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The Pesticide Monitoring Subcommittee consists of representatives of the Agricultural Research Service, Consumer and Marketing Service, Federal Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Federal Water Pollution Control Administration, Food and Drug Administration, Public Health Service, and the Tennessee Valley Authority.

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Mrs. Sylvia P. O'Rear
Editorial Manager

PESTICIDES MONITORING JOURNAL
Pesticides Program
Food and Drug Administration
1600 Clifton Rd., N.E.
Atlanta, Georgia 30333

CONTENTS

Volume 3 June 1969 Number 1

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Chlorinated Hydrocarbon Pesticides in California Bays and Estuaries

John C. Modin [1]

ABSTRACT

As part of a nationwide program to monitor organochlorine pesticide residues in estuaries, the U. S. Bureau of Commercial Fisheries in January 1966 contracted to the California Department of Fish and Game the responsibility to monitor selected estuaries in California for pesticides. Analyses of oysters, mussels, and clams sampled at points of interest within each estuary revealed DDT, DDD, DDE, dieldrin, and endrin in concentrations from 10 to 3,600 ppb. Calculations are based on the laboratory wet weight of homogenized tissue. In studies of offshore exposure, high levels of DDT, DDD, and DDE were found in a king crab (2,739 ppb) and in ova from a king salmon (668 ppb). Pesticides were also measured in the ova of prawn, flounder, halibut, and sole; of these, halibut ova were the most highly contaminated, with DDE, DDD, and DDT measuring 591 ppb.

Introduction

As part of a nationwide program to determine the seasonal and geographical variation of organochlorine residues in estuaries (*3*), the U. S. Bureau of Commercial Fisheries in January 1966 contracted to the California Department of Fish and Game the responsibility to monitor selected California estuaries for pesticides. A monthly sampling program began in January 1966 and continued through 1967 in nine California estuaries located from Humboldt Bay in northern California to Hedionda Lagoon in southern California (Fig. 1). In 1968, emphasis was placed on monitoring estuaries with comparatively high pesticide pollution.

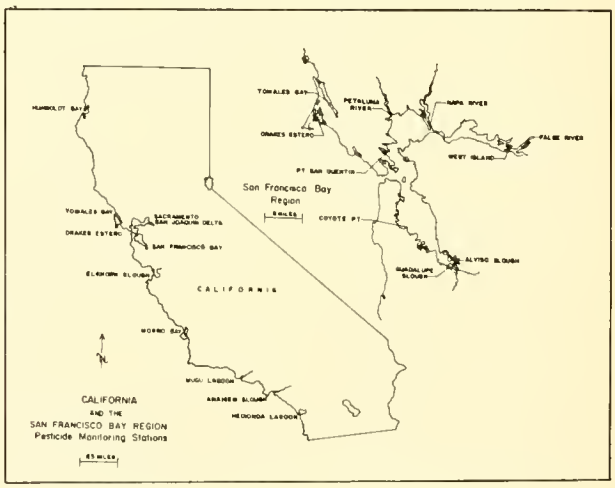

FIGURE 1.—*Pesticides monitoring stations*

Methods and Materials

Shellfish rapidly concentrate minute amounts of pesticides present in estuarine waters. In laboratory studies pesticides were found to accumulate in oysters at levels as much as 70,000 times those present in surrounding waters (*2*). It should be pointed out that shellfish purge themselves rapidly of pesticide residues and therefore represent only recent pollution levels. Butler (*5*) reports three seasonal peaks in residues in shellfish at the mouth of the Arroyo Colorado on the southern coast of Texas

[1] California Department of Fish and Game, Marine Resources Operations, Menlo Park, Calif. 94025.

where much of the rich farm land is harvested three times a year. The filter-feeding characteristic of sedentary shellfish insures a continuous uptake of pesticide residues in the area of observation. Because of this special trait the giant Pacific oyster, *Crassostrea gigas*, the Asiatic clam, *Corbicula fluminea*, and the bay mussel, *Mytilus edulis*, were selected for sampling. Analyses of routine samples were conducted at the Bureau of Commercial Fisheries Laboratory, Gulf Breeze, Fla., and duplicate analyses of all samples were made by the California Department of Fish and Game Laboratory, Menlo Park. Similar results have been obtained at each laboratory; for example, analysis of shellfish samples by the Bureau of Commercial Fisheries in May, June, July, and August of 1968 showed 28, 66, 60, and 25 ppb DDT, respectively. Duplicate analyses of these samples by the California Department of Fish and Game revealed 28, 81, 58, and 23 ppb DDT, respectively. Data presented in Tables 1 thru 4 are the results of the Bureau of Commercial Fisheries Laboratory; Tables 5 and 6 present data from the California Department of Fish and Game.

TABLE 1.—*Chlorinated pesticides in the giant Pacific oyster,* Crassostrea gigas

Year	Pesticide	Residues in PPB (µg/kg)											
		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
HUMBOLDT BAY													
1966	DDE	—	—	—	—	—	<10	11	<10	<10	<10	<10	<10
	DDD	—	—	—	—	—	<10	17	—	21	<10	<10	<10
	DDT	<10	10	—	47	11	14	—	11	—	18	14	20
1967	DDE	10	<10	<10	<10	<10	<10	<10	<10	—	<10	<10	<10
	DDD	<10	—	—	<10	—	<10	<10	—	<10	<10	<10	<10
	DDT	30	28	12	19	19	19	24	12	16	15	21	22
DRAKES ESTERO													
1966	DDE	—	13	<10	10	13	10	17	11	12	<10	<10	11
	DDD	—	15	<10	17	16	10	13	11	<10	<10	<10	10
	DDT	—	<10	—	—	<10	—	—	—	—	—	—	—
1967	DDE	10	11	17	14	16	12	13	<10	13	15	14	<10
	DDD	10	14	20	18	17	14	15	12	16	18	17	<10
	DDT	—	—	10	10	11	10	—	10	10	<10	<10	—
MORRO BAY													
1966	DDE	83	58	43	88	65	40	43	53	73	10	71	72
	DDD	33	27	17	39	25	16	16	22	34	27	33	31
	DDT	23	21	14	30	20	—	—	14	23	23	25	37
	Dieldrin	—	—	—	27	10	—	—	—	—	—	—	—
1967	DDE	62	120	63	110	93	130	64	81	56	43	37	29
	DDD	29	47	43	42	57	56	46	44	33	20	14	10
	DDT	41	96	130	120	92	80	52	49	72	25	20	12

TABLE 2.—*Chlorinated pesticides in the Pacific oyster,* Crassostrea gigas

Year	Pesticide	Residues in PPB (µg/kg)											
		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
ELKHORN SLOUGH													
1966	DDE	160	220	96	96	89	88	86	72	79	84	130	190
	DDD	160	220	120	110	95	82	79	77	66	65	77	160
	DDT	250	290	110	96	85	65	64	55	41	56	76	210
	Dieldrin	—	20	11	20	18	—	—	—	—	10	—	30
1967	DDE	200	220	200	230	210	300	160	200	190	62	190	250
	DDD	160	230	200	260	340	390	200	260	210	55	150	230
	DDT	260	440	390	690	860	920	390	500	390	110	340	370
	Dieldrin	26	25	29	30	39	33	10	10	15	—	14	17

TABLE 3.—*Chlorinated pesticides in the Bay mussel,* Mytilus edulis

Year	Pesticide	Residues in PPB (μg/kg)								
		Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June
MUGU LAGOON										
1967-1968	DDE	130	160	220	250	200	370	170	320	207
	DDD	150	230	280	230	210	350	180	280	168
	DDT	270	440	650	460	340	790	430	510	363
	Dieldrin	—	—	<10	—	—	16	—	—	—
ANAHEIM SLOUGH										
1967-1968	DDE	360	330	200	270	110	170	310	430	203
	DDD	100	150	87	91	45	62	110	120	102
	DDT	85	120	120	160	43	110	77	76	52
	Dieldrin	—	—	—	—	31	—	—	—	<10
HEDIONDA LAGOON										
1967-1968	Toxaphene [1]	—	11,000	970	—	—	—	—	—	—
	DDE	100	130	90	130	52	200	210	130	130
	DDD	72	240	84	73	31	88	220	120	154
	DDT	130	3,600	740	92	200	440	300	53	86

[1] Due to the presence of toxaphene all values for DDT and metabolites are approximated.

TABLE 4.—*Chlorinated pesticides in the Pacific oyster,* Crassostrea gigas *from San Francisco Bay and the Asiatic clam,* Corbicula fluminea *from West Island and False River*

Year	Pesticide	Residues in PPB (μg/kg)											
		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
SAN FRANCISCO BAY													
1966	DDE	12	30	47	52	69	59	37	52	57	51	55	55
	DDD	20	37	60	83	120	62	47	82	90	88	84	110
	DDT	14	13	19	23	45	38	24	43	49	33	40	98
	Dieldrin	—	—	—	14	20	—	—	—	—	11	15	20
1967	DDE	52	34	30	42	23	39	45	53	30	31	100	45
	DDD	130	65	59	75	55	85	120	130	74	68	50	84
	DDT	88	49	49	70	34	64	89	63	38	36	85	45
	Dieldrin	23	11	15	19	13	21	19	17	11	—	10	11
WEST ISLAND													
1967	DDE	280	330	320	270	320	230	170	140	170	180	690	390
	DDD	250	370	350	250	250	210	130	93	150	150	490	310
	DDT	210	300	320	250	260	270	150	130	230	270	1,100	770
	Dieldrin	21	20	22	17	12	18	<10	15	20	10	20	18
	Endrin	10	<10	<10	—	—	—	—	—	—	—	—	—
FALSE RIVER													
1967	DDE				470	460	320	420	270				400
	DDD		No		410	320	200	260	180		No		350
	DDT		Samples		1,000	910	640	780	500		Samples		210
	Dieldrin				28	19	20	16	16				17
	Endrin				—	—	—	—	—				—

TABLE 5.—*Chlorinated pesticides in the Dungeness Crab,* Cancer magister, *in the San Francisco Region*

Sampling Site	Pesticide Residues in PPB (μG/KG)		
	DDE	DDD	DDT
OCTOBER 1967			
Point Bonita (San Fran. Bay Entrance)			
Stripped female	62	—	—
Ova	430	—	—
Double Point (17 mi. north of San Fran.)			
Stripped female	54	—	—
Ova	210	—	—
Bodega Bay (43 mi. north of San Fran.)			
Stripped female	40	—	—
Ova	54	—	—
JANUARY 1968			
Fourfathom Bank (Off San Fran.)			
Stripped female	130	10	—
Ova	220	22	19
South Bank (Off San Fran.)			
Stripped female	—	—	—
Ova	420	65	46
Drakes Bay (25 mi. north of San Fran.)			
Stripped female	110	10	10
Ova	190	15	11

TABLE 6.—*Pesticides in offshore fish and shellfish*

Species and Sample Location	Date of Collection	Pesticide Residues in PPB (μG/KG)		
		DDE	DDD	DDT
Spot Prawn ova Monterey Bay [1]	12/30/67	106	20	ND
Spot Prawn ova Monterey Bay [1]	1/13/68	141	23	ND
Spot Prawn ova Monterey Bay [1]	1/20/68	143	22	65
Spot Prawn ova Monterey Bay [1]	2/09/68	113	25	10
Starry Flounder ova Point Reyes	2/05/68	70	10	ND
Halibut ova Outer Drakes Bay	2/01/68	407	108	76
Sand Sole ova Point Reyes	2/05/68	61	42	30
King Salmon ova (anadromous) American River	1/20/68	475	92	101
King Crab Santa Barbara [2]	2/14/68	2,430	98	211

[1] Fished by commercial fishermen in the Monterey canyon, depth 150 fathoms.
[2] Fished by commercial fishermen in the Santa Barbara channel, 50-100 fathoms.

Samples were refrigerated at 35 to 40 F and were desiccated within 48 hours after collection. Oysters, mussels, and clams were shucked into a clean blender jar and homogenized for approximately 1 minute. Thirty grams of homogenized tissue were mixed with 90% sodium sulfate (anhydrous powder) and 10% Quso, a fine precipitated silica, to equal exactly 90 g (*4*). Crab and fish samples were prepared similarly with the exception that twice the amount of desiccant mix described above was added. The sediment samples were prepared as prescribed for oysters, clams, and mussels. The sample and desiccant were mixed thoroughly and placed in a freezer for approximately 1 hour. The sample was then removed from the freezer, capped with a cutting assembly, and blended until a free flowing mixture was obtained. A duplicate sample of this material was folded in aluminum foil and sealed in a self-sealing plastic bag, removing as much air as possible during the sealing operation. This unfrozen desiccated sample was then packed in a cardboard container and mailed to the Bureau of Commercial Fisheries Laboratory for analysis.

All samples were routinely screened for lindane; heptachlor; aldrin; heptachlor epoxide; the *o,p′* and *p,p′* isomers of DDT, DDD, and DDE; dieldrin; endrin; and methoxychlor. Each sample was weighed in an extraction thimble, placed in a Soxhlet extraction assembly and refluxed with 250 ml of petroleum ether for at least 4 hours. The petroleum ether extract was evaporated to approximately 10 ml and transferred to a separatory funnel for partitioning with two 50-ml aliquots of acetonitrile saturated with petroleum ether. The two acetonitrile partitions were drained into a crystal dish, evaporated to dryness, and transferred to a Florisil elution column. The Florisil was stored at 135 C prior to use. DDT and its metabolites DDD and DDE, lindane, heptachlor, aldrin, heptachlor epoxide, and methoxychlor were eluted from the Florisil column with 200 ml of 6% ethyl ether in petroleum ether; endrin and dieldrin were eluted with 200 ml of 15% ethyl ether in petroleum ether. Further cleanup of the 15% extract on an MgO-Celite column was required. This extract was evaporated to approximately 10 ml and transferred to a 25-ml graduated cylinder for analysis.

Analyses by the California Department of Fish and Game were determined on an F and M model 402 gas chromatograph equipped with a tritium-foil electron capture detector cell. A dual-column system was employed to identify and confirm suspected pesticides. A 1:1 ratio of 3% DC-200 and 5% QF-1 on 80/100 mesh Gas Chrom Q in a 5-foot 3 mm column was used to separate the *o,p′* and *p,p′* isomers of DDT, DDD, and DDE. A 3-foot column of 3% DC-200 on 80/100 mesh Gas Chrom Q was used for confirmation. Ancillary confirmation techniques were not employed. Operating parameters were as follows:

Temperature:	Detector	210 C
	Flash heater	280 C
	Column oven	175 C
Carrier Gas:	95% argon, 5% methane operated at 40 psi and a flow rate of 70 ml/min. A purge gas was not used.	
Instrument Settings:	Pulse interval 150 micro seconds Range 10 Attenuator 16	

Recoveries of the *o,p′* and *p,p′* isomers of DDT, DDD, and DDE ranged between 82% and 111%. A sample of homogenized Pacific oyster tissue free of measurable levels of pesticides was spiked with a standard solution of *o,p′* and *p,p′* DDT, DDD, and DDE. Analysis of the spiked sample recovered 89% *p,p′*-DDE, 102% *o,p′*-DDE, 102% *p,p′*-DDD, 111% *o,p′*-DDD, 92% *p,p′*-DDT, and 82% *o,p′*-DDT. No corrections for recoveries were made.

Although all samples were screened for 10 organochlorine pesticides, only DDT, DDD, and DDE were routinely found. Toxaphene was found in two samples and endrin in only one. Quantitative measurements were recorded as low as 10 ppb and were based on the laboratory wet weight of a single sample of 12 homogenized shellfish. Pesticides identified at lower concentrations are indicated as less than 10 ppb. Polychlorinated biphenyls reported by Risebrough *et al.* (*7*), were not found in samples submitted to the Bureau of Commercial Fisheries for analysis. Polychlorinated biphenyls were not considered in the data presented in Tables 5 and 6.

Results and Discussion

Data collected during the study period show significantly higher pesticide pollution in estuaries receiving runoff from large agricultural and urban areas than in estuaries which are isolated from agricultural and urban drainage. Humboldt Bay, Morro Bay, and Drakes Estero are geographically isolated from extensive agricultural lands. Pesticides in shellfish from these areas seldom exceeded 100 ppb (Table 1). Shellfish in small estuaries receiving irrigation return waters from regions with extensive agricultural operations were found with much higher pesticide levels. Pesticide levels in Elkhorn and Anaheim Sloughs, Mugu, and Hedionda Lagoons reflected the increased exposure to pesticide pollution from nearby agricultural and urban areas; for example, in November 1967, a mussel sample taken in Hedionda Lagoon contained approximately 11,000 ppb toxaphene. DDT and its metabolites DDD and DDE in shellfish

from these areas frequently exceeded 100 ppb (Tables 2 and 3).

Expected high levels of pesticides were not found in San Francisco Bay, the terminating point for the Sacramento and San Joaquin Rivers which drain over 6 million acres of agricultural land in the Sacramento and San Joaquin Valleys. The dilution of highly polluted irrigation water by a voluminous tidal exchange probably retards the accumulations of pesticides in San Francisco Bay shellfish. The greatest accumulation in oysters which occurred in January and August 1967 measured only 130 ppb DDD (Table 4). Additional sampling at the Petaluma and Napa Rivers and Alviso and Guadalupe Sloughs within San Francisco Bay failed to indicate pollution levels comparable with the smaller estuaries influenced by agriculture. Significantly higher pesticide levels were found in shellfish from waters of the Sacramento-San Joaquin River Delta entering San Francisco Bay. In November 1967, a sample of the Asiatic clam from West Island, located in the delta region, contained 1,100 ppb DDT, nearly 10 times the highest level found in San Francisco Bay (Table 4).

PESTICIDE ACCUMULATION IN THE DUNGENESS CRAB, *CANCER MAGISTER*

Commercial fishermen speculate that pesticide pollution may be a factor contributing to the decline of the commercial crab fishery in the San Francisco area where average annual landings dropped from 5.4 million pounds between 1953 and 1960 to 895,000 lb between 1963 and 1968. A similar decline did not occur in the Fort Bragg area, 150 miles north of San Francisco, where extensive pesticide pollution does not exist. Annual landings at Fort Bragg averaged 328,000 lb between 1953 and 1960. Fort Bragg landings increased between 1963 and 1968 averaging 504,000 lb annually.

A preliminary study was initiated in October 1967 to measure pesticide accumulation in adult crabs and in the ova of gravid females. Pesticides in ova and stripped females decreased sharply in samples collected at increasing distances from the entrance to San Francisco Bay (Table 5). Ova collected at Point Bonita near the bay entrance contained 430 ppb DDE. At Double Point, 17 miles north of Point Bonita, ova contained 210 ppb DDE; and at Bodega Bay, 43 miles north of Point Bonita, ova contained only 54 ppb DDE. Lowe (*6*) found that juvenile blue crabs, *Callinectes sapidus*, could survive in flowing sea water containing 0.25 ppb DDT but perished in a few days in water containing DDT in excess of 0.5 ppb DDT. Laboratory studies will be necessary to determine if the much higher levels of less toxic DDE found in ova of the Dungeness crab in the San Francisco area are of sufficient magnitude to lower survival of larvae.

PESTICIDES IN OCEAN MUD, FISH, AND SHELLFISH

Bottom sediments were taken at a depth of 200 feet off Ano Nuevo Island and Bodega Bay to obtain pesticide data in two areas being considered for receiving waters from a proposed central California agricultural drain. Two samples comprising 50% to 75% ophiuroids and miscellaneous marine invertebrates were found with 12 and 19 ppb DDE. Pesticides were not found in the sediment samples with a small proportion of animal material. Pesticides with a retention time less than the *o,p'* isomer of DDE could not be measured. Highly electronegative, unidentified compounds present in these sediments obscured the identification of rapidly eluting pesticides. Since it is unlikely that pesticides other than members of the DDT family would be found in the study area, no effort was made to remove or identify the interference.

Ova from a king salmon, *Oncorhynchus tshawytscha*, taken in the American River in January 1968, contained 668 ppb DDT, DDD, and DDE (Table 6). These residues probably were deposited in the ova prior to the salmon's spawning migration up the American River. Burdick and co-workers (*1*), investigating hatchery losses of lake trout fry in a New York State fish hatchery, found mortalities beginning in fry containing 2,900 ppb DDT. A slight increase in environmental pollution could increase the pesticide burden in king salmon ova to levels that might result in the loss of fry.

Unusually high pesticide levels were found in a California king crab, *Paralithodes californiesis*, taken in the Santa Barbara channel nearly 5 miles off the southern California coast. This specimen had accumulated in its body tissue 2,430 ppb DDE, 98 ppb DDD, and 211 ppb DDT (Table 6). During 2 years of inshore estuarine monitoring, shellfish were seldom found with pesticide residues in excess of 1,000 ppb. It is suspected that an incidental exposure to an unknown but unusually high level of pollution resulted in the pesticide levels observed in the king crab.

Pesticides also were measured in the ova of the spot prawn, *Pandalus platyceros;* starry flounder, *Platichthys stellatus;* California halibut, *Paralichthys californicus;* and the sand sole, *Psettichthys melanostictus*. DDT was found in six of the nine samples collected; and DDE and DDD were found in all samples. Halibut ova were the most highly contaminated, with DDE, DDD, and DDT measuring 407, 108, and 76 ppb, respectively (Table 6).

Plans are being made to investigate how current pesticide pollution in California estuaries affects important sport and commercial species. This information is essential to insure the protection of fisheries and wild-

life resources from the chronic, sublethal pesticide levels prevailing in the marine environment.

Summary

This study is part of a nationwide surveillance program conducted by the Bureau of Commercial Fisheries to determine the extent of pesticide pollution in estuaries.

Shellfish are used as sampling organisms because of their ability to concentrate extremely low pesticide levels commonly present in the marine environment. The filter feeding characteristic of sedentary shellfish insures a continuous uptake of pesticides in the areas of observation. All samples were routinely screened for lindane; heptachlor; aldrin; heptachlor epoxide; the *o,p'* and *p,p'* isomers of DDT, DDD, and DDE; dieldrin; endrin; and methoxychlor. DDT, DDD, DDE, and dieldrin were routinely identified in California estuaries. The voluminous dilution of pesticides and the time lapse from pesticide application prevent identification of other pesticides in estuarine shellfish.

Pesticide residues in estuaries geographically isolated from agricultural areas seldom exceeded 100 ppb. Pesticide residues frequently exceeded this level in agricultural regions and were found as high as 11,000 ppb in shellfish from polluted areas.

Studies revealed 430 ppb DDE in the ova of Dungeness crab taken in the San Francisco area. This level decreased to 54 ppb in samples collected 43 miles north of San Francisco.

Acknowledgments

The author wishes to acknowledge the Pesticides Monitoring Program of the Bureau of Commercial Fisheries for the full financial support of this program. Special credit is given Mr. Alfred Wilson, Jr. for the chemical analysis of these samples.

See Appendix for chemical names of compounds mentioned in this paper.

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PESTICIDES IN WATER

Pesticide Residues in Sediments of the Lower Mississippi River and its Tributaries [1]

W. F. Barthel[2], J. C. Hawthorne[3], J. H. Ford[3],
G. C. Bolton[4], L. L. McDowell[4], E. H. Grissinger[4], and D. A. Parsons[4]

ABSTRACT

Studies of the chlorinated hydrocarbon content of sediments and water from the lower Mississippi River and its tributaries were conducted in 1964, 1966, and 1967 to determine the extent and possible sources of agricultural pesticides in the streams of the Delta.

The Mississippi River bed was sampled at 11 sites located between Tiptonville, Tenn., and New Orleans, La. Tributaries of the Mississippi in the Delta were sampled in Tennessee, Mississippi, Louisiana, and Arkansas.

Pesticides residues were detected from both agricultural and nonagricultural sources; however, no evidence was found of a general buildup of chlorinated hydrocarbons in the sediments of these streams from farm use. Dieldrin, aldrin, endrin, endrin keto, isodrin, chlordane, heptachlor, hexachloronorbornadiene, and heptachloronorbornene were found in sediment and water samples collected from Cypress Creek and Wolf River at Memphis, Tenn., near a primary manufacturer of endrin and heptachlor. Lower concentrations of several of these compounds were detected in sediments collected from tributary streams in Mississippi near formulating plants that prepare the technical pesticides for agricultural use. DDT analogs and metabolites were found in some of the tributary streams where no known formulators are located.

[1] Cooperative study: USDA Agricultural Research Service, Mississippi Agricultural Experiment Station, and the University of Mississippi. Food and Drug Administration, Public Health Service, Department of Health, Education, and Welfare, Atlanta, Ga. 30333. Formerly with the Plant Pest Control Division, U. S. Department of Agriculture, Gulfport, Miss. 39501.

[2] Plant Pest Control Division, U. S. Department of Agriculture, Gulfport, Miss. 39501.

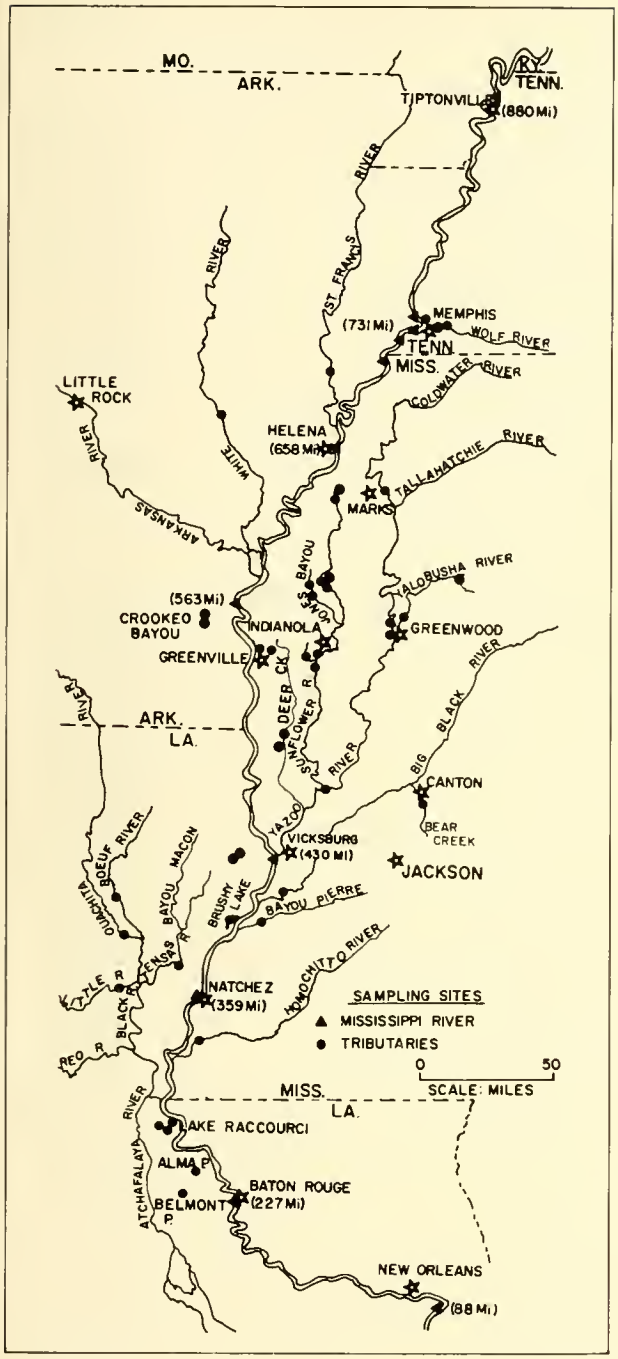
[3] Sedimentation Laboratory, Soil and Water Conservation Research Division, U. S. Department of Agriculture, Oxford, Miss. 38655.

Introduction

A study of the chlorinated hydrocarbon insecticide contamination of streambed materials in the lower Mississippi River and its tributaries was conducted in June and July 1964. This study was part of a planned program to investigate the fate of pesticides in our environment. The area of sampling was principally within the Mississippi River Delta (Fig. 1) a productive agricultural area where relatively large quantities of pesticides are used. Results of this investigation indicated two distinct sources of contamination (*1*). One was in the region of manufacturing operations in the Wolf River-Cypress Creek complex in Memphis, Tenn. The second was associated with several pesticide formulating plants, located on other tributaries, that prepare the pesticide materials for agricultural use. Perhaps the most significant finding of the 1964 study was that the large quantities of pesticides previously applied to crops in the Mississippi River Delta had not caused measurable widespread contamination of the streambed materials.

A second study of the pesticide contamination of streambed materials in the Mississippi River Delta was conducted in June and July 1966 and was essentially a repeat of the 1964 study. A supplemental study of contamination of the Wolf River-Cypress Creek complex in Memphis, Tenn., was conducted in April 1967. The results of the 1964, 1966, and 1967 studies are included in this report. The 1964 data have been published previously (*1*) but are included for comparison with the 1966 and 1967 data.

FIGURE 1.—*Streambed sampling locations on the Mississippi River and its tributaries*



Sampling Sites and Methods

The general sampling pattern was the same in 1964, 1966, and 1967. Separate sets of samples were taken upstream and downstream from possible sources of pesticide pollution. Specific industrial and municipal areas were bracketed to separate possible contributions of these sources from those of agriculture. Although sparsely distributed over many miles of stream channels (Fig. 1), the pattern of sampling at each of the selected sampling sites was designed to present a representative portrayal of conditions at each site.

The Mississippi River was sampled at 11 sites between Tiptonville, Tenn., and New Orleans, La. In Table 1, both the 1964 and 1966 sampling sites are designated by river miles upstream from the Head of Passes on the Gulf of Mexico. River miles were obtained from the 1962 Flood Control and Navigation Maps of the Mississippi River (*2*).

Bed material of a meandering stream usually differs in characteristics from one side of the stream to the other and from one cross section to another along its length; therefore, 12 samples were collected at each Mississippi River site. Samples were taken at three cross sections (U—upstream, M—middle, and D—downstream) which were usually one or more stream widths apart. At each of the three cross sections, samples were taken at two water depths (2 feet and 7 feet below mean low water elevation) and on both sides of the river (L—left bank and R—right bank). Deviations in this procedure are shown in Table 1. A total of 127 samples were collected in 1964 and 132 samples in 1966.

The equipment shown in Fig. 2 was used, generally, from a boat to obtain bed material samples. The weighted sampler was dragged along the bottom until it was partly filled. Six or seven grab samples were mixed to obtain approximately 1½ gallons of bed material for each sample.

The Corps of Engineers from the Memphis, Vicksburg, and New Orleans Districts assisted in collecting the samples from the Mississippi River in 1964. The U. S. Coast Guard assisted in taking the samples from the Mississippi River at Memphis in 1966.

Several tributaries were sampled in Tennessee, Louisiana, Mississippi, and Arkansas (Table 2). A total of 119 samples were collected in 1964, and 146 samples were collected in the 1966 sampling. Usually three cross sections were sampled at each site and a composited 1½-gallon sample obtained from the low water perimeter at each cross section. A distance of several stream widths usually separated the sampling sections. Deviations in procedure between the 1964 and 1966 sampling are noted in Table 2. Sampling sites on the tributaries are indicated on the accompanying maps (see Map Section).

TABLE 1.—*Sampling sites on the lower Mississippi River—1964 and 1966*

Sample No.	Year	River Mile	Field Designation [1]
	Tiptonville, Tenn.		
OX- 1	1964 and 1966	879.9	UR-2
2	1964 and 1966		UR-7
3	1964 and 1966		UL-2
4	1964 and 1966		UL-7
5	1964 and 1966	879.6	MR-2
6	1964 and 1966		MR-7
7	1964 and 1966		ML-2
8	1964 and 1966		ML-7
9	1964 and 1966	879.1	DR-2
10	1964 and 1966		DR-7
11	1964 and 1966		DL-2
12	1964 and 1966		DL-7
	Redman Bar, Tenn.		
13	1964 and 1966	740.8	UR-2
14	1964 and 1966		UR-7
15	1964 and 1966		UL-2
16	1964 and 1966		UL-7
17	1964 and 1966	740.4	MR-2
18	1964		MR-4
19	1964 and 1966		MR-7
20	1964 and 1966		ML-2
21	1964 and 1966		ML-7
22	1964 and 1966	737.7	DR-2
23	1964 and 1966		DR-7
24	1964 and 1966		DL-2
25	1964 and 1966		DL-7
	Memphis, Tenn.		
26	1964 and 1966	732.8	UR-2
27	1964 and 1966		UR-7
28	1964 and 1966		UL-2
29	1964 and 1966		UL-7
30	1964 and 1966	731.0	MR-2
31	1964 and 1966		MR-7
32	1964 and 1966		ML-2
33	1964 and 1966		ML-7
34	1964 and 1966	730.4	DR-2
35	1964 and 1966		DR-7
36	1964 and 1966		DL-2
37	1964 and 1966		DL-7
	West Memphis, Ark.		
38	1964 and 1966	727.7	UR-2
39	1964 and 1966		UR-7
40	1964 and 1966		UL-2
41	1964 and 1966		UL-7
42	1964 and 1966	723.6	MR-2
43	1964 and 1966		MR-7
44	1964 and 1966		ML-2
45	1964 and 1966		ML-7
46	1964 and 1966	723.0	DR-2
47	1964 and 1966		DR-7
48	1964 and 1966		DL-2
49	1964 and 1966		DL-7
	State Line, Tenn.-Miss.		
50	1964 and 1966	714.8	UR-2
51	1964 and 1966		UR-7
52	1964 and 1966		UL-2
53	1964 and 1966		UL-7
54	1964 and 1966	714.0	MR-2
55	1964 and 1966		MR-7
56	1964 and 1966		ML-2
57	1964 and 1966		ML-7
58	1964 and 1966	712.5	DR-2
59	1964 and 1966		DR-7
60	1964 and 1966		DL-2
61	1964 and 1966		DL-7
	Helena, Ark.		
62	1964	657.9	No Sample
63	1964		No Sample
64	1964		UL-2
65	1964		UL-7
66	1964	657.5	No Sample
67	1964		No Sample
68	1964		ML-2
69	1964		ML-7
70	1964	657.1	No Sample
71	1964		No Sample
72	1964		DL-2
73	1964		DL-7
62	1966	670.2	UR-2
63	1966		UR-7
64	1966		UL-2
65	1966		UL-7
66	1966	670.0	MR-2
67	1966		MR-7
68	1966		ML-2
69	1966		ML-7
70	1966	667.7	DR-2
71	1966		DR-7
72	1966		DL-2
73	1966		DL-7
	Greenville, Miss. (Arkansas City, Ark.)		
74	1964	567.0	UR-2
75	1964		UR-7
76	1964		UL-2
77	1964		UL-7
74	1966	567.6	UR-2
75	1966		UR-7
76	1966		UL-2
77	1966		UL-7
78	1964 and 1966	563.2	MR-2
79	1964 and 1966		MR-7
80	1964 and 1966		ML-2
81	1964 and 1966		ML-7
82	1964 and 1966	562.0	DR-2
83	1964 and 1966		DR-7
84	1964 and 1966		DL-2
85	1964 and 1966		DL-7

TABLE 1.—*Sampling sites on the lower Mississippi River—1964 and 1966*—Continued

Sample No.	Year	River Mile	Field Designation [1]
	Vicksburg, Miss.		
86	1964 and 1966	430.7	UR-2
87	1964 and 1966		UR-7
88	1964 and 1966		UL-2
89	1964 and 1966		UL-7
90	1964 and 1966	429.8	MR-2
91	1964 and 1966		MR-7
92	1964 and 1966		ML-2
93	1964 and 1966		ML-7
94	1964 and 1966	429.1	DR-2
95	1964 and 1966		DR-7
96	1964 and 1966		DL-2
97	1964 and 1966		DL-7
	Natchez, Miss.		
98	1964 and 1966	360.9	UR-2
99	1964 and 1966		UR-7
100	1964 and 1966		UL-2
101	1964 and 1966		UL-7
102	1964 and 1966	358.7	MR-2
103	1964 and 1966		MR-7
104	1964 and 1966		ML-2
105	1964 and 1966		ML-7
106	1964 and 1966	356.8	DR-2
107	1964 and 1966		DR-7
108	1964 and 1966		DL-2
109	1964 and 1966		DL-7
	Baton Rouge, La.		
110	1964 and 1966	227.9	UR-2
111	1964 and 1966		UR-7
112	1964 and 1966		UL-2
113	1964 and 1966		UL-7
114	1964 and 1966	227.2	MR-2
115	1964 and 1966		MR-7
116	1964 and 1966		ML-2
117	1964 and 1966		ML-7
118	1964 and 1966	226.7	DR-2
119	1964 and 1966		DR-7
120	1964 and 1966		DL-2
121	1964 and 1966		DL-7
	New Orleans, La.		
122	1964 and 1966	88.9	UR-2
123	1964 and 1966		UR-7
124	1964 and 1966		UL-2
125	1964 and 1966		UL-7
126	1964 and 1966	88.0	MR-2
127	1964 and 1966		MR-7
128	1964 and 1966		ML-2
129	1964 and 1966		ML-7
130	1964 and 1966	86.7	DR-2
131	1964 and 1966		DR-7
132	1964 and 1966		DL-2
133	1964 and 1966		DL-7

[1] U—upstream cross section; M—middle cross section; D—downstream cross section; R and L indicate right and left bank, respectively, looking downstream; the last digit is sampling depth in feet.

FIGURE 2.—*Bed material sampler*

The 1967 sampling program was restricted to the Wolf River-Cypress Creek area at Memphis, Tenn. Sediment and water samples were collected both upstream and downstream from (a) a pesticides manufacturing plant, and (b) the confluence of Cypress Creek and Wolf River (see Map Section). Twenty-four sediment and 10 water samples were collected, compared with 16 sediment samples collected in 1966 and 14 in 1964. Deviations in the 1967 sampling program from that conducted in 1964 and 1966 are shown in Tables 3 and 4.

