South Dakota State University

Electronic Theses and Dissertations

1969

Ecological and Trophic Distribution of Pesticides in Lack Poinsett, South Dakota

Michael Robert Hannon

Recommended Citation

ECOLOGICAL AND TROPHIC DISTRIBUTION OF PESTICIDES

IN LAKE POINSETT, SOUTH DAKOTA

BY

MICHAEL ROBERT HANNON

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Wildlife Biology, South Dakota
State University

1969

ECOLOGICAL AND TROPHIC DISTRIBUTION OF PESTICIDES

IN LAKE POINSETT, SOUTH DAKOTA

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

_//_   Date

                              Thesis Adviser's   Date

                    Head, Department of Wildlife   Date
                         and Fisheries Sciences

ACKNOWLEDGMENTS

ECOLOGICAL AND TROPHIC DISTRIBUTION OF PESTICIDES

IN LAKE POINSETT, SOUTH DAKOTA
Abstract

MICHAEL ROBERT HANNON

Ecological and trophic distributions of chlorinated hydro-
carbon residues in Lake Poinsett, South Dakota were studied. Com-
ponents of the ecosystem analyzed were water, bottom sediment,
zooplankton, benthic algae, crayfish, aquatic insects and fish.
Concentrations of aldrin, DDD, DDE, DDT, dieldrin, endrin, hepta-
chlor, heptachlor epoxide, lindane, methoxychlor and toxaphene
were determined by gas chromatography and thin-layer chromatography.

DDT and its metabolites, DDD and DDE, were the highest
residues detected in all trophic levels examined. Heptachlor,
heptachlor epoxide, aldrin, dieldrin and lindane were present in
the majority of sample types, while neither endrin nor methoxychlor
was detected above analytical confidence limits in any sample.
Toxaphene was present in only four fish.

The DDT complex was found to increase in percentage of total
residue with higher trophic levels. A change in ratio of DDT to
DDD plus DDE was found with increase in trophic level. While DDT
was most abundant in water, fish and bottom sediment had greater
concentrations of DDD plus DDE. Higher trophic levels had greater
percentages of the epoxide form of heptachlor and aldrin.

Water had the lowest total residue reported. Bottom sediment
and crayfish had 18 times the residue level of water, while zooplankton

and benthic algae showed a 37-fold increase over water. Total residue in fish averaged 790 times that of water, and aquatic insects had the highest magnification over water (7300-fold).

Analysis of fish tissue gave the order of increasing residue concentration as testes, muscle, liver, egg and depot fat.

Fish fat content was correlated (r = 0.40, d.f. = 72) with higher insecticide levels. Analysis of variance showed residue levels increased with age (P < .05). No significant difference was found by analysis of variance between sexes, or between fall and spring collections.

Residue levels in Lake Poinsett water were similar to levels reported for other areas, but fish displayed a much lower magnification over water than has been reported in the literature.

DDT complex levels detected in Lake Poinsett fish were well below the Food and Drug Administration's tentative 5 ppm tolerance limit set on a wet-weight, whole-body basis (Sager pers. comm. 1969). No residues were found above tentative Food and Drug Administration tolerance limits in any sample.

TABLE OF CONTENTS

LIST OF FIGURES

Figure   Page

LIST OF TABLES

INTRODUCTION

Man has always struggled to control his environment. In the last two decades this struggle has been augmented by a new array of biocides for pest control. Chlorinated hydrocarbon pesticides are one of these. Woodwell (1967) reported evidence that pesticides are spread over the earth by wind and water in much the same pattern as radioactive fallout. Migrating fish and birds transport residues thousands of miles, as do oceanic currents. Chlorinated hydrocarbon pesticides have become an integral part of the biological system (Breidenbach, 1965; Weaver et al., 1965).

Since their introduction in the 1940's chlorinated hydrocarbon pesticides have been economically desirable for pest control on agricultural lands because of their low cost and long residual nature. In South Dakota, a predominately agricultural state, pest control is of great economic significance and pesticides have been used since their introduction. Because of this wide use it is important to know residue levels of chlorinated hydrocarbons in the environment. Lakes are of prime recreational and commercial value, and the presence of toxic chemicals in a lake could affect both plant and animal life and decrease desirability of the lake.

Lake Poinsett, the largest natural lake in South Dakota, is economically important for its recreation areas and for its commercial fishery. It is similar to a number of other lakes in the Great Plains region which adjoin crop lands and are shallow, warm

water, alkaline, eutrophic lakes. Lake Poinsett and the Big Sioux
River, which is occasionally diverted into the lake, are surrounded
by cultivated land. The lake acts as a settling basin for much of
the material carried into it by the Big Sioux diversion channel.
Herbicides, insecticides, and other agricultural chemicals have been
used in these areas for many years.

This study was initiated to determine levels and examine
ecological and trophic distribution of chlorinated hydrocarbon
residues in Lake Poinsett.

REVIEW OF LITERATURE

DDT was the first chlorinated hydrocarbon used for pest control. Synthesized in 1874, its insecticidal properties were not discovered until 1939 by Paul Muller in Switzerland. Additional synthetic chlorinated hydrocarbon insecticides were soon developed and now several hundred compounds in thousands of formulations are registered for use in the United States (President's Science Advisory Committee, 1963).

Chlorinated hydrocarbon residues have been found almost universally, even where applications have never been made: in the oil of abyssal fish (President's Science Advisory Committee, 1963); in every major U. S. river system (Weaver et al., 1965); in the air (Antommaria et al., 1965); and in the rain (Wheatly and Hardman, 1965).

Harrington and Bidlingmayer (1958) reported that an application of one pound of dieldrin per acre to a salt marsh killed 1,175,000 fish and nearly annihilated the crab population. Populations of brook trout and other fishes were reduced considerably as a result of DDT spraying to control the spruce budworm in northern Maine (Warner and Fenderson, 1962).

Some chronic effects of chlorinated hydrocarbons observed have been damage to liver and kidney and restricted growth (Andrews et al., 1966), increased susceptibility to disease (Schoenthal, 1963), abnormal appetite (Allison et al., 1963), slowed response to external

stimuli (Cairns and Scheier, 1964), and reduced reproduction (Burdick et al., 1964). Olgilvie and Anderson (1965) reported behavioral changes in temperature selection for salmon exposed to sublethal doses of DDT. Endrin residues in resistant forage fish have been reported to cause mortality to predator fish many times their own weight (Rosato and Ferguson, 1968).

