Agr. Food Chem. 8:452-456 (1960).

23. Lichtenstein, E. P. and K. R. Schulz.
Residues of Aldrin and Heptachlor in Soils and Their Translocation into various Crops. J. Agr. Food Chem. 13:57-63 (1965).

24. Lowe, P.
Personal Communication. The University of Arizona (1968).

25. Matsumura, F. and G. M. Boush.
Dieldrin. Degradation by Soil Microorganisms. Science. 156(3777):959-961 (1967).

26. McCollom, G. B.
Orchard Air Dusting and Drift Residues on Adjacent Hayfields. J. Econ. Entomology. 55:999-1000 (1962).

27. Metcalf, R. L.
Organic Insecticides. Interscience Publishers, Inc., New York, p 239 (1955).

28. Mills, P. A., Onley, J. H. and R. A. Gaither.
Rapid Method for Chlorinated Pesticide Residues in Non-fatty Foods. J. Assoc. Offic. Agr. Chemists. 46:186 (1963).

29. Mitchell, G. C.
Personal Communication. The University of Arizona (1967).

30. Moubry, R. J., Myrdal, G. R. and J. A. Jensen.
Rapid Screening Method for Detecting Chlorinated Hydrocarbon Pesticide Residues in the Fat of Milk, Cheese and Butter. Paper presented at Meeting of Assoc. of Offic. Anal. Chemists (1966).

31. Nelson, J. and A. Milun.
Gas Chromatography of High Molecular Weight Fatty Primary Amines. Chem. and Ind. (London) pp 663-664 (1960).

32. Pillmore, R. E., Peterson, J. E., Wilson, R. A., Mohn, M. A., Ise, G. H. and C. W. Hall.
Residues in Forest Birds in New Mexico. Pesticide-Wildlife studies. U. S. Dep. Int. Fish and Wildlife Circ. 199 (1963).

33. Saha, J. G. and H. McDonald.
Insecticide Residues in Wheat Grown in Soil Treated with Aldrin and Endrin. J. Agr. Food Chem. 15(2):205-207 (1967).

34. Thom, J.
Personal Communication. Community Studies Pesticide Project, Berkeley, Calif. (1968).

35. Turner, N.
DDT in Connecticut Wildlife. Conn. Agr. Expt. Sta. Bull. 62 (1965).

36. U. S. Dept. of Health, Education and Welfare, Public Health Service, Bureau of State Services (Environmental Health). Guide to the Analysis of Pesticide Residues. Office of Pesticides, Washington, D. C. Vol. I, Sec. IV A.L.(1) (1965).

37. U. S. Dept. of Health, Education and Welfare, Public Health Service, Bureau of State Services (Environmental Health). Guide to the Analysis of Pesticide Residues. Office of Pesticides, Washington, D. C. Vol. I, Sec. II B.1.a(1) (1965).

38. U. S. Dept. of Health, Education and Welfare, Public Health Service, Bureau of State Services (Environmental Health). Guide to the Analysis of Pesticide Residues. Office of Pesticides, Washington, D. C. Vol. I, Sec. II A.2.(1) (1965).

39. U. S. Dept. of Health, Education and Welfare, Public Health Service, National Communicable Disease Center, Atlanta, Ga. Chemical Methods for the Determination of Pesticide Residues in Human Tissues and in Environmental Samples (1968).

40. Van Middelem, C. H. Fate and Persistence of Organic Pesticides in the Environment. Amer. Chem. Soc. Series 60:228-249 (1966).

41. Walker, C. H., Hamilton, G. A. and R. B. Harrison. Organochlorine Insecticide Residues in Wild Birds in Britain. J. Sci. Food Agr. 18(3):123-129 (1967).

42. West, I. Biological Effects of Pesticides in the Environment. Amer. Chem. Soc. Series 60:38-53 (1966).

43. Westlake, W. E. and F. A. Gunther. Occurrence and Mode of Introduction of Pesticides in the Environment. Amer. Chem. Soc. Series 60:110-121 (1966).

44. Wheatley, G. A. and J. A. Hardman. Indications of the Presence of Organochlorine Insecticides in Rainwater in Central England. Nature. 207:486 (1965).

45. Wheeler, W. B., Frear, D. E. H., Mumma, R. O., Hamilton, R. H. and R. C. Cotner. Absorption and Translocation of Dieldrin by Forage Crops. J. Agr. Food Chem. 15(2):231-234 (1967).