In the 1966 and 1967 sampling programs the sediment samples were frozen immediately upon coming ashore. At the USDA Sedimentation Laboratory, the samples were thawed, well stirred, and subsampled. The subsamples were refrozen and delivered to the Plant Pest Control Division Laboratory at Gulfport, Miss., for pesticide analysis.

TABLE 2.—*Sampling sites on tributaries of the Lower Mississippi River—1964 and 1966*

Sample No.	Year	Field Site Designation [1]	Field Location
		TENNESSEE	
Wolf River, Memphis			
134	1964 and 1966	U	At Hwy. 64, 70, 79 Bridge.
135	1964 and 1966	M	250 feet upstream from Hollywood Road Bridge.
136	1964	D	50 feet upstream from Hollywood Road Bridge.
136	1966	D	Under Hollywood Road Bridge.
300	1966	O	Old channel cutoff by Hollywood Road Bridge.
137	1964 and 1966	U	U, M, and D Sec. are downstream from confluence with Cypress Creek
138	1964 and 1966	M	at condemned North Bellevue Blvd. Bridge.
139	1964 and 1966	D	
140	1964 and 1966	D	50 feet upstream from North Watkins Bridge.
Old Wolf River, Memphis			
301	1966	U	2.4 miles upstream from Memphis Harbor Entrance.
302	1966	M	1.7 miles upstream from Memphis Harbor Entrance.
303	1966	D	1.1 miles upstream from Memphis Harbor Entrance.
Cypress Creek, Memphis			
141	1964 and 1966	U	U, M, and D Sec. are between Summer Ave. and L & N Railroad.
142	1964 and 1966	M	
143	1964 and 1966	D	
144	1964 and 1966	U	Jackson Avenue.
145	1964 and 1966	M	North Bingham.
146	1964 and 1966	D	200 feet above pumping station.
304	1966	X	Spoils; left bank; 300—450 feet downstream from Meager St. (Meagher St.).
147	1964 and 1966		Deposition area on right bank 200 feet upstream from pumping station.
McKellar Lake, Memphis			
305	1966	U	0.25 mile upstream from confluence with Nonconnah Creek.
306	1966	D	0.5 mile downstream from confluence with Nonconnah Creek.
Industrial Channel, Memphis			
307	1966		0.75 mile upstream from confluence with McKellar Lake.
Tennessee Chute, Memphis			
308	1966		1.5 miles downstream from confluence with McKellar Lake.
Nonconnah Creek, Memphis			
309	1966		400 feet upstream from Airways Road Bridge.
		LOUISIANA	
Alma Plantation Bayou near Lakeland, Pointe Coupee Parish			
149	1964 and 1966	1 and 2	1, 2, 3 and 4 Sec. are 1.2 miles S of Hwy. 416.
150	1964 and 1966	3 and 4	
Borrow Pit for Belmont Plantation near Maringouin, Pointe Coupee Parish			
151	1964 and 1966	U	U and D Sec. are 50 feet SE of confluence with Belmont Plantation
152	1964 and 1966	D	ditch.
153	1964 and 1966		0.2 mile NW from confluence with Belmont Plantation ditch.
Belmont Plantation Ditch near Maringouin, Pointe Coupee Parish			
154	1964 and 1966		0.2 mile upstream from confluence with borrow pit.
Brushy Lake near St. Joseph, Tensas Parish			
155	1964 and 1966	U	U and D Sec. are 2.5 miles N of St. Joseph; 0.2 mile NE of Hwy.
156	1964 and 1966	D	605; 0.2 mile SW of Hwy. 606; and 0.5 mile upstream from confluence with Lake Bruin (S29, T11N, R12E).

TABLE 2.—*Sampling sites on tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Year	Field Site Designation [1]	Field Location
		LOUISIANA—Continued	
Little River near Jonesville, Catahoula Parish			
157	1964 and 1966	U	U, M and D Sec. are 4 miles SW of Jonesville; 0.2 mile N of Hwy. 84; and 0.2 mile N of Utility (S6, T7N, R6E).
158	1964 and 1966	M	
159	1964 and 1966	D	
Ouachita River near Duty, Catahoula Parish			
160	1964 and 1966	U	U, M and D Sec. are 0.5 mile upstream from ferry connecting Hwy. 124 and Hwy. 559 (S23, T11N, R5E).
161	1964 and 1966	M	
162	1964 and 1966	D	
Boeuf River near Winnsboro, Franklin Parish			
163	1964 and 1966	U	U, M and D Sec. are 12.5 miles SW of Winnsboro and 0.5 mile upstream from Hwy. 4 bridge (S26, T13N, R5E).
164	1964 and 1966	M	
165	1964 and 1966	D	
Raccourci (Old River) near Batchelor, Pointe Coupee Parish			
166	1964 and 1966	UR- 5	The four sections are 1 mile N of Batchelor.
167	1964 and 1966	UR-10	
168	1964 and 1966	UL- 5	
169	1964 and 1966	UL-10	
170	1964 and 1966	MR- 5	The four sections are 7 miles downstream from where samples 166-169 were taken.
171	1964 and 1966	MR-10	
172	1964 and 1966	ML- 5	
173	1964 and 1966	ML-10	
174	1964 and 1966	DR- 5	The four sections are 12 miles downstream from where samples 166-169 were taken.
175	1964 and 1966	DR-10	
176	1964 and 1966	DL- 5	
177	1964 and 1966	DL-10	
Tensas River near Clayton, Concordia Parish			
178	1964 and 1966	U	U, M and D Sec. are 0.5 mile upstream from Hwy. 15 bridge and 0.2 mile NW of Hwy. 566. (S27, T9N, R9E).
179	1964 and 1966	M	
180	1964 and 1966	D	
Brushy Bayou near Tallulah, Madison Parish			
310	1966	U	0.8 mile E of city limits where Bayou crosses Hwy. 80 (S6, T16N, R13E).
311	1966	D	0.9 mile SW of city limits at spillway by Bayou Drive (S29, T16N, R12E).
		MISSISSIPPI	
Bayou Pierre near Port Gibson, Claiborne County			
181	1964 and 1966	U	U, M and D Sec. are 2 miles NW of Port Gibson and 1 mile downstream from confluence with Little Bayou Pierre (S12, T12N, R2E).
182	1964 and 1966	M	
183	1964 and 1966	D	
184	1964 and 1966	U	U, M and D Sec. are 1 mile west from where samples 181-183 were taken (S12, T12N, R2E).
185	1964 and 1966	M	
186	1964 and 1966	D	
Big Black River, Warren County			
187	1964 and 1966	U	U, M and D Sec. are 2 miles east of Hwy. 61 (S19, T13N, R3E)
188	1964 and 1966	M	
189	1964 and 1966	D	
Bear Creek near Canton, Madison County			
312	1966	UU	UU Sec. is 6.4 miles S of Canton city limits on Hwy. 51 south (S27, T8N, R2E).

TABLE 2.—*Sampling sites on tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Year	Field Site Designation [1]	Field Location
		MISSISSIPPI—Continued	
Bear Creek near Canton, Madison County (Continued)			
193	1964	U [2]	U and D Sec. are 4 miles south of Canton and 0.2 mile downstream from bridge (S14, T8N, R2E).
327	1966	U	
192	1964	D [2]	
328	1966	D	
191	1964	U [2]	U and D Sec. are 2.5 miles S of Canton and 200 feet downstream from bridge (S6, T8N, R3E).
329	1966	U	
190	1964	D [2]	
330	1966	D	
Coldwater River near Marks, Quitman County			
194	1964 and 1966	U	U, M and D Sec. are 600 feet upstream from bridge on Hwy. 6. (S25, T28N, R1W).
195	1964 and 1966	M	
196	1964 and 1966	D	
197	1964 and 1966	U	300 feet upstream from powerline which is 0.5 mile downstream from Hwy. 6 bridge (S36, T28N, R1W).
198	1964 and 1966	M	At powerline (S36, T28N, R1W).
199	1964 and 1966	D	300 feet downstream from powerline (S1, T27N, R1W).
Homochitto River, Wilkinson County			
200	1964 and 1966	U	U, M and D Sec. are 15 miles S of Natchez, Miss. on Hwy. 61 and 0.2 mile downstream from bridge. (S10, T4N, R2W).
201	1964 and 1966	M	
202	1964 and 1966	D	
Sunflower River near Clarksdale, Coahoma County			
203	1964 and 1966	U	U, M and D Sec. are 300 feet upstream from railroad bridge (S23, T27N, R4W).
204	1964 and 1966	M	
205	1964 and 1966	D	
206	1964 and 1966	U	U, M and D Sec. are 1 mile downstream from Hwy. 61 bridge, near Bramlette and Son Cotton Gin (S35, T27N, R4W).
207	1964 and 1966	M	
208	1964 and 1966	D	
Ditch A near Clarksdale, Coahoma County			
313	1966		2 miles SE of Clarksdale at Hwy. 322 bridge (S5, T26N, R3W).
Ditch B near Clarksdale, Coahoma County			
314	1966		0.6 mile S of Clarksdale by Hwy. 49E bridge (S30, T27N, R3W).
Sunflower River, Sunflower County			
209	1964 and 1966	U	U, M and D Sec. are 4.5 miles E of Cleveland (S20, T22N, R4W).
210	1964 and 1966	M	
211	1964 and 1966	D	
212	1964 and 1966	U	U, M and D Sec. are 2 miles downstream from where samples 209-211 were taken and 2 miles upstream from Hwy. 8 bridge (S32, T22N, R4W).
213	1964 and 1966	M	
214	1964 and 1966	D	
Jones Bayou near Cleveland, Bolivar County			
215	1964 and 1966	U	U and D Sec. are 1 mile N of Cleveland and 1 mile W of Hwy. 61 (S8, T22N, R5W).
216	1964 and 1966	D	
217	1964 and 1966	U	U and D Sec. are 1 mile S of Cleveland and 0.8 mile W of Hwy. 61 (S32, T22N, R5W).
218	1964 and 1966	D	
Ditch A near Cleveland, Bolivar County			
315	1966	U	U and D Sec. are 0.3 mile NE of Cleveland on gravel road, just E of Brenner Mfg. Co. (S9 & 15, T22N, R5W).
316	1966	D	

TABLE 2.—*Sampling sites on tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Year	Field Site Designation [1]	Field Location
		MISSISSIPPI—Continued	
Sunflower River near Indianola, Sunflower County			
219	1964	U	U, M, and D Sec. are 0.3 mile upstream from bridge (S22, T18N, R5W).
220	1964	M	
221	1964	D	
219	1966	U	U, M and D Sec. are 1.8 miles upstream from confluence with Bay Lake Run and 2 miles downstream from where samples 219-221 were taken in 1964 (S33, T18N, R5W).
220	1966	M	
221	1966	D	
222	1964 and 1966	U	U, M and D Sec. are 0.3 mile upstream from bridge at Kinlock and 2 miles S of confluence with Bay Lake Run (S22, T17N, R5W).
223	1964 and 1966	M	
224	1964 and 1966	D	
Ditch 24 near Indianola, Sunflower County			
317	1966	U	5.5 miles W of Indianola and 0.7 mile N of Hwy. 82 where Greenville Railroad crosses Ditch (S6, T18N, R5W).
225	1964 and 1966	D	3 miles S of Hwy. 82 and 1.8 miles E of Washington-Sunflower County line (S20, T18N, R5W).
Tallahatchie River near Greenwood, Leflore County			
226	1964 and 1966	U	U, M and D Sec. are 1.2 miles E of Hwy. 49E and 0.3 mile upstream from bridge (S12, T20N, R1W).
227	1964 and 1966	M	
228	1964 and 1966	D	
Yalobusha River near Greenwood, Leflore County			
229	1964 and 1966	U	U, M and D Sec. are 5.3 miles NW of Greenwood and 1.8 miles W of Leflore—Carroll County line (S18, T20N, R2E).
230	1964 and 1966	M	
231	1964 and 1966	D	
Yazoo River near Greenwood, Leflore County			
232	1964 and 1966	U	U, M and D Sec. are 4 miles SW of Greenwood and 0.3 mile upstream from bridge (S6, T18N, R1E).
233	1964 and 1966	M	
234	1964 and 1966	D	
Yazoo River near Satartia, Yazoo County			
235	1964 and 1966	U	U, M and D Sec. are 0.5 mile W of Satartia and 0.5 mile downstream from bridge (S36, T10N, R4W).
236	1964 and 1966	M	
237	1964 and 1966	D	
238	1964 and 1966	No Sample	
239	1964 and 1966	No Sample	
240	1964 and 1966	No Sample	
Horseshoe Bayou near Greenville, Washington County			
241	1964 and 1966	U	U and D Sec. are 300 feet W of Hwy. 1 and 1 mile N of Greenville, across street from stockyards (S2, T18N, R8W).
242	1964 and 1966	D	
243	1964 and 1966	U	U and D Sec. are 0.5 mile downstream from where samples 241 and 242 were taken and 0.5 mile E of Hwy. 1, near bridge (S10, T18N, R8W).
244	1964 and 1966	D	
Fish Lake near Greenville, Washington County			
245	1964 and 1966	U	U, M and D Sec. are 1.3 miles N of Hwy. 82 and 1.8 mile E of Hwy. 1 (S12, T18N, R8W).
246	1964 and 1966	M	
247	1964 and 1966	D	
248	1964 and 1966	U	U, M and D Sec. are 0.8 mile E of site where samples 245-247 were taken (S13, T18N, R8W).
249	1964 and 1966	M	
250	1964 and 1966	D	
Ditch 6 near Greenville, Washington County			
318	1966	D	At Hwy. 82 bridge (S25, T18N, R8W).

TABLE 2.—*Sampling sites on tributaries of the Lower Mississippi River—1964 and 1966* Continued

Sample No.	Year	Field Site Designation [1]	Field Location
		MISSISSIPPI—Continued	
Bogue River near Grenada, Grenada County			
319	1966	U	U and D Sec. are 4 miles SE of Grenada (S34, T22N, R5E).
320	1966	D	
321	1966	U	U and D Sec. are 400 feet upstream from confluence with Yalobusha (S8, T22N, R5E).
322	1966	D	
Deer Creek near Rolling Fork, Sharkey County			
323	1966	U	1 mile N of city limits (S35, T13N, R7W).
Rolling Fork Creek near Rolling Fork, Sharkey County			
324	1966	D	0.4 mile E of Hwy. 61 (S12, T12N, R7W).
		ARKANSAS	
St. Francis River, Lee County			
251	1964 and 1966	U	U, M and D Sec. are 2 miles upstream from Hwy. 79 bridge (S22 and 23, T3N, R4E).
252	1964 and 1966	M	
253	1964 and 1966	D	
White River near Clarendon, Monroe County			
254	1964 and 1966	U	U, M and D Sec. are 0.5 mile upstream from boat landing at Clarendon (S22, T1N, R3W).
255	1964 and 1966	M	
256	1964 and 1966	D	
Crooked Bayou near McGehee, Desha County			
325	1966	U	150 feet upstream from the corner of Spruce and 1st Street (S21, T12S, R3W).
326	1966	D	0.8 mile S of McGehee and 600 feet downstream from Missouri Pacific Railroad bridge (S34, T12S, R3W).

[1] U—upstream cross section; M—middle cross section; D—downstream cross section.
The field designations for the 1964 Bear Creek samples are listed correctly in this report. They were previously published in error (see W. F. Barthel, D. A. Parson, L. L. McDowell, and E. H. Grissinger, 1966. Surface Hydrology and Pesticides. *In* Pesticides and Their Effects on Soils and Water ASA Special Publ. No. 8, pp. 128-144). Field reconnaissance at Bear Creek since 1964 indicates a surface drainage pattern different than believed in 1964.

TABLE 3.—*Sediment sampling sites on Wolf River and Cypress Creek, Memphis, Tenn.—1964, 1966, and 1967*

Sample No.			Field Site Designation	Field Location
1964	1966	1967		
		Wolf River		
134	134	400	U	U Sec. at Hwy. 64, 70, 79 Bridge.
		401	U	Bank deposit at U Sec. at Hwy. 64, 70, 79 Bridge.
135	135	402	M	M Sec. 250 feet upstream from Hollywood Road Bridge.
136	136	403	D	D Sec. at Hollywood Road Bridge.
		404	D	Bank deposit at D Sec. at Hollywood Road Bridge.
	300	405	O	Old channel cutoff by Hollywood Road Bridge.
140	140	406		50 feet upstream from North Watkins Bridge.
		407		Bank deposit at North Watkins Bridge.
137	137	408	U	U, M and D Sec. downstream from confluence with Cypress Creek at condemned North Bellevue Blvd. Bridge.
138	138	409	M	
139	139	410	D	
		411	D	Bank deposit at D Sec. downstream from confluence with Cypress Creek at condemned North Bellevue Blvd. Bridge.

TABLE 3.—*Sediment sampling sites on Wolf River and Cypress Creek, Memphis, Tenn.—1964, 1966, and 1967*—Continued

Sample No.			Field Site Designation	Field Location
1964	1966	1967		
			Cypress Creek	
141	141		U	U Sec. downstream from Summer Avenue.
142	142		M	M Sec. downstream from Summer Avenue at end of Glankler Street.
143	143	412	D	D Sec. upstream from Scott Street.
144	144	413	U	U Sec. at Jackson Avenue.
145	145	414	M	M Sec. between Meager (Meagher) St. and end of North Bingham Street.
		415	A	A Sec. downstream from Meager (Meagher) Street.
	304	416	X	X Sec. on spoil bank 300-450 feet downstream from Meager (Meagher) St. and 20-60 feet SW of Cypress Creek.
		417	B	B Sec. in deposit area 350-500 feet downstream from Meager (Meagher) St. and 200-500 feet SW of Cypress Creek.
		418	C	C Sec. in deposit area 350-500 feet downstream from Meager (Meagher) St. and 250-600 feet SW of Cypress Creek.
146	146		D	D Sec. 200 feet upstream from pumping station.
		419	D	D Sec. 330 feet upstream from confluence with Leath Bayou; upstream from pumping station.
147	147			Deposition area on right bank 200 feet upstream from pumping station.
		420		Sample taken from top 6 inches of deposition area on left bank 300-400 feet upstream from confluence with Leath Bayou; upstream from pumping station.
		421		Samples taken from 12-18 inches of deposition area on left bank 300-400 feet upstream from confluence of Leath Bayou; upstream from pumping station.
		422		Samples taken from top 6 inches of deposition area on right bank 250-350 feet upstream from pumping station.
		423		Sample taken from 12-18 inches of deposition area on right bank 250-350 feet upstream from pumping station.

TABLE 4.—*Water sampling sites on Wolf River and Cypress Creek, Memphis, Tenn.—1967*

Sample No.	Field Site Designation	Field Location
	Wolf River	
426	U	Hwy. 64, 70, 79 Bridge; same location as sediment sample 400.
427	D	Hollywood Road Bridge; same location as sediment sample 403.
428		Watkins Bridge; same location as sediment sample 406.
429		Downstream from confluence with Cypress Creek at condemned North Bellevue Blvd. Bridge same location as sediment samples 408-410.
	Cypress Creek	
430		45 feet upstream from Summer Avenue.
431		Scott Street.
432		Meager (Meagher) Street
433		330 feet upstream from confluence with Leath Bayou; same location as sediment sample 419.
424		0.2 mile downstream from pumping station.
425		0.2 mile downstream from pumping station.

SEDIMENT: EXTRACTION AND FORTIFICATION

Samples were arranged in sets, each containing from 24 to 36 samples, including 5 controls. All samples contained sediment, except the first 3 controls. Subsamples of moist sediment were taken from each set, and a 300-g composite of moist sediment was weighed into a half-gallon glass jar; 600 ml of a 3:1 mixture of hexane and isopropanol and approximately 250 g of anhydrous Na_2SO_4 were added. The jar was closed with a screw lid backed with aluminum foil and rotated concentrically for 4 hours. The contents were then filtered through Na_2SO_4 and Celite into a 1-liter separatory funnel equipped with a Teflon stopcock and washed three times with distilled water. The hexane remaining in the separatory funnel was dried by the addition of 10 to 20 g of anhydrous Na_2SO_4, and 5 to 10 g of Celite, followed by vigorous shaking. A 300-ml aliquot of the extract was filtered into an amber glass sample bottle using a filter tube containing a cotton plug, Na_2SO_4, and Celite, in that order. Sample bottles were sealed with foil-lined crown caps backed with aluminum foil.

Each milliliter of the bottled extract contained the chlorinated hydrocarbons derived from 0.67 g of moist soil. The moisture content of the original sediment was determined separately. Concentrations reported are on a dry sediment weight basis. In most cases the extract needed no further cleanup before screening by gas chromatographic analysis. In fact, it is only by such screening that need for further cleanup is ascertained. When extracts could not be analyzed immediately, they were stored at 3 C.

Five controls were processed and analyzed with each group of samples. These controls were arranged as follows:

Control 1: Solvent, 300 ml; fortified but not processed. This control was used as a standard for measurement.

Control 2: Solvent, 300 ml; not fortified, but processed. This control checked for contamination at any stage in processing.

Control 3: Solvent, 300 ml; fortified, processed. This control checked on processing loss.

Control 4: Composite of sediment samples, processed as a sample. This control showed the average concentration of pesticides in the group and provided a base on which to calculate recovery data with Control 5.

Control 5: Composite of sediment, fortified and processed. This control, together with Control 4, provided data for calculation of recovery of pesticides in the group of samples.

Routinely, control samples 1, 3, and 5 were fortified just before the extraction stage with 9 ml of a composite standard hexane solution containing nine of the most commonly found insecticides. The concentration of insecticides in this standard were as follows:

Lindane Heptachlor Heptachlor epoxide Dieldrin	10 μg/ml
p,p'-DDE	20 μg/ml
p,p'-DDT *o,p'*-DDT Endrin *p,p'*-TDE	50 μg/ml

Selection of the standard mixture depended on the previous history of the area from which the samples were taken. All pesticides likely to be encountered in the sample were included in the composite standard. Standard solutions used for fortification were checked periodically for degradation of pesticides.

WATER: EXTRACTION AND FORTIFICATION

Water samples, including five control samples, were arranged in a set for extraction of the chlorinated hydrocarbon pesticides. A single batch of redistilled solvent (pentane-ether 3:1) was used in the extraction of each set. Routinely, 1 liter of solvent was added to 11.3 kg (4 gallons) of the water sample contained in the original 5-gallon sample carboy. The carboy was rotated on a ball mill for 20 minutes at 30 rpm. Subsequently, a 750-ml aliquot of the solvent extract was concentrated to 50 ml, using a Snyder column, and transferred to a sample bottle for gas chromatographic analysis.

Five controls were processed and analyzed with each group of unknown water samples. These controls were arranged as follows:

Control 1: Solvent, 1000 ml; fortified, but not processed. Exactly 1 ml of a composite pesticide standard was added to 100 ml of solvent contained in a 2-liter Erlenmeyer flask. After mixing, a 750-ml aliquot was concentrated to 50 ml as in the unknown sample extraction procedure. The gas chromatographic peaks were calibrated on the basis of the different pesticides contained in the Control 1 concentrate.

Control 2: Solvent, 1000 ml; not fortified, but processed. The solvent was added to a clean, empty 5-gallon carboy. The carboy was rotated on a ball

mill for 20 minutes at 30 rpm. A 750-ml aliquot of the solvent was concentrated to 50 ml and transferred to a labeled sample bottle. This control sample served as an analytical blank. Any pesticides analyzed in this extract represented contamination by glassware and handling.

Control 3: Solvent, 1000 ml; fortified, processed. This control was prepared in the same manner as Control 2, except that 1 ml of the composite pesticide standard was added to the solvent at the beginning of the procedure. The pesticide concentrations analyzed in this extract, compared with traces present in Control 2, provided recovery data in the absence of water.

Control 4: Solvent, 1000 ml; not fortified, but processed. This control was prepared in the same manner as Control 2, except that 11.3 kg of distilled water plus 100 ml of redistilled acetone, were added to the carboy prior to the addition of the solvent.

Control 5: Solvent, 1000 ml; fortified, processed. This control was prepared in the same manner as Control 4, except that 1 ml of the composite pesticide standard contained in 100 ml of redistilled acetone, was added to the water prior to the addition of the solvent. The pesticide concentrations determined in this extract permitted calculation of recovery data obtained in the presence of water, when compared to (a) the known quantities added in the fortifying standard, and (b) the traces of contaminants recovered in Control 4.

The recovery data obtained from the analyses of the control samples were used in computing the concentrations of pesticides. Concentrations are reported on a total weight basis.

GAS CHROMATOGRAPHIC ANALYSES

Analyses were perfomed on standard gas chromatographs using electron affinity detectors and glass columns with column injection. Each sample was analyzed using two separate columns: 3% DC-200 on Gas Chrom Q and 9% QF-1 on Diatoport S. Column temperature for 3% DC-200 was maintained at 180 C to insure separation of endrin, dieldrin, and *p,p'*-DDE. The 9% QF-1 column was maintained at about 166 C to insure separation of *p,p'*-TDE, endrin, and *p,p'*-DDT. Sulfur interference was eliminated by using a column of 5% XE-60 on Chromosorb W at 180 C. Because of partly fused peaks, even under these ideal conditions, all calculations were based on peak heights rather than on peak area. Confirmation of specific residues was made by thin layer chromatography, *p* values, and by conversion to other products.

Results and Discussion

Pesticide concentrations of bed material samples collected in 1964 and 1966 from the lower Mississippi River and its tributaries are given in Tables 5 and 6, respectively. In Table 5, only those Mississippi River samples contaminated with pesticides are listed. Table 6 lists all samples from each tributary site where pesticide residues were detected. Pesticide concentrations of sediment and water samples collected in 1967 from Wolf River and Cypress Creek are given in Tables 7 and 8.

The pesticide analyses of the sediment and water samples indicate two major areas of pesticide contamination—one in association with manufacturing operations in the Memphis Wolf River-Cypress Creek complex and the other in association with a group of pesticide formulating plants located on other tributaries in Mississippi.

MEMPHIS WOLF RIVER-CYPRESS CREEK COMPLEX

Several chlorinated hydrocarbons including dieldrin, aldrin, endrin, endrin keto, isodrin, chlordane, heptachlor, hexachloronorbornadiene (X), heptachloronorbornene (Y), and Z, were found in sediment and water samples collected in 1966 and 1967 from Cypress Creek and Wolf River, near the manufacturing operations in Memphis, Tenn. High concentrations of several of these compounds were detected in bottom sediments, spoils, and flood plain deposits (see Tables 6 and 7) from Cypress Creek, downstream from a primary manufacturer of endrin and heptachlor. In general these results are in agreement with the 1964 data.

Isodrin, X, and Y are intermediates in the manufacture of endrin (Fig. 3). Compound Z is believed to be the reaction product of hexachlorocyclopentadiene with X, but this has not been confirmed. Aldrin, the *endo-exo* isomer of isodrin, and dieldrin, the *endo-exo* isomer of endrin, may be minor by-products in the manufacture of heptachlor.

Since the bulk of the intermediate compounds (isodrin, X, Y, and Z) is removed during the manufacturing process, they are essentially absent from technical endrin sold to formulating plants for insecticide purposes. No contamination was found in 1966 in the Mississippi River sediments upstream from the confluence with Wolf River. Thus the only chlorinated hydrocarbons found in the Mississippi River sediments were those apparently coming from Wolf River and Cypress Creek (isodrin, X, Y, and chlordane). Traces of X were found in sediments at Baton Rouge, La., about 500 river miles downstream from the source at Memphis.

Manufacturing wastes were detected in the Wolf River sediment samples in 1966 and 1967 upstream from the confluence with Cypress Creek. These residues

may have originated from three sources: (a) Cypress Creek — transported upstream by backwater from the Mississippi River, (b) industrial waste sewers — direct discharge of manufacturing wastes into the Wolf River or into the Mississippi River with subsequent transport upstream during high stages of the Mississippi River, and (c) seepage from wastes buried in recent years at the Hollywood dump (see Map Section).

The immediate source of pesticide residues in McKellar Lake and Tennessee Chute is unknown. Contamination may have come from Cypress Creek and Wolf River by way of backwater flow from the Mississippi River. More plausibly, it may have come from industrial dumps along Nonconnah Creek which drains into McKellar Lake.

In 1967 recent deposition of a dark deposit, ¼ to 3 inches in depth, on the upper banks of Wolf River from Summer Avenue (well upstream from the industrial area) to the confluence with the Mississippi River was observed and sampled. This deposition was undoubtedly due to the slowing up of floodwaters in the Wolf River by high stages in the Mississippi. Upstream at Summer Avenue this recently deposited layer looked like ordinary mud of the region. Downstream from Hollywood Street the deposits became increasingly dark colored (Fig. 4 and 5). The dark colored layer was contaminated with pesticide residues at three of the sampling locations along the River: Hollywood St., Watkins St., and North Bellevue Crossings (see "Bank deposits," Table 7).

The dark colored deposits appeared to be a mixture of several industrial organic wastes, largely nonpesticidal. Such nonpesticidal organic compounds could play a major role in the transport of the chlorinated hydrocarbon pesticides.

The extent and magnitude of the chlorinated hydrocarbon deposits associated with the manufacturing operations in the Memphis area is difficult to assess quantitatively. The difficulty rests largely with the procurement of samples that are representative of the deposits in the area. Several factors contribute to this sampling problem: (a) the variability in the nature of the deposits, (b) continuous dredging operations, and (c) unknown locations of industrial sewage outfalls. The results of the 1964, 1966, and 1967 surveys indicate the presence of a variety of chlorinated hydrocarbon residues, some in locally high concentrations, in the Memphis area. Clearly, it is impossible to predict the long term effects of this potential source of industrial pollution on water quality in the immediate area and in the downstream sections of the Mississippi River.

When the Mississippi River is at low stage, it is plausible that intense flood flows in Cypress Creek or in the Wolf River due to local rain storms would flush contaminated sediments from the bed and banks into the Mississippi River. The susceptibility of the contaminated sediments along Cypress Creek to erosion and transport decreased during the 1964-1967 sampling period, because the concrete lining in the channel was extended and uncontaminated fill was spread over the highly contaminated areas.

TRIBUTARIES IN MISSISSIPPI, LOUISIANA, AND ARKANSAS

A total of 125 sediment samples were collected from tributary streams in Mississippi, Louisiana, and Arkansas in 1966. About 50% of these samples were contaminated with chlorinated hydrocarbons. DDT analogs and metabolites were detected in all of the contaminated samples and were the only contaminants in about 25% of the 125 tributary samples.

It is difficult in some locations to separate the industrial, municipal, and agricultural sources of pesticide pollution; nevertheless, certain significant findings with regard to sources of pesticide residues are evident:

1. Industrial pollution is indicated by the variety of chlorinated hydrocarbon residues detected in close proximity to formulating plants in Mississippi.
2. With one exception, DDT analogs and metabolites were the only residues originating from nonindustrial sources, i.e., municipal and agricultural.

Contamination apparently associated with pesticide formulating plants was found at five locations on tributary streams in Mississippi: Horseshoe Bayou and Fish Lake at Greenville, Jones Bayou at Cleveland, and the Sunflower River at Clarksdale and Indianola (Tables 6 and 9). Pesticide residues included dieldrin, aldrin, endrin, isodrin, X, Y, chlordane, and lindane in addition to the DDT analogs and metabolites. Residues of isodrin were found in association with formulating plants at Greenville, Clarksdale, and Indianola. A trace of Y was found in sediments from Horseshoe Bayou, and traces of X and Y were detected in sediments from Ditch A at Cleveland. The presence of isodrin, X, and Y in association with other pesticide compounds in the sediments near formulating plants was unexpected, but confirmed by reanalysis (Table 9). Small amounts of these compounds may be present in some technical chlorinated hydrocarbons supplied by the primary manufacturers.

Pesticide residues were found in sediments both upstream and downstream from the formulating plants in Mississippi. Reconnaissance of the areas since the 1964 sampling revealed that some of the formulators had been dumping waste materials in city sewers, city dumps, privately owned dump areas, and in channels and sloughs upstream from the plant site. At some locations the reversal of normal streamflow by backwater from other tributaries may also account for the apparent

transport and deposition of pesticide wastes upstream from the plants.

Residues of DDT analogs and metabolites originating from nonindustrial sources, i.e., urban spray programs or from agricultural usage were found in the following streams in Louisiana, Mississippi, and Arkansas:

Louisiana
Tensas River, near Clayton, Concordia Parish
Brushy Bayou, near Tallulah, Madison Parish

Mississippi
Bayou Pierre, near Port Gibson, Claiborne County
Deer Creek, near Rolling Fork, Sharkey County
Rolling Fork Creek, near Rolling Fork, Sharkey County
Sunflower River, Sunflower County
Coldwater River, near Marks, Quitman County
Bear Creek, near Canton, Madison County

Arkansas
Crooked Bayou, near McGehee, Desha County
St. Francis River, Lee County

Traces of dieldrin were also detected in the sediments from the St. Francis River in Arkansas (Table 9). DDT analogs and metabolites were found in 1964 and 1966 in sediments from the Coldwater River at Marks, Miss., and Bear Creek at Canton, Miss. Because formulating plants are located on both of these streams, it is impossible to determine whether the residues originated from formulation wastes or from other sources.

The absence of contamination in samples from several streams indicates that the large amounts of pesticides previously applied to crops in the Delta have not created widespread contamination of streambed materials. No contamination was detected at the following locations:

Louisiana
Alma Plantation
Belmont Plantation
Brushy Lake
Little River
Ouachita River
Boeuf River
Raccourci (Old River)

Mississippi
Big Black River
Homochitto River
Tallahatchie River
Yalobusha River
Yazoo River
Bogue River

Arkansas
White River

The lack of contamination in the samples from the Alma and Belmont Plantations and from Brushy Lake is especially significant. Endrin had been used on the sugar-cane fields on the Alma and Belmont Plantations 5 or 6 years before the 1964 sampling. Five or six applications of 12-16 lb per acre of 2% endrin had been applied during the period 1959-1964. Aquatic life was observed in the bayous and borrow pits at the time of sampling in 1964. Data on insecticide applications between 1964 and 1966 were not obtained. Brushy Lake received the drainage water from about 5000 acres of cotton on which endrin had been applied for a number of years.

The results of the 1966 analyses indicate contamination of the streambed materials to a greater extent and magnitude than that observed in 1964. This is a reflection, in part, of improvements in analytical procedures that enabled better identification and measurement of the chlorinated hydrocarbon residues. In the 1964 analyses the detection limit was 0.1 ppm. This was lowered to 0.05 ppm in the analyses of the 1966 samples. Near the completion of the analyses of the 1966 samples, the overall methodolgy and experience had developed significantly enabling further lowering of the detection limit to 0.01 ppm for certain residues in a multi-component analysis.

Improvements in the analytical methods that developed during the analysis of the 1966 samples prompted an additional study to (a) evaluate the methods of sample storage and subsampling and (b) reevaluate the original analyses of several of the 1966 samples. Twenty-four samples of sediment were selected for reanalysis. These samples had been stored in tin-lined steel containers at 25 C for about 9 months. The samples were permitted to thaw, stirred to a uniform consistency, and subsampled. The results of these analyses are presented in Table 9.

In general, analyses of the new subsamples agreed with the original analyses indicating that storage at —25 C prevented any appreciable loss of pesticide residues. Traces of aldrin, dieldrin, endrin, isodrin, Y, and lindane were detected in several samples upon (a) reevaluation of the gas chromatographic records from the original analyses, (b) reanalysis of the original hexane-isopropanol extracts, and (c) analyses of new subsamples of the sediment. Original reports of toxaphene/strobane were in error because of sulfur interference in the colorimetric method employed. The colorimetric method was replaced by gas chromatography using a column of 5% XE-60 on Chromosorb W to eliminate sulfur interference. Chlordane was detected in some samples after eliminating the sulfur interference.

Summary

Chlorinated hydrocarbon analyses were performed on a total of 548 sediment samples collected in 1964, 1966, and 1967 from the lower Mississippi River and several of its tributaries. These analyses indicated two localized areas of significant pesticide contamination—one in association with manufacturing operations in the Wolf River-Cypress Creek complex at Memphis, Tenn., and the other in association with a group of pesticide formulating plants in Mississippi.

Except for the contamination from Wolf River and Cypress Creek, there is no buildup or increasing pesticide contamination of the sediments in the lower Mississippi River. High concentrations of chlorinated hydrocarbon residues were detected in bottom sediments, spoils, and flood-plain deposits from Cypress Creek, downstream from a primary manufacturer of endrin and heptachlor. These were residues of dieldrin, aldrin, endrin, endrin keto, isodrin, chlordane, heptachlor, hexachloronorbornadiene (X), and heptachloronorbornene (Y). Traces of X, an intermediate compound in the manufacture of endrin, were detected in sediments from Baton Rouge, La., about 500 river miles downstream from the source at Memphis. Most of the Mississippi River samples below West Memphis, Ark., however, showed no pesticide residues in tests sensitive enough to detect 0.05 ppm.

Contamination apparently associated with pesticide formulating plants was found in sediments at five locations on tributary streams in Mississippi. Chlorinated hydrocarbon residues included dieldrin, aldrin, endrin, isodrin, X, Y, chlordane, lindane, and DDT analogs and metabolites. Many of these residues were found in low concentrations, i.e., <0.05 ppm.

Residues of DDT analogs and metabolites originating from urban spray programs or from agricultural usage were found in several streams in Louisiana, Mississippi, and Arkansas. With one exception, DDT analogs and metabolites were the only residues originating from nonindustrial sources, i.e., municipal and agricultural.

The most significant conclusion from these investigations is that the large amounts of chlorinated hydrocarbons previously applied to crops in the Mississippi River Delta have not created widespread contamination of streambed materials.