One of the least obvious effects of pesticides has been on food chain organisms. Schoenthal (1963) reported drastic reductions in bottom-dwelling organisms after DDT spraying in Montana. Change in fauna may involve species composition, but more often affects relative abundance and size distributions (Hynes, 1964).

Ferguson and Bingham (1966) found combinations of insecticides more toxic to resistant fish than individual compounds. Higher mortality was an apparent result of differences in mode of action of insecticides and production of a greater over-all stress.

Hunt and Bischoff (1960) demonstrated the concept of biological magnification of pesticides in an aquatic ecosystem. Hickey et al. (1966) found a 50-fold increase in the amount of DDT and its metabolites in the bottom fauna, as compared to bottom sediment in a Lake Michigan ecosystem. Fish feeding on the invertebrates averaged an 11-fold concentration as compared to bottom fauna. DDT and its metabolites were present in all levels of a salt marsh ecosystem (Woodwell et al., 1967). Meeks (1968) reported data showing an over-all increase of DDT concentrations with higher trophic levels.

METHODS AND MATERIALS

Insecticide residue levels in the Lake Poinsett ecosystem were measured from June 1967 to June 1968. Components of the ecosystem examined were water, bottom sediment, zooplankton, benthic algae, crayfish, aquatic insects, and fish. Six sampling stations were established on the lake (Appendix A). Water samples were collected with Kemmerer water sampler. An orange peel dredge was used to collect bottom sediments. Plankton was collected with a Miller sampler and the Birge-Juday sampler equipped with No. 10 nets. Fish were collected by Otter trawl, gill net, beach seine, frame net and electroshocker. All samples were analyzed for aldrin, DDD, DDE, DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, lindane, methoxychlor, and toxaphene (Appendix B).

Water and bottom sediments from each of the sampling stations and composite plankton samples were analyzed. The species composition of plankton was mainly _Daphnia pulex, Chydorus sphaericus, Bosmina, Diaphanasoma_, and _Copepoda_.

Aquatic insects examined were midge larvae (Tendipedidae) and whirligig beetles (Gyrinidae).

Species of fish analyzed included northern pike (_Esox lucius_), carp (_Cyprinus carpio_), spottail shiner (_Natropis hudsonius_), fathead minnow (_Pimephales promelas_), white sucker (_Catostomus commersoni_), bigmouth buffalo (_Ictiobus cyprinellus_), black bullhead (_Ictalurus melas_), channel catfish (_Ictalurus punctatus_), white bass (_Roccus_

chrysops), bluegill (Lepomis macrochirus), white crappie (Pomoxis annularis), black crappie (Pomoxis nigromaculatus), yellow perch (Perca flavescens), and walleye (Stizostedion vitreum).

Whole-body analyses were made. Frozen fish were put through a meat grinder until a homogenous sample was obtained. Fifty grams of each sample were refrozen in pre-treated (washed in detergent and rinsed in distilled water, acetone and hexane) plastic bags.

Lipids were removed from 25 g aliquots of the whole-body samples by successive extraction with 200, 100 and 100 ml 1:9 (v/v) ethyl ether and petroleum ether in a VirTis blendor. Total lipid content was determined by drying the extract with anhydrous sodium sulfate and evaporating to a constant weight.

Samples were extracted and purified for chlorinated hydro-carbon residues by the Florisil column method (Stemp et al., 1964) after fat determination. The lipid extract was placed on top of 50 g of Florisil in a 20 mm x 600 mm Pyrex chromatographic column. Chlorinated hydrocarbon residues were eluted with 750 ml of 1:4 (v/v) dichloromethane in petroleum ether. The eluant was evaporated to near dryness and transferred to a calibrated test tube using hexane as a solvent. Samples were then analyzed for insecticide residues by electron capture gas chromatography (ECGC).

The instrument used for ECGC was a Varian Aerograph HY-FI model 600 equipped with an electron capture detector with a 250-millicurie tritium source. Identification of all samples was made with two

columns: a 1/8 inch o.d. x 5 ft Pyrex column packed with 5% Dow-11 silicone, and a 1/8 inch o.d. x 10 ft Pyrex column packed with 2% QF-1 silicone (Flouro); both on 60/80 mesh (HMDS) treated chromosorb W. Quantitative calculations were made from the Dow-11 column. Identical procedures for ECGC analyses were employed throughout the study.

Identification and quantitative analyses were accomplished from the chromatograms by comparing retention time and peak area of the sample with the retention time and peak area of the reference standard. Parts per million were calculated using the formula:

$$ppm = \frac{V \, w \, A_1}{W \, v \, A_2 \, e}$$

where:

W = weight of sample in grams

V = volume of extract in milliliters

v = volume of extract injected in microliters

w = weight of standard injected in nanograms

A_1 = area of sample peak

A_2 = area of standard peak

e = procedure efficiency correction

Two-gram samples of fat, muscle, liver, testes and egg were also extracted for pesticide residues by the Florisil column method (Stemp et al., 1964).

Methods for extracting insecticide residues from water were taken from Breidenbach et al. (1964). After particulate matter

settled, 750 ml of water were placed in a 1-liter separatory funnel. The sample was acidified with concentrated hydrochloric acid and extracted successively with 100, 50, 35 and 35 ml of hexane. The extracts were combined and dried with anhydrous sodium sulfate, concentrated and subjected to thin-layer chromatography (TLC).

Commercial pre-coated silica gel glass plates were spotted with 0.25 ug of TLC standard (0.025 g aldrin, heptachlor epoxide, endrin; 0.050 g lindane; 0.0125 g heptachlor; all in 25 ml of hexane) and one-half of the concentrated extract. Plates were developed with carbon tetrachloride, dried and sprayed with a 0.1 mg/ml solution of Rhodamine B in ethanol. When viewed under ultraviolet light, the TLC standard indicated the location of possible residues from the sample. The area of the plate containing the sample was then divided into five sections (Fig. 1). Silica gel within each section was removed and the residues were eluted with a mixture of 1:1 (v/v) diethyl and petroleum ether. The eluant was then brought to desired volume and analyzed by ECGC.