FIGURE 3.—*The manufacture of endrin*

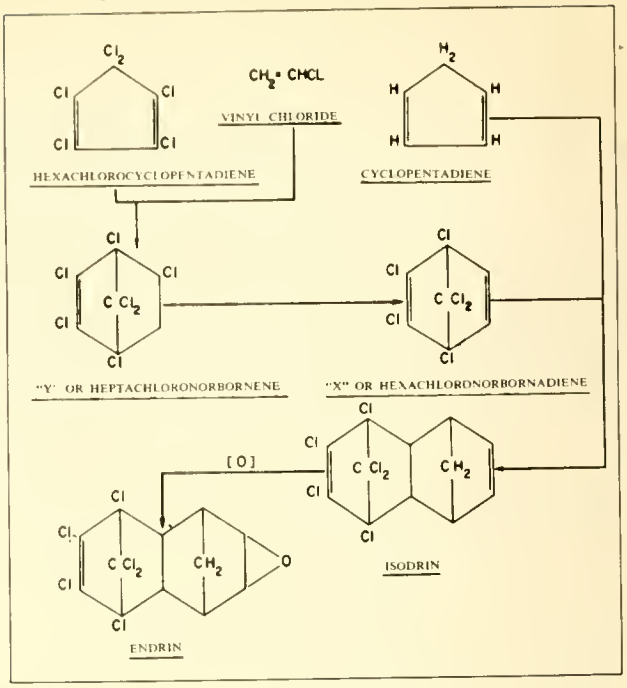


TABLE 5.—*Pesticide concentrations of bed material samples from the Lower Mississippi River—1964 and 1966*

Sample No.	River Mile	Field Designation [1]	Pesticide (ppm) [2] 1964	Pesticide (ppm) [2] 1966
		Tiptonville, Tenn.		
OX- 7	879.6	ML-2	Trace BHC	
9	879.1	DR-2	2.9 BHC	
		Redman Bar, Tenn.		
19	740.4	MR-7	0.6 BHC	
		Memphis, Tenn.		
28	732.8	UL-2	23.4 Isodrin	0.63 X 0.48 Y 0.28 Isodrin 2.20 Chlordane
29	732.8	UL-7	0.4 Isodrin 0.6 Toxaphene/ Strobane	0.52 X 1.10 Y 0.41 Isodrin 2.80 Chlordane
32	731.0	ML-2	0.2 X 0.4 Y 3.9 Isodrin	0.35 X 1.30 Y 0.08 Isodrin 2.10 Chlordane
33	731.0	ML-7	0.2 Y 0.8 Isodrin	0.28 X 0.13 Y 0.08 Isodrin 0.80 Chlordane
36	730.4	DI-2	2.9 Isodrin	
37	730.4	DI-7	0.9 Isodrin	

[1] See Appendix for chemical names of compounds mentioned in this paper.

[2] Mention of trade products or companies in this paper does not imply that they are recommended or endorsed by the Department of Agriculture over similar products of other companies not mentioned. Trade names are used here for convenience in reference only.

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(2) U.S. Army, Corps of Engineers, Mississippi River Commission, Vicksburg, Miss. 1962. (30 ed.) Flood Control and Navigation Maps of the Mississippi River; Cairo, Ill. to the Gulf of Mexico.

TABLE 5.—*Pesticide concentrations of bed material samples from the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	River Mile	Field Designation [1]	Pesticide (ppm) [2]	
			1964	1966
West Memphis, Ark.				
40	727.7	UL-2	0.4 Toxaphene/ Strobane	
41	727.7	UL-7	0.1 Toxaphene/ Strobane	
43	723.6	MR-7	0.8 Isodrin	0.16 X
47	723.0	DR-7		0.08 X
State Line, Miss.-Tenn.				
50	714.8	UR-2	Trace BHC	
51	714.8	UR-7	Trace BHC	
53	714.8	UL-7	Trace BHC	
55	714.0	MR-7	Trace BHC	
58	712.5	DR-2	Trace BHC	
59	712.5	DR-7	Trace X & Y	
60	712.5	DL-2	Trace X & Y	
61	712.5	DL-7	Trace X & Y	
Helena, Ark.				
72	657.1	DL-2	Trace Y	
Greenville, Miss.				
76	567.0	UL-2	Trace X & Y	
80	563.2	ML-2	1.1 Isodrin	
81	563.2	ML-7	1.3 Isodrin	
82	562.0	DR-2	Trace Y	
83	562.0	DR-7	Trace Y	
85	562.0	DL-7	Trace Y	
Vicksburg, Miss.				
86	430.7	UR-2	Trace Y	
94	429.1	DR-2	Trace BHC	
95	429.1	DR-7	Trace BHC	
96	429.1	DL-2	Trace BHC	
Natchez, Miss.				
99	360.9	UR-7		0.10 X
100	360.9	UL-2		0.10 X
102	358.7	MR-2		0.22 X
103	358.7	MR-7		0.31 X
104	358.7	ML-2		0.20 X
105	358.7	ML-7		0.18 X
106	356.8	DR-2		0.24 X
108	356.8	DL-2	Trace BHC	
109	356.8	DL-7	Trace BHC	
Baton Rouge, La.				
110	227.9	UR-2	Trace BHC	
112	227.9	UL-2	Trace X & Y	1.10 X
113	227.9	UL-7	Trace X & Y	
114	227.2	MR-2	Trace X & Y	
115	227.2	MR-7		0.08 X
116	227.2	ML-2		0.09 X
117	227.2	ML-7		0.05 X
118	226.7	DR-2		0.24 X
119	226.7	DR-7		0.14 X
120	226.7	DL-2		0.05 X
121	226.7	DL-7		0.09 X

[1] U—upstream cross section; M—middle cross section; D—downstream cross section; R and L indicate right and left bank, respectively, looking downstream; the last digit is sampling depth in feet.

[2] Trace quantities are defined as 0.05 to 0.1 ppm; parts pesticide per oven-dry sediment weight.

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
TENNESSEE			
Wolf River, Memphis			
OX-134	U	No Residue	No Residue
135	M	No Residue	0.25 Y
136	D	No Residue	No Residue

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
TENNESSEE—Continued			
Wolf River, Memphis (Continued)			
300	O	No Sample	0.05 Y 0.09 Aldrin 2.20 Chlordane 1.57 *p,p'*-TDE 0.37 *p,p'*-DDE 0.83 *o,p'*-TDE
137	U	13.2 X 16.0 Y 10.9 Heptachlor epoxide	7.10 X 9.90 Y 13.0 Isodrin 0.30 Aldrin
138	M	7.5 X 8.7 Y 14.9 Heptachlor epoxide	3.40 X 5.00 Y 12.00 Isodrin 0.21 Aldrin
139	D	3.4 X 4.6 Y	4.70 X 5.30 Y 6.90 Isodrin 0.16 Aldrin
140	D	No Residue	No Residue
Old Wolf River, Memphis			
301	U	No Sample	0.68 X 3.27 Y 5.94 Isodrin 1.50 Aldrin 0.57 Endrin 0.14 Dieldrin 3.10 Chlordane
302	M	No Sample	0.08 X 0.62 Y 0.58 Isodrin 0.26 Endrin 0.10 Dieldrin 2.24 Chlordane
303	D	No Sample	0.13 X 0.28 Y 0.28 Isodrin 0.31 Endrin 0.26 Dieldrin 2.31 Chlordane
Cypress Creek, Memphis			
141	U	No Residue	No Residue
142	M	0.4 X 1.2 Y 2.4 Isodrin	2.20 *p,p'*-TDE 1.00 *o,p'*-TDE
143	D	2.4 X 3.4 Y 1.6 Isodrin	1.90 *p,p'*-TDE 1.30 *o,p'*-TDE
144	U	1,160.0 X 594.0 Y 34.9 Isodrin 824.0 Endrin	8.00 X 6.70 Y 9.10 Isodrin 0.28 Aldrin

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
	TENNESSEE—Continued		
Cypress Creek, Memphis (Continued)			
145	M	33,400.0 X 28,100.0 Y 1,140.0 Isodrin 12,800.0 Endrin	273.00 X 173.00 Y 183.00 Isodrin 3.40 Aldrin
146	D	515.0 X 475.0 Y 1,090.0 Heptachlor epoxide 172.0 Endrin 218.0 Isodrin	31.0 X 274.0 Y 1,000.0 Isodrin 6.2 Aldrin
147		426.0 X 766.0 Y 537.0 Heptachlor epoxide	298.0 X 668.0 Y 354.0 Isodrin 22.0 Aldrin
304	X	No Sample	110,000.0 X 85,000.0 Y 12,000.0 Isodrin 3,000.0 Aldrin 10,200.0 Endrin 9,000.0 Dieldrin 30,000.0 Chlordane
McKellar Lake, Memphis			
305	U	No Sample	0.12 X 0.10 Y 0.18 Isodrin 0.05 *p,p'*-TDE
306	D	No Sample	0.06 X 0.06 Y 0.06 Isodrin 0.05 *p,p'*-TDE
Tennessee Chute, Memphis			
308		No Sample	0.07 Isodrin
	LOUISIANA		
Alma Plantation Bayou, near Lakeland, Pointe Coupee Parish			
149	1 and 2	0.4 Heptachlor epoxide	No Residue
150	3 and 4	0.6 Heptachlor epoxide	No Residue
Little River near Jonesville, Catahoula Parish			
157	U	No Residue	No Residue
158	M	No Residue	No Residue
159	D	0.3 Heptachlor epoxide	No Residue
Tensas River, near Clayton, Concordia Parish			
178	U	No Residue	0.22 *p,p'*-TDE 0.14 *p,p'*-DDE
179	M	No Residue	0.20 *p,p'*-TDE 0.14 *p,p'*-DDE
180	D	No Residue	0.17 *p,p'*-TDE 0.10 *p,p'*-DDE

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
	LOUISIANA—Continued		
Brushy Bayou, near Tallulah, Madison Parish			
310	U	No Sample	0.67 *p,p'*-DDE 0.32 *o,p'*-TDE 1.16 *p,p'*-TDE 0.41 *p,p'*-DDT
311	D	No Sample	0.09 *p,p'*-DDE 0.06 *o,p'*-TDE 0.21 *p,p'*-TDE
	MISSISSIPPI		
Bayou Pierre, near Port Gibson, Claiborne County			
181	U	No Residue	No Residue
182	M	No Residue	No Residue
183	D	No Residue	No Residue
184	U	No Residue	0.05 TDE
185	M	No Residue	No Residue
186	D	No Residue	No Residue
Bear Creek, near Canton, Madison County			
312	UU	No Sample	No Residue
[3] 327 (193)	U	No Residue	0.24 TDE 0.05 DDE
[3] 328 (192)	D	No Residue	0.11 TDE
[3] 329 (191)	U	No Residue	0.07 TDE 0.05 DDE
[3] 330 (190)	D	0.2 TDE	No Residue
Coldwater River, near Marks, Quitman County			
194	U	No Residue	0.11 *p,p'*-TDE 0.06 *p,p'*-DDE
195	M	No Residue	0.09 *p,p'*-TDE
196	D	No Residue	0.12 *p,p'*-TDE 0.06 *p,p'*-DDE
197	U	0.4 TDE	0.12 *p,p'*-TDE
198	M	0.4 TDE	0.11 *p,p'*-TDE
199	D	0.5 TDE	0.07 *p,p'*-TDE
Sunflower River, near Clarksdale, Coahoma County			
203	U	Trace BHC	0.42 *p,p'*-TDE 0.17 *o,p'*-TDE
204	M	No Residue	0.06 Dieldrin 11.19 Toxaphene/Strobane 0.46 *p,p'*-TDE 0.09 *o,p'*-TDE 0.19 *p,p'*-DDE

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
MISSISSIPPI—Continued			
Sunflower River, near Clarksdale, Coahoma County (Continued)			
205	D	No Residue	0.08 Dieldrin 8.85 Toxaphene/Strobane 0.67 *p,p'*-TDE 0.17 *o,p'*-TDE 0.38 *p,p'*-DDE
206	U	No Residue	0.27 Dieldrin 0.91 *p,p'*-TDE 0.19 *o,p'*-TDE 0.33 *p,p'*-DDE
207	M	No Residue	0.29 Dieldrin 11.93 Toxaphene/Strobane 1.34 *p,p'*-TDE 0.39 *o,p'*-TDE 0.48 *p,p'*-DDE
208	D	No Residue	0.24 Dieldrin 10.87 Toxaphene/Strobane 1.09 *p,p'*-TDE 0.21 *o,p'*-TDE 0.38 *p,p'*-DDE
Ditch A, near Clarksdale, Coahoma County			
313		No Sample	0.09 Dieldrin 0.55 *p,p'*-TDE 0.21 *p,p'*-DDT 0.27 *o,p'*-TDE 0.19 *p,p'*-DDE
Ditch B, near Clarksdale, Coahoma County			
314		No Sample	1.21 Dieldrin 2.08 Isodrin 2.92 Aldrin 6.44 Chlordane 17.40 *p,p'*-TDE 10.22 *o,p'*-TDE 1.12 *p,p'*-DDE
Sunflower River, Sunflower County			
209	U	No Residue	0.14 *p,p'*-TDE
210	M	No Residue	0.11 *p,p'*-TDE
211	D	No Residue	0.14 *p,p'*-TDE 0.07 *p,p'*-DDE
212	U	No Residue	0.13 *p,p'*-TDE
213	M	No Residue	0.13 *p,p'*-TDE 0.06 *p,p'*-DDE
214	D	No Residue	0.16 *p,p'*-TDE 0.12 *p,p'*-DDE
Jones Bayou, near Cleveland, Bolivar County			
215	U	No Residue	0.17 *p,p'*-TDE 0.16 *p,p'*-DDE
216	D	No Residue	0.20 *p,p'*-TDE 0.15 *p,p'*-DDE

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
	MISSISSIPPI—Continued		
Jones Bayou, near Cleveland, Bolivar County (Continued)			
217	U	No Residue	0.70 Dieldrin 4.52 Toxaphene/Strobane 0.84 *p,p'*-TDE 0.18 *o,p'*-TDE 0.25 *p,p'*-DDE
218	D	No Residue	3.91 Toxaphene/Strobane 0.65 *p,p'*-TDE 0.17 *o,p'*-TDE 0.21 *p,p'*-DDE
Ditch A, near Cleveland, Bolivar County			
315	U	No Sample	0.16 *p,p'*-TDE 0.04 *o,p'*-TDE
316	D	No Sample	0.09 X 0.07 Y 1.20 *p,p'*-TDE 0.59 *o,p'*-TDE
Sunflower River, near Indianola, Sunflower County			
219	U	No Residue	No Residue
220	M	No Residue	No Residue
221	D	No Residue	No Residue
222	U	0.5 TDE	2.45 Toxaphene/Strobane 0.42 *p,p'*-TDE 0.15 *p,p'*-DDE
223	M	0.4 TDE	0.34 *p,p'*-TDE 0.12 *p,p'*-DDE
224	D	0.4 TDE	6.57 Toxaphene/Strobane 0.27 *p,p'*-TDE 0.10 *p,p'*-DDE 0.12 *p,p'*-DDT
Ditch 24, near Indianola, Sunflower County			
317	U	No Sample	0.46 *p,p'*-TDE 0.16 *o,p'*-TDE 0.15 *p,p'*-DDE 0.09 *p,p'*-DDT
225	D	1.4 TDE 0.2 DDE	0.05 Dieldrin 13.18 Toxaphene/Strobane 1.07 *p,p'*-TDE 0.29 *o,p'*-TDE 0.25 *p,p'*-DDE 0.49 *p,p'*-DDT
Horseshoe Bayou, near Greenville, Washington County			
241	U	No Residue	0.06 Dieldrin 0.56 Chlordane 0.09 *p,p'*-DDE 0.44 *p,p'*-TDE 0.18 *o,p'*-TDE

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2]	
		1964	1966
	MISSISSIPPI—Continued		
Horseshoe Bayou, near Greenville, Washington County (Continued)			
242	D	No Residue	0.15 Dieldrin 1.55 Chlordane 1.41 Aldrin 0.31 *p,p'*-DDE 5.33 *p,p'*-TDE 2.41 *o,p'*-TDE
243	U	No Residue	0.69 Dieldrin 1.31 Chlordane 0.18 Aldrin 0.59 *p,p'*-DDE 5.80 *p,p'*-TDE 3.31 *o,p'*-TDE
244	D	0.2 DDE 3.3 TDE	1.04 Dieldrin 1.16 Chlordane 0.41 Aldrin 0.86 *p,p'*-DDE 6.61 *p,p'*-TDE 3.94 *o,p'*-TDE
Fish Lake, near Greenville, Washington County			
245	U	No Residue	0.19 *p,p'*-DDT 0.06 *o,p'*-DDT 0.39 *p,p'*-DDE 0.46 *p,p'*-TDE 0.08 *o,p'*-TDE
246	M	No Residue	0.19 *p,p'*-DDT 0.05 *o,p'*-DDT 0.40 *p,p'*-DDE 0.56 *p,p'*-TDE 0.11 *o,p'*-TDE
247	D	No Residue	0.08 *p,p'*-DDT 0.05 *o,p'*-DDT 0.39 *p,p'*-DDE 0.48 *p,p'*-TDE 0.13 *o,p'*-TDE
248	U	No Residue	0.07 *o,p'*-DDT 0.48 *p,p'*-DDE 0.57 *p,p'*-TDE 0.14 *o,p'*-TDE
249	M	No Residue	0.07 *o,p'*-DDT 0.34 *p,p'*-DDE 0.28 *p,p'*-TDE 0.06 *o,p'*-TDE
250	D	No Residue	0.24 *p,p'*-DDE 0.22 *p,p'*-TDE
Ditch 6, near Greenville, Washington County			
318	D	No Sample	0.18 Dieldrin 0.29 *p,p'*-DDE 1.05 *p,p'*-TDE 1.19 *o,p'*-TDE

TABLE 6.—*Pesticide concentration of bed material samples from the tributaries of the Lower Mississippi River—1964 and 1966*—Continued

Sample No.	Field Site Designation [1]	Pesticides (ppm) [2] 1964	1966
		MISSISSIPPI—Continued	
Deer Creek near Rolling Fork, Sharkey County			
323	U	No Sample	0.59 *p,p'*-DDE 1.75 *o,p'*-TDE 4.03 *p,p'*-TDE
Rolling Fork Creek, near Rolling Fork, Sharkey County			
324	D	No Sample	0.30 *p,p'*-DDE 0.30 *o,p'*-TDE 0.78 *p,p'*-TDE
		ARKANSAS	
St. Francis River, Lee County			
251	U	No Residue	0.05 *p,p'*-DDE 0.11 *p,p'*-TDE
252	M	No Residue	0.20 *p,p'*-DDE 0.13 *p,p'*-TDE
253	D	No Residue	0.12 *p,p'*-TDE
Crooked Bayou, near McGehee, Desha County			
325	U	No Sample	0.13 *p,p'*-DDE 0.05 *o,p'*-TDE 0.21 *p,p'*-TDE 0.17 *p,p'*-DDT
326	D	No Sample	0.09 *p,p'*-DDE 0.09 *o,p'*-TDE 0.21 *p,p'*-TDE

[1] U—upper cross section; M—middle cross section; D—downstream cross section.
[2] Trace quantities are defined as 0.05 to 0.1 ppm; parts pesticide per oven-dry sediment weight.
[3] See Table 2 for explanation of sample numbers.

TABLE 7.—*Pesticide concentrations of sediments from Wolf River and Cypress Creek, Memphis, Tenn.—1967*

Sample No.	Pesticides (ppm) [1] Dieldrin	Aldrin	Endrin	Endrin Keto	Isodrin	Chlordane	Hepta-chlor	X	Y	Z
					Wolf River					
OX-400										
[2] 401										
402										
403						0.12	0.07	0.13		
[3] 404		0.16				5.08	0.60	0.41	0.07	0.29
[4] 405		0.12				0.62	0.09	0.17		
406		0.19				3.96	0.33	0.83	0.32	0.06
407	0.33	23.70	1.01		1.80	128.40	11.10	35.00	14.20	2.00
408		0.09				2.32	0.32	0.58	0.25	
409					0.18	1.88	0.13	0.65	0.44	
410						1.62	0.30	0.17	0.13	
[2] 411		1.09				12.41	3.11	5.48	1.71	0.23

TABLE 7.—*Pesticide concentrations of sediments from Wolf River and Cypress Creek, Memphis, Tenn.—1967*—Continued

Sample No.	Pesticides (ppm) [1]									
	Dieldrin	Aldrin	Endrin	Endrin Keto	Isodrin	Chlordane	Hepta-chlor	X	Y	Z
					Cypress Creek					
[5] 412	0.15		0.24							
413	3.48	1.09	10.00	2.12	11.60	5.87	2.25	22.50	42.50	
414	5.59	4.07	23.60		59.70	8.81	2.44	140.00	118.00	4.51
415	3.27	2.80	22.20	2.80	48.00	10.47	2.66	47.40	49.10	2.70
[6] 416	4.60	2.79	47.40	24.80	71.00					
[6] 417	931.00	567.00	10,676.00	3,509.00	24,123.00					
[6] 418	63.10	39.00	631.00	242.00	1,660.00					
419	2.26	7.70	9.65	2.08	105.70	9.58	1.18	124.80	194.60	6.20
[7] 420	68.60	26.40	73.40	89.00	24.5					
[7] 421	0.47	1.33	1.93	4.78						
[7] 422	73.70	16.60	294.00	96.10	181.0					
[7] 423	12.10	32.80	24.20	66.10	523.0					

[1] Parts pesticide per oven-dry sediment weight.
[2] Bank deposits.
[3] Also contains in ppm: 0.06 heptachlor epoxide.
[4] Also contains in ppm: 0.12 *p,p'*-DDT; 0.41 *o,p'*-TDE; 0.12 *p,p'*-DDE.
[5] Also contains in ppm: 1.62 *p,p'*-DDT; 0.41 *o,p'*-DDT; 1.83 *p,p'*-TDE; 0.32 *p,p'*-DDE.
[6] Spoils; apparently dredged from Cypress Creek.
[7] Stream deposition area.

TABLE 8.—*Pesticide concentrations in water samples from Wolf River and Cypress Creek, Memphis, Tenn.—1967*

Sample No.	Pesticides (ppb) [1]								
	Dieldrin	Aldrin	Endrin	Endrin Keto	Isodrin	Heptachlor	X	Y	Z
				Wolf River					
OX-426									
427									
428						6.10	1.18	3.55	0.50
429						1.02	5.54	0.95	
				Cypress Creek					
430									
431									
432	0.37		2.03	5.04	0.09	0.22	0.93	0.10	0.28
433	0.32	0.15	1.98	6.50	0.73	2.40	4.83	3.15	0.17
424	0.04	0.29	0.25		0.09	0.12	0.47	0.42	
425	0.05		0.27				0.38	0.70	

[1] Parts pesticide per total-sample weight.

TABLE 9.—*Pesticide concentrations of selected bed material samples from the tributaries of the Lower Mississippi River; collected and analyzed in 1966; reanalyzed in 1967*

Sample No.	Subsample [2]	Pesticides (ppm) [1]															
		p,p'-DDT	*o,p'*-DDT	*p,p'*-DDE	*o,p'*-DDE	*p,p'*-TDE	*o,p'*-TDE	Aldrin	Dieldrin	Endrin	Isodrin	X	Y	Z	Lindane	Chlordane	Toxaphene/ Strobane
Tensas River near Clayton, Concordia Parish, La.																	
OX-178	O-1			0.14		0.22											
	O-2			0.14		0.22											
	R-S			0.20		0.23	0.07										
179	O-1			0.14		0.20											
	O-2			0.14		0.20											
	R-S			0.27		0.24	0.06										
Coldwater River near Marks, Quitman County, Miss.																	
194	O-1			0.06		0.11											
	O-2			0.06		0.11											
	R-S			0.07		0.08	0.02										
195	O-1					0.09											
	O-2			0.04		0.09											
	R-S			0.06		0.08	0.02										
196	O-1			0.06		0.12											
	O-2			0.06		0.12											
	R-S			0.07		0.08	0.03										
197	O-1					0.12											
	O-2			0.05		0.12											
	R-S			0.05		0.10	0.03										
198	O-1					0.11											
	O-2			0.05		0.11											
	R-S			0.10		0.15	0.04										
199	O-1					0.07											
	O-2			0.05		0.07											
	R-S			0.05		0.09	0.03										
Sunflower River near Clarksdale, Coahoma County, Miss.																	
203	O-1					0.42	0.17										
	O-2			0.19		0.46	0.08	0.03	0.06							0.25	
	R-S			0.27		0.40	0.09	0.07	0.06							0.22	
204	O-1			0.19		0.46	0.09		0.06								11.19
	O-2			0.19		0.46	0.09	0.03	0.06							0.44	
	R-S			0.22		0.29	0.07	0.03	0.02							0.33	
205	O-1			0.38		0.67	0.17		0.08								8.85
	O-2			0.38		0.67	0.17	0.04	0.08							0.38	
	R-S			0.38		0.43	0.09	0.08	0.04							0.28	
206	O-1			0.33		0.91	0.19		0.27								
	O-2			0.33		0.91	0.19	0.03	0.27							0.36	
	R-S			0.33		0.65	0.13	0.03	0.36							0.37	
207	O-1			0.48		1.34	0.29		0.29								11.93
	O-2			0.48		1.34	0.29	0.04	0.29							0.53	
	R-S			0.55		0.91	0.45	0.04	0.37							0.88	
208	O-1			0.38		1.09	0.21		0.24								10.87
	O-2			0.38		1.09	0.21	0.04	0.24							0.49	
	R-S			0.50		0.85	0.34	0.01	0.36							1.08	

TABLE 9.—*Pesticide concentrations of selected bed material samples from the tributaries of the Lower Mississippi River; collected and analyzed in 1966; reanalyzed in 1967*—Continued

Sample No.	Subsample [2]	Pesticides (ppm) [1]															
		p,p'-DDT	*o,p'*-DDT	*p,p'*-DDE	*o,p'*-DDE	*p,p'*-TDE	*o,p'*-TDE	Aldrin	Dieldrin	Endrin	Isodrin	X	Y	Z	Lindane	Chlordane	Toxaphene/ Strobane
Horseshoe Bayou near Greenville, Washington County, Miss.																	
241	O-1			0.09		0.44	0.18		0.06							0.56	
	R-E			0.10		0.41	0.18	0.04	0.06	0.05					0.01	0.56	
	R-S			0.22		0.41	0.02	0.12	0.13	0.21					0.10	0.40	
242	O-1			0.31		5.33	2.41	1.41	0.15							1.55	
	R-E			0.31		4.90	2.41	1.41	0.15	0.15	0.09		0.02		0.03	1.55	
	R-S			0.11		3.45	1.01	0.38	0.18	0.17	0.04		0.03		0.07	0.84	
243	O-1			0.59		5.80	3.31	0.18	0.69							1.31	
	R-E			0.57		5.80	3.31	0.18	0.69	0.50						1.31	
	R-S			0.34	0.30	3.57	1.59	0.20	0.49	0.33						0.26	
244	O-1			0.86		6.61	3.94	0.41	1.04							1.16	
	R-E			0.86		6.61	3.94	0.41	1.04	0.46					0.10	1.16	
	R-S			0.29	0.40	3.59	1.77	0.02	0.63	0.37					0.07	0.43	
Fish Lake, near Greenville, Washington County, Miss.																	
245	O-1	0.19	0.06	0.39		0.46	0.08										
	R-E	0.19	0.06	0.39		0.46	0.08		0.03	0.13							
246	O-1	0.19	0.05	0.40		0.56	0.11										
	R-E	0.19	0.05	0.40		0.56	0.11		0.04	0.04							
247	O-1	0.08	0.05	0.39		0.48	0.13										
	R-E	0.08	0.05	0.39		0.48	0.13		0.03	0.05							
248	O-1		0.07	0.48		0.57	0.14										
	R-E	0.04	0.07	0.48		0.57	0.14		0.03	0.06							
249	O-1		0.07	0.34		0.28	0.06										
	R-E	0.03	0.07	0.34		0.28	0.06		0.03	0.10							
250	O-1			0.24		0.22											
	R-E	0.02	0.07	0.24		0.22	0.06		0.03	0.02							
St. Francis River, Lee County, Ark.																	
251	O-1			0.05		0.11											
	R-E			0.05		0.11			0.02								
252	O-1			0.20		0.13											
	R-E			0.20		0.13			0.01								
Old Wolf River, Memphis, Tenn.																	
301	O-1							1.50	0.14	0.57	5.94	0.68	3.27			3.10	
	O-2							0.20	0.14	0.57	5.94	0.68	3.27	0.85	0.27	3.10	
	R-S							0.50	0.18	0.18	9.48	1.10	4.88	1.37	0.22	3.12	
302	O-1								0.10	0.26	0.58	0.08	0.62			2.24	
	O-2							0.02	0.10	0.26	0.58	0.08	0.62	0.16	0.06	2.24	
	R-S							0.08	0.09	0.12	0.95	0.03	0.98	0.20	0.09	1.07	
303	O-1								0.26	0.31	0.28	0.13	0.28			2.31	
	O-2							0.05	0.26	0.31	0.28	0.13	0.28	0.07	0.07	2.31	
	R-S							0.04	0.15	0.38	0.31	0.08	0.22	0.06	0.06	1.20	

TABLE 9.—*Pesticide concentrations of selected bed material samples from the tributaries of the Lower Mississippi River; collected and analyzed in 1966; reanalyzed in 1967*—Continued

Sample No	Subsample [2]	Pesticides (ppm) [1]															
		p,p'-DDT	*o,p'*-DDT	*p,p'*-DDE	*o,p'*-DDE	*p,p'*-TDE	*o,p'*-TDE	Aldrin	Dieldrin	Endrin	Isodrin	X	Y	Z	Lindane	Chlordane	Toxaphene/ Strobane
Ditch A, near Clarksdale, Coahoma County, Miss.																	
313	O-1	0.21		0.19		0.55	0.27		0.09								
	O-2	0.48		0.21		0.41	0.13	0.05	0.16	0.13	0.05						
	R-S	0.19		0.18		0.48	0.15	0.05	0.15	0.08	0.01						
Ditch B, near Clarksdale, Coahoma County, Miss.																	
314	O-1			1.12		17.40	10.22	2.92	1.21		2.08					6.44	
	O-2	1.76		0.24		12.28	5.22	1.15	2.23		0.97					6.44	
	R-S	1.54		0.57		14.80	5.50	4.35	4.39		1.94					5.76	
Ditch 24, near Indianola, Sunflower County, Miss.																	
317	O-1	0.09		0.15		0.46	0.16										
	O-2	0.23		0.22		0.43	0.11		0.03		0.05						
	R-S	0.17		0.14		0.41	0.09		0.03		0.01						

[1] Parts pesticide per oven-dry sediment weight.

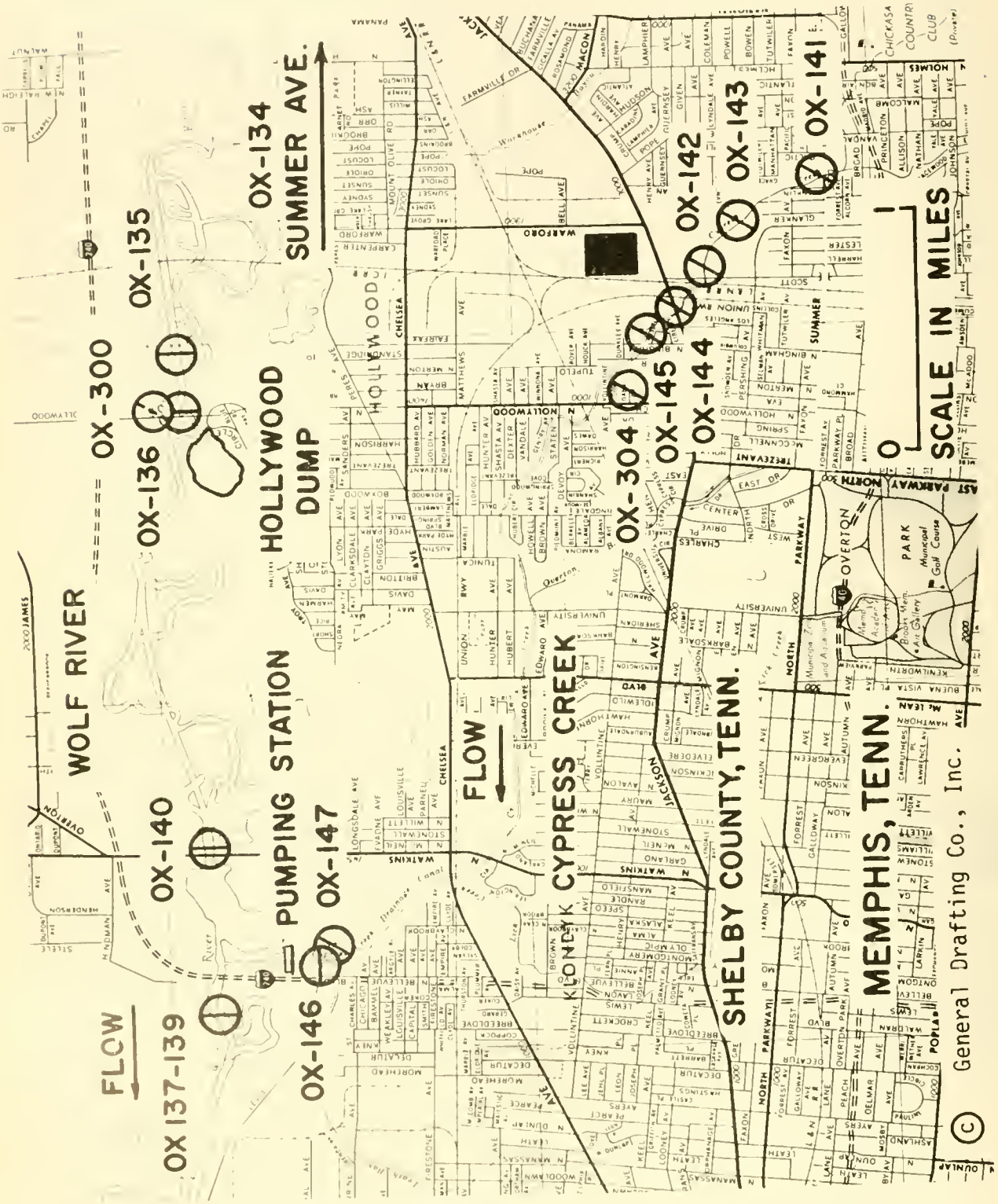
[2] O-1 refers to the original subsample of sediment analyzed in 1966 or early 1967; O-2 is a re-evaluation in late 1967 of O-1 gas chromatographic charts; R-E is a reanalysis in late 1967 of the hexane-isopropanol extracts of O-1 subsample; and R-S is a new subsample of O-1 sediment analyzed in late 1967.

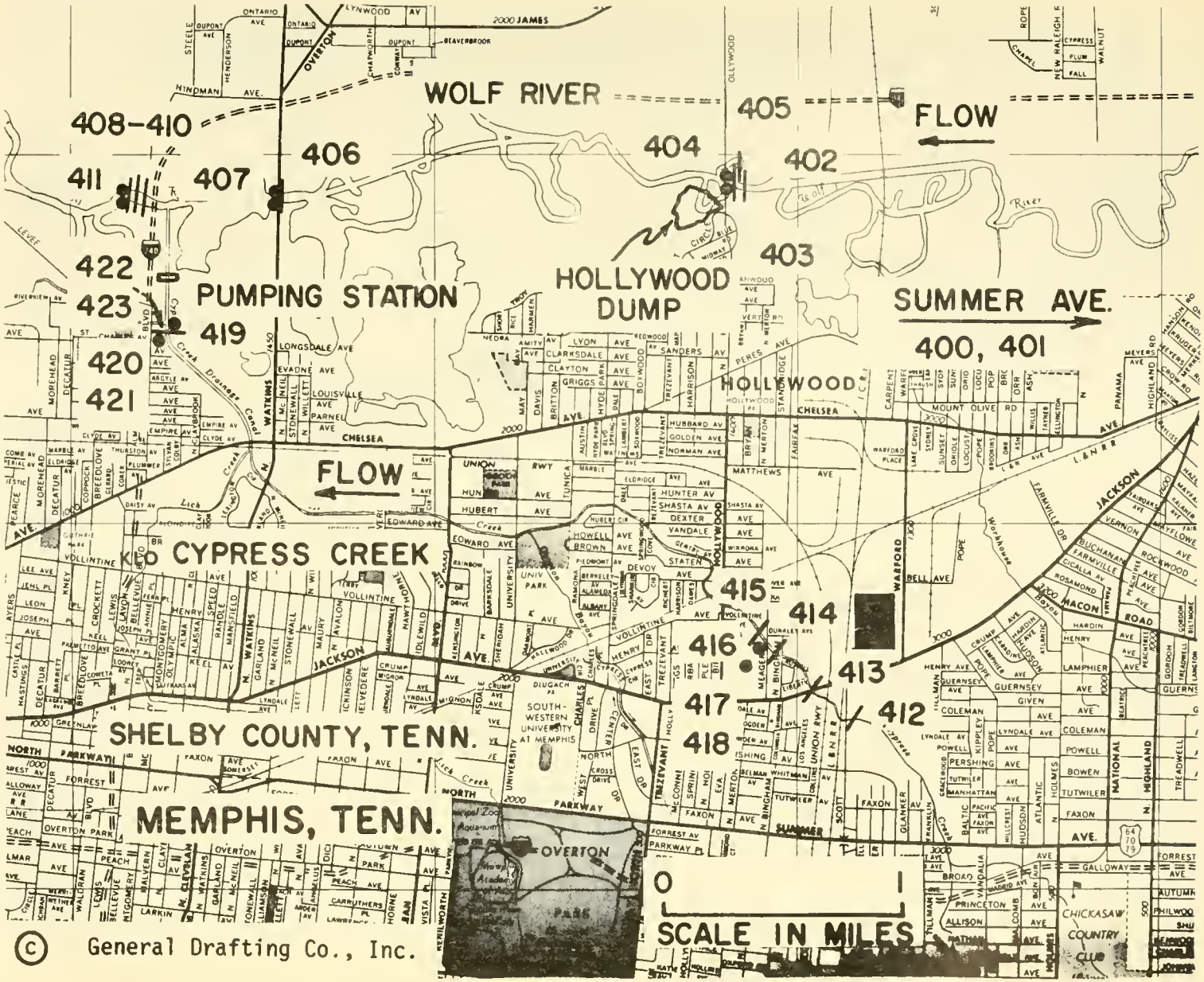
FIGURE 4.—*Dark, greasy deposits on bank of Wolf River near old North Bellevue Boulevard Crossing, Memphis, Tenn.*

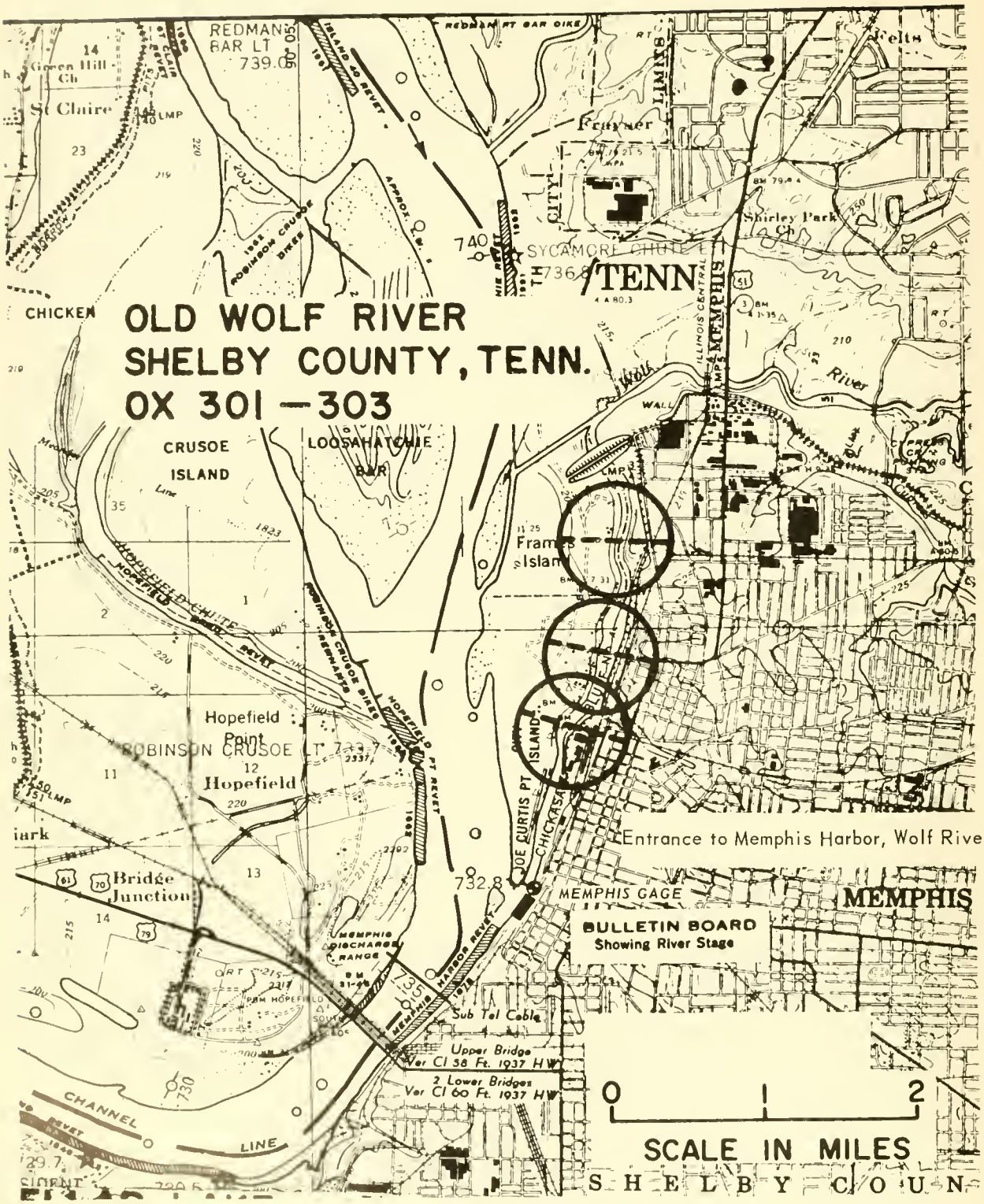
FIGURE 5.—*Dark, greasy deposits on bank of Wolf River near confluence with Mississippi River, Memphis, Tenn.*

MAP SECTION

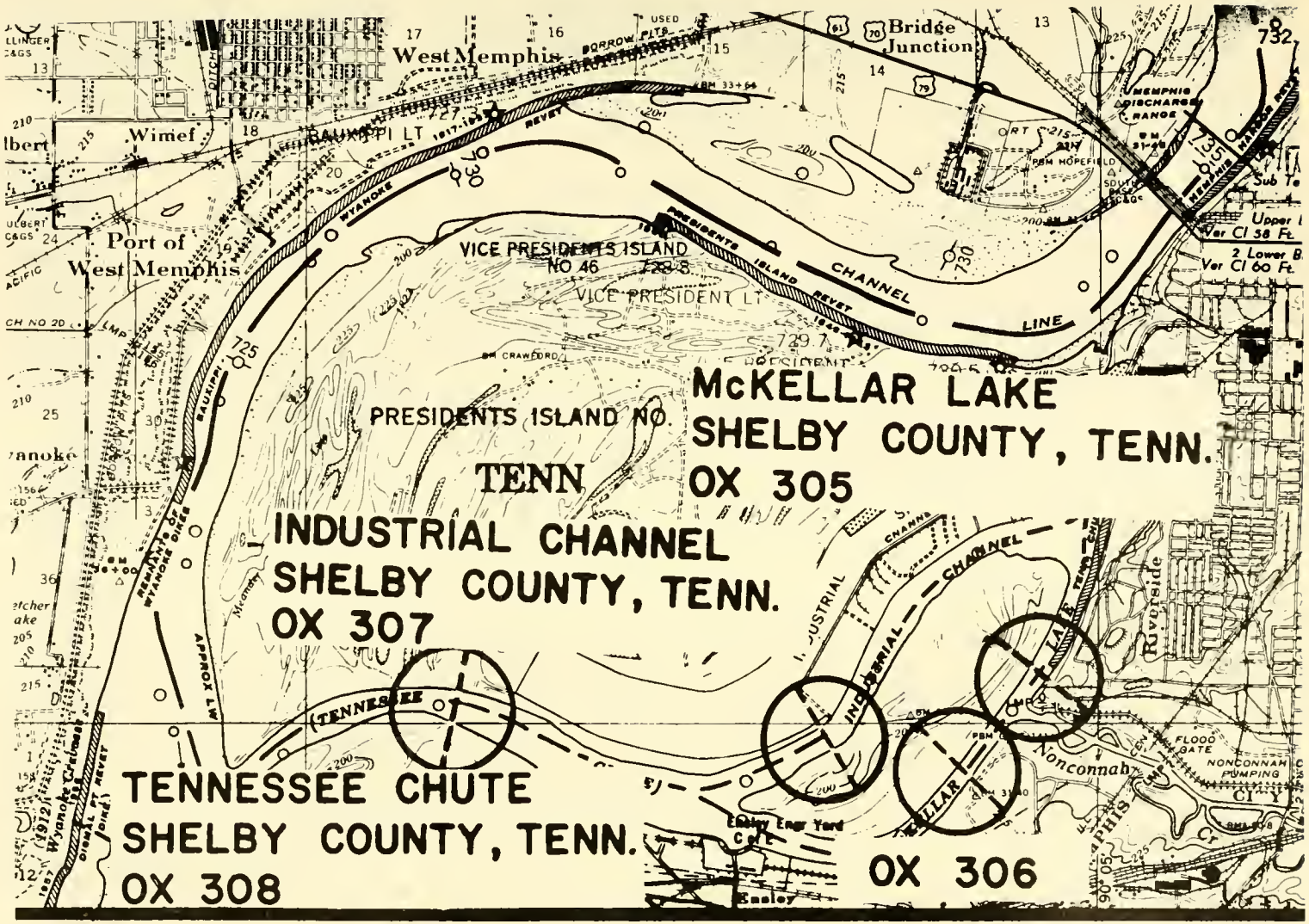
Maps of Sampling Sites on the Tributaries of the Lower Mississippi River—Arranged in Order of Listings in Tables 2 and 3




WOLF RIVER
FLOW
408–410
411
407
406
405
404
402
403
422
423
419
420
421
PUMPING STATION
HOLLYWOOD DUMP
SUMMER AVE.
400, 401
HOLLYWOOD
FLOW
CYPRESS CREEK
415
414
416
413
417
412
418
SHELBY COUNTY, TENN.
MEMPHIS, TENN.
SOUTH-WESTERN UNIVERSITY AT MEMPHIS
OVERTON PARK
0
1
SCALE IN MILES
© General Drafting Co., Inc.

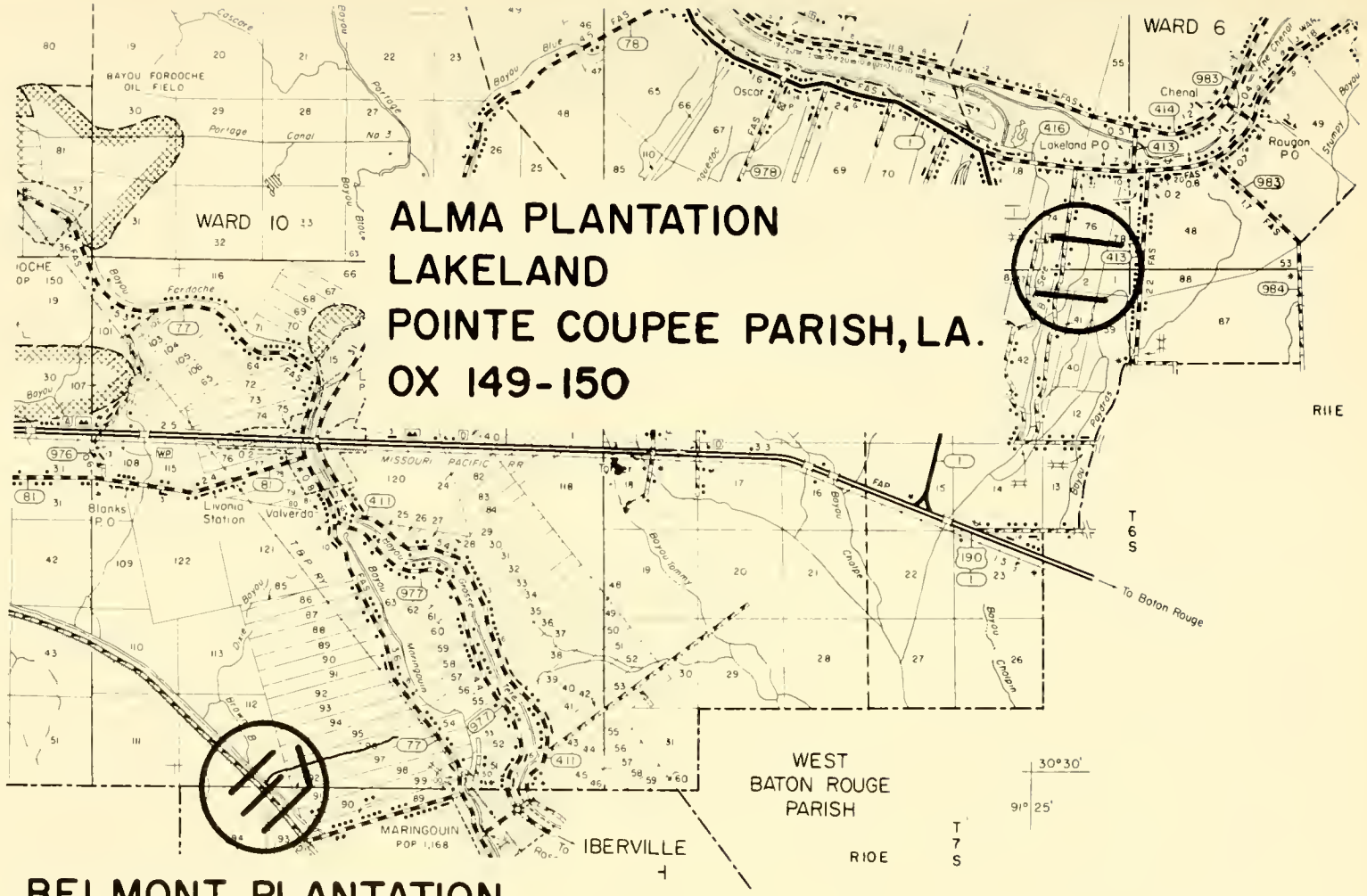


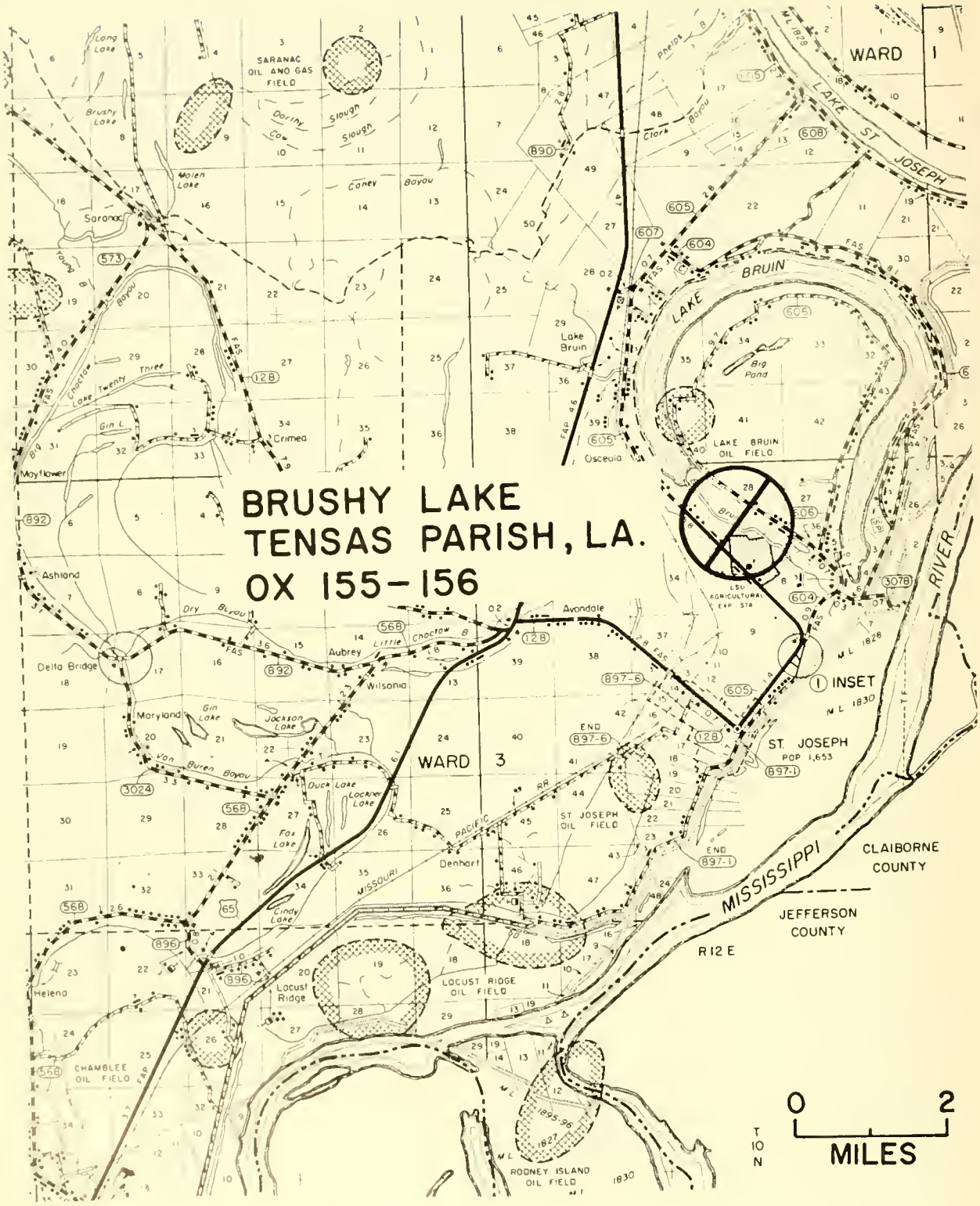
Entrance to Memphis Harbor, Wolf River

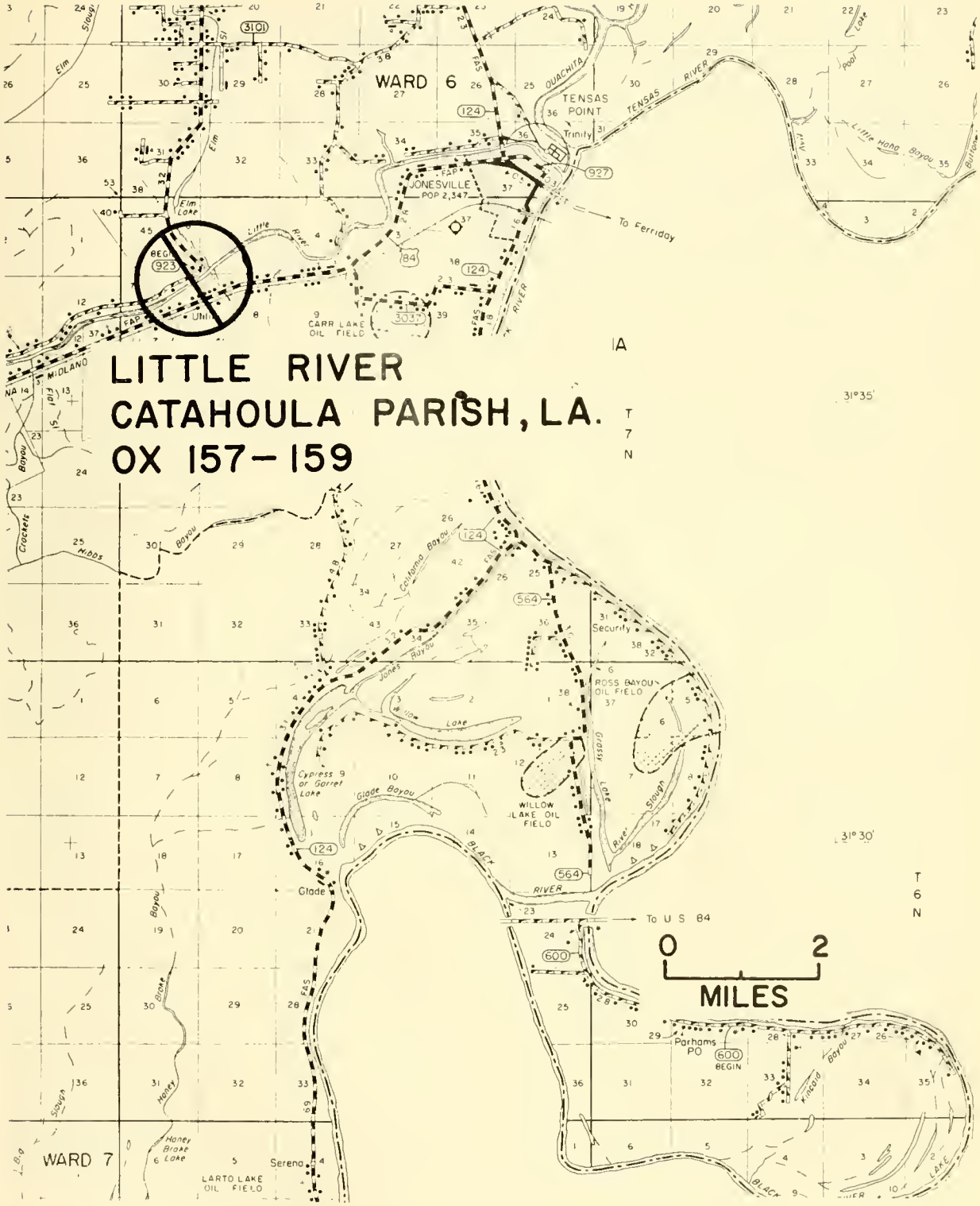

West Memphis
Bridge Junction
Wimef
Port of West Memphis
VICE PRESIDENTS ISLAND NO 46
VICE PRESIDENT LT
PRESIDENTS ISLAND NO.
TENN
McKELLAR LAKE
SHELBY COUNTY, TENN.
OX 305
INDUSTRIAL CHANNEL
SHELBY COUNTY, TENN.
OX 307
TENNESSEE CHUTE
SHELBY COUNTY, TENN.
OX 308
OX 306
PRESIDENTS ISLAND REVET
CHANNEL LINE
TENNESSEE
Riverside
Nonconnah
Scale 1/62500
1 0 1 2 3 4 Miles

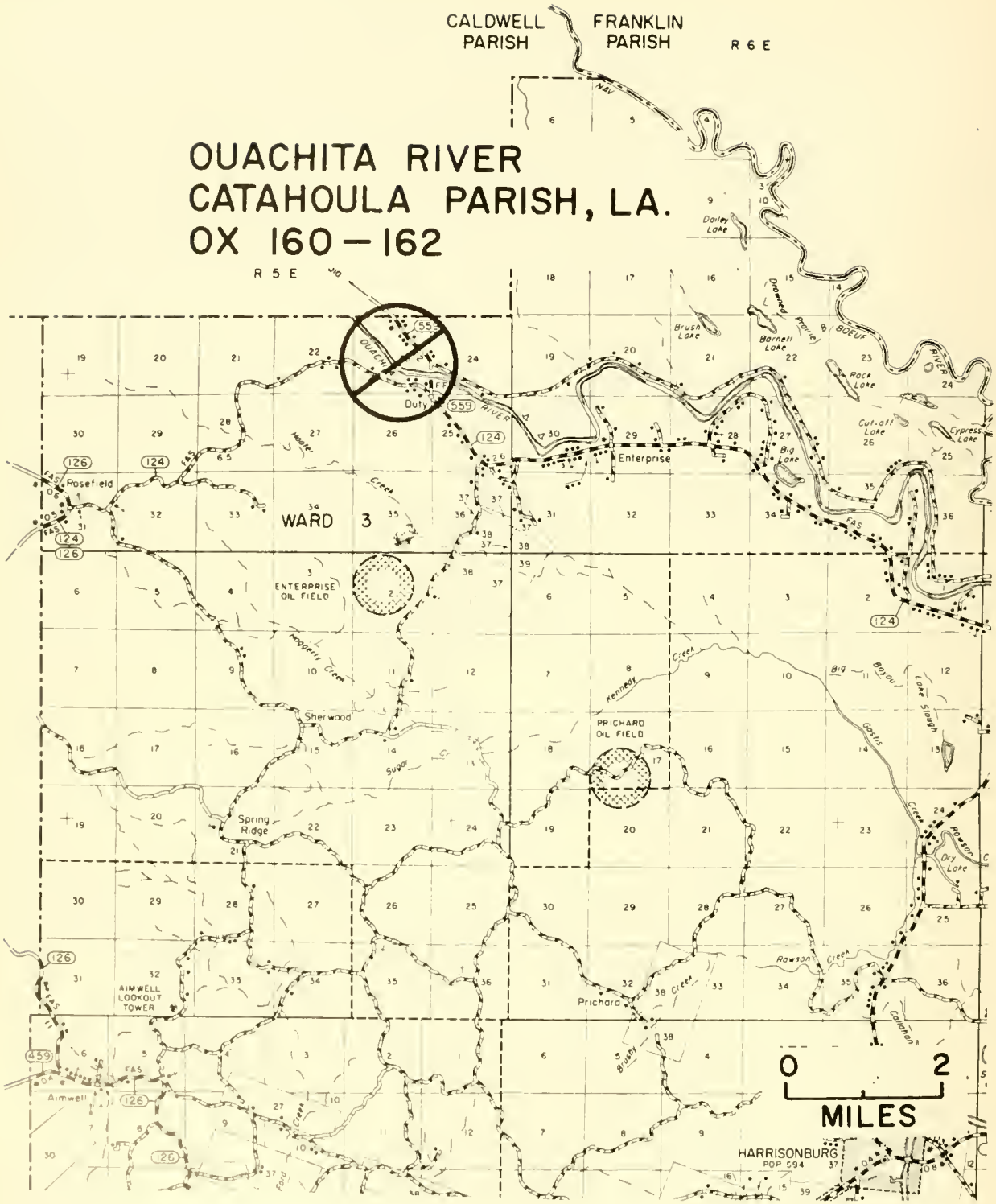
1963

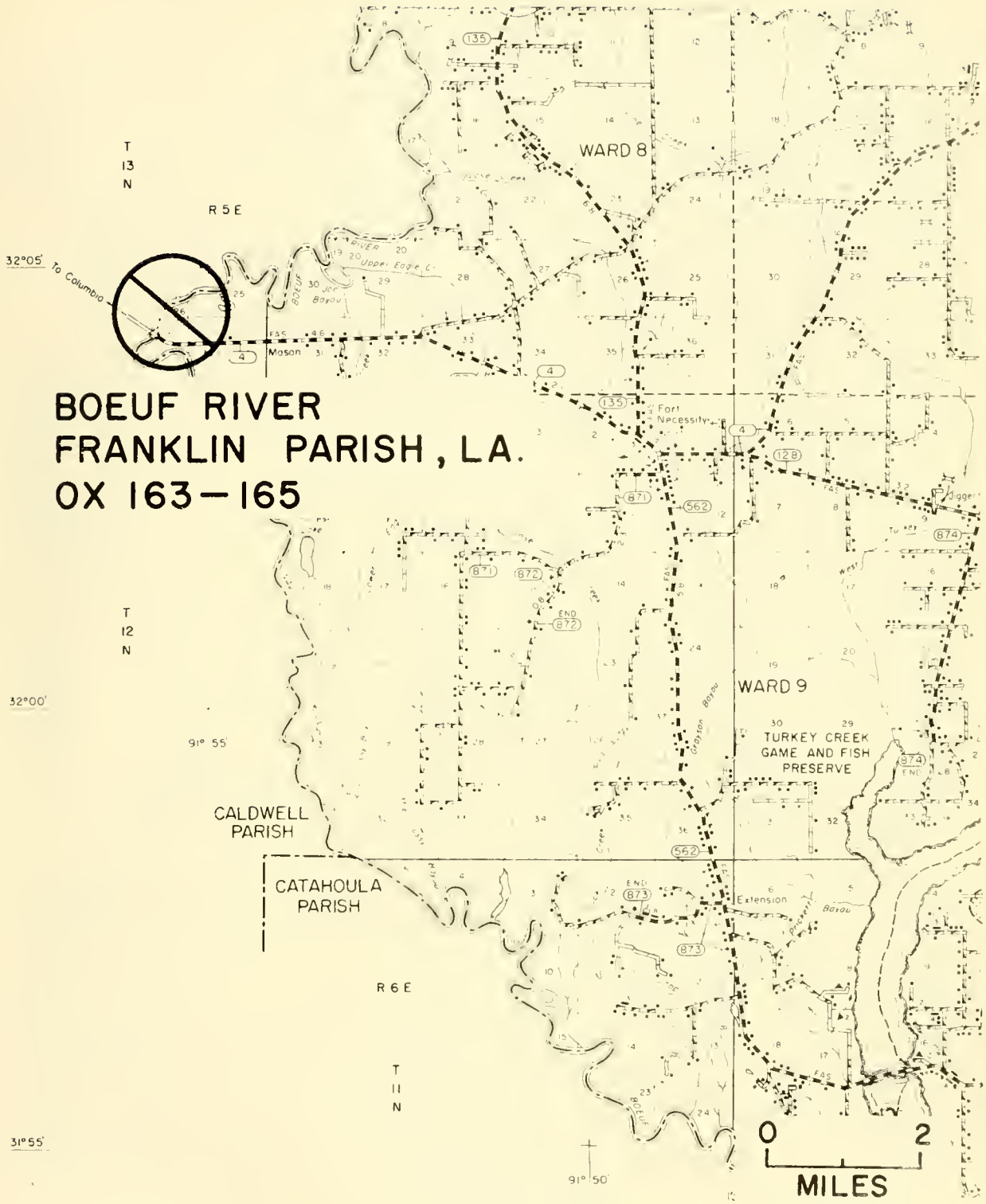
MEMPHIS, TENN.
SHELBY COUNTY, TENN.
NONCONNAH CREEK
OX-309
DUMP
McKELLAR LAKE
MEMPHIS METROPOLITAN AIRPORT
DOGWOOD HILLS
HICKORY HILLS
CANADA GARDENS
SCALE IN MILES
© General Drafting Co., Inc.

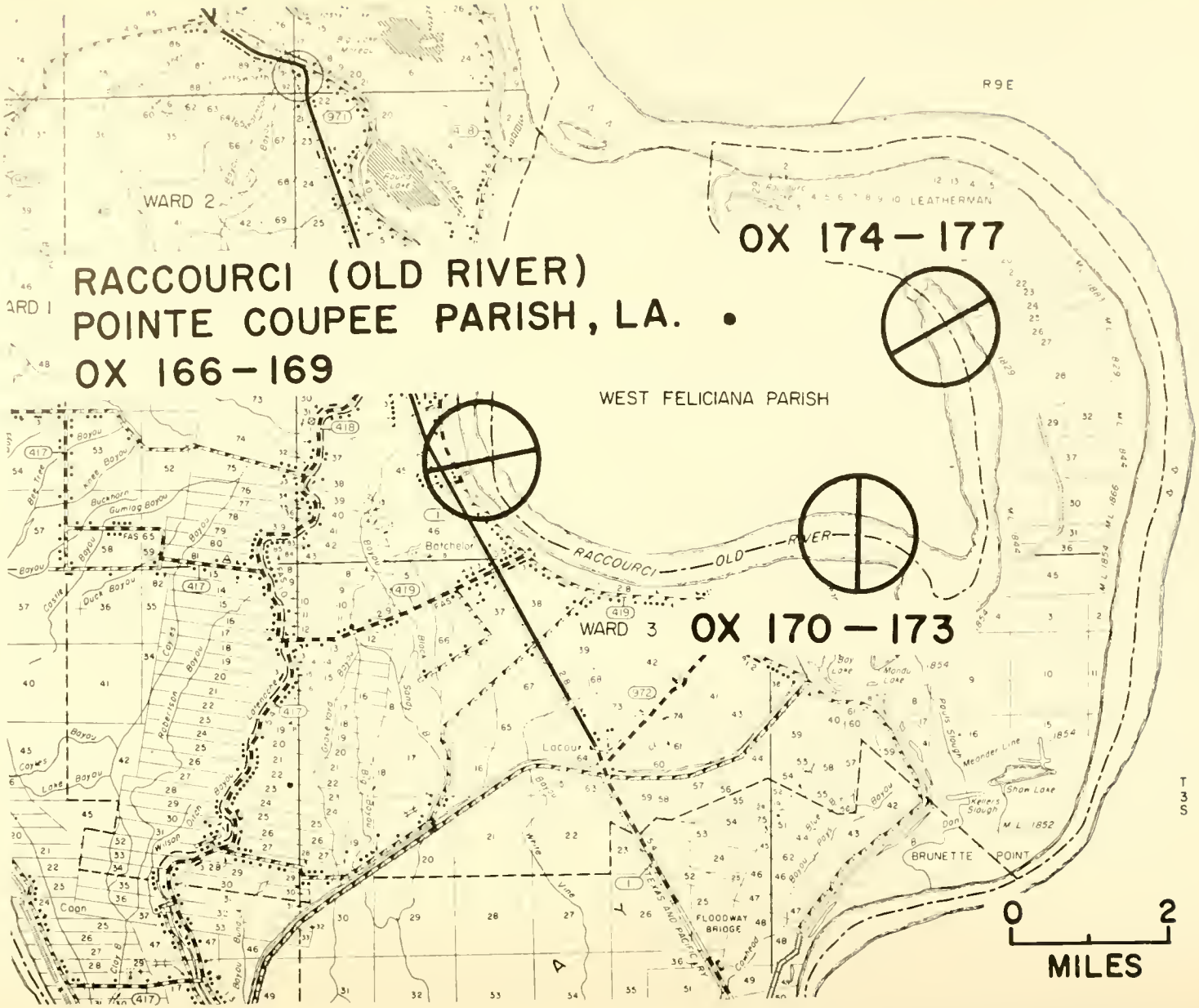

WARD 6
WARD 10
ALMA PLANTATION
LAKELAND
POINTE COUPEE PARISH, LA.
OX 149-150
BELMONT PLANTATION
MARINGOUIN
POINTE COUPEE PARISH, LA.
OX 151-154
BAYOU FOROOCHE OIL FIELD
Oscar
Lakeland PO
Chenal
Rougon PO
Blanks PO
Livonia Station
Valverde
MISSOURI PACIFIC RR
T B P RY
To Baton Rouge
WEST BATON ROUGE PARISH
MARINGOUIN POP 1,168
To IBERVILLE
30°30'
91° 25'
T 6 S
T 7 S
R11E
R10E
0 2
MILES
POINTE COUPE

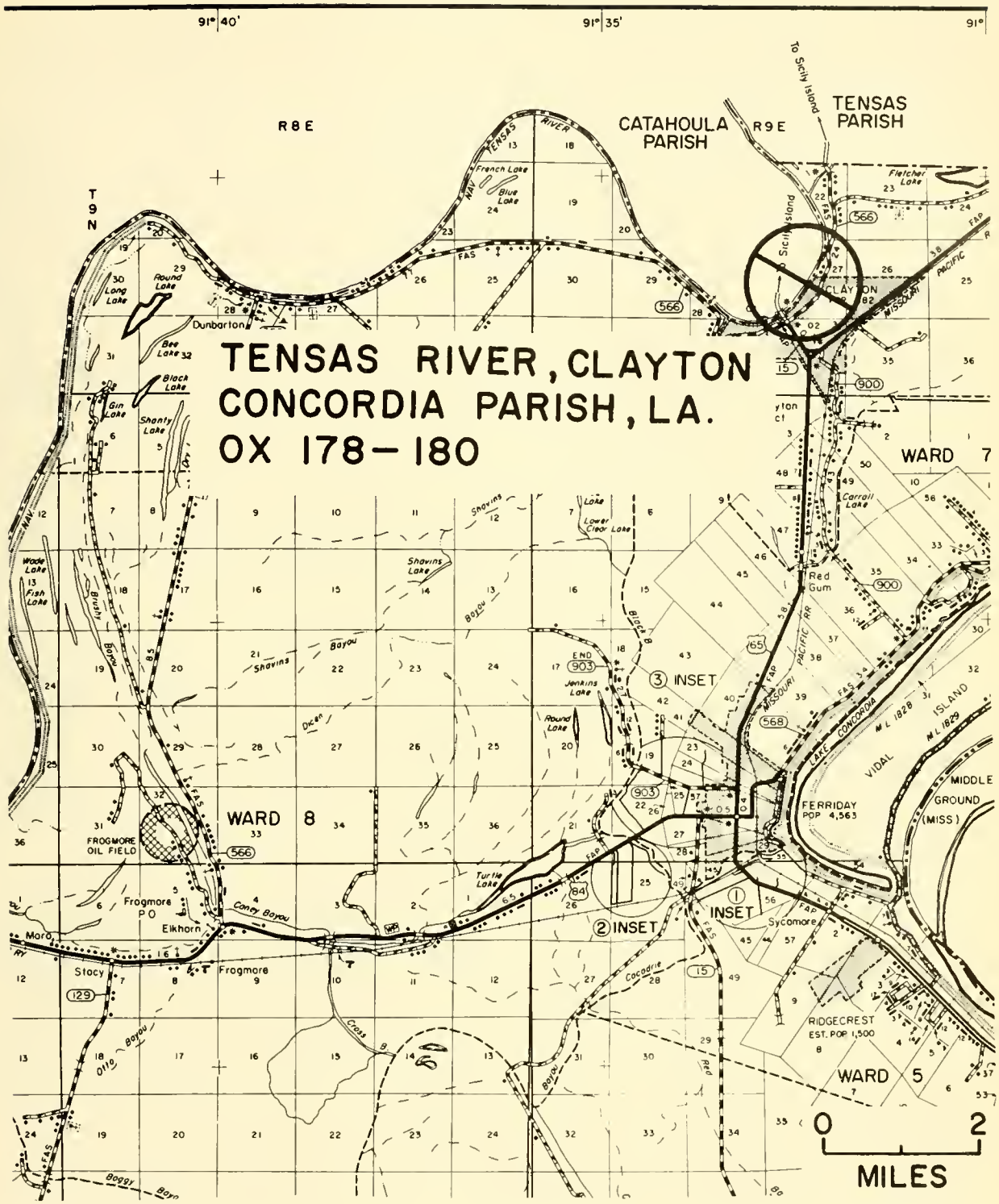

BRUSHY LAKE
TENSAS PARISH, LA.
OX 155-156
WARD 1
WARD 3
SARANAC OIL AND GAS FIELD
LAKE BRUIN OIL FIELD
ST. JOSEPH OIL FIELD
LOCUST RIDGE OIL FIELD
CHAMBLEE OIL FIELD
RODNEY ISLAND OIL FIELD
LAKE ST JOSEPH
LAKE BRUIN
Saranac
Crimea
Mayflower
Ashland
Delta Bridge
Aubrey
Wilsonia
Maryland
Avondale
Osceola
Denhart
Locust Ridge
Helena
ST. JOSEPH
POP 1,653
INSET 1
MISSISSIPPI RIVER
CLAIBORNE COUNTY
JEFFERSON COUNTY
R12E
T 10 N
0 2 MILES