Insecticides were removed from bottom sediment by extracting into 3:1 (v/v) hexane/propanol-2 and washing the extract with dis- tilled water (Shell Development Co., 1964). Samples were dried with anhydrous sodium sulfate, evaporated to 0.5 ml and thin-layered the same as water with one modification. When carbon tetrachloride was used as the developing solvent large quantities of an unknown com- pound interfered with insecticide separation. Use of hexane as the solvent moved this compound above the insecticides.

SECT. V	(UNKNOWN)	
SECT. IV	ALDRIN, DDE, DDT HEPTACHLOR	
SECT. III	HEPTACHLOR EPOXIDE DDD LINDANE	
SECT. II	DIELDRIN	
SECT. I	SPOTTING LINE	

Figure 1. Diagram of the sections of separation for
chlorinated hydrocarbon insecticides on thin-
layer chromatography plate.

Zooplankton and benthic algae were analyzed according to procedures of Mills et al. (1963). Insecticide residues were extracted into acetonitrile and partitioned into petroleum ether. Cleanup procedures and EOGC were identical with those for tissue. Dry weight analyses were made following the methods described in the AOAC Manual (1965).

Aquatic insects were extracted for insecticides by the Florisil column method (Stemp et al., 1964) in the same manner as fish tissue.

Random samples of fish, plankton and algae were thin-layered as described by Breidenbach et al. (1964) for further verification of chlorinated hydrocarbon residues. Also a method of identification based on the distribution of insecticides between two immiscible phases was employed on samples having residues difficult to identify (Beroza and Bowman, 1965).

Efficiencies of extraction were determined for all materials analyzed. Samples of each type were divided into two equal parts. Known quantities of insecticides were added to one portion, and the unfortified portion served as a blank. By knowing amounts added and by calculating amounts recovered it was possible to determine percent recovery.

Analytical reference standards (99+ purity) obtained from manufacturers were used throughout the experiment as references and for fortification.

Standards were formulated as follows:

Standard No. 1
.00010 mg/ml heptachlor, dieldrin
.00030 mg/ml DDD
.00050 mg/ml DDT

Standard No. 2
.00010 mg/ml lindane, aldrin, heptachlor
                epoxide
.00015 mg/ml DDE

Standard No. 3
.00175 mg/ml endrin
.00100 mg/ml methoxychlor

Standard No. 4
.00200 mg/ml toxaphene

Florisil, 60/100 mesh, activated at 650 C (Fisher Scientific

Company) was heated at 130 C for 12-14 hours, mixed with 3 percent

distilled water and stored in airtight containers.

Solvents were either Nanograde (Malinkrodt Chemical Works) or

distilled in glass (Burdick and Jackson Laboratories, Inc.).

TLC plates, 20 x 20 cm glass, pre-treated with 0.25 mm

silica gel without a flourescent indicator were obtained from Brink-

man Instruments, Inc.

RESULTS AND DISCUSSION

Fortified samples or controls are commonly used to determine efficiency of extraction and isolation of pesticide residues from biological tissues. This method assumes that insecticides metabolically incorporated into tissues are extracted with equal efficiency as insecticides added to tissue just prior to analysis. Greichus et al. (1968) working with dieldrin-C^{14} concluded that ECGC analysis of fortified control samples gave an accurate measurement of the recovery of insecticide from pheasant tissues in which dieldrin was metabolically incorporated. This was assumed to be true for all samples analyzed in this study, and procedure efficiencies were determined using fortified controls (Table 1).

Average insecticide residue levels (wet weight) for the Lake Poinsett ecosystem are given in Table 2. Neither endrin nor methoxychlor was detected above analytical confidence limits. Toxaphene was found in only four fish, with levels ranging from 0.09 ppm to 1.05 ppm. Toxaphene has been used as a piscicide in adjoining lakes and these fish may have come into Lake Poinsett from previously treated areas. DDT and its metabolites, DDD and DDE, were detected in all trophic levels examined. The heptachlor-heptachlor epoxide and aldrin-dieldrin complexes were present in all types of samples analyzed except crayfish. Lindane was detected in water, plankton and benthic algae, crayfish, and fish, but not in bottom sediment or aquatic insects.

Table 1. Percent recovery of insecticides from components of the
Lake Poinsett ecosystem.

| | Sample | | | |
	Fish	Plankton-Algae	Water	Bottom Sediment
Lindane	62	54	80	48
Heptachlor	68	42	95	32
Heptachlor Epoxide	71	52	70	43
Aldrin	56	50	81	40
Dieldrin	70	66	97	68
DDT	50	74	72	74
DDD	60	63	77	58
DDE	70	66	75	36
Toxaphene	96	60	90	50
Endrin	62	24	92	41
Methoxychlor	67	48	85	41

Table 2. Average insecticide residue levels in the Lake Poinsett ecosystem in ppm.

	No. of samples	Residue					Average total residue
		Lindane	Heptachlor, heptachlor epoxide	Aldrin dieldrin	DDT, DDD,DDE	Toxaphene	
Water	12	.00003	.00006	.00002	.00008	--[1]	.00019
Bottom sediment	12	—	.0008	.0004	.0022	—	.0034
Plankton-algae	7	.0002	.0011	.0007	.0050	—	.007⌐
Aquatic insects	98	—	.312	.164	.919	—	1.395
Crayfish	10	.001	—	—	.002	—	.003
Fish	87	.003	.008	.016	.100	.023	.150

[1]Less than analytical confidence limits (Appendix C)

DDT and its metabolites were the most prevalent insecticide residues detected. These residues are found world-wide and have been reported in remote, non-treated areas (Cole et al., 1967). Aldrin and dieldrin were also present in a majority of samples analyzed. These have both been extensively used in South Dakota. Heptachlor or heptachlor epoxide were found frequently in the analyses. Heptachlor has been used over a large area of eastern South Dakota. Conversion of heptachlor to its epoxide has been reported as common in animals (Davidow et al., 1953), plants (Gannon and Decker, 1958), and soil (Wilkinson et al., 1964). Lindane was found at relatively low concentrations in about one fourth of all samples analyzed. It has had limited use in South Dakota, mainly in cattle oilers, alone or in combination with other chlorinated hydrocarbons.