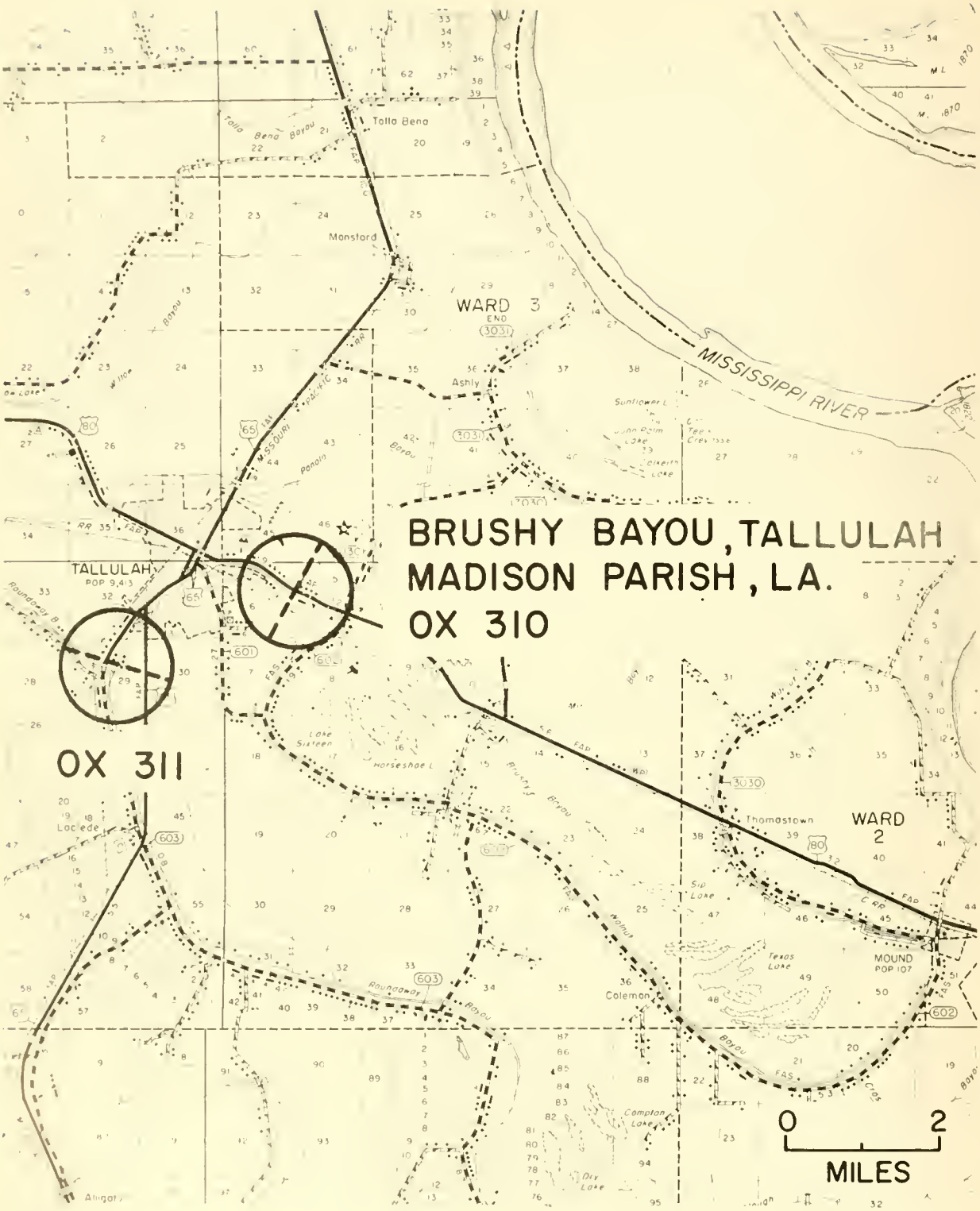

LITTLE RIVER
CATAHOULA PARISH, LA.
OX 157-159
WARD 6
WARD 7
TENSAS POINT
JONESVILLE
POP 2,347
CARR LAKE OIL FIELD
ROSS BAYOU OIL FIELD
WILLOW LAKE OIL FIELD
LARTO LAKE OIL FIELD
Parhams PO
Glade
Serena
Securify
To Ferriday
To U S 84
0 2
MILES
T 7 N
T 6 N
31°35'
31°30'

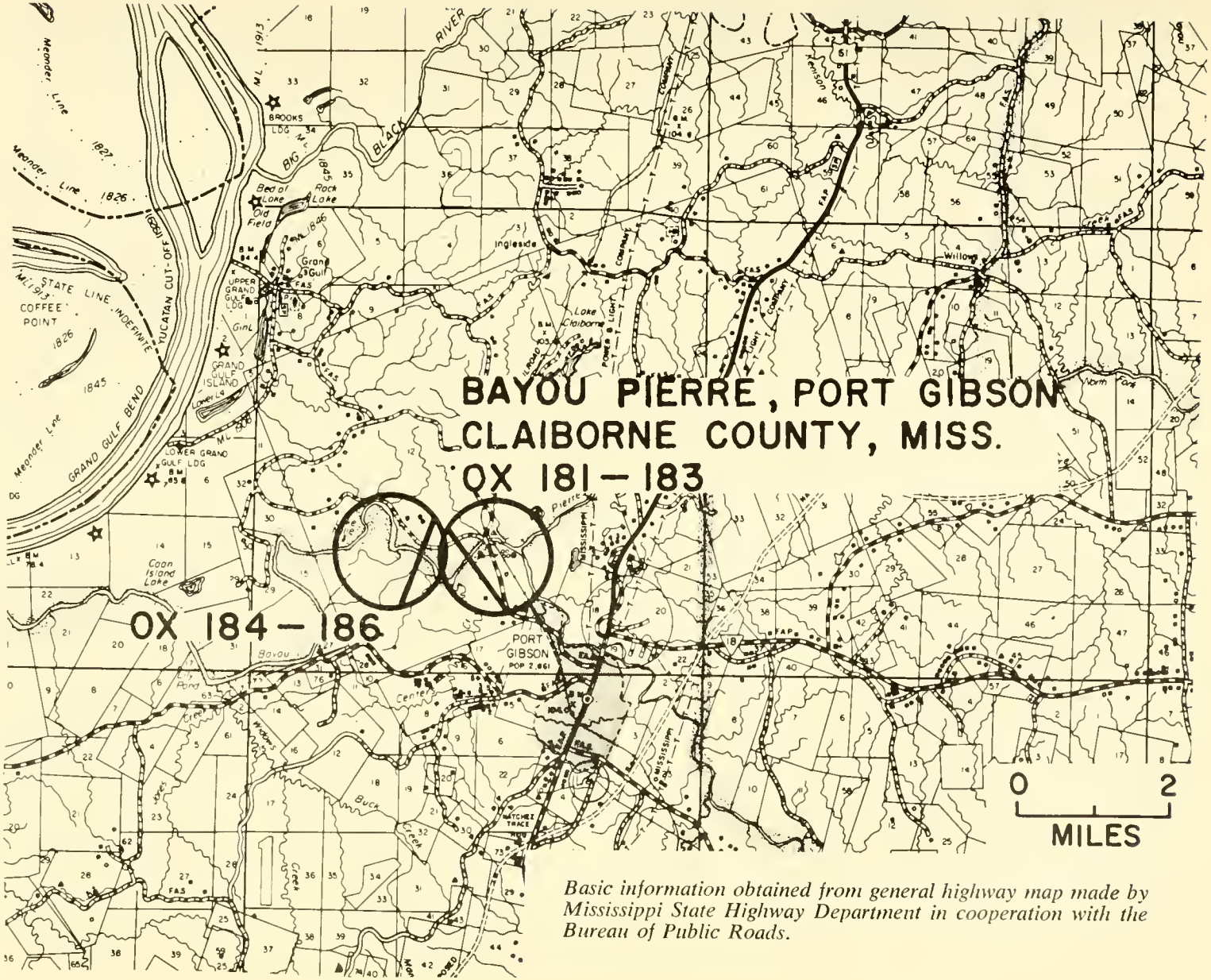

CALDWELL PARISH
FRANKLIN PARISH
R 6 E
OUACHITA RIVER
CATAHOULA PARISH, LA.
OX 160 — 162
R 5 E
WARD 3
ENTERPRISE OIL FIELD
PRICHARD OIL FIELD
Rosefield
Enterprise
Sherwood
Spring Ridge
AIMWELL LOOKOUT TOWER
Aimwell
Prichard
HARRISONBURG
POP 594
0 2
MILES


BOEUF RIVER
FRANKLIN PARISH, LA.
OX 163–165
T 13 N
R 5 E
32°05'
To Columbia
WARD 8
Upper Eagle C.
Boeuf River
Jct. Bayou
Mason
Fort Necessity
T 12 N
32°00'
91° 55'
WARD 9
Grayson Bayou
TURKEY CREEK GAME AND FISH PRESERVE
CALDWELL PARISH
CATAHOULA PARISH
Extension
Bayou
R 6 E
T 11 N
31°55'
91° 50'
0
2
MILES

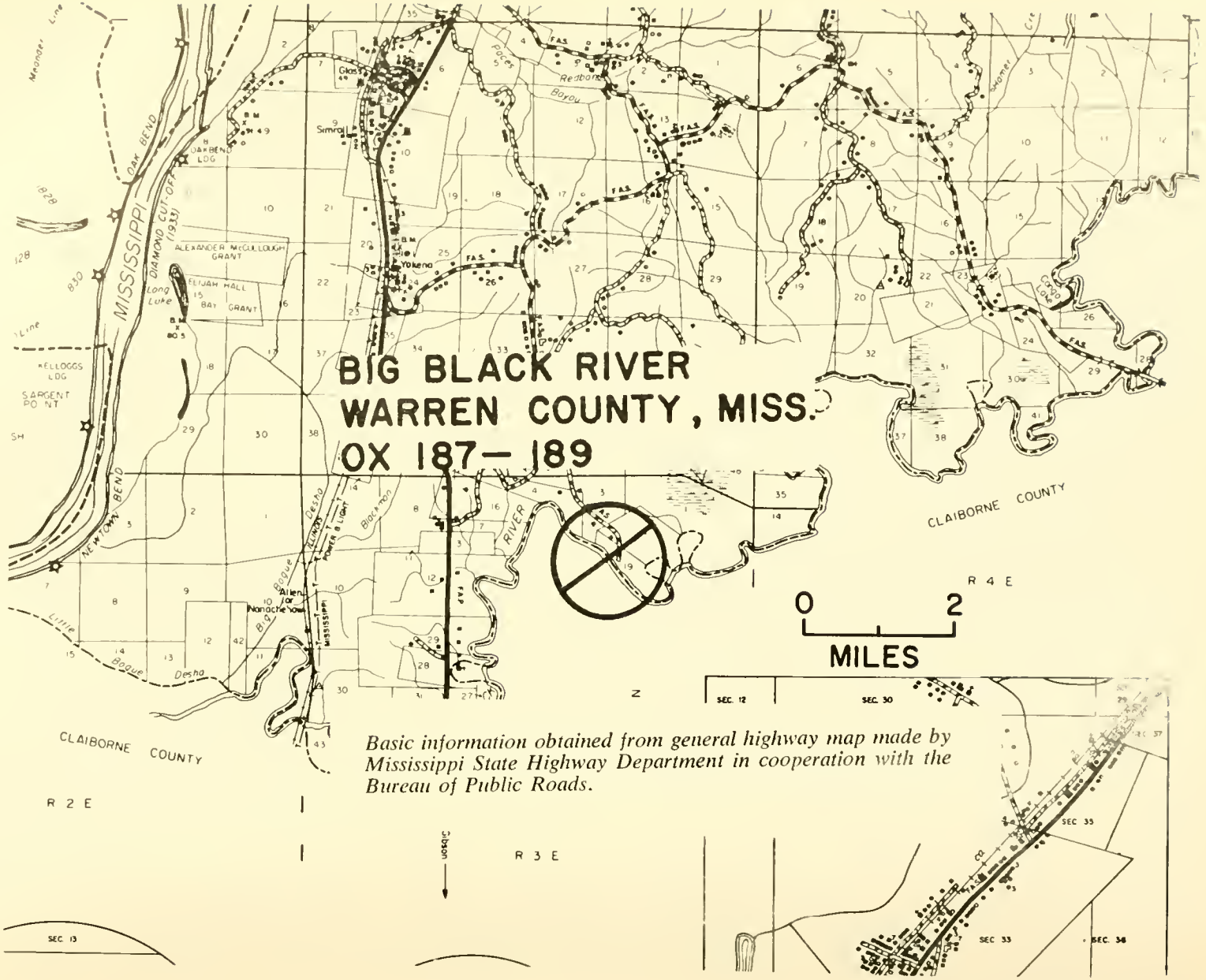

RACCOURCI (OLD RIVER)
POINTE COUPEE PARISH, LA.
OX 166-169
OX 174-177
OX 170-173
WEST FELICIANA PARISH
WARD 2
WARD 3
R9E
T2S
T3S
RACCOURCI OLD RIVER
BRUNETTE POINT
FLOODWAY BRIDGE
0 2
MILES


TENSAS RIVER, CLAYTON
CONCORDIA PARISH, LA.
OX 178–180
91° 40'
91° 35'
91°
R8E
R9E
CATAHOULA PARISH
TENSAS PARISH
T 9 N
To Sicily Island
Dunbarton
Clayton
Ferriday
Pop 4,563
Ridgecrest
Est. Pop 1,500
Frogmore
Oil Field
Frogmore P.O.
Elkhorn
Stacy
Moro
Sycamore
Vidal
Middle Ground (Miss.)
Ward 5
Ward 7
Ward 8
Inset 1
Inset 2
Inset 3
0
2
Miles


BRUSHY BAYOU, TALLULAH
MADISON PARISH, LA.
OX 310
OX 311
MISSISSIPPI RIVER
TALLULAH
POP 9,413
Monsford
Ashly
WARD 3
END
WARD 2
Thomastown
Coleman
MOUND
POP 107
Lake Sixteen
Horseshoe L.
Texas Lake
Compton Lake
Dry Lake
Roundaway Bayou
Bruchys Bayou
Walnut Bayou
Tolla Bena Bayou
Panola
Sid Lake
0
2
MILES



Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



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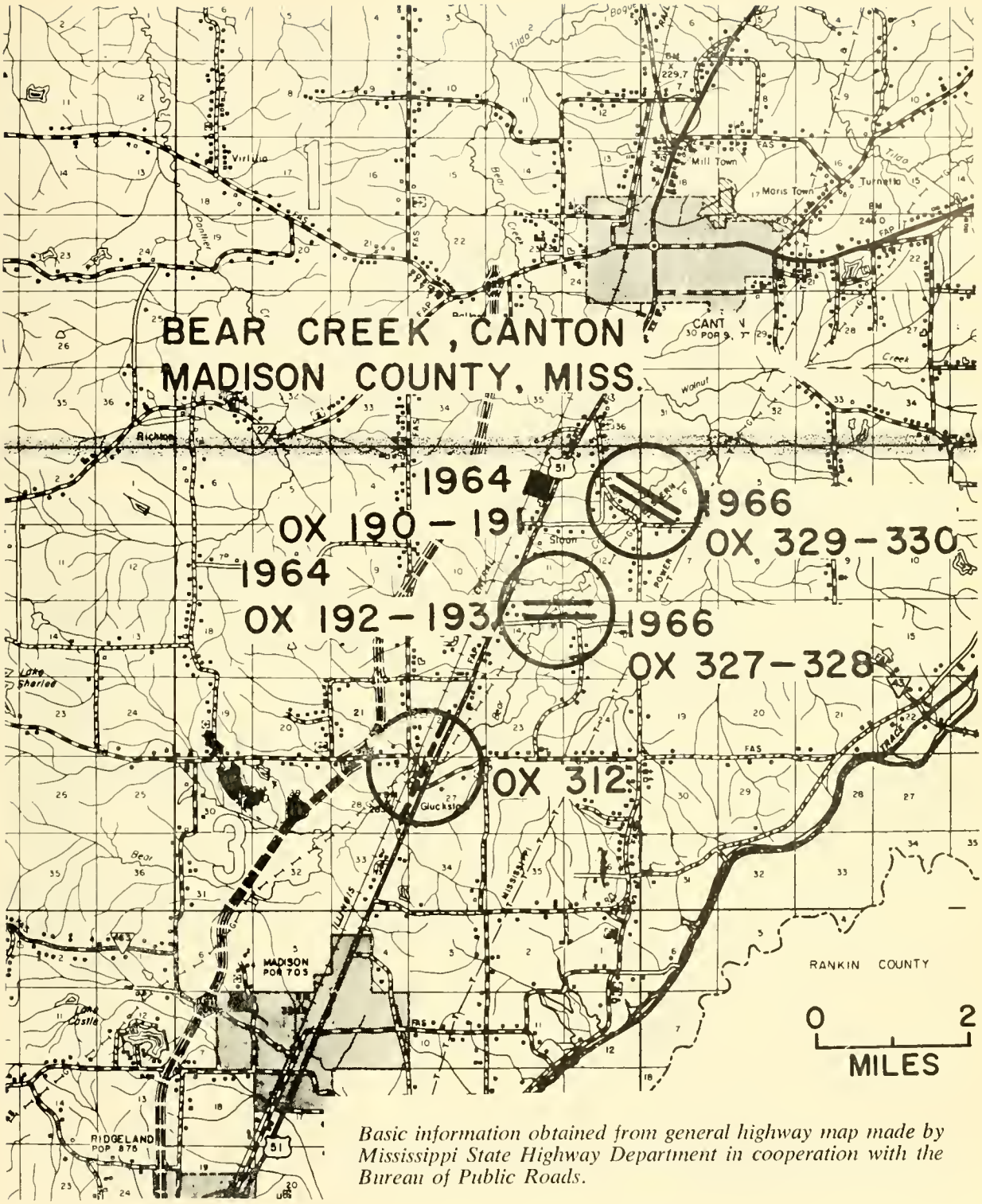
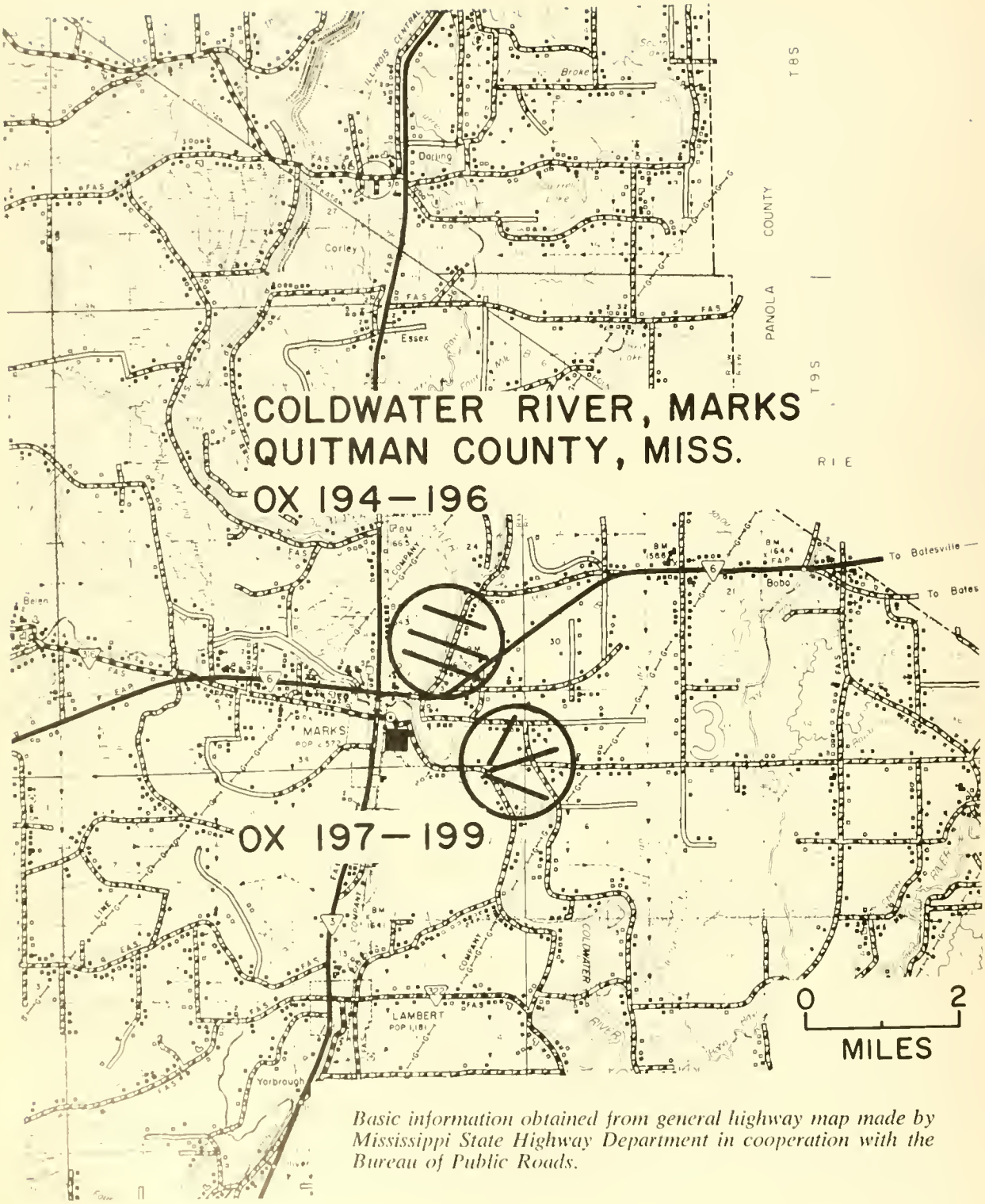


Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



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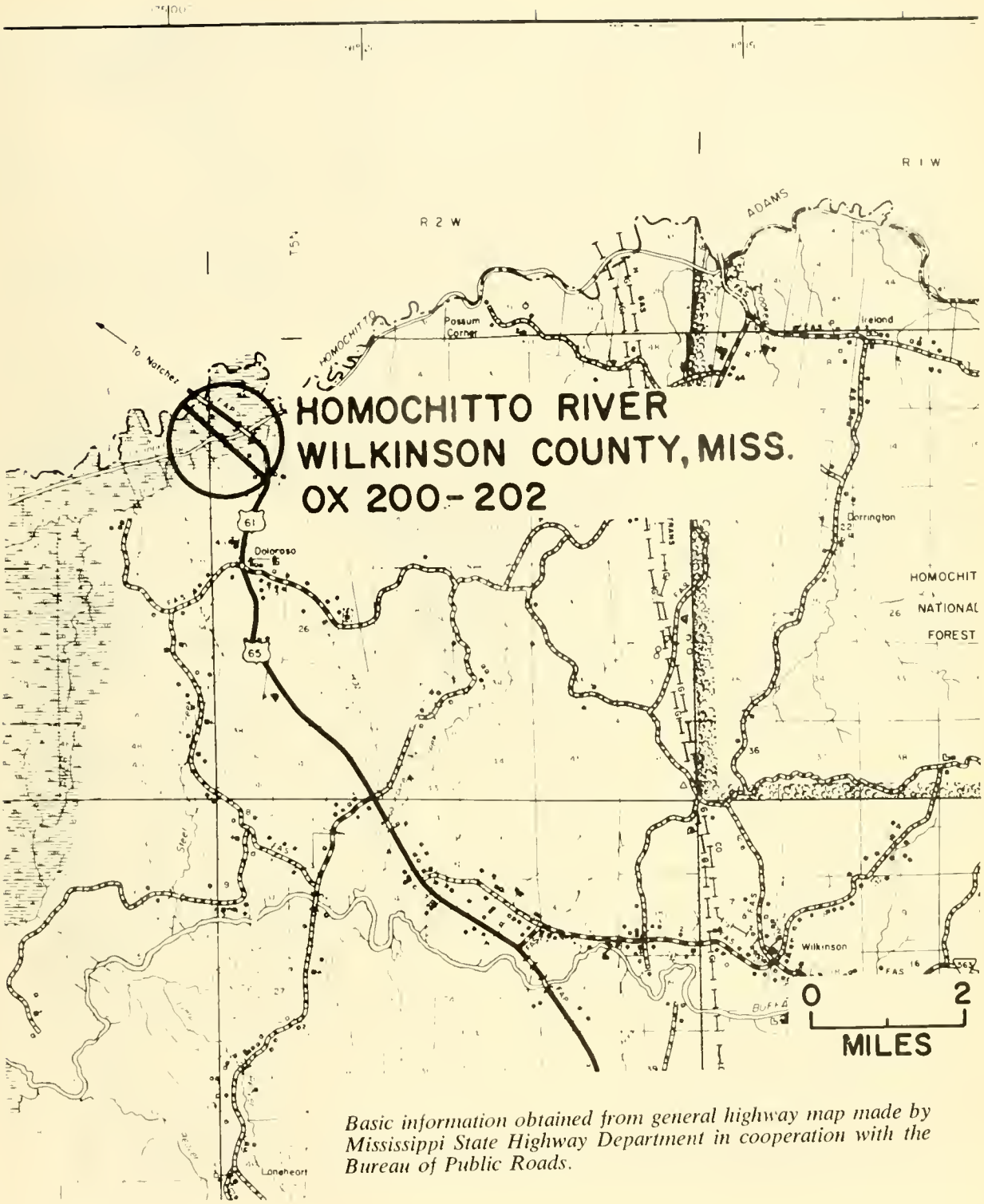
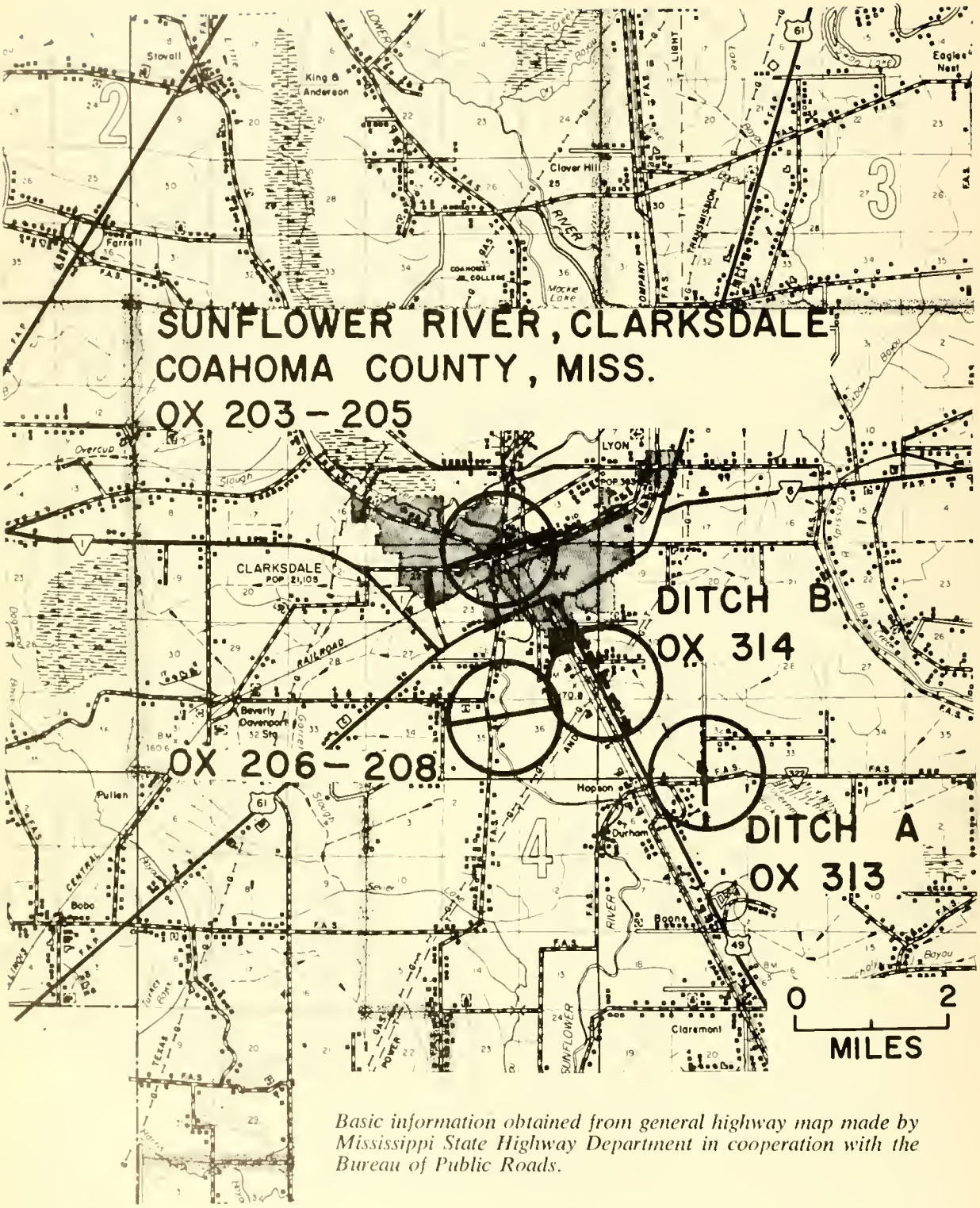
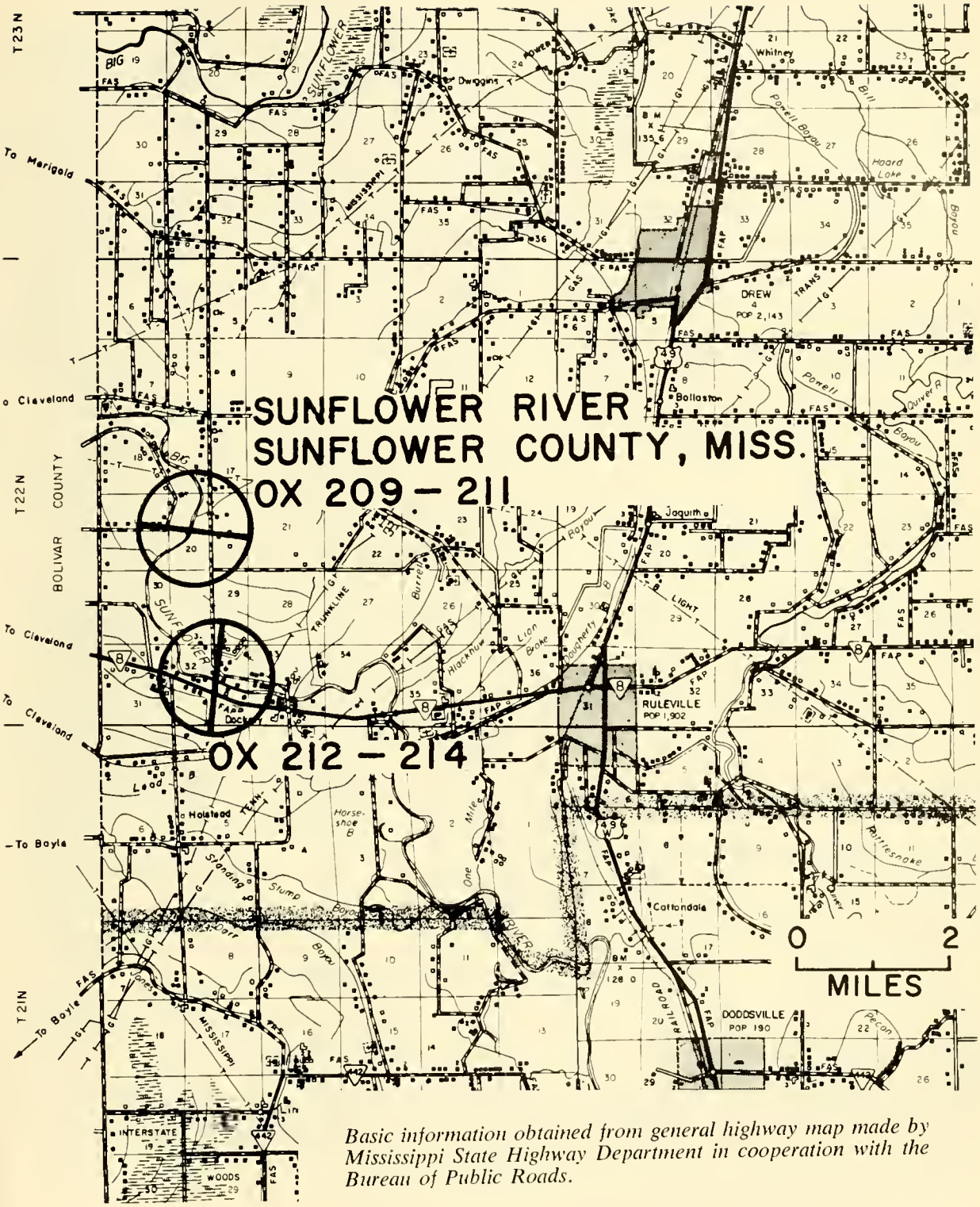


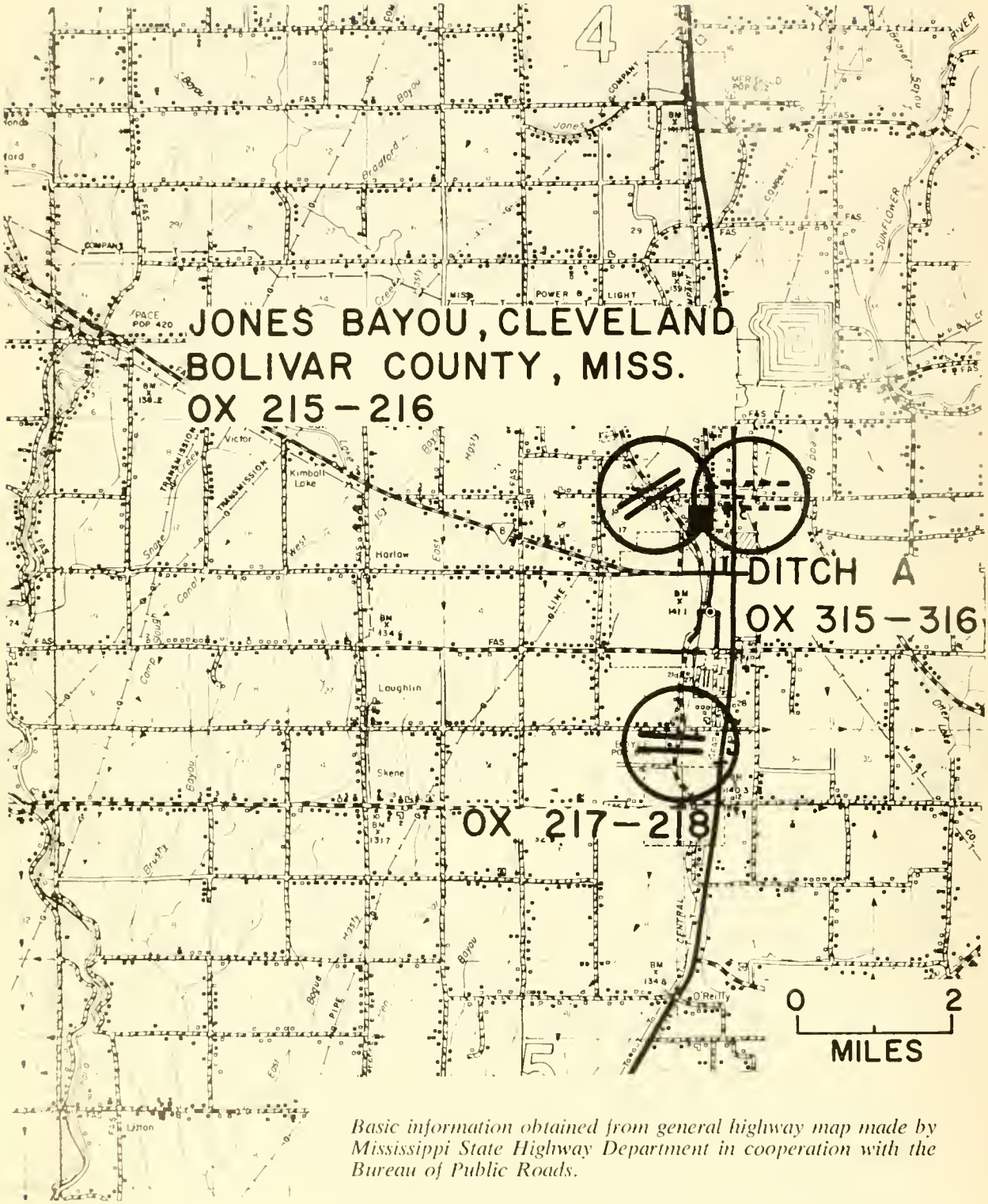
Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



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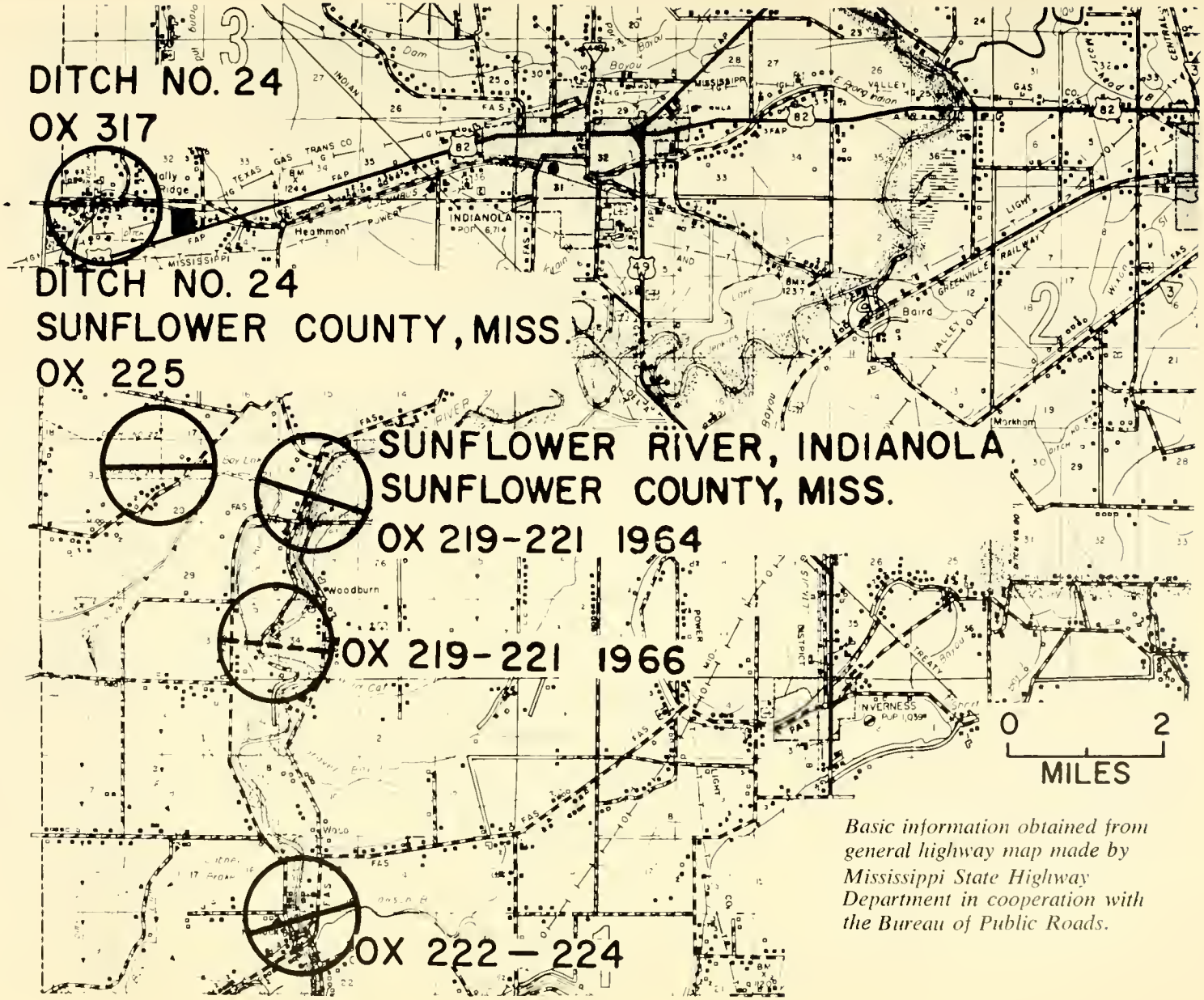

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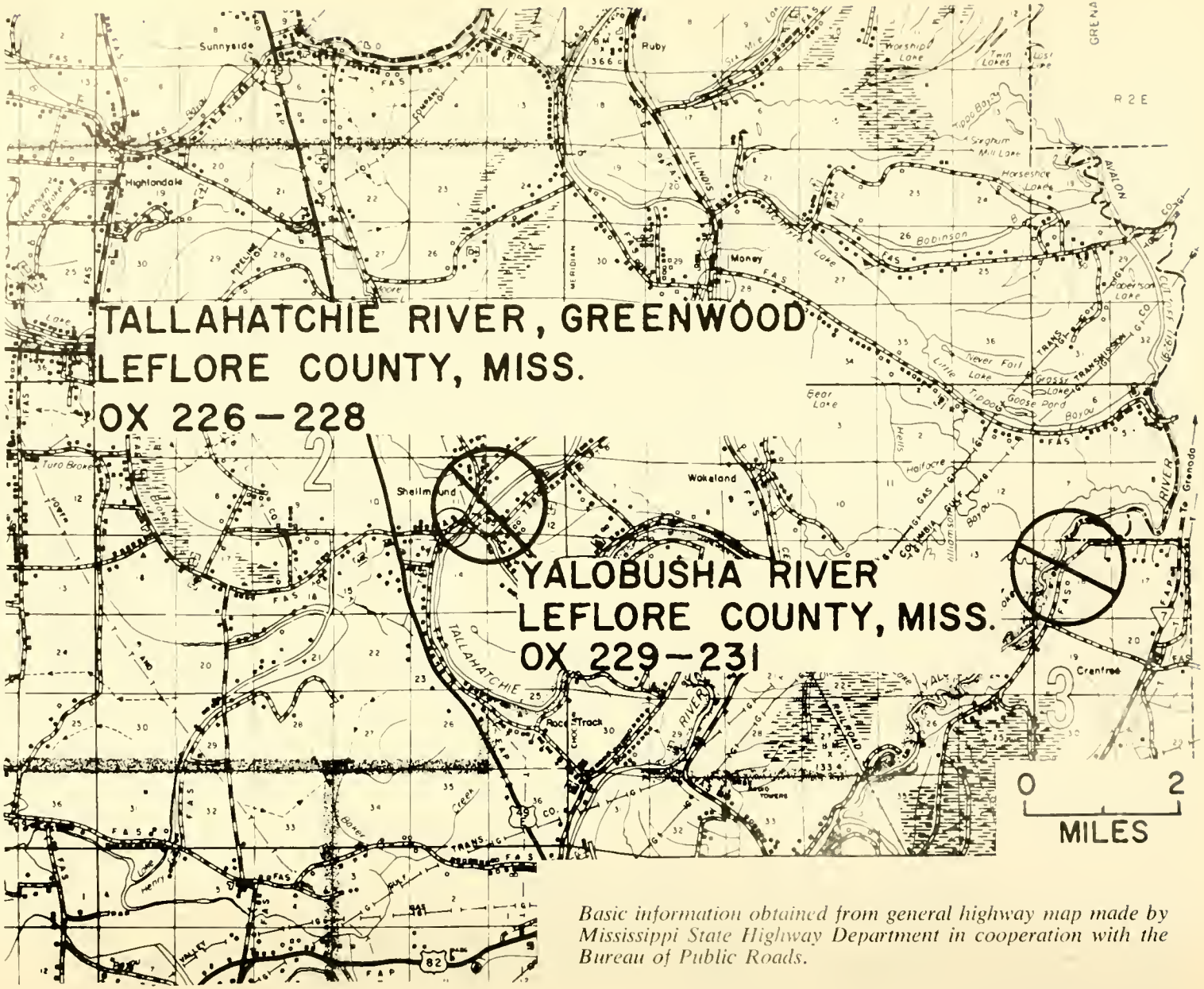

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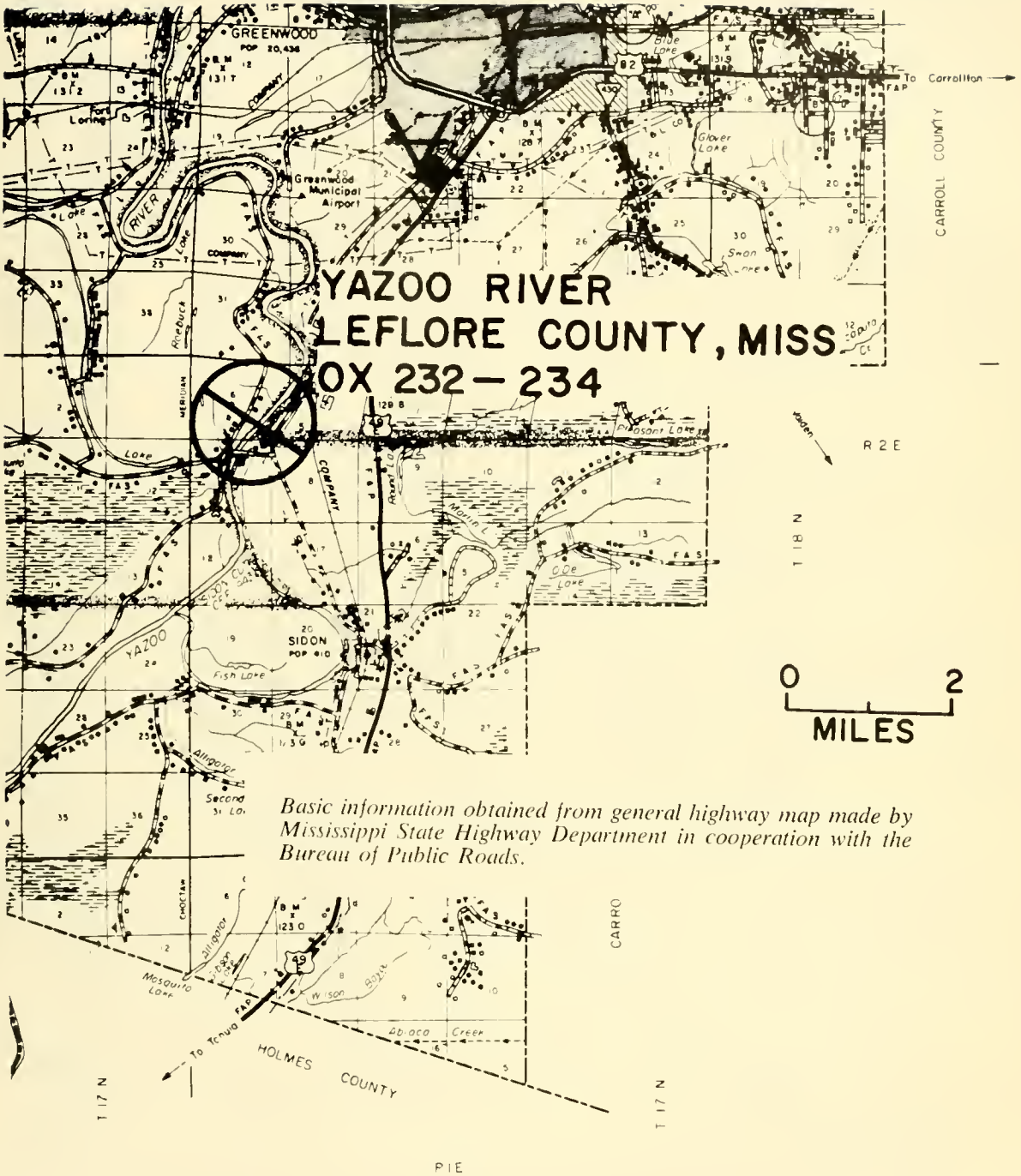
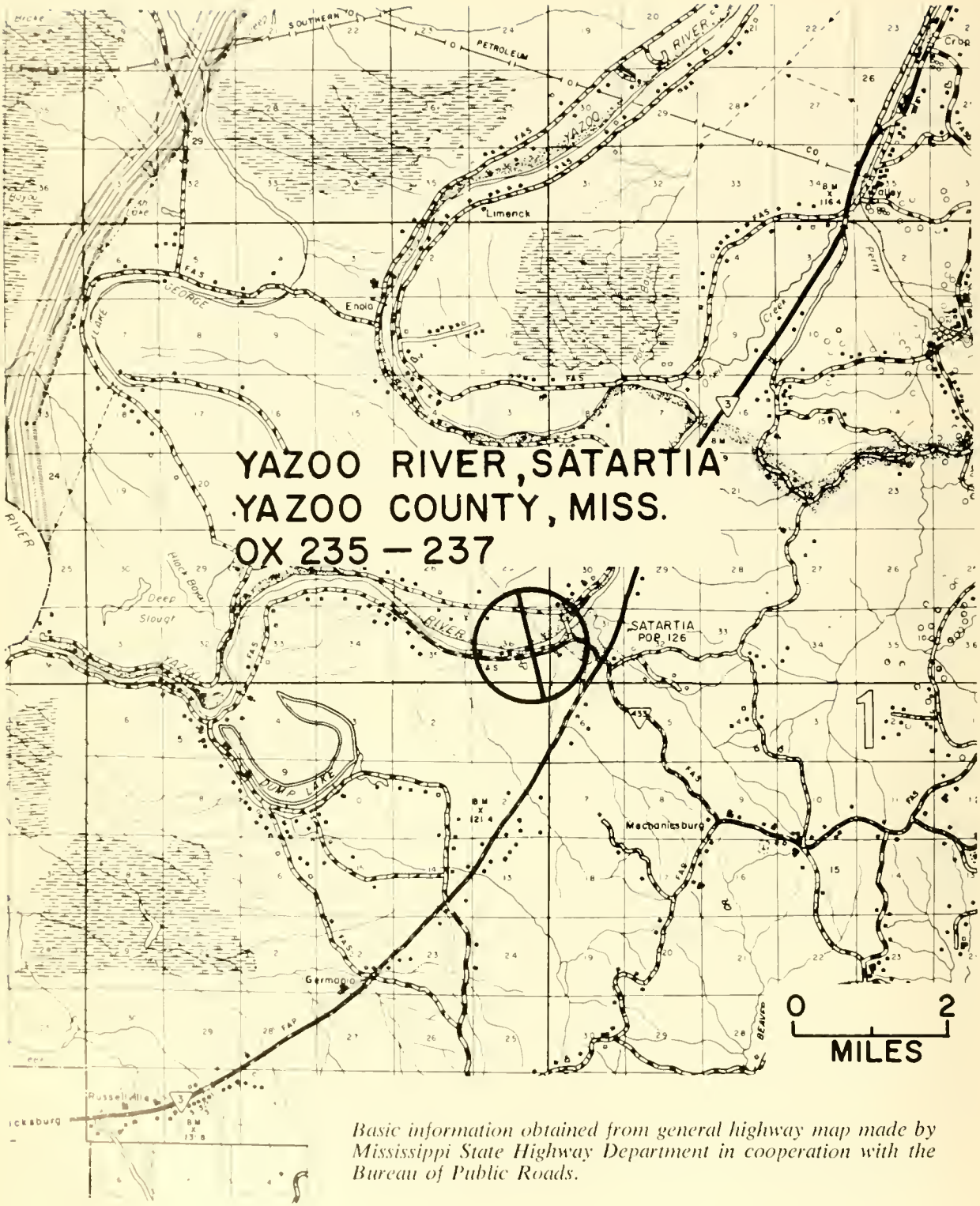

YAZOO RIVER
LEFLORE COUNTY, MISS.
OX 232–234
GREENWOOD
POP 20,456
To Carrollton
CARROLL COUNTY
Greenwood Municipal Airport
Glover Lake
Blue Lake
Pleasant Lake
Morin L.
Coe Lake
Fish Lake
SIDON
POP 610
YAZOO
RIVER
Lake
COMPANY
R 2 E
T 18 N
0
2
MILES
Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.
Alligator
Second
Mosquito Lake
To Tchula
HOLMES COUNTY
CARRO
Abiaca Creek
T 17 N
T 17 N
PIE



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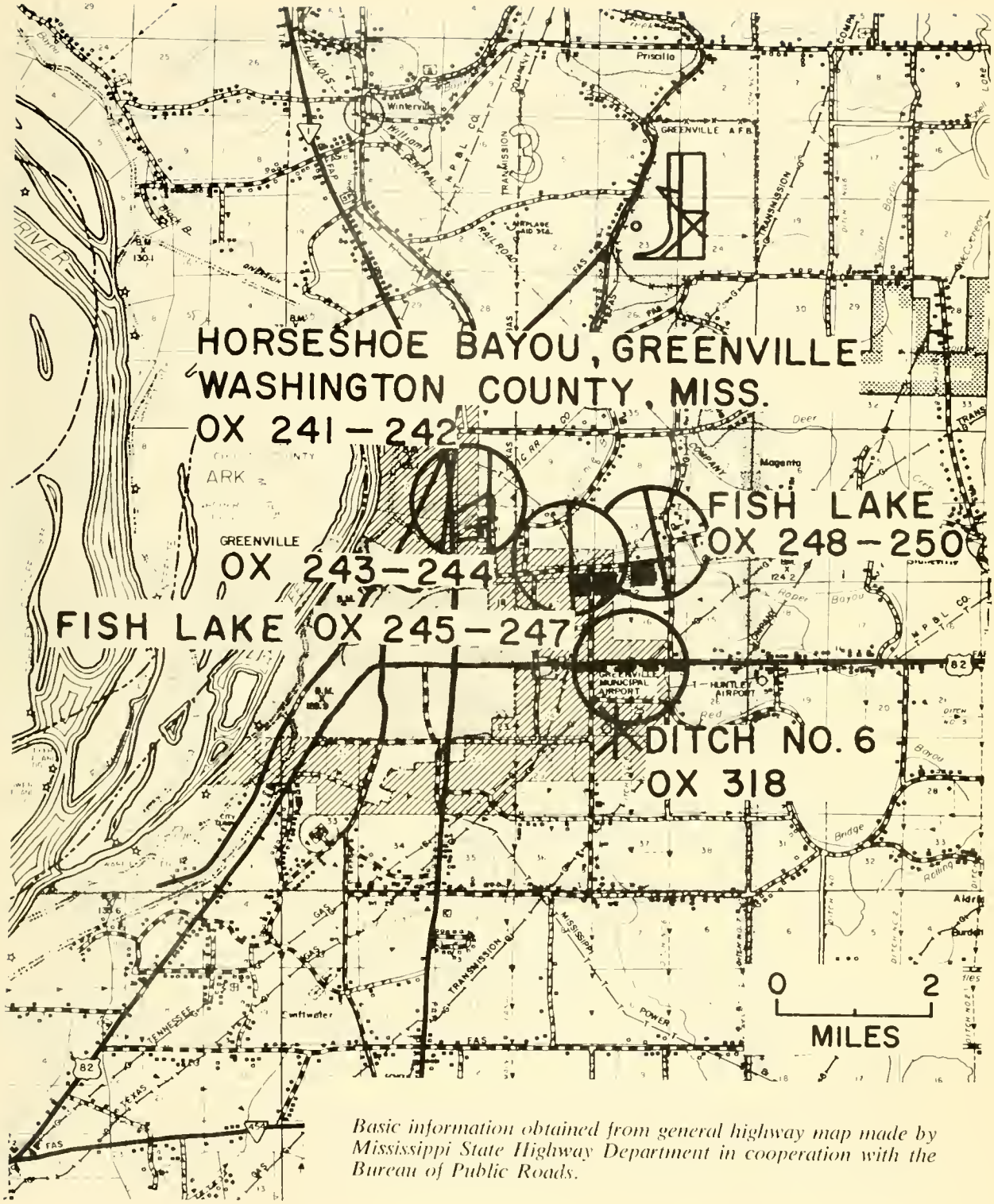
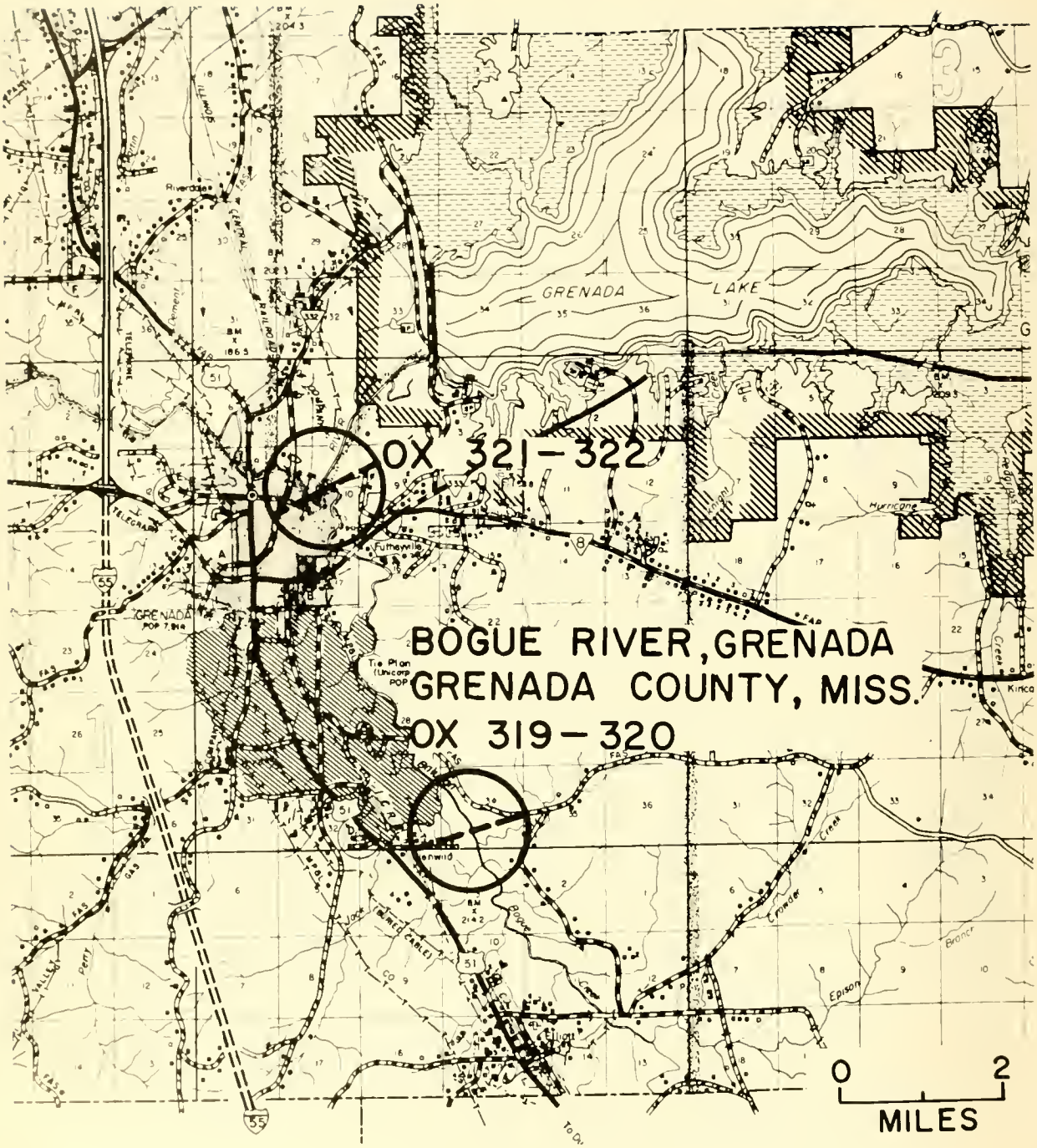


Basic information obtained from general highway map made by Mississippi State Highway Department in cooperation with the Bureau of Public Roads.



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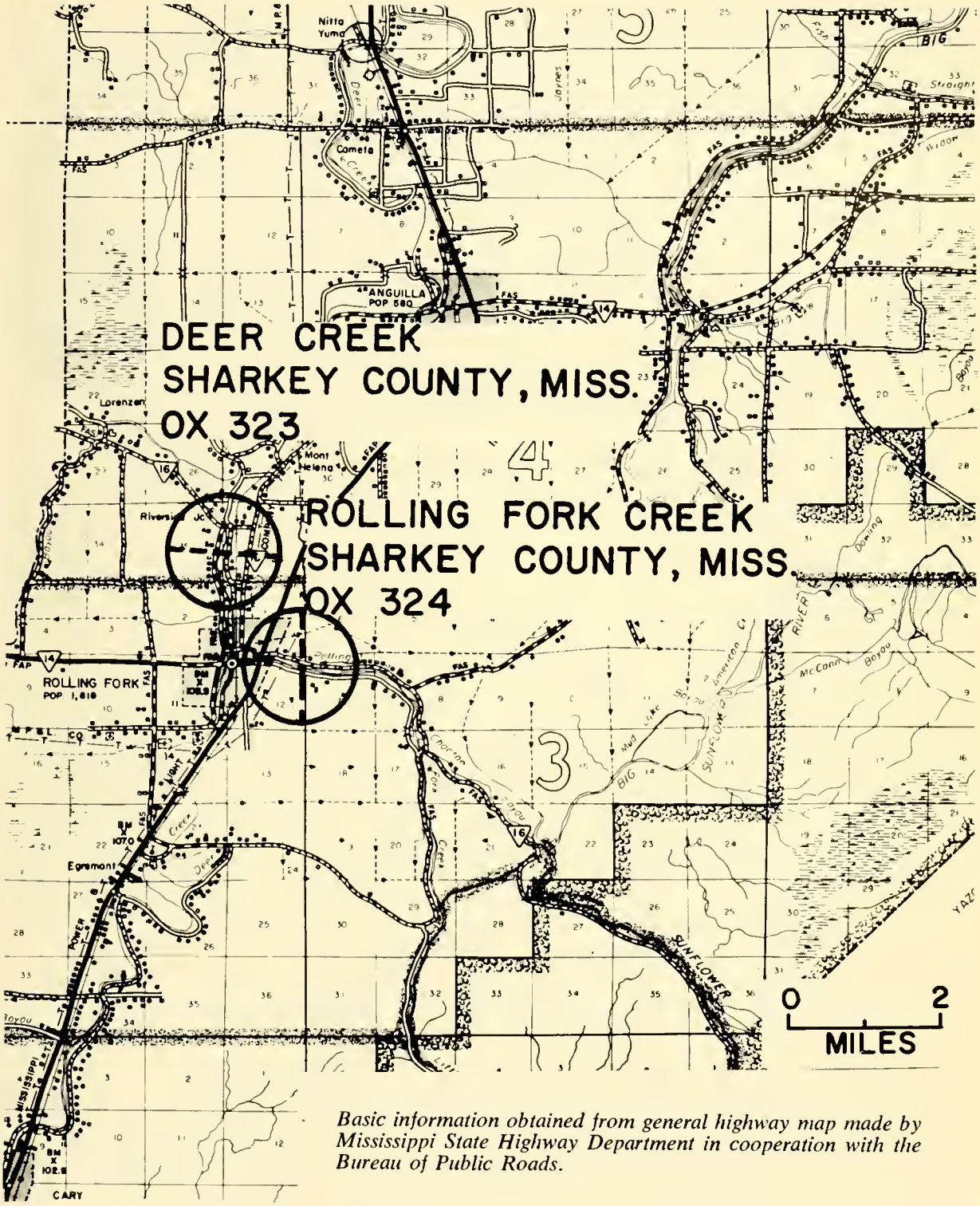

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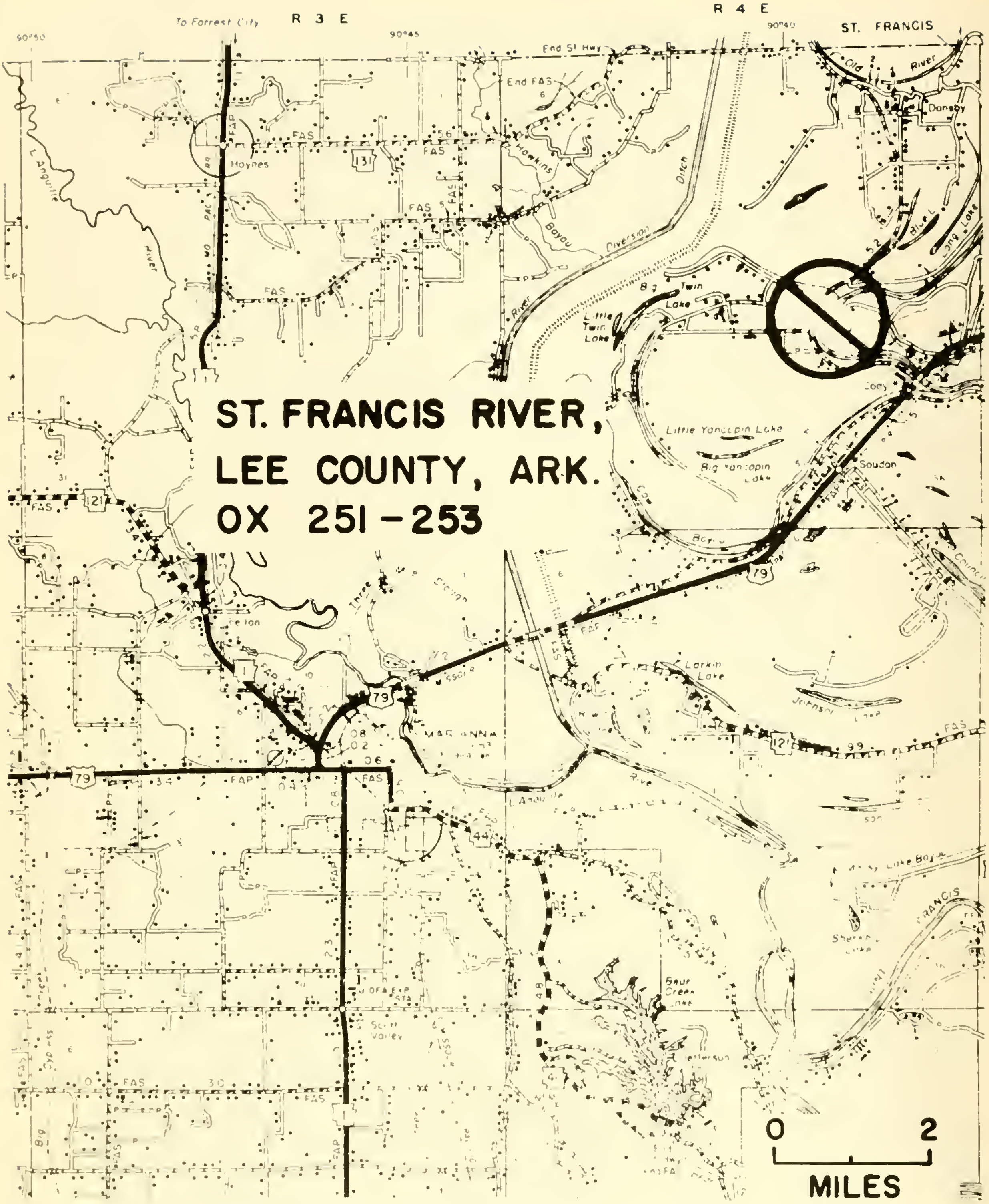
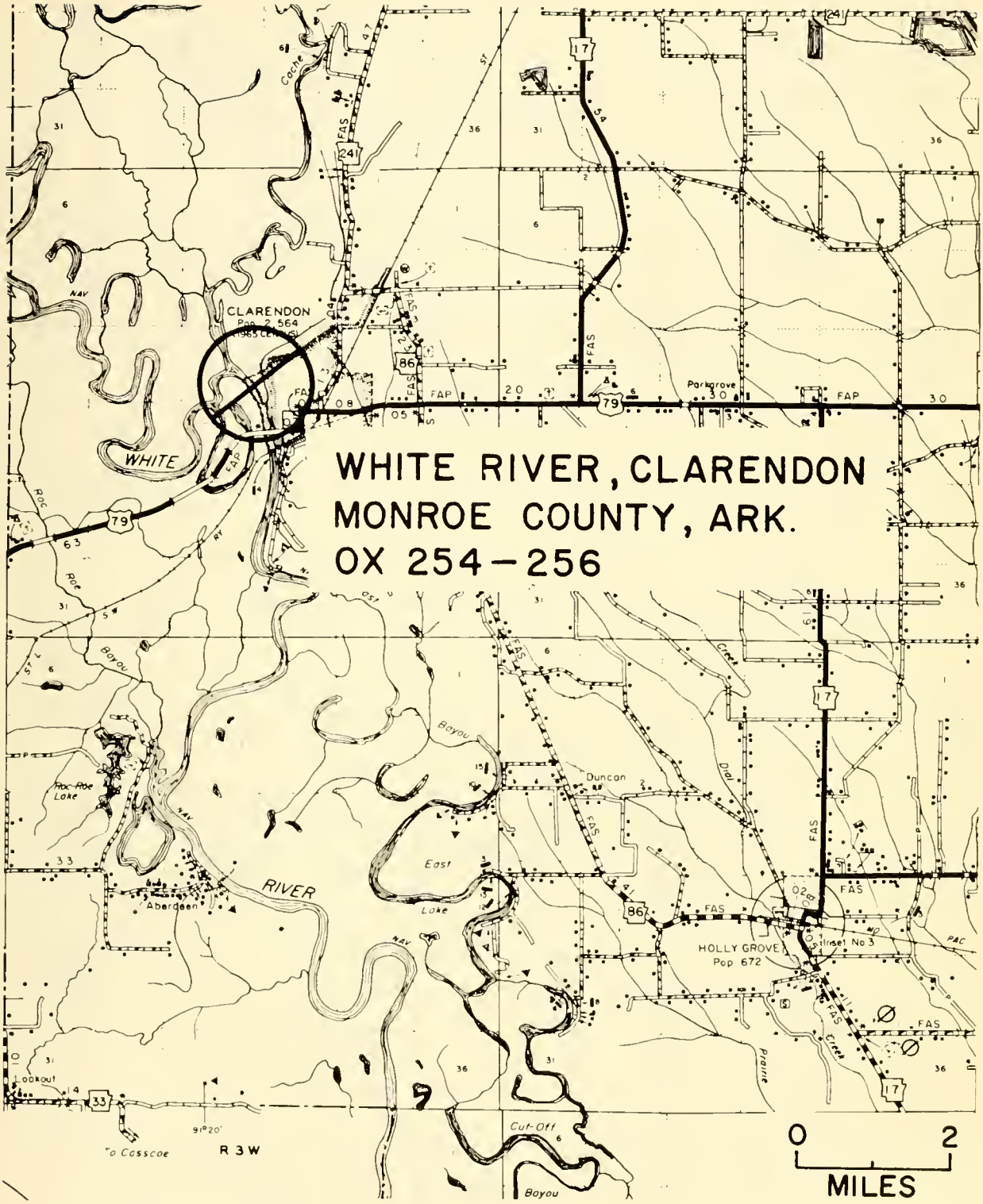
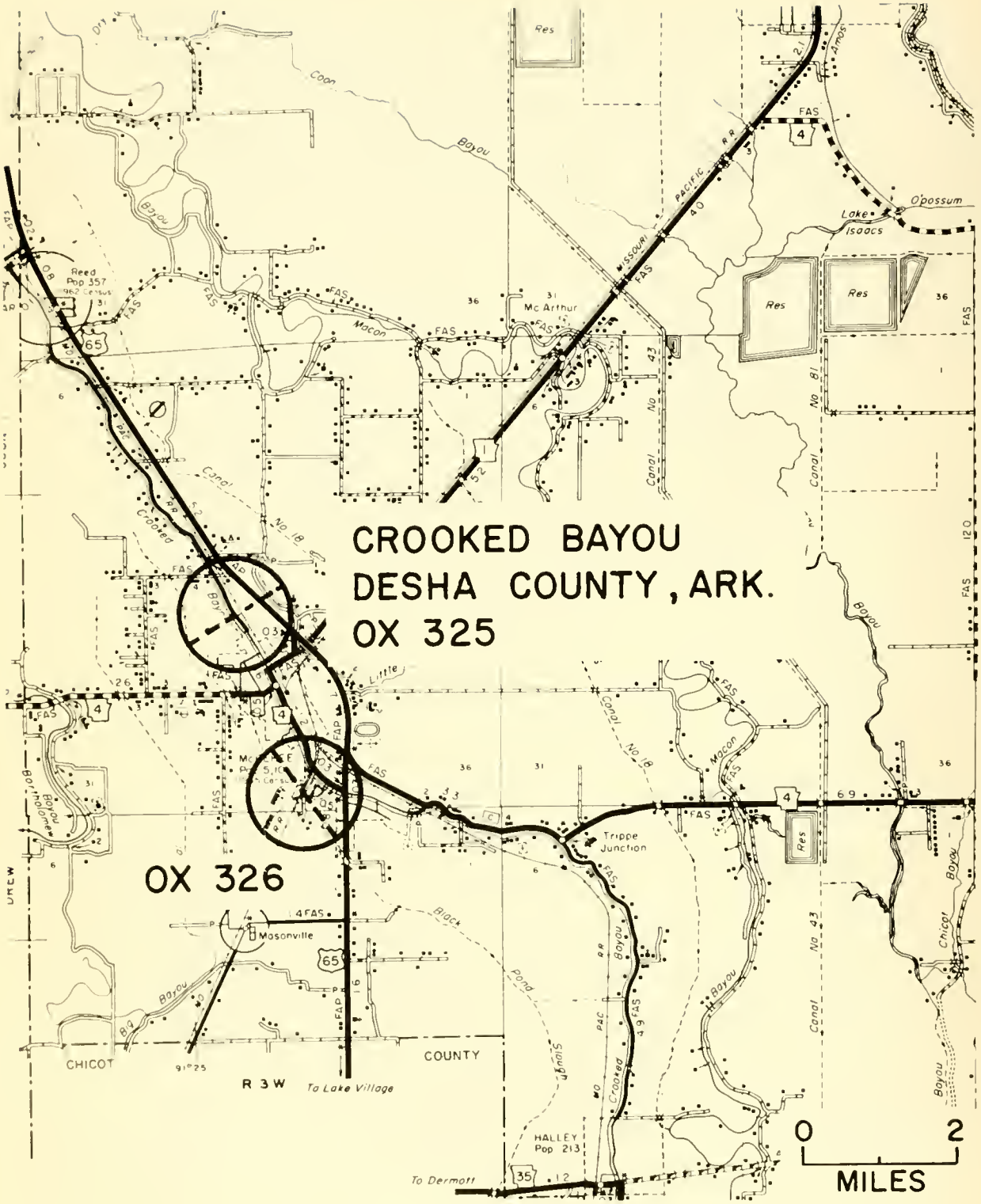

R 3 E
R 4 E
To Forrest City
ST. FRANCIS
End St Hwy
Haynes
Old River
Hawkins
Bayou
Diversion
Ditch
Twin Lake
Little Twin Lake
Soudan
Larkin Lake
ST. FRANCIS RIVER,
LEE COUNTY, ARK.
OX 251-253
0 2
MILES


WHITE RIVER, CLARENDON
MONROE COUNTY, ARK.
OX 254-256
CLARENDON
Pop 2,564
WHITE
RIVER
Duncan
East
Lake
Bayou
Aberdeen
HOLLY GROVE
Pop 672
Parkgrove
Cut-Off
Bayou
Prairie
Creek
Roc-Roe
Lake
Lookout
To Casscoe
R 3W
0
2
MILES


CROOKED BAYOU
DESHA COUNTY, ARK.
OX 325
OX 326
Reed
Pop 357
1962 Census
McArthur
Trippe Junction
Masonville
CHICOT
COUNTY
R 3 W
To Lake Village
HALLEY
Pop 213
To Dermott
Lake Isaacs
O'possum
Res
Macon
Canal No. 18
Canal No. 43
Canal No. 81
Missouri Pacific R.R.
Crooked Bayou
Black Pond
Johnson Bayou
Chicot Bayou
Bartholomew Bayou
Bayou B-4
FAS
FAP
0
2
MILES

APPENDIX

Chemical Names of Compounds Mentioned in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1, 4-*endo-exo*-5,8-dimethanonaphthalene
BHC	1,2,3,4,5,6-hexachlorocyclohexane, mixer isomers
CHLORDANE	1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane
DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
DDT (including its isomers and dehydrochlorination products)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in a ratio of about 3 or 4 to 1)
DIELDRIN	Not less than 85% of 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-dimethano=naphthalene
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-dimethanonaphthalene
ENDRIN KETO	Structure uncertain
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
ISODRIN	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo, endo*-5,8-dimethanonaphthalene
LINDANE	1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer
METHOXYCHLOR	1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane
STROBANE®	terpene polychlorinates (65% chlorine)
TDE (DDD) (including its isomers and dehydrochlorination products)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical TDE contains some *o,p'*isomer also
TOXAPHENE	chlorinated camphene containing 67% to 69% chlorine
X	hexachloronorbornadiene
Y	heptachloronorbornene

Information for Contributors

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and interlaboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

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The *Pesticides Monitoring Journal* is published quarterly under the auspices of the Federal Committee on Pest Control and its Subcommittee on Pesticide Monitoring as a source of information on pesticide levels relative to man and his environment.