Comparison of residue composition in Lake Poinsett samples (Table 3) yielded several trends. In all trophic levels analyzed the DDT complex accounted for the greater percentage of total insecticide residues. There was an increase in this percentage from water (44%) to bottom sediment (63%), to plankton and benthic algae (72%), to fish (79%). There was a change in the ratio of DDT to DDD plus DDE with higher trophic levels. DDT was the most abundant in water, while plankton and benthic algae had approximately equal ratios. Fish and bottom sediment had greater concentrations of DDE and DDD. Conversion of the parent compound, DDT, to its metabolites by enzyme systems may account for this change in ratio. Bridges et al.

Table 3. Percent composition of insecticides in components of the Lake Poinsett ecosystem

	Lindane	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	DDT	DDD	DDE
			Average percent composition					
Water	15	10	19	6	6	38	--[1]	6
Bottom sediment	—	8	16	—	13	23	23	17
Plankton-algae	2	1	15	2	8	34	19	19
Fish	2	—	6	1	12	31	25	23

[1]Less than analytical confidence limits (Appendix C)

(1963) reported a marked degradation of DDT to DDD and DDE in fish. Dechlorination of DDT by anaerobic soil microbes has also been reported (Chacko et al., 1966; Guenzi and Beard, 1967).

The aldrin-dieldrin percentage was relatively constant for all trophic levels shown. The heptachlor-heptachlor epoxide complex showed a decrease in percent of total residue with increase in trophic level. In both of these complexes the epoxide showed an increase in percentage while the parent compound declined with trophic level. Lindane decreased in percent of total residue with higher trophic levels. Gakstatter and Weiss (1967) reported that absorption of lindane from water by fish was slower and elimination was faster than that of dieldrin or DDT. They related absorption and elimination to water solubility of the pesticide. Robeck et al. (1965) reported the order of increasing solubility as DDT (16-40 ppb), dieldrin (140-180 ppb), and Lindane (500-6600 ppb). This implies that biological concentration would less likely occur with rapidly excreted insecticides such as lindane than with those having longer residual lives in biological tissues such as dieldrin or the DDT complex.

Average total chlorinated hydrocarbon residues for each type of sample analyzed are given in Table 4. Water had the lowest average residue of all components analyzed from the Lake Poinsett ecosystem. Chlorinated hydrocarbons are only slightly soluble in water, adhere to silt and tend to settle. Water, being basic to the aquatic ecosystem, served as standard of comparison. Bottom sediment had total

Table 4. Average concentration of insecticides in the Lake Poinsett
ecosystem

	ppm	Concentration factor over water
Water	.00019	
Bottom sediment	.0034	18 X
Crayfish	.0034	18 X
Plankton-algae	.007	37 X
Fish	.150	790 X
Aquatic insects	1.395	7300 X

residues approximately 18 fold greater than water. Contributing
factors to bottom sediment residues are siltation, plankton fallout
and decaying organisms. Crayfish also showed an 18-fold increase
over water. Zooplankton and benthic algae had residues 37 times
that of water, while fish exhibited a 790-fold increase over residue
levels in water. Fish concentrate insecticides through feeding or
by direct uptake from water via the gills, while insignificant
residue enters through the skin or by ingestion of water (Ferguson
et al., 1966).

The highest concentration of residues over those of water
occurred in aquatic insects. They showed a 7300-fold increase. The
high levels may have been partly due to comparatively low water

content in these insects as compared to other types of samples. Although Lake Poinsett bottom sediments would be considered excellent habitat for bottom fauna, only a scarce population is in evidence. It is possible that the more susceptible species have been unable to survive the high residue levels indicated. This would explain the apparent discrepancy in bottom fauna levels relative to fish levels. Fish normally feeding on bottom fauna may have altered their feeding habits due to its scarcity.

Insecticide residue concentrations for fish were calculated on both a tissue and a fat basis (Table 5). Tissue basis expresses residues as ug of residue per gram of whole body weight, while fat basis is an expression of ug of residue per gram of lipid present in the tissue sample analyzed. Both tissue (wet weight) and lipid bases are commonly reported in the literature and are shown both ways in this study for reasons of comparison.

Certain trends were apparent in the average insecticide residue levels of fish. DDT complex residues were the highest concentrations detected in all species analyzed. Average levels in species ranged from 35 to 214 ppb. Aldrin and dieldrin were the next highest ranging from 6 to 42 ppb. The heptachlor-heptachlor epoxide complex and lindane ranged from 2 to 26 ppb and 1 to 25 ppb respectively.

Highest average total residue levels were found in carp, channel catfish, northern pike and white sucker in that order. Bluegill had the lowest average levels, followed by spottail shiner, yellow perch

Table 5. Average residue levels for Lake Poinsett fish expressed on a tissue basis (T) and on a fat basis (F) in ppb

| | No. of samples analyzed | Residue | | | | | | | | | | Average total residue | |
| | | Lindane | | Heptachlor, Heptachlor epoxide | | Aldrin dieldrin | | DDT, DDD,DDE | | Toxaphene | | | |
		T	F	T	F	T	F	T	F	T	F	T	F
Fathead minnow	13	9	592	20	810	10	152	89	1742	—[1]	—	128	3296
Spottail shiner	5	5	245	4	59	15	703	47	1279	—	—	71	2286
White sucker	6	2	52	2	59	13	306	91	2388	83	2705	191	5510
Buffalo	11	1	35	8	114	19	246	104	1540	—	—	132	1937
Carp	6	4	42	26	174	30	268	151	1417	176	1152	387	3053
Bluegill	3	1	256	—	—	6	629	35	3819	—	—	42	4704
Yellow perch	6	—	—	3	143	9	422	76	3095	—	—	88	3660
White crappie	7	1	24	3	81	14	396	105	3539	—	—	123	4040
Black crappie	5	25	671	6	168	11	304	92	2518	—	—	134	3661
White bass	6	2	17	10	132	14	183	124	1806	—	—	150	2138
Black bullhead	6	1	32	2	90	8	281	82	3134	—	—	93	3537
Channel catfish	5	2	18	21	156	42	309	214	1561	—	—	279	2044
Walleye	15	2	58	5	229	14	607	81	3912	—	—	102	4806
Northern pike	6	2	58	4	74	8	325	115	3860	74	1382	203	5699

[1]Less than analytical confidence limits (Appendix C)

and black bullhead. Sufficient data were not available for statistical comparisons between species.