The parent committee is composed of representatives of the U. S. Departments of Agriculture, Defense, the Interior, and Health, Education, and Welfare.

The Pesticide Monitoring Subcommittee consists of representatives of the Agricultural Research Service, Consumer and Marketing Service, Federal Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Federal Water Pollution Control Administration, Food and Drug Administration, Public Health Service, and the Tennessee Valley Authority.

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Address correspondence to:
Mrs. Sylvia P. O'Rear
Editorial Manager

PESTICIDES MONITORING JOURNAL
Pesticides Program
Food and Drug Administration
1600 Clifton Rd., N.E.
Atlanta, Georgia 30333

CONTENTS

Volume 3 September 1969 Number 2

EDITORIAL

In recent years public and scientific attention has focused mainly on DDT and the other chlorinated hydrocarbon insecticides as causes of environmental contamination. The singling out of this group of pesticides has resulted in the present controversy over whether or not the use of persistent insecticides should be curtailed or discontinued. There has been an actual decrease in the use of such chemicals, accompanied by an increase in the number of projects designed to develop biological controls and nonpersistent insecticides.

The interest in possible hazards from persistent insecticides has no counterpart where persistent herbicides are concerned. Herbicides that persist for more than one crop season may inhibit growth of subsequent crops and reduce crop yields.

One of the threats to the environment from persistent herbicides is the possibility of their leaching into the soil where the rate of degradation would be much slower. If herbicides reach ground water supplies used for irrigation, crop damage may result.

In the past 5 years, herbicide usage has more than doubled. At the present time nearly 300 million pounds are used annually. In 1967, herbicide sales were nearly 55% of the value of all sales of synthetic organic pesticides, and the value of herbicide sales exceeded the value of insecticide sales for the first time. More acres of land in the conterminous United States are treated with herbicides than are treated with all other pesticides combined. With the increased demand for food and fiber and a probable decrease in hand labor, it is likely that the use of herbicides will continue to grow.

As new herbicides are developed their effect on the environment should be established. The potential hazards from persistent herbicides have been recognized by the U. S. Department of Agriculture, and its soil monitoring program has been expanded to include the detection of more herbicides. Increased monitoring of herbicides to determine their distribution and concentration in the environment is a step toward preventing problems similar to those encountered with persistent insecticides. Those responsible for pesticide monitoring programs should keep abreast of pesticide usage and adjust their programs accordingly.

Paul F. Sand
Member, Editorial Advisory Board

RESIDUES IN FOOD AND FEED

Cooperative Study on Uptake of DDT, Dieldrin, and Endrin by Peanuts, Soybeans, Tobacco, Turnip Greens, and Turnip Roots

SECTION A: FLORIDA
SECTION B: MISSISSIPPI
SECTION C: NORTH CAROLINA
SECTION D: SOUTH CAROLINA
SECTION E: TEXAS
SECTION F: VIRGINIA

GENERAL INTRODUCTION

Crops may acquire excessive pesticide residues through direct or indirect contamination. Excessive pesticide residues can usually be avoided by observing the proper number of applications and the recommended dosage and time interval between the last application and harvest. However, indirect or inadvertent illegal residues may result from absorption and/or translocation of pesticides by plants growing in soils that have been contaminated by repeated applications to previous crops.

Pesticides, particularly the chlorinated hydrocarbons, have been applied rather intensively in the southern region of the United States during the past 2 decades for the control of insects on such crops as cotton and tobacco. It is well known that certain chlorinated insecticides and their toxic metabolites may persist in soils for months and even years following applications, depending on a number of interrelated factors. These factors include the physical properties and chemical reactivity of the toxicant as well as the formulation and mode of application; the soil type, moisture, temperature, and microorganisms; the cover crops and the degree of cultivation.

It is well established that root crops absorb certain chlorinated insecticides from soils. Absorption of these soil residues has been reported in such crops as carrots, beets, sugarbeets, onions, potatoes, radishes, sweet potatoes, turnips, etc. Efforts have also been made to analyze aerial portions of plants growing in contaminated soil in order to determine if any absorption and translocation occurred from the soil into the developing plant. Translocation of a number of chlorinated insecticides from the soil into the aerial portions of lettuce, cabbage, celery, peas, beans, soybeans, cucumbers, tomatoes, peppers, peanuts, rice, wheat, cotton, alfalfa, etc., has been reported. In most instances care was taken to prevent surface contamination of the crop by windblown pesticide residues from the soil. Although some of the pesticide residues were found to be extremely low, there appears to be significant evidence that some limited absorption and translocation can occur in some plants, at least under certain conditions. It should also be noted that improved methodology in recent years has resulted in the detection of positive pesticide residues where previously negative or unrealistic values were obtained. More efficient extraction techniques have recently been reported for the quantitative removal of field-weathered pesticide residues from soil, animal, and plant substrates. In addition, recent improvements in gas chromatographic detection systems have significantly increased the sensitivity and selectivity for detecting pesticide chemicals. These improvements in methodology have contributed substantially to the many recent reports of low levels of chemical residues in certain crops grown in pesticide-contaminated soils. It is not always apparent from the data presented whether the residues in the aerial plant portions are due to direct or indirect contamination.

Obviously, there are many interacting factors which contribute to the "uptake" of pesticides from the soil by plants. Since these factors undoubtedly vary in different plants, soils, climatic conditions, etc., it is important that individual persistent pesticides be evaluated under local

or regional conditions. For these reasons the S-58 regional committee on pesticide residue research decided to undertake cooperative field and laboratory studies.

The objective of the studies was to determine the extent of contamination of several commercially important crops grown in soils containing known concentrations of several pesticides. Six State residue laboratories (Florida, Mississippi, North Carolina, South Carolina, Texas, and Virginia) participated in this cooperative study. Three commonly used chlorinated hydrocarbons (DDT, endrin, and dieldrin) and several commercial crops (soybeans, peanuts, turnip greens, and tobacco) were selected. Each State selected one or two pesticides and one or two crops for their individual experiments. Three pesticide application rates were selected: DDT at 2, 8, and 16 lb/acre; endrin and dieldrin at 1, 2, and 4 lb/acre. Each pesticide formulation was obtained from a single source and distributed to each cooperating State for application in the field. Three separate randomized block designs were prepared for the field experiments depending on the number of crops and insecticides selected by the individual State. Each experimental field treatment was replicated three times. The central laboratory in Florida analyzed not only the three replications of their own field experiments, but also one replication from each of the cooperating States' experiments.

A preliminary soil analysis was conducted by the individual laboratories prior to the actual incorporation of pesticides into the soil to determine the existing level of residual pesticides at each location. Another purpose of the preliminary soil study was to provide each analytical laboratory an opportunity to obtain experience in soil analyses for the pesticides under study. The Florida laboratory analyzed duplicate samples of the preliminary soils from each of the cooperating State experiment plots.

Because of the diversity of the crops under study, complete standardization of the crop extraction and cleanup was not always possible or practical. It is also realized with the extraction procedures employed in these cooperative studies, that complete extraction of the pesticide from the soil or plant substrates was not usually achieved. All cooperating States standardized as many variables in the cooperative experiments as was feasible. Following completion of the laboratory phase, statistical analyses of the data were conducted at North Carolina State University.

C. H. Van Middelem[1]
Chairman, S-58 Technical Committee

[1] Pesticide Research Laboratory, Department of Food Science, University of Florida, Gainesville, Fla. 32601.

Residues of Endrin and DDT in Turnips Grown in Soil Containing These Compounds[1]

W. B. Wheeler[2], H. A. Moye[2], C. H. Van Middelem[2], N. P. Thompson[2], and W. B. Tappan[3]

ABSTRACT

Turnips grown in soils fortified with 1, 2, and 4 lb/acre endrin and 2, 8, and 16 lb/acre DDT were analyzed to determine the degree of crop contamination. The maximum levels of endrin in turnip peels, peeled turnips, and turnip greens were 0.12, 0.04, and 0.02 ppm, respectively. The highest levels of DDT in turnip peels, peeled turnips, and turnip greens were 0.10, 0.03, and 0.02 ppm, respectively.

Introduction

Large quantities of pesticides have been applied to tobacco and tobacco soil for pest control in the production of cigar wrapper tobacco. Pesticide treatments of this type have been shown to result in the accumulation of rather high insecticide levels in soils. After rates of 15 to 75 lb/acre active DDT were applied to tobacco soils the previous spring, Kincaid *et al. (3)* found from 5.0 to 21.1 lb/acre DDT residues remaining in the soil 1 year later. Since DDT is quite persistent, months and even years of weathering might be required before soil levels are significantly reduced. Kincaid *et al. (3)* reported that in North Florida soils this insecticide disappeared at an average annual rate of approximately 18%.

Whether or not these cumulative soil residues might cause above tolerance residues in or on vegetables or forage crops grown in the soil is of concern in Florida and elsewhere. Dupree and Beckham *(1)* reported low levels of DDT in squash (0.02 ppm), lima beans (0.07 ppm), turnip greens (0.08 ppm), and turnip roots (0.04 ppm) when grown in soil containing this chemical.

Endrin has been used also to control tobacco pests and may be a more significant problem than DDT since its tolerance level on crops is zero. Endrin has been reported by Kincaid *et al. (3)* to disappear from North Florida soil at an annual rate of approximately 11%. Thus, the opportunity exists for vegetables grown in endrin-contaminated soils to accumulate detectable endrin residues. In fact, endrin has been detected in pole beans grown on Florida soil previously treated with this pesticide for the control of tobacco insects. Furthermore, low levels of endrin have also been reported by Dupree and Beckham *(1)* in turnip greens, turnip roots, summer squash, and lima beans following growth in soils which had received previous applications of endrin. The State Department of Agriculture has also occasionally encountered low levels of endrin on and in such crops as squash, cucumber, and eggplant. Since these crops had no history of any foliar application of endrin during the growing season, translocation of endrin by these vegetables was suspected. The detection of endrin in the seeds of these crops supported this assumption.

Materials and Methods

The experimental soil at the North Florida Experiment Station, Quincy, is a loamy, fine sand of the Orangeburg type. The pH, organic matter, cation exchange capacity and clay content were 5.2, 1.94%, 4.09 meq/100g, and 8.8%, respectively. A randomized block design was followed for one crop and two pesticides at one location. There were three replications of each pesticide at each level of soil fortification. Experimental plots were 16 x 20 feet with 4-foot alleys between plots and 6- to 10-inch ditches around plots. The alleys and ditches were designed to prevent the contamination of one plot by runoff from another.

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[1] Florida Agricultural Experiment Station Journal Series No. 3191.

[2] Pesticide Research Laboratory, Department of Food Science, University of Florida, Gainesville, Fla. 32601.

[3] North Florida Experiment Station, Quincy, Fla. 32351

Granular formulations of either endrin or DDT were incorporated into the soil of separate plots. Endrin was applied at rates of 0, 1, 2, and 4 lb/acre and DDT at 0, 2, 8, and 16 lb/acre. (The rates of 1, 2, 4, 8, and 16 lb/acre will sometimes be used interchangeably with 0.5, 1, 2, 4, and 8 ppm, respectively. This conversion is based on the assumption that a 6-inch deep acre of soil weighs 2×10^6 lb). The granules (4.7% DDT and 3.2% endrin) were roto-tilled to a depth of 4 to 6 inches to insure uniform incorporation.

The turnips, Just Right F variety, were planted on Septemper 26 and harvested on December 1, 1966. Climatological conditions during this period are shown in Table 1. The only rainfall of any consequence during the crop-growing period was as follows: September 28—1.94 inches, October 10—0.64 inches, October 19—2.02 inches, November 2—1.05 inches, and November 28—0.34 inches. No supplemental irrigation was applied during the course of this experiment.

TABLE 1.—*Climatological data for the experimental area (Quincy, Fla.) during the 1966 growing season*

Date	Temperature (°F)			Rainfall (Inches)
	Average Maximum	Average Minimum	Degree Days [1]	
September 26-30	85.8	65.6	0	1.99
October 1-31	78.9	57.2	57	3.02
November 1-30	71.4	46.1	223	1.73
December	63.0	35.0	16	0.00

[1] Monthly degree-day totals are the sums of negative departures of average daily temperatures from 65° F.

SAMPLING

Soil samples were taken for pesticide residue analysis within 24 hours after the turnips were planted and on the day of harvest. These samplings will be referred to henceforth as "planting" and "harvest" soils. Twenty cores (1 x 6 inches) were systematically selected from the center of the experimental plot. The cores were taken in 2 rows extending the 20-foot length. All samples were kept sealed and frozen until time for analysis.

Turnip foliage and root samples consisted of 12 mature plants per plot. The roots and foliage were separated in the field and refrigerated until transported to the laboratory (usually within 24 hours). Upon arrival, the turnips were water-washed, peeled, and frozen until extracted and analyzed.

EXTRACTION OF DDT AND ENDRIN FROM SOIL

The moisture content of soil has been shown to affect the extraction efficiency of chlorinated insecticides if it deviates more than 1 to 2% from an optimum of 12%. In this study the original moisture content of each soil sample was determined by heating in a muffle furnace at 110 C for 16 hours. Moisture was added or removed by evaporation to bring all soils to approximately 12% moisture prior to extraction.

Soil samples weighing 100 g each were extracted by tumbling end-over-end at 64 rpm for 1 hour with 200 ml of a 1:1 hexane-acetone mixture. The soil extract was filtered through fluted filter paper (E & D, #515) into a 500-ml separatory funnel equipped with a Teflon stopcock. Following washing of the extract three times with 100-ml portions of distilled water, the hexane layer was retained and passed through a 65-mm Buchner funnel (topped with Whatman #42 filter paper) containing a mixture of 30 ml anhydrous sodium sulfate, 15 ml Hyflo Supercel and 15 ml Celite 545. Extracts were analyzed by gas chromatography without further cleanup or concentration.

EXTRACTION OF DDT AND ENDRIN FROM TURNIP ROOTS AND TOPS

Fifty-gram subsamples were blended at high speed in a Lourdes homogenizer for 3 minutes with 200 ml of 2:1 hexane-isopropyl alcohol. Following removal of the solvent, the residue was reblended using an additional 200 ml of 2:1 hexane-isopropyl alcohol. The slurry was filtered and the two extracts combined. After three washings with 100-ml portions of distilled water (a few milliliters of saturated NaCl solution were added in the event emulsions formed), the hexane extract was dried over anhydrous sodium sulfate at 35 F for 1 to 2 hours. The extract was passed through a cleanup column consisting of a mixture of 1:2:1 by weight activated Nuchar carbon, alumina, and Celite 545, respectively, and topped with a 1-inch layer of anhydrous sodium sulfate. The chromatographic column was pre-rinsed with 50 ml of hexane prior to the elution of the insecticides with 400 ml of 5% acetone in hexane (v/v). The extracts were then concentrated in a Kuderna-Danish apparatus on a steam bath to a known volume prior to analysis.

DETERMINATION OF RESIDUES OF ENDRIN AND DDT

A Packard gas chromatograph, Model 7610, equipped with dual linear columns and electron capture detectors was used to quantitate the residues of endrin and DDT. The operating parameters for the instrument were as follows:

Columns:	Pyrex, 5′ x ¼″ packed with 60/80 Gas Chrom Q	
	1. 5% DC-200	
	2. 4% SE-30 plus 6% QF-1	
Temperatures:	Inlet	230 C
	Column	190 C
	Detector	215 C
Carrier Gas:	N_2 at 100 ml/min.	

The limit of sensitivity of the instrument was 0.01 ppm for all compounds (endrin and *p,p'*-DDE, *o,p*-DDE, *o,p*-DDT, *p,p'*-DDT).

Results of separate extractions of a single sample were considered acceptable if average deviations from the mean did not exceed ±20%. If one of the replicate analyses resulted in a deviation in excess of 20%, the value was subjected to a statistical test described by Sachs (5) to determine if elimination of the value was valid. In several instances when data were discarded as a result of this test, additional replicate samples were processed to replace these values.

Results

Efficiencies of the extraction and detection methods utilized in this study were established by adding known amounts of endrin or DDT to untreated soil or crop samples and following the procedures as outlined in the *Materials and Methods* section. The pesticides were added to the substrates (soil or turnips) prior to extraction, and the percentages recovered are indicated in Table 2. Since *p,p'*-DDE and *o,p*-DDT are commonly found in soils and crops treated with DDT, these analyses were included in the recovery studies.

In all instances, an average of 75% or more of the added insecticide survived the cleanup and extraction steps. The lowest recoveries, averaging 75-80%, were obtained from turnip tops and roots. However, the reproducibility of results was considered satisfactory and, therefore, the described extraction and cleanup procedures were followed. No corrections were made for any deviations of recovery values from 100%.

ENDRIN IN SOILS

The levels of endrin in the planting soils (Table 3) were 0.01, 0.64, 0.74, and 1.98 ppm at application rates of 0, 1, 2, and 4 lb/acre, respectively. These data illustrate the difficulty in obtaining predetermined soil levels of insecticide even under carefully controlled experimental conditions. Only the 4 lb/acre rate was found to be close to the expected level of 2.0 ppm. Statistical analyses indicate a significant difference between all planting soil levels of endrin and the control. Although the 1 and 2 lb/acre applications were not statistically different at the 95% confidence level, the 4 lb/acre application was found to be significantly greater than the next lower level of treatment with a 99% level of confidence.

The harvest soil levels of endrin were 0.03, 0.77, 1.59 and 3.71 ppm, respectively, for the 0, 1, 2, and 4 lb/acre application rates. The two low levels at planting and harvest were similar, but the two higher levels found in harvest soils were significantly greater than found in planting soils and were in excess of the amount of endrin originally applied.

TABLE 2.—*Recoveries of endrin and DDT from soil, turnip tops, and roots*

Soil or Plant Part	Pesticide	Number of Samples	Percent Recovery		Standard Deviation
			Range [1]	Average [1]	
Soil [1]	*p,p'*-DDE	4	90-95	92	3
	o,p'-DDT	4	82-88	84	3
	p,p'-DDT	4	90-94	92	2
	endrin	4	92-103	96	6
Turnip tops [2]	p,p'-DDT	3	84-95	90	6
	endrin	4	75-76	75	1
Turnip roots [2]	p,p'-DDT	8	92-111	104	7
	endrin	8	70-84	80	5

[1] Levels of sample fortification ranged from 1.0 to 4.0 ppm.
[2] Levels of sample fortification ranged from 0.01 to 0.10 ppm.

TABLE 3.—*Levels of endrin in soil at planting and at harvest in turnip peels, peeled turnips, and turnip greens*

Rate of Application (lb/acre)	Residues in ppm				
	Soil		Turnips		
	At Planting	At Harvest	Peels	Peeled	Greens
0	0.01	0.03	0.00	0.00	0.00
1	0.64	0.77	0.03	0.02	0.01
2	0.74	1.59	0.07	0.02	0.01
4	1.98	3.71	0.12	0.04	0.02
LSD (05)	0.49	0.60	0.021	0.009	0.007
(01)	0.81	0.91	0.033	0.014	0.011
CV (%)	19	20	18	22	15

[1] Dry weight.
[2] Fresh weight.
NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

ENDRIN IN TURNIPS

The levels of endrin detected varied depending on the plant part (Table 3). The peels contained the highest insecticide level (0.12 ppm) of the three plant parts analyzed. As would be expected, the untreated soil resulted in no residue in the peels, and the highest endrin level in the soil caused the highest level in the peel.

The peeled turnips had endrin accumulations statistically greater than zero (99% confidence level) in each case. The same pesticide levels (0.02 ppm) were detected in peeled turnips grown in soil containing 1 and 2 lb/acre. The highest level of soil fortification resulted in endrin residues of 0.04 ppm in the peeled turnips.

Levels of endrin detected in turnip greens were low (0.01 to 0.02 ppm), but were higher than the check values obtained from crops grown in untreated soils. Application rates of 0, 1, 2, and 4 lb/acre endrin to the soil produced levels in turnip greens of 0.00, 0.01, 0.01, and 0.02 ppm, respectively. At the 99% confidence level, only the highest rate was significantly different from the control.

DDT IN SOILS

DDT levels in planting soils are presented in Table 4. The "total DDT" present was 0.14, 0.66, 2.61, and 6.30

ppm in soils treated at rates of 0, 2, 8, and 16 lb/acre, respectively. These data illustrate again the difficulty in obtaining desired levels of fortification under field conditions. Moreover, the statistical analysis of the data indicated that the 0, 2, and 8 lb/acre levels were not significantly different even at the 95% confidence level. However, the two highest planting soil levels of DDT were significantly different at the 95% confidence level.

The total DDT (Table 4) detected in harvest soil samples was 0.09, 1.22, 4.92, and 13.35 ppm in plots treated at rates of 0, 2, 8, and 16 lb/acre, respectively. As was the case with endrin, the DDT levels in harvest soils statistically were significantly greater than planting levels. Moreover, harvest soil levels were similar to the planting DDT levels in that the two lowest DDT rates (0 and 1 ppm) were not statistically different at the 95% confidence level. Furthermore, the 2 and 8 lb/acre rates were not significantly different. The 8 lb/acre DDT rate was different from the zero rate, and the highest application (16 lb/acre) was statistically different from the 4 ppm rate at the 99% level of confidence.

DDT IN TURNIPS

The levels of DDT and its analogs found in turnip peels, peeled turnips, and tops are presented in Table 5. Again, only the levels of total DDT will be discussed. The highest levels of insecticide detected were in the turnip peels as was the case with endrin. There were no statistical differences (95% confidence level) for total DDT levels in peels between the 0 and 1 ppm rates. The two highest soil application rates (8 and 16 lb/acre) resulted in statistically different DDT levels in peels (0.06 ppm and 0.10 ppm, respectively) at the same level of confidence.

There were not statistical differences in DDT levels among the peeled turnips grown in soils containing different insecticide levels. The levels were all low (0.01 to 0.03 ppm), demonstrating that widely different soil concentrations of DDT (0.1 to 13 ppm) did not cause differences in residues in the peeled crop.

Small quantities of total DDT (.02 ppm) were detected in turnip greens grown in soil fortified at the three rates. Again, it is apparent that even high soil levels of this insecticide did not cause significant residues in the aerial portions of this crop. If any DDT residues were absorbed and translocated from the soil into the turnip plant, it occurred only to a very limited extent.

TABLE 4.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT and total DDT in soil at planting and at harvest*

Rate of Application (lb/acre)	Residues in ppm [1]							
	Planting Soil				Harvest Soil			
	p, p′-DDE	o,p-DDT	p,p′-DDT	Total DDT	p,p′-DDE	o,p-DDT	p,p′-DDT	Total DDT
0	0.03	0.04	0.07	0.14	0.02	0.02	0.05	0.09
2	0.04	0.12	0.50	0.66	0.06	0.25	0.91	1.22
8	0.12	0.47	2.02	2.61	0.14	1.32	3.46	4.92
16	0.27	1.22	4.81	6.30	0.58	2.55	10.22	13.35
LSD (05)	0.13	0.47	2.26	2.89	0.07	0.67	3.06	3.76
(01)	0.20	0.71	3.42	4.38	0.11	1.05	4.80	5.89
CV (%)	6	51	61	59	17	31	40	36

[1] Dry weight.
NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

TABLE 5.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT and total DDT in turnip peels, peeled turnips, and turnip greens*

Rate of Soil Application (lb/acre)	Residues in ppm [1]											
	Peels				Peeled Turnips				Turnip Greens			
	p,p′-DDE	o,p-DDT	p,p′-DDT	Total DDT	p,p′-DDE	o,p-DDT	p,p′-DDT	Total DDT	p,p′-DDE	o,p-DDT	p,p′-DDT	Total DDT
0	0.00	0.01	0.02	0.03	0.00	0.01	0.02	0.03	0.00	0.01	0.01	0.02
2	0.00	0.01	0.01	0.02	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.02
8	0.00	0.03	0.03	0.06	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.02
16	0.00	0.04	0.06	0.10	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.02
LSD (05)	—	0.01	0.02	0.03	—	—	—	—	—	—	—	0.010
(01)	—	0.02	0.03	0.05	—	—	—	—	—	—	—	0.014
CV (%)	—	33	31	30	—	—	—	—	—	—	—	17

[1] Fresh weight.
NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

Discussion

The recovery data in Table 2 have the usual limitations in that crop or soil fortification was followed shortly by extraction, cleanup, and analysis. The extraction efficiencies were not determined using weathered residues nor were exhaustive extraction procedures utilized. The possibilities of inefficient extractions have been pointed out by several investigators (*2,4,6,7* and *Lichtenstein, E. P. 1966. Personal communication*).

The soil analyses yielded some unexpected data, particularly with reference to the harvest residue levels being greatly in excess of planting levels. Possible explanations for this discrepancy were: pesticide drift from adjacent fields during the growing period; runoff from neighboring plots or fields; poor sampling or mixing procedures at planting or at harvest; poor methodology (i.e., inefficient extraction of freshly incorporated insecticide and/or ineffective mixing of soil and insecticide during plot preparation). Each of these possibilities has has been carefully investigated, and none appears to be a valid explanation.

The levels of DDT or endrin in turnips were low. As would be expected because of the direct contact with the soil, the peels did contain the highest insecticide levels, while the peeled turnips and the greens contained very small quantities of these chemicals. If these very low levels are considered in light of the method sensitivity (0.01 ppm for each insecticide) and the fact that levels ranging from 0.01 to 0.03 ppm are commonly considered to be the same in magnitude, then only the two higher soil treatment rates of endrin and DDT resulted in significant crop residues as reflected by the turnip peel data.

Under the experimental conditions described, it cannot be concluded that absorption and translocation of endrin or DDT was the sole mechanism by which the turnip plants were contaminated. There is the possibility that above-ground plant parts could have been contaminated by several other mechanisms such as vaporization and co-distillation of the insecticide from the soil as well as splashing or blowing of the contaminated soil onto leaves and stems. The experiment was not designed to differentiate or measure the effects of each of these possible avenues of pesticide contamination of the plant.

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Residues of Endrin and DDT in Soybeans Grown on Soil Treated with These Compounds[1]

B. F. Barrentine and Jimmie D. Cain

ABSTRACT

Endrin and DDT were disced into the soil at rates of 2, 4, and 8 lb/acre and 8, 16, and 32 lb/acre, respectively. Soybeans were grown in the treated soils and analyzed at harvest to determine the degree of uptake by this crop. Data obtained indicated that DDT was not taken up by the soybeans. A small but significant amount of endrin (maximum, 0.12 ppm) was found in the beans grown on endrin-treated soil.

Introduction

Reports of endrin in soybeans in 1963 and 1964 caused serious concern in agricultural and regulatory agencies. In 1966 the Food and Drug Administration, U. S. Department of Health, Education, and Welfare, seized a tank car of crude soybean oil that contained residues of endrin reported to be about 1.0 ppm.

Endrin has never been approved for insect control on soybeans but has been approved and widely used for cotton insect control in Mississippi. The occurrence of endrin in soybeans suggested the possibility that endrin present in the soil, from areas formerly planted to cotton, were being picked up by the soybean plant and translocated to the bean. It had been assumed previously that the chlorinated hydrocarbons were not translocated from soil to crops.

The purpose of this study was to determine the uptake of endrin by soybeans grown in soils treated at planting with various levels of endrin. DDT was also included in the study.

Materials and Methods

The experimental area was located on a Leeper clay loam soil. This soil is 25 to 40% clay and contains about 1 to 1.5% organic matter. This soil usually has a cation exchange capacity of 20 to 25 meq of Ca^{++} per 100 g of soil. The pH of the soil varied from 7.5 to 7.9, averaging 7.7. A randomized block design for one crop and two pesticides was used. There were seven treatments, three levels of DDT, three levels of endrin, and one common check plot. There were three replicates making a total of 21 plots. Each plot was 13.3 by 32.7 feet or 0.01 of an acre. The area was disced and the plots laid off. DDT was diluted and applied as a spray to give levels of 8, 16, and 32 lb/acre. Endrin was applied in a similar manner to give levels of 2, 4, and 8 lb/acre. These are higher levels than used by the other States. The area was then disced again to a depth of 6 inches. Four rows of Lee soybeans were planted on each plot by conventional methods.

Climatological data from a weather station in the experimental area is shown in Table 1. Rainfall and temperatures were about normal for this period.

TABLE 1.—*Climatological data for the experimental area during the 1966 growing season*

Month	Temperature (°F)		Evaporation (Inches)	Rainfall (Inches)
	Average Maximum	Average Minimum		
June	86.7	64.7	7.09	2.24
July	93.9	71.7	8.28	3.19
August	88.4	67.4	6.48	2.74
September	82.9	63.2	4.37	4.33
October	73.8	48.8	4.14	2.67
November	66.5	45.3	3.08	1.65

[1] Mississippi Agricultural Experiment Station, Department of Agricultural Chemistry, Mississippi State University, State College, Miss. 39762.

TABLE 2.—*Levels of p,p'-DDE, o,p-DDT, p,p'DDT, and total DDT in soil (0- to 6-inch depth) at planting and harvest and in soybeans*

Rate of Application (lb. acre)	Residues in ppm							
	Planting Soil [1]			Harvest Soil				Soybeans
	o,p-DDT	p,p'-DDT	Total DDT	p,p'-DDE	o,p-DDT	p,p'-DDT	Total DDT	Total DDT
0	0.03	0.09	0.12	0.03	0.02	0.07	0.12	<0.01
8	0.67	2.54	3.21	0.38	0.51	1.52	2.41	<0.01
16	1.18	4.27	5.45	0.73	1.07	4.20	6.00	<0.01
32	3.25	11.36	14.61	1.22	2.60	9.91	13.73	<0.01
LSD (05)	0.68	3.22	3.89	0.30	0.72	2.48	3.44	ns
(01)	1.03	4.88	5.90	0.46	1.09	3.76	5.21	ns
CV (%)	27	35	33	26	34	32	31	—

[1] No DDE found in planting soil.

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = not significant

SAMPLING PROCEDURE

The soils were sampled immediately after planting and at harvest of the beans. Twenty cores of soil 1-inch in diameter and 6 inches deep were taken from each experimental plot. The soil cores were composited and passed through a coarse screen to remove trash. The soils, weighing about 1 kg, were then passed through a ¼-inch screen and stored in a sealed container for analysis.

Enough beans were stripped from the two inside rows to yield about 1 quart of shelled beans. The beans were shelled by hand or through a small mechanical sheller and stored in quart fruit jars for analysis.

EXTRACTION

The soil samples, each weighing 100 g, were extracted with hexane-acetone essentially as suggested by the Pesticide Research Laboratory, Gainsville, Fla. The extract was washed with water and passed through a column containing layers of anhydrous sodium sulfate, Celite 545, and Hyflo-Supercel. One to six microliters of the eluant was injected into the gas chromatograph.

The soybeans were ground, and 25-g samples were extracted with petroleum ether. One gram of the oil thus extracted was cleaned up on a Florisil column as outlined by Langlois (*1*) with some modifications. The eluant was concentrated in a Kuderna-Danish concentrator to 5 ml, and 5 μl were injected into the gas chromatograph.

GAS CHROMATOGRAPHY

Determination of DDT and its metabolites and endrin was by gas-liquid chromatography using an electron capture detector. The instrument was a Barber-Colman Model 5360 gas chromatograph with a tritium detector. The operating conditions were as follows:

Columns: Glass, 6' x ¼", packed with a mixture of 4% SE-30 and 6% QF-1 on Anakrom ABS. Other column packings were used for verification.

Temperature: Column 200 C
Detector 215 C

Carrier Gas: N_2 at 110 ml/min

The sensitivity level for endrin is about 0.003 ppm and for *p,p'*-DDT about 0.005 ppm under the conditions of this work. Recovery of endrin from fortified samples of oil ranged from 93 to 102%. The recovery of *p,p'*-DDT ranged from 89 to 113%. The soybean data are not corrected for recovery.

Statistical Evaluation

The statistical evaluation of the data is presented in Tables 2 and 3. It will be noted that the coefficient of variability is rather high. As expected, the levels of "total DDT" and endrin were highly correlated with the treatments, but in the case of DDT the difference between treatments was highly significant only between the two highest levels.

TABLE 3.—*Levels of endrin in soil (0- to 6-inch depth) at planting and harvest and in soybeans*

Rate of Application (lb. acre)	Residues in PPM		
	Soil		Soybeans
	At Planting	At Harvest	
0	0	0	0.01
2	0.59	0.34	0.04
4	1.20	1.04	0.08
8	1.49	1.79	0.12
LSD (05)	0.43	0.95	0.02
(01)	0.66	1.44	0.03
CV (%)	26	60	15

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

No significant uptake of DDT by the soybean was observed. A small but highly significant uptake of endrin by the soybean occurred.

Results and Discussion

The application of 8, 16, and 32 lb of DDT per acre (top 6 inches) should have resulted in 4, 8, and 16 ppm of total DDT in the soil. Values shown in Table 2 for total DDT both at planting and harvest are in fair agreement for the 8- and 32-lb treatment. The soils from the 16-lb treatment of DDT were lower in total DDT than expected; no explanation for this can be offered. It will be noted in Table 2 that no DDE was found in the soil at planting; but DDE was found at harvest as expected.

The time between planting and harvest was approximately 5 months. No significant drop in total DDT in the soil occurred during this period. No DDT was detected in the soybeans grown in this soil.

Endrin application of 2, 4, and 8 lb/acre in the top 6 inches of soil should have resulted in soils containing 1, 2, and 4 ppm of endrin. The values found were for the most part less than half the expected values (Table 3). The soils from the 2- and 4-lb treatments showed some drop in endrin from planting to harvest. The 8-lb treatment showed an apparent increase which was probably due to sampling variation. The amount of endrin in the beans, although small, was highly significant for treatments (Table 3). The amount of endrin found in the soybeans approximated 10% of that found in the soil.

The results of this study on DDT in soybeans is not in agreement with the other States, as most of them found small amounts of DDT and its metabolites present in the beans. The occurrence of endrin in soybeans grown in soil containing endrin is in agreement with the monitoring studies of the U. S. Department of Agriculture (*2*). In a study near Greenville, Miss., they reported soil levels of endrin ranging from 0.04 to 1.12 ppm. Soybeans from these soils contained endrin in varying amounts from 0.17 ppm to a high of 0.54 ppm.

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Residues of DDT and Dieldrin in Peanuts and Tobacco Grown on Contaminated Soil [1]

T. J. Sheets[2], M. D. Jackson[2], W. J. Mistric[3], and W. V. Campbell[3]

ABSTRACT

Nuts, hulls, and green forage of peanut plants grown in soil fortified with DDT or dieldrin contained residues of these insecticides. At harvest, dieldrin was more concentrated in nuts than DDT. Nuts from plots sprayed with 1 lb/acre of dieldrin had 0.22 ppm at harvest. On conversion of analytical values to a dry-stemless basis, green tobacco leaves from the same plots contained 0.18 ppm of dieldin at harvest. DDT was also present in tobacco leaves, but contamination of controls prevented an unqualified conclusion on DDT absorption from soil and transport to leaves. In those plant parts with significant residues attributable to soil contamination, concentrations of the insecticides increased in a direct linear relation with rate of application.

At peanut harvest 5 months after application of 2, 8, and 16 lb/acre of DDT, the upper 6 inches of soil contained 44, 44, and 52%, respectively, of the "total DDT" in the soil at planting. About 31% of the o,p-DDT remained in the soil at the end of the 5-month season, whereas about 50% of the p,p'-DDT remained. Dieldrin residues present at peanut harvest were 42, 56, and 40% of the initial concentrations resulting from applications of 1, 2, and 4 lb/acre, respectively.

Introduction

Chlorinated hydrocarbon insecticides have been employed extensively in North Carolina to control insects in cotton (*Gossypium hirsutum* L.), peanuts (*Arachis hypogaea* L.), tobacco (*Nicotiana tabacum* L.), and several other crops. DDT and toxaphene remain the most widely used pesticides for insect control in cotton. TDE is still a major insecticide for tobacco, but DDT is no longer recommended for use on this crop. With the occurrence of insect resistance to endrin and recognition of the persistence of endrin in the environment, it was dropped from recommendations for tobacco in 1964.