Fish tissues in order of increasing concentration of residues were testes, muscle, liver, egg and depot fat (Table 6). Levels in depot fat were approximately ten times greater than those of whole-body samples. Bridges et al. (1963) studying DDT and its metabolites reported the order of increasing concentration in tissues to be muscle, liver, ovary and fat.

Statistical analysis showed a correlation ($r = 0.40$, d.f. = 72) of insecticide content to fat level within species. Fish with greater lipid levels tended to have higher residue levels. Holden (1962) reported that residue levels in tissue were directly related to lipid content. Analysis of variance showed insecticide levels increased with age, older fish within species having higher levels ($P < .05$). In these analyses interaction between age and fat level were not analyzed. No significant difference was found by analysis of variance between sexes. Fish collected in the spring did not have levels of insecticide residues significantly different from those collected in the fall.

Table 6. Insecticide residue levels in several tissues of Lake Poinsett Fish

Tissue	Fat	Egg	Liver	Muscle	Testes
Residue (ppm)	1.08	0.30	0.06	0.05	0.03

Residue levels detected in the Lake Poinsett ecosystem are compared to those reported by others in Table 7. Hickey et al. (1966) studying a Lake Michigan ecosystem reported bottom sediment levels for the DDT complex seven times those observed in Lake Poinsett. DDT concentrations reported by them in bottom fauna were about half those detected in Lake Poinsett aquatic insects. Lake Michigan fish were approximately 40 times higher in these residues than Lake Poinsett fish. Their study area was surrounded by agricultural land receiving significant annual applications of DDT and DDD for many years.

Cole et al. (1967) reported pretreatment levels of DDT and its metabolites in water and bottom sediments of an isolated watershed in Pennsylvania similar to those of Lake Poinsett. Levels for fish averaged 22 times higher in their study area. Woodwell et al. (1967) reported DDT complex residue levels in water nearly identical to those of Lake Poinsett and levels in fish approximately eight times higher in a New York estuary.

In the Pennsylvania watershed there was a 22000-fold increase in fish over water, while fish in the New York estuary showed about a 16000-fold increase over water. Lake Poinsett fish, however, showed a much lower magnitude of concentration over water (1200-fold). Possible factors influencing the relatively low magnification of fish levels over water levels could be water chemistry and lymnological characteristics. Also high productivity of fish and plankton in the lake may result in lower individual concentrations.

Table 7. Comparative levels of DDT complex in Lake Poinsett and other aquatic eco-
systems (wet weight basis) in ppm.

	Lake Poinsett ecosystem	Lake Michigan[1] ecosystem	Pennsylvania[2] watershed	New York Estuary[3] ecosystem
Water	.00008	--[4]	.0001	.00005
Bottom sediment	.0022	.014	.0013	—
Bottom fauna	.919	.410	—	—
Fish	.100	4.220	2.240	.79

[1]Hickey et al. (1966)

[2]Cole et al. (1967)

[3]Woodwell et al. (1967)

[4]Not reported

No pesticide residues were found above tentative Food and Drug Administration tolerance limits in any sample (Sager pers. comm. 1969). DDT complex levels detected in fish were well below the 5 ppm tentative tolerance limit set on a wet-weight, whole-body basis.

SUMMARY

Insecticide residues were measured in the Lake Poinsett eco-
system from June 1967 to June 1968. Ecological and trophic distri-
butions were studied. Components of the ecosystem examined were
water, bottom sediment, zooplankton and benthic algae, crayfish and
fish.

After extraction and purification samples were analyzed for
aldrin, DDD, DDE, DDT, dieldrin, endrin, heptachlor, heptachlor
epoxide, lindane, methoxychlor and toxaphene by electron capture gas
chromatography and thin-layer chromatography. Results were expressed
on a wet-weight basis for all samples analyzed. Residues in fish
were also determined on a fat basis.

Neither endrin nor methoxychlor was detected above analytical
confidence limits, while toxaphene was found in only four fish. DDT
and its metabolites, DDD and DDE, were detected in all trophic levels
examined. The heptachlor-heptachlor epoxide and aldrin-dieldrin com-
plexes were present in all types of samples except crayfish. Lindane
was detected in water, zooplankton and benthic algae, crayfish, and
fish, but not in bottom sediment or aquatic insects.

The DDT complex accounted for the greatest percentage of total
insecticide residues in all trophic levels examined. This percentage
increased from water (44%) to bottom sediment (63%), to zooplankton
and benthic algae (72%), to fish (79%). The ratio of DDT to DDD plus
DDE decreased in higher trophic levels. DDT was most abundant in

water, while fish had higher concentrations of DDD plus DDE. Zooplankton and benthic algae had approximately equal ratios. The aldrin plus dieldrin percentage was relatively constant for all trophic levels, while the heptachlor-heptachlor epoxide percentage decreased. The epoxide form of aldrin and heptachlor increased in percentage with higher trophic levels. Lindane decreased in percentage in higher trophic levels.

Water had the lowest total residue detected. Bottom sediment and crayfish had 18 times the residue level of water, while zooplankton and benthic algae showed a 37-fold increase over water. Total residue in fish averaged 790 times that of water, and aquatic insects had the highest magnification over water (7300-fold).

DDT and metabolites were the highest residues in fish and ranged from 35 to 214 ppb. Aldrin plus dieldrin ranged from 6 to 42 ppb, heptachlor plus heptachlor epoxide from 2 to 26 ppb and lindane from 1 to 25 ppb in fish.

Highest average total residue levels were found in carp, channel catfish, northern pike and white sucker in that order. Bluegill had the lowest average levels followed by spottail shiner, yellow perch and black bullhead.

Analysis of fish tissues showed the order of increasing residue concentration to be testes, muscle, liver, egg and depot fat.

Increasing fat level was correlated ($r = 0.40$, d.f. $= 72$) with higher insecticide levels. Analysis of variance showed residue

levels increased with age (P < .05). No significant difference was found by analysis of variance between sexes, or between fall and spring collections.

Residue levels in Lake Poinsett water were similar to levels reported for other areas, but fish levels showed a much lower magnification over water levels than has been reported in the literature.

DDT complex levels detected in Lake Poinsett fish were well below the Food and Drug Administration's tentative 5 ppm tolerance limit set on a wet-weight, whole-body basis (Sager pers. comm. 1969). No residues were found above tentative Food and Drug Administration tolerance limits in any sample.

LITERATURE CITED

Allison, D. B., J. Kallman, O. B. Cope, and C. C. Van Valin. 1963. Insecticides: effects on cutthroat trout of repeated exposure to DDT. Science 142: 958-961.

Andrews, A. K., C. C. Van Valin, and B. E. Stebbings. 1966. Some effects of heptachlor on bluegills (Lepomis macrochirus). Trans. Amer. Fish. Soc. 95: 297-306.

Antommaria, P., M. Corn, and L. DeMaio. 1965. Airborne particulates in Pittsburgh: association with p,p'-DDT. Science 150: 1476-1477.

A.O.A.C. 1965. Official Methods of Analysis. Association of Official Agricultural Chemists, Washington, D. C.

Beroza, M. and M. C. Bowman. 1965. Identification of pesticide residues at nanogram level by extraction p-values. Anal. Chem. 37(2): 291-292.

Breidenbach, A. W. 1965. Pesticide residues in air and water. Arch. Env. Health. 10: 827-830.

Breidenbach, A. W., J. J. Lichtenberg, C. F. Henke, D. J. Smith, J. W. Eichelberger, Jr., and H. Stierle. 1964. The identification and measurement of chlorinated hydrocarbon pesticides in surface waters. Rev. ed. U. S. Dept. Health, Education and Welfare, Public Health Service Publ. 1241: 63-69.

Bridges, W. R., B. J. Kallman, and A. K. Andrews. 1963. Persistence of DDT and its metabolites in a farm pond. Trans. Amer. Fish. Soc. 92: 421-427.

Burdick, G. E., E. J. Harris, H. J. Dean, T. M. Walker, J. Skea, and D. Colby. 1964. The accumulation of DDT in lake trout and the effect on reproduction. Trans. Amer. Fish. Soc. 93: 127-136.

Cairns, J. Jr., and A. Scheier. 1964. The effect upon the pumpkin-seed sunfish (Lepomis gibbosus) of chronic exposure to lethal sublethal concentrations of dieldrin. Notulae Natur (Philadelphia) 370. 1-10.

Chacko, C. I., J. L. Lockwood, and M. Zabik. 1966. Chlorinated hydrocarbon pesticides; degradation by microbes. Science 154: 893-895.

Cole, H., D. Barry and D. E. H. Frear. 1967. DDT levels in fish streams, stream sediments, and soil before and after DDT aerial spray application for fall cankerworm in northern Pennsylvania. Bull. Environ. Contam. Toxicol. 2(3): 127-146.

Davidow, B. and J. L. Radomski. 1953. Isolation of an epoxide metabolite from fat tissues of dogs fed heptachlor. J. Pharmacol. Exptl. Therap. 107: 259-265.

Ferguson, D. E. and C. R. Bingham. 1966. The effects of pesticides on susceptible and resistant mosquitofish. Bull. Environ. Contam. Toxicol. 1: 97-103.

Ferguson, D. E., J. L. Ludke and G. C. Murphy. 1966a. Dynamics of endrin uptake and release by resistant and susceptible strains of mosquitofish. Trans. Amer. Fish. Soc. 95: 335-344.

Gakstatter, J. H. and C. M. Weiss. 1967. The elimination of DDT-C^{14} and lindane-C^{14} from fish following a single sublethal exposure in aquaria. Trans. Amer. Fish. Soc. 96: 301-307.

Gannon, N. and G. C. Decker. 1958. The conversion of heptachlor to its epoxide in plants. J. Econ. Entomol. 51(1): 3-7.

Greichus, Y., D. Lamb and C. Garrett. 1968. Efficiency of extraction of metabolically incorporated HEOD (Carbon-14) from pheasant tissues, eggs, and faeces. Analyst 93(1106): 323-325.

Guenzi, W. D. and W. E. Beard. 1967. Anaerobic biodegradation of DDT to DDD in soil. Science 156: 1116-1117.

Harrington Jr., R. W. and W. L. Bidlingmayer. 1958. Effects of dieldrin on fishes and invertebrates of a salt march. J. Wildl. Mgmt. 22(1): 76-82.

Hickey, J. J., J. A. Keith and F. B. Coon. 1966. An exploration of pesticides in a Lake Michigan ecosystem. J. Appl. Ecol. 3 (Suppl.): 141-154.

Holden, A. V. 1962. A study of the absorption of C^{14} labelled DDT from the water by fish. Ann. Appl. Biol. 50: 467-477.

Hunt, E. G. and A. I. Bischoff. 1960. Inimical effects on wildlife of periodic DDD applications to Clear Lake. Calif. Fish Game 46: 91-106.

Hynes, H. B. N. 1964. The use of biology in the study of water pollution. Chem. Indust., 1964: 435-436.

Meeks, R. L. 1968. The accumulation of ^{36}Cl ring-labeled DDT in a freshwater marsh. J. Wildl. Mgmt. 32(2): 376-398.

Mills, P. A., J. H. Onley and R. A. Gaither. 1963. Rapid method for chlorinated pesticides residues in nonfatty foods. J. Assoc. Offic. Agr. Chem. 46(2): 186-191.

Olgilvie, D. M. and J. M. Anderson. 1965. Effect of DDT on temperature selection by young Atlantic salmon (<u>Salmo salar</u>). J. Fish. Res. Ed. Canada, 22(2), 1965.

President's Science Advisory Committee, 1963. Use of pesticides. GPO, Wash. 25, D. C. 25p.

Robeck, C. G., K. A. Dostal, J. M. Cohen and J. F. Kreissel. 1965. Effectiveness of water treatment processes in pesticide removal. J. Amer. Water Works Assn. 57: 181-200.

Rosato, P. and D. E. Ferguson. 1968. The toxicity of endrin-resistant mosquitofish to elevin species of vertebrates. Bioscience 18(8): 783-784.

Schoenthal, N. D. 1963. Some effects of DDT on cold water fish and fishfood organisms. Proc. Mont. Acad. Sci. 23: 63-95.

Shell Development Company. 1964. Determination of chlorinated pesticide residues in water, soil, crops, and animal products. Shell Devel. Co., Agr. Research Div., Analytical Methods MMS-43/64. Modesto Methods Series. 15p.

Stemp, A. R., B. J. Liska, B. E. Langlois and W. J. Stadelman. 1964. Analysis of egg yolk and poultry tissues for chlorinated insecticide residues. Poult. Sci. 43(1): 273-275.

Warner, K. and O. C. Fenderson. 1962. Effects of DDT spraying for forest insects on Maine trout streams. J. Wildl. Mgmt. 26(1): 86-93.

Weaver, L., C. G. Gunnerson, A. W. Breidenbach and J. J. Lichtenberg. 1965. Chlorinated hydrocarbon pesticides in major U. S. river basins. Public Health Rep. 80: 481-493.

Wheatly, G. A. and J. A. Hardman. 1965. Indications of the presence of organochloride insecticides in rain-water in central England. Nature 207: 486-487.

Wilkinson, A. T. S., D. G. Finlayson and H. V. Morley. 1964. Toxic residues in soil 9 years after treatment with aldrin and heptachlor. Science 143: 681-682.

Woodwell, G. M. 1967. Toxic substances and ecological cycles. Scientific American 216(?): 24-29.

Woodwell, G. M., C. E. Wurster, Jr. and P. A. Isaacson. 1967. DDT residues in an East Coast Estuary: a case for biological concentration of a persistent insecticide. Science 156: 821-824.
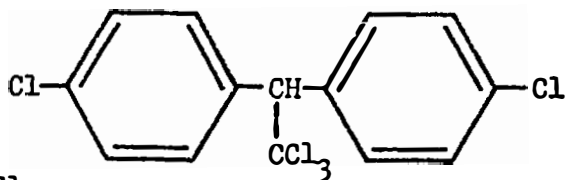
APPENDIXES

Appendix A. Map of Lake Poinsett and Dry Lake, South Dakota showing sampling stations
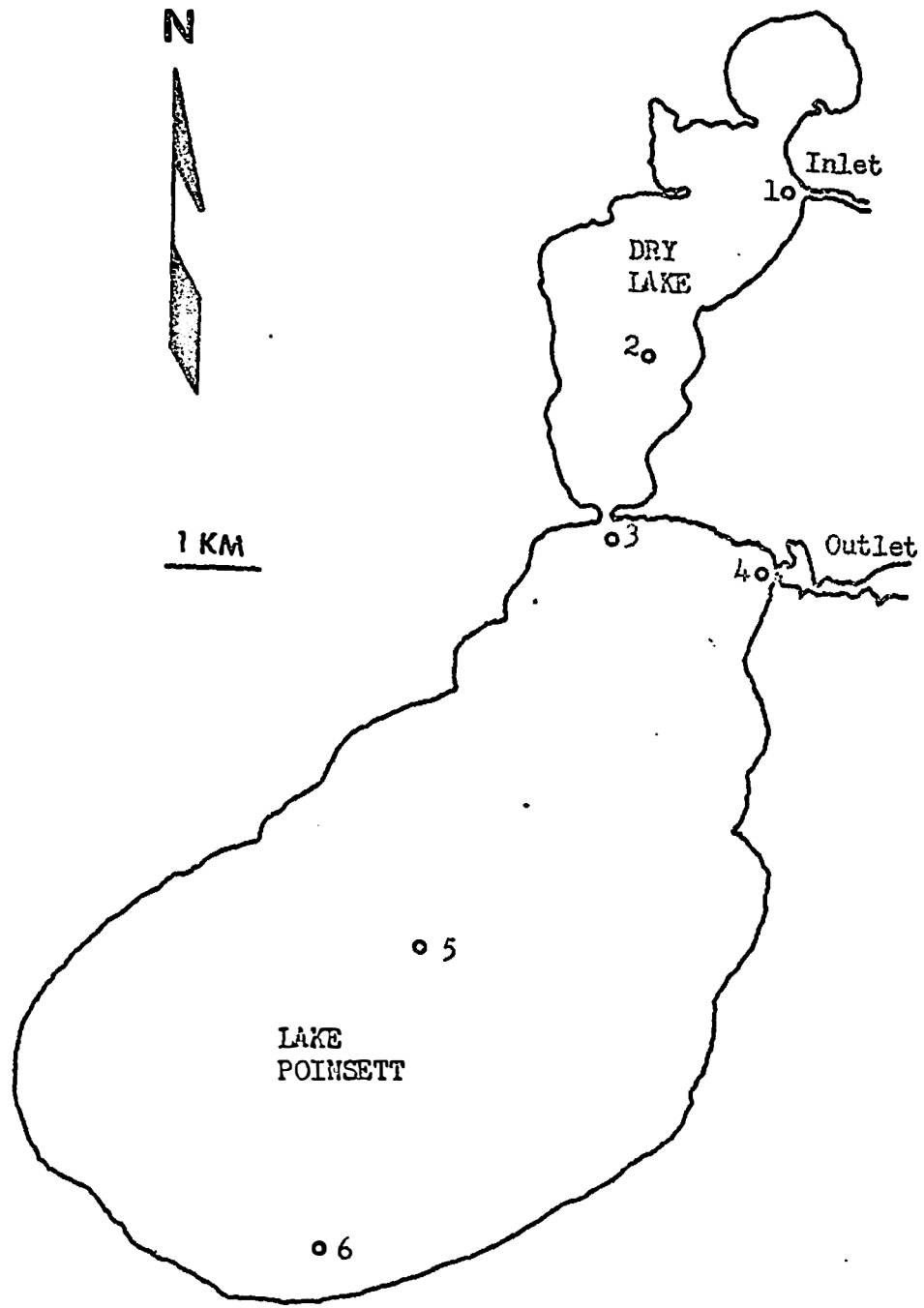
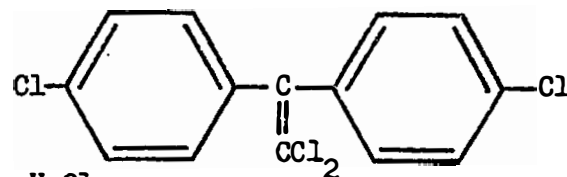Appendix B. Chemical formulas, structures, and scientific names for chlorinated hydrocarbons
investigated

p,p'-DDT   1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane

$C_{14}H_9Cl_5$

M.W. = 354.49

p,p'-DDE   1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene

$C_{14}H_8Cl_4$

M.W. = 318.02

p,p'-DDD   2,2-bis(p-chlorophenyl)-1,1-dichloroethane
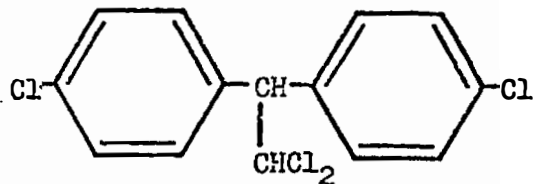
$C_{14}H_{10}Cl_4$

M.W. = 320.05

METHOXYCHLOR   2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane
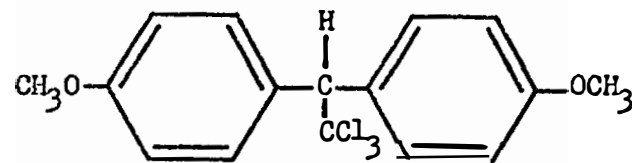
$C_{16}H_{15}Cl_3O_2$

M.W. = 345.65

Appendix B. (Continued).

ALDRIN   1,2,3,4,10,10-hexachloro-
          1,4,4a-5,8,8a-hexahydro-
          endo-1,4-exo-5,8-dimethano-
          naphthalene

$C_{12}H_8Cl_6$
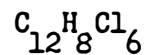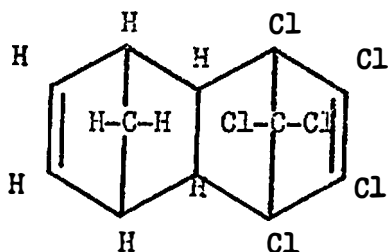
M.W. = 364.93

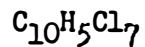DIELDRIN   1,2,3,4,10,10-hexachloro-
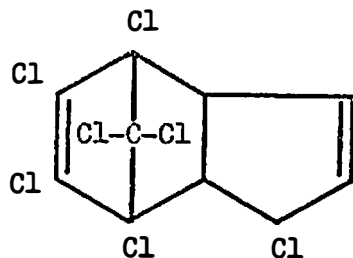   exo-6,7-epoxy-1,4,4a,5,6-
            7,8,8a-octahydro-1,4-endo,
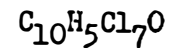   exo-5,8-dimethanonaph-
            thalene

$C_{12}H_8Cl_6O$
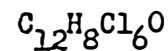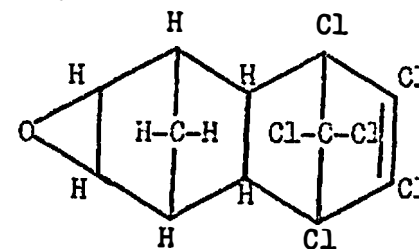
M.W. = 380.9

HEPTACHLOR   1,4,5,6,7,8,8-hepta-
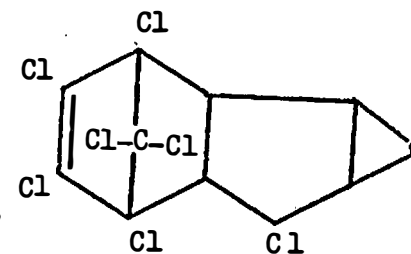   chloro-3a,4,7,7a-tetra-
              hydro-4,7-methanoindene

$C_{10}H_5Cl_7$

M.W. = 373.3

HEPTACHLOR EPOXIDE   1,4,5,6,7,8,8a-
                      heptachloro-2,3-epoxy-3a,
                      4,7,7a-tetrahydro-4,7-
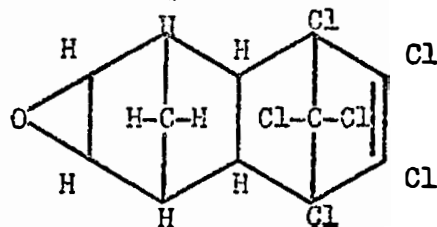   methanoindene

$C_{10}H_5Cl_7O$

M.W. = 389.33

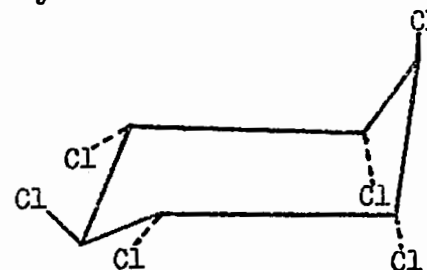Appendix B.   (Continued).

ENDRIN   1,2,3,4,10,10-hexachloro-
6,7-epoxy-1,4,4a,5,6,7,8,8a-
octahydro-endo-1,4-endo-5,8-
dimethanonaphthalene

$C_{12}H_8Cl_6O$

M.W. = 380.9

LINDANE   a,a,a,e,e,e-Hexachloro-
cyclohexane

$C_6H_6Cl_6$

M.W. = 290.85

TOXAPHENE   a mixture of chlorinated
camphenes

Precise nature of the
compounds present is
unknown

$C_{10}H_{10}Cl_8$

M.W. = 413

Appendix C. Minimum analytical confidence limits in ppb (wet weight
basis)

	Fish	Plankton–algae	Water	Bottom sediment
Lindane	1.0	0.1	0.02	0.2
Heptachlor	1.0	0.1	0.02	0.2
Heptachlor epoxide	1.0	0.1	0.02	0.2
Aldrin	1.0	0.1	0.02	0.2
Dieldrin	1.0	0.1	0.02	0.2
DDT	4.0	0.4	0.08	0.8
DDD	4.0	0.4	0.08	0.8
DDE	1.0	0.1	0.02	0.2
Toxaphene	20.0	5.0	1.00	10.0
Endrin	10.0	2.0	0.40	4.0
Methoxychlor	10.0	2.0	0.40	4.0