Due to extensive use and persistent nature of the chlorinated hydrocarbons many of the agricultural soils in North Carolina may be expected to contain low levels of these insecticides. A limited survey conducted over several counties in eastern North Carolina in 1966 (*Campbell, W. V., T. J. Sheets, and M. D. Jackson. 1966. Unpublished results, Dep. Entomol. and Pesticide Residue Res. Lab., N. C. State Univ. Agr. Exp. Sta., Raleigh, N. C.*) showed that 31% of the soil samples from a total of 39 fields contained residues of aldrin and dieldrin >0.1 ppm; and 36% had "total DDT" residues >1.0 ppm.

Approximately 170,000 acres of peanuts and about 400,000 acres of flue-cured tobacco are grown for market in North Carolina. The cash value of these two crops amounts to about $530 million annually; therefore, peanuts and tobacco were selected for study as a part of the regional experiment on the contamination of crops growing in soil containing residues of insecticides. Dieldrin and DDT were chosen for the experiment because, based on past and present pest control practices, low levels might be expected in many soils.

Materials and Methods

TREATMENT OF THE SOIL

A coastal plain soil with no record of pesticide use was selected for the experimental site in North Carolina. The soil type was Norfolk loamy sand in replication 1 and Norfolk sandy loam in replications 2 and 3. The pH of the soil in the experimental area was 5.0. Organic matter content was 0.8, 1.6, and 2.3% in replications 1, 2, and

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Pesticide Residue Research Laboratory, North Carolina State University, Raleigh, N.C. 27607.
[3] Department of Entomology, North Carolina State University, Raleigh, N.C. 27607

3, respectively, and averaged 1.6%. Cation exchange capacity varied from 1.75 meq per 100 g in replication 1 to 3.45 in replication 2 and 4.55 in replication 3. The average cation exchange capacity over replications was 3.25 meq per 100 g. The sand, silt, and clay contents were 83, 13, and 4%, respectively. After the field was plowed, 1000 lb of lime, 500 lb of 0-20-0 fertilizer, and 1000 lb of 4-8-12 fertilizer were applied per acre. The lime and fertilizer were mixed in the soil by discing. During July calcium sulfate (gypsum, containing boron) was applied to the foliage of the peanuts at the rate of 800 lb/acre.

DDT and dieldrin were applied on May 6, 1966, to plots 28 feet wide (8 rows) and 30 feet long. Rates of application were 2, 8, and 16 lb/acre of DDT and 1, 2, and 4 lb/acre of dieldrin. The insecticides were incorporated by discing twice, and rows were prepared for transplanting tobacco and seeding peanuts. One unsprayed plot in each replication served as a control. The experimental design was a randomized split plot with insecticides and rates as the main plots and crops (tobacco and peanuts) as the subplots. Four of the eight rows in each main plot were planted to peanuts (variety NC-2) May 9, 1966; tobacco (variety Coker 319) was transplanted in the other four rows May 11, 1966. Rainfall and temperature records were kept for the experimental period (Table 1).

SAMPLING

One soil sample consisting of thirty 1-inch cores was taken from the surface soil (0- to 6-inch depth) of each replication prior to application of the insecticides. Immediately after application and incorporation of the insecticides and again at the time of peanut harvest, one sample consisting of 20 cores was taken from each main plot (0- to 6-inch depth) in each replication. The soils were dried in the laboratory to a water content of 4% or less (oven-dry basis), screened through a 2-mm screen and stored at −5 to −8 C.

The fifth and sixth leaves (3rd priming) of the tobacco plants were harvested July 13, 1966, and placed in cold storage at −5 to −8 C. Leaves 19 through 22 (last priming) were harvested August 18 and stored.

On October 10, 1966, 2 to 3 lb of peanuts were harvested from each plot. The peanuts were shelled, and nuts and hulls were saved for analysis. Green forage samples were also collected October 10, 1966. All samples were stored at −5 to −8 C.

Subsamples of soil, tobacco leaves, and hulls, nuts, and green forage of peanuts from all samples of the first replication were shipped to the S-58 Regional Laboratory at Gainesville, Fla., for insecticide analyses.

EXTRACTION OF DDT AND DIELDRIN FROM SOIL

The method described in the initial report on the monitoring program of the U. S. Department of Agriculture (*10*), with slight modifications, was employed for analysis of the soils. The soils were removed from storage, and subsamples weighing 100 g on an oven-dry basis were placed in 1-quart jars. A 200-ml mixture of hexane-isopropanol (3:1) was added. The jars were sealed, set vertically on a reciprocating shaker, and agitated for 1 hour. After removing the jars from the shaker, the soil was allowed to settle. Approximately 100 ml of the extraction solution was decanted through a plug of glass wool into a separatory funnel. The extracts were washed twice with a solution of 2% NaCl in water. The water washings and unbroken emulsions remaining were discarded. The washed solution was drained into a storage container. The solution at this point was ready for injection into the gas chromatograph. Each milliliter of the solvent was equivalent to 0.67 g of soil.

EXTRACTION OF DDT AND DIELDRIN FROM PEANUTS

The method of analysis for peanuts was modified from that published in the Food and Drug Administration Pesticide Analytical Manual (*1*). After the samples were removed from storage, 100-g subsamples of peanuts were chopped, and the undried nuts were blended with 100 ml of ethanol (95%) and 50 ml of water. The mixture was shaken with 50 ml of ethyl ether. Fifty milliliters of petroleum ether was added and the mixture shaken again. After centrifugation the mixed ether layer was removed and washed three times with a solution of 2% NaCl in water. The mixed ether extract was filtered through anhydrous Na_2SO_4 and evaporated. The peanut oil remained.

A 3-g sample of peanut oil was dissolved in 15 ml of petroleum ether, and the pesticide was partitioned into acetonitrile (four partitions). The acetonitrile portions were added to 500-600 ml of a solution of 2% NaCl in water, and the insecticides were partitioned into 100 ml of petroleum ether. The partitioning step was repeated once. The combined petroleum ether solution was washed twice with 2% NaCl solution, filtered through anhydrous Na_2SO_4 and reduced to a small volume (less than 10 ml) in a Danish-Kuderna evaporator. The petroleum ether remaining was placed on a 10-cm Florisil column and the pesticides eluted with 6% diethylether in petroleum ether. Columns containing samples from dieldrin plots also were eluted with 200 ml of 15% diethylether in petroleum ether. The ether was evaporated and the residue dissolved in hexane for gas chromatography.

The oil content of the nuts was determined (*6*). For presentation, the concentrations of insecticides for peanuts were converted from ppm in oil to ppm in nuts.

EXTRACTION OF DDT AND DIELDRIN FROM HULLS AND GREEN FORAGE OF PEANUTS AND FROM TOBACCO

Samples of peanut hulls, green forage of peanuts, or green tobacco leaves were chopped, and subsamples weighing 25 g were blended with 300 ml of petroleum ether for 2 minutes. The ether was decanted through an anhydrous Na_2SO_4 column into a Danish-Kuderna evaporator. The residues were extracted twice more with 200-ml portions of petroleum ether. The ether extracts were filtered through anhydrous Na_2SO_4 and combined with the original ether extract. The volume was reduced for acetonitrile partition. The remainder of the cleanup steps were identical to those described for peanut oil.

DETERMINATION OF RESIDUES

Determinations in the clean extracts were accomplished with a Jarrell Ash 28-731 gas chromatograph equipped with an electron capture (tritium) detector. The instrument parameters for the analyses were as follows:

Detector voltage: 15 volts

Column: Glass, ¼" x 6', packed with 5% DOW 11 on Chromosorb W HDMS (60/80 mesh)

Carrier Gas: Prepurified nitrogen at 100 ml/min

Temperature: Inlet 220 C
Column 175 C
Detector 205 C

The amounts of insecticides were measured from peak areas, estimated by triangulation, on the chromatographic charts. For each sample, two injections were made into the gas chromatograph except for those that were negative on the first injection. All finite values are averages of the two injections.

Recoveries of *p,p'*-DDE, the two major isomers of DDT (*o,p*-DDT and *p,p'*-DDT), and dieldrin were determined for each commodity. Samples from untreated plots were fortified with the insecticides at the initial extraction step and were carried through the analysis with samples from sprayed plots. Values in the tables were not corrected for incomplete recoveries.

STATISTICAL EVALUATION

Standard deviations were calculated for recoveries. Analyses of variance were performed for all other data. Each pesticide or metabolite within each crop was analyzed separately. In each analysis, variation attributed to replications, rate of application of insecticide, and error was calculated. The change in the insecticide residue level in each commodity with the rate of insecticide application was tested for a significant linear or quadratic relation. Least significant differences (LSD) and the coefficients of variation (CV) were computed to aid interpretation. A combined analysis of variance was performed on the two tobacco primings for each insecticide.

Results and Discussion

Climatological data for the 1966 growing season indicate that temperatures were typical for the coastal plain of North Carolina (Table 1). Rainfall patterns deviated somewhat from the long term average; July and October were drier and May wetter than normal.

The range, mean, and standard deviation for recoveries of *p,p'*-DDE, *o,p*-DDT, *p,p'*-DDT, *and dieldrin from* soil, vegetable oil (for peanuts), peanut hulls, green peanut forage, and green tobacco leaves are given in Table 2. Mean recoveries equaled or exceeded 80% except for dieldrin in green tobacco leaves.

TABLE 1.—*Climatological data for the experimental area during the 1966 growing season*

Month	Temperature (°F)			Rainfall (Inches)
	Average Maximum	Average Minimum	Degree Days [1]	
April	72.9	46.9	179	2.87
May	79.0	56.6	35	6.14
June	85.3	61.7	8	3.89
July	92.2	68.1	0	1.23
August	86.7	68.4	0	4.51
September	83.6	60.6	5	3.93
October	73.9	48.9	135	1.45

[1] Monthly degree-day totals are the sums of the negative departures of average daily temperatures from 65°F.

TABLE 2.—*Recoveries of DDT and dieldrin from soil, vegetable oil (for peanuts), peanut hulls, peanut green forage, and tobacco leaves*

Soil or Plant Part	Pesticide	Number of Samples	Range (Percent)	Mean Recovery ± Standard Deviation (Percent)
Soil	*p,p'*-DDE	3	82-106	97 ± 13
	o,p-DDT	3	101-104	102 ± 2
	p,p'-DDT	7	81-115	98 ± 11
	Dieldrin	4	78- 90	82 ± 5
Vegetable oil (for peanuts)	*p,p'*-DDE	7	84- 94	88 ± 3
	o,p-DDT	7	91- 99	96 ± 3
	p,p'-DDT	7	95- 97	96 ± 1
	Dieldrin	10	83-109	90 ± 7
Peanut hulls	*p,p'*-DDE	4	84- 92	88 ± 4
	o,p-DDT	4	86- 90	88 ± 2
	p,p'-DDT	4	84- 90	88 ± 3
	Dieldrin	4	81- 94	86 ± 6
Peanut green forage	*p,p'*-DDE	5	74- 88	82 ± 5
	o,p-DDT	5	71- 91	81 ± 10
	p,p'-DDT	5	66- 90	80 ± 9
	Dieldrin	6	72-100	80 ± 12
Tobacco leaves	*p,p'*-DDE	10	77- 89	85 ± 4
	o,p-DDT	10	78-104	88 ± 10
	p,p'-DDT	10	74- 94	84 ± 7
	Dieldrin	10	62- 92	76 ± 10

Levels of DDT in the soil at planting and at harvest are recorded in Table 3. Differences among residue levels at different rates of application were significant at the 5% level of probability for *p,p'*-DDE, *o,p*-DDT, *p,p'*-DDT, and total DDT. At peanut harvest 5 months after application, the concentration of total DDT in soil from

the upper 6 inches of plots sprayed with 2, 8, and 16 lb/acre was 0.87, 2.31, and 4.89 ppm, respectively. From the low to high rate of application, 44, 44, and 52% of the total DDT present in the soil at planting remained at peanut harvest.

The *o,p*-DDT disappeared from the surface soil more rapidly than *p,p'*-DDT. Calculations from the values in Table 3 revealed that at each of the three rates of application 31% of the *o,p*-DDT remained in the surface soil at peanut harvest; whereas, levels of *p,p'*-DDT remaining at harvest from application of 2, 8, and 16 lb/acre were 47, 46, and 58%, respectively (an average of 50%). Disappearance of *o,p'*-DDT over the 5-month period was proportional to the concentration at planting. We cannot determine from the statistical computations if the high percent recovery of *p,p'*-DDT after 5 months at the 16 lb/acre rate was significantly different from that at the 2 and 8 lb/acre rates. At the two lowest rates, disappearance was proportional to the initial concentration. Coefficients of variation (CV) indicate that the data for residues at harvest were more variable than those for residues at planting.

Peanut hulls were contaminated with DDT through absorption or translocation or by direct adherence to the peanut hulls. Hulls from control plots contained *p,p'*-DDT (Table 4). Levels in the hulls increased linearly as the rate of application increased. Although each DDT component was detected in nuts from the 16 lb/acre plots and *p,p'*-DDT in the 8 lb/acre plots, none of the residues in the nuts was significantly different (statistically) from the levels in the control. The three DDT components were present in green peanut forage from all plots, including the control, but differences were too small for statistical significance except those for total DDT. Hulls for the 16 lb/acre plots contained an average of 1.00 ppm of total DDT; nut samples from the same plot contained an average of 0.13 ppm; and green forage samples averaged 0.10 ppm for total DDT. These data indicate that, although quite significant amounts of DDT may be absorbed into peanut hulls, only very small quantities reach the nuts and green forage. Residues of chlorinated hydrocarbons, especially DDT and dieldrin, have rendered peanut hulls and hay unsuitable as feed for dairy cattle and for poultry, cattle, and other animals for slaughter. Meat and milk have become contaminated with these insecticides when such feeds were used.

Individual values for *p,p'*DDE, *o,p*-DDT, and *p,p'*-DDT were low for tobacco leaves and varied little with the rate of application (Table 4). Trends for the two primings were identical; therefore, only total DDT data averaged over the two primings are reported.

TABLE 3.—*Levels of* p,p'-*DDE*, o,p-*DDT*, p,p'-*DDT and total DDT in soil (0- to 6-inch depth) at planting and at harvest*

Rate of Application (lb/acre)	Residues in Planting Soil (ppm)				Residues in Harvest Soil (ppm)			
	p,p'-DDE	*o,p'*-DDT	*p,p*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT
0	<0.04	<0.04	<0.10	<0.18	<0.05	<0.05	<0.10	<0.20
2	0.03	0.36	1.59	1.98	<0.05	0.11	0.74	0.87
8	0.08	0.97	4.24	5.29	0.06	0.30	1.95	2.31
16	0.08	2.15	7.15	9.38	0.10	0.66	4.13	4.89
LSD (05)	0.03	0.23	1.36	1.41	0.02	0.26	2.25	2.51
(01)	ns	0.36	2.06	2.13	0.03	0.39	3.41	3.81
CV (%)	24	13	21	17	15	46	65	61

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

TABLE 4.—*Levels of* p,p'-*DDT*, o,p-*DDT*, p,p'-*DDT, and total DDT in hulls, nuts, and green forage of peanuts and in green leaves of tobacco*

Rate of Application (lb/acre)	Peanuts (ppm)												Tobacco (ppm)	
	Hulls				Nuts [1]				Green forage					
	p,p'-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	Green Leaf (Total DDT)	Dry-stemless basis (Total DDT)
0	<0.01	<0.02	0.03	0.04	<0.02	<0.02	<0.04	<0.08	0.01	0.02	0.02	0.05	0.16	1.47
2	0.02	0.02	0.07	0.11	<0.02	<0.02	<0.04	<0.08	0.01	0.01	0.03	0.05	0.15	1.38
8	0.04	0.08	0.28	0.40	<0.02	<0.02	0.05	0.07	0.02	0.03	0.04	0.09	0.16	1.47
16	0.09	0.19	0.73	1.00	0.02	0.02	0.09	0.13	0.02	0.03	0.05	0.10	0.18	1.66
LSD (05)	0.03	0.09	0.29	0.42	ns	ns	ns	ns	ns	ns	ns	0.03	ns	—
(01)	0.05	0.14	0.44	0.64	ns	ns	ns	ns	ns	ns	ns	ns	ns	—
CV (%)	44	61	53	53	[2]	[2]	54	44	30	28	24	19	24	—

[1] PPM expressed on whole-nut basis.
[2] Actual values of all samples were very small and without variation; therefore, coefficients of variation were not computed.

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = no significant

The level of total DDT in green tobacco leaves from control plots averaged 0.16 ppm for two primings (Table 4) and leaves from the 16 lb/acre plot averaged 0.18 ppm. This difference was not significant. Over the range of soil concentrations employed and the prevailing environmental conditions in this experiment, DDT levels were relatively low and were unrelated to the residue level in the soil at planting.

At the end of the 5-month growing season dieldrin concentrations in the upper 6 inches of soil were 42, 56, and 40% of the initial concentrations, respectively, in plots sprayed with 1, 2, and 4 lb/acre (Table 5). Residues in the soil varied from 1.00 to 4.11 ppm at planting and 0.42 to 1.64 ppm at harvest.

Concentration of dieldrin in nuts were about equal to those in hulls, and green forage contained small but significant amounts (Table 5). These results are in general agreement with those of Beek *et al.* (*2*) and Bruce *et al.* (*4*).

There was a direct linear relation between the concentration of dieldrin in nuts at harvest and the concentration in soil at planting (Fig. 1). In Fig 1, extrapolation of the line to zero provides an estimate of residues in peanuts that could occur at dieldrin concentrations in the soil below 1 ppm. A dieldrin concentration of about 0.22 ppm in this soil at planting would cause a residue

TABLE 5.—*Levels of dieldrin in soil at planting and at harvest and in hulls, nuts, and green forage of peanuts, and in leaves of tobacco*

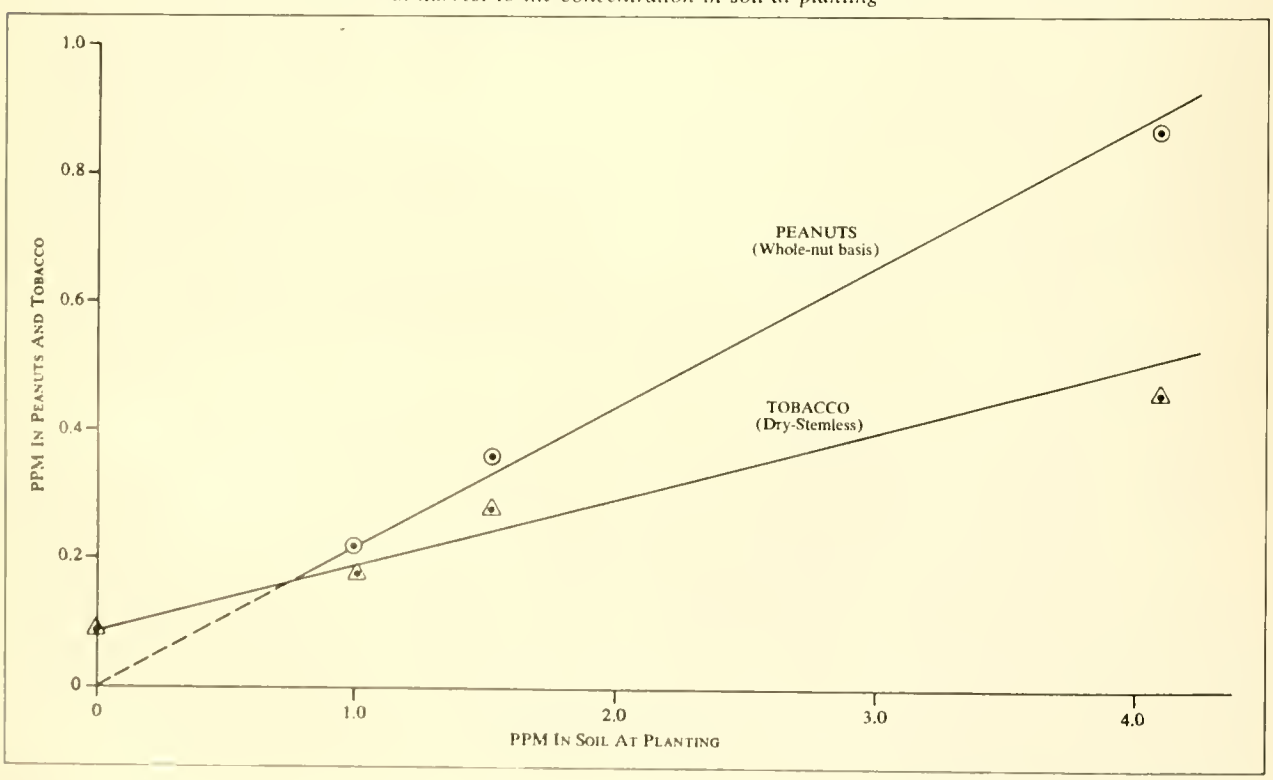
	Dieldrin Residues in ppm						
	Soil		Peanuts			Tobacco	
Rate of Application (lb/acre)	At Planting	At Harvest	Hulls	Nuts [1]	Green forage	Green leaf	Dry-stemless basis
0	<0.05	<0.05	<0.02	<0.04	<0.01	0.01	0.09
1	1.00	0.42	0.21	0.22	0.01	0.02	0.18
2	1.53	0.85	0.49	0.36	0.03	0.03	0.28
4	4.11	1.64	0.81	0.87	0.04	0.05	0.46
LSD (05)	1.00	0.44	0.31	0.39	0.014	0.014	—
(01)	1.52	0.67	0.47	0.59	0.021	0.021	—
CV (%)	30	30	41	53	33	34	—

[1] PPM expressed on whole-nut basis.

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

of 0.05 ppm in the nuts at harvest. A residue of 0.03 ppm would appear in nuts from a soil concentration of about 0.13 ppm. Since absorption of aldrin and dieldrin by plant roots is influenced by soil type (*5,7*) and probably climate also, the concentration of dieldrin in soil required to cause a specific residue in peanuts would, in all likelihood, vary widely. In a limited survey conducted in 1965 in the Eastern United States, residues of dieldrin ranging from 0.05 to 0.26 ppm were found in soil from 28 of 49 fields sampled (*9*). In that survey dieldrin residues in five composite samples of peanuts aver-

FIGURE 1.—*Relation of dieldrin concentration in peanuts (whole-nut basis) and tobacco leaves at harvest to the concentration in soil at planting*



aged 0.10 ppm. Because sampling was limited, Seal *et al.* (9) were unable to resolve the magnitude and significance of the problem.

Dieldrin was present in low concentrations in leaves of tobacco (Table 5). This result is in agreement with that of Schmid and Rastetter (8) who found dieldrin in leaves of tobacco that had been grown in aldrin-treated soil. There was no significance between primings nor was the interaction (treatment x priming) significant. There was a significant linear relation between the concentration of dieldrin in the green leaf of tobacco and the rate of application. Because dieldrin residues in tobacco from the two primings were so similar, only the average values for the two primings are given in Table 5.

From the results in Table 5, there is little question that dieldrin was absorbed by roots of peanuts and tobacco and translocated to the tops. Levels in the tops of the two plants are about the same. Significant amounts of DDT were transported into the tops of peanuts also (Table 4). At equal concentrations in the soil dieldrin apparently was present in peanut forage and tobacco leaves in greater concentrations than DDT. Concentrations for controls must be subtracted from those for the other treatments for an accurate comparison.

According to Bowery *et al.* (3), residues of several insecticides including TDE and endrin decrease during the flue-curing of tobacco. Before computing losses of residues during curing, they converted all analytical values for TDE and endrin to a "dry-stemless basis." TDE residues decreased from 780 ppm on green tobacco to 463 ppm on cured tobacco; those for endrin dropped from 101 to 60 ppm. The decreases were 41 and 42%, respectively, for TDE and endrin. Since DDT is similar to TDE and dieldrin to endrin in structure, reactivity, and persistence, we used the percent losses obtained by Bowery *et al.* (3) to calculate the residue expected on cured tobacco. If losses of 42% occurred during the curing of tobacco containing 0.46 ppm of dieldrin (equivalent to 0.05 ppm on a green-weight basis, see Table 5), the cured tobacco would have about 0.27 ppm. The same conversions for 0.18 and 0.28 ppm of dieldrin (0.02 and 0.03 ppm on a green-weight basis) showed that the cured leaf would contain 0.10 and 0.16 ppm, respectively. Hence, residues of dieldrin present in some agricultural soils of North Carolina may cause significant contamination of flue-cured tobacco through absorption into the roots and translocation to the leaves. Calculation for 1.66 ppm of DDT (0.18 on a green-weight basis, see Table 4) showed that the cured product would contain about 0.98 ppm of DDT. However, this value was not significantly different from that of the control; and the question of significant DDT residues in leaves of tobacco grown on contaminated soil remains unresolved.

The greatest unexplained contamination in this experiment was the DDT on tobacco leaves from control plots. Since the plants were not sprayed with DDT, we assumed this contamination occurred by (a) drift during spray operations on adjacent fields or (b) movement of contaminated dust within the experimental area. The latter explanation seems least plausible since so little cross-contamination was encountered with dieldrin. The unexplained contamination of tobacco leaves may have masked low levels of DDT in the leaves arising from absorption into roots and transport to leaves.

Values obtained by the Regional Laboratory at Gainesville, Fla. for dieldrin in soil samples from the first replication agreed with those from our laboratory, whereas our values for DDT in most soil samples were less than those obtained in the Regional Laboratory (Table 6). Data are given only for residues in soil at planting. The greatest discrepancies between results of the laboratories occurred with green tobacco (data not reported); our values were greater than those from the Regional Laboratory for dieldrin and DDT. There is no clear explanation for the differences. With green tobacco, drying during shipping or processing for analysis could alter the green, or "as received," weight and in consequence result in different concentrations without a change in the actual amounts of insecticides. To explain the differences between concentrations reported by the Regional Laboratory and those obtained in North Carolina, the excessive drying would have had to occur in North Carolina instead of during shipment to Florida.

TABLE 6.—*Values obtained by the North Carolina State University laboratory and by the Regional Laboratory at the University of Florida for total DDT and dieldrin in soil from the first replication at planting*

Total DDT			Dieldrin		
Rate of Application (lb/acre)	NCSU (ppm)	Univ. of Fla. (ppm)	Rate of Application (lb/acre)	NCSU (ppm)	Univ. of Fla. (ppm)
0	<0.18	0.18	0	<0.05	<0.05
2	0.94	1.88	1	0.95	0.96
8	3.72	6.91	2	1.30	1.35
16	8.16	12.53	4	3.48	3.34

Acknowledgment

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DDT Residues in Tobacco and Soybeans Grown in Soil Treated With DDT [1]

John K. Reed[2] and L. E. Priester[3]

ABSTRACT

DDT was incorporated into Norfolk fine sandy loam soil to a depth of 6 inches at concentrations of 2, 8, and 16 lb/acre. Tobacco leaves harvested from plants grown in this soil contained up to 0.70 ppm "total DDT," and beans from soybeans contained up to 0.65 ppm total DDT. Soil contamination of the plant parts may be responsible for some of these high residues. The loss of DDT from the soil was not great from planting to harvesting of the crops.

Introduction

The purpose of this study was to determine to what extent pesticide residues in the soil could be transferred to tobacco leaves or soybeans. Tobacco was chosen to represent a crop with a large leaf surface, and beans of soybeans were chosen to represent a crop product containing a concentration of oil which tends to accumulate nonpolar chlorinated hydrocarbon pesticides. Both crops are important to the agricultural economy of South Carolina and other areas of the Southeast. DDT was chosen as the pesticide, because it has been widely used in recent years and has accumulated in soils where these two crops are likely to be grown.

Materials and Methods

The study plan called for tobacco and soybeans to be grown in plots fortified with 0, 2, 8, and 16 lb/acre of DDT. Each plot was replicated three times in a randomized block design. Soil samples were taken before treatment and analyzed for DDT content. Approximately 2 lb/acre of DDT was found to be present in the soil prior to treatment. Therefore, the check and the plot that would have received the first treatment both contained 2 lb/acre of DDT. Sufficient DDT was then applied by spraying onto the soil to bring the concentration in the other plots to the desired levels of 8 and 16 lb/acre. The material was thoroughly disced into the top 6 inches of soil, and samples of soil from all plots were taken to a depth of 6 inches at planting and harvesting. A 1-inch soil sampling tube was used to take sufficient samples to fill a 1-quart container. Weather data for the growing period are shown in Table 1. The tobacco and soybeans were planted on May 15, 1966. The crops were allowed to grow to maturity following usual agricultural practices, except that no additional pesticides were applied at any time during the growing season.

TABLE 1.—*Climatological data for the experimental area during the 1966 growing season*

Month	Temperature (°F)		Rainfall (Inches)
	Average Maximum	Average Minimum	
May	78.1	59.7	5.29
June	83.8	62.7	3.75
July	90.4	69.9	5.25
August	86.6	68.3	6.02
September	82.7	60.8	1.94
October	75.8	48.4	1.03
November	66.8	37.7	0.91

Prime tobacco leaves were harvested August 13, 1966, and then were stored at near 0° C until analyzed. The soybeans were harvested by hand November 18, 1966. The soybeans were threshed after drying by flailing the entire plant, and the beans were then separated from the trash. The threshing resulted in a considerable amount of dust being mixed with the beans.

[1] Technical contribution number 775, South Carolina Agricultural Experiment Station, Clemson, S. C. 29631.

[2] Department of Entomology and Zoology, Clemson University, Clemson, S. C. 29631.

[3] Present adress: Medical College of South Carolina, Charleston, S.C. 29401.

In the laboratory the three types of samples were extracted, followed by cleanup procedures as necessary. Cleanup by acetonitrile partition was based on the original technique reported by Jones and Riddick (*1*) as modified by Mills (*2*). The routine was as follows:

To each 10-g sample of air-dried soil, 20 ml of 1:1 hexane-acetone solution was added. The samples were capped, shaken, and allowed to stand for 30 minutes, then shaken again, and a 10-ml aliquot was taken for analysis. The 10-ml aliquot was placed in a separatory funnel and washed with two 25-ml portions of distilled water. The hexane layer was adjusted to 10 ml and an aliquot injected directly into the gas chromatograph for analysis.

Samples of fresh tobacco, weighing 100 g each, were chopped in a food chopper and then placed in a gallon jar with 200-ml of 1:1 hexane-acetone solution. The jar was capped with a mylar liner and rolled on a rolling machine for 1 hour. A 100-ml aliquot was placed in a 1-liter separatory funnel and washed with two 500-ml portions of distilled water. The hexane extract was dried over sodium sulfate, evaporated almost to dryness under a stream of dry air, and adjusted to 10 ml with hexane. An aliquot was taken from this solution for injection into the gas chromatograph.

A portion of the shelled beans from each plot was ground in a Servall homogenizer. A 25-g sample of the ground beans was weighed into a small flask and 50 ml of 1:1 hexane-acetone solution added. The flasks were capped and placed on a Burrell wrist-action shaker and shaken for 1 hour. The samples were allowed to stand until a 25-ml portion could be pipetted from the top relatively free of suspended particles. The aliquot was washed with three 25-ml portions of water followed by three 5-ml portions of acetonitrile. The acetonitrile extracts were adjusted to a known volume and an aliquot injected into the gas chromatograph for analysis.

Residue determinations were make by gas chromatography using a MicroTek 220 with a Ni^{63} electron capture detector. Operating parameters were as follows:

Columns: Glass, 6′ x ¼″
1. 5% DC 200 on 60/80 Chromport XXX
2. 5% DC QF-1 on 68/80 Chromport XXX

Temperatures: Column 195 C
Inlet 230 C
Detector 275 C

Carrier gas: N_2 at 120 cc/min

Inlet pressure: 40 psi

Detector voltage: 1.6×10^{-9} AFS

TABLE 2.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT and total DDT in soil (0- to 6-inch depth) at planting and at harvest*

Rate of Application (lb/acre)	Residues in ppm							
	Planting soil				Harvest soil			
	p,p′-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT	*p,p′*-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT
2 (Check)	0.35	0.13	0.53	1.01	0.33	0.17	0.57	1.07
2	0.32	0.20	1.74	2.26	0.30	0.18	0.56	1.04
8	0.39	0.54	3.80	4.73	0.35	0.24	2.62	3.21
16	0.47	1.28	6.18	7.93	0.25	0.14	4.80	5.19
LSD (05)					0.05	ns	0.64	0.76
(01)					0.07	ns	0.97	1.14
CV (%)					24	29	26	14

NOTE: LSD = Least Signicant Differences
CV = Coefficients of Variation
ns = not significant

TABLE 3.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT, and total DDT in green leaves of tobacco and in beans of soybeans*

Rate of Application (lb/acre)	Residues in ppm							
	Tobacco leaves [1]				Soybeans [2]			
	p,p′-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT	*p,p′*-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT
2 (Check)	0.06	0.14	0.23	0.43	0	0.05	0.37	0.42
2	0.09	0.18	0.29	0.56	trace	0.08	0.48	0.56
8	0.08	0.18	0.32	0.58	trace	0.07	0.57	0.64
16	0.13	0.19	0.37	0.69	trace	0.08	0.49	0.57
LSD (05)	0.03	0.03	0.07	0.07		ns	ns	ns
(01)	ns	ns	ns	0.10		ns	ns	ns
CV (%)	19	7	11	6		35	18	19

[1] Net weight
[2] Whole beans

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = no significant

Confirmation of the analysis of the analogs of DDT was checked on the two types of column packing listed above. Resolution of the DDT products was uncomplicated by the presence of other pesticides except traces of BHC isomers. The sensitivity of the method allowed detection of DDT at 0.01 ppm in soil, tobacco, and soybeans. Recovery of *p,p'*-DDT, when added at the rate of 1 ppm, was as follows:

Soil	92.7 - 93%
Tobacco	92.4%
Soybeans	78.3 - 80.8%

Results and Discussion

The levels of DDT and related compounds applied in these tests were sufficiently high to allow ready detection by the methods used. Levels of *p,p'*-DDE, *o,p*-DDT, *p,p'*-DDT, and total DDT in the soil are reported in Table 2. Since approximately 2 lb/acre of total DDT was detected in the soil as a residue from previous usage, the check and the 2-lb/acre experimental plot are replicates as no insecticide was added. Results in Table 2 show that the loss of DDT from the soil was not great from planting to harvesting of the crops. This soil was classified as Norfolk fine sandy loam with a pH of 6.0 - 6.5. It contained little organic matter but retained the insecticide well. The levels of DDT transferred to the leaves of tobacco and the beans of soybeans are considerable (Table 3). A high of 0.70 ppm total DDT in tobacco leaves and 0.65 ppm total DDT in beans does not indicate that translocation alone was responsible for the presence of the residue. The tobacco leaves were sticky and would have retained dust blown or splashed on them from the surrounding soil. Similarly, dust and splashed soil particles could have been deposited on the bean plant, especially the bean pods. During threshing much of the dust from the plant was mixed with the beans and was not blown off in the hand processing.

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Residues of DDT and Endrin in Peanuts and Soybeans Grown in Soil Containing These Pesticides[1]

H. Wyman Dorough and N. M. Randolph

ABSTRACT

Peanuts and soybeans were grown in soils which, on the day of planting, were treated with either DDT or endrin. When DDT was applied to the soils at rates of 2, 8, and 16 lb/acre, "total DDT" residues did not exceed 0.17 ppm in mature peanuts or 0.09 ppm in soybeans. Maximum endrin residues in peanuts and soybeans grown in soils treated with 1, 2, and 4 lb/acre of this insecticide were 0.1 ppm and 0.03 ppm, respectively. Although these maximum levels of residues resulted from the highest treated rates of DDT and endrin, only peanuts from the endrin plots contained residues which were significantly different as the rates increased.

Introduction

There are many methods by which food and feed crops may be contaminated with pesticides. Fortunately, contamination is usually avoided by good farm practices and by the proper use of toxic materials. Possibly the most unexpected source of contamination is from residues remaining in soil following application of a recommended pesticide. The user generally assumes that there are no hazards if the material is applied as directed. In most cases this is true; however, harmful side effects can occur.

In Texas, DDT and endrin have played an important role in the successful production of many agricultural commodities. In many areas they have been used season after season for many years. This is especially true for DDT on cotton where multiple applications of the insecticide have been common practice. Endrin has been used to a lesser extent on cotton, but prior to 1963 it was used as a routine pest control agent in the cotton-producing areas of South Texas. In addition to being used on cotton, DDT and endrin are used to control insect pests on many other crops. Thus, a large proportion of the farmland in Texas has been exposed to deposits of DDT and endrin and must be considered as a potential source of crop contamination. Soybeans and peanuts are often grown in these soils, and the level of pesticides in the soil that will result in residues in the crops grown therein is not known.

Previous studies have indicated that the translocation of DDT and endrin from the soil would account for little, if any, insecticide contamination of certain crops. Eden and Arthur (*1*) reported that, although no residues of DDT were translocated in soybeans grown in soils treated at 5, 10, and 20 lb/acre, residues of heptachlor and heptachlor epoxide were found in soybeans harvested from soils treated with heptachlor. DDT was not translocated to corn kernels harvested from plants dusted with this insecticide (*2*). However, Randolph *et al.* (*4*) found traces of DDT, toxaphene, dieldrin, and BHC residues in the oil and meal of cottonseed produced on soils treated with these insecticides. Nash (*3*) found that concentrations of endrin in soybeans grown in soils treated with endrin-C^{14} increased almost linearly with time when the entire plant was considered. He also reported that soybean shoots from plants grown in Lakeland sandy loam soil contained about twice as much endrin as found in plants grown in Hagerstown soil.

Obviously, there are many factors which attribute to the uptake of insecticides from the soil by plants. Because these factors may vary in number or in importance in different areas, it is necessary that each crop and each pesticide be evaluated under local conditions. The present research was designed to determine the magnitude of insecticide residues in peanuts and soybeans grown in our area in soils containing three different levels of DDT and endrin.

[1] From Department of Entomology, Texas A&M University, College Station, Tex. 77843.

Materials and Methods

SOIL TREATMENT

Emulsifiable concentrates of DDT and endrin were applied to the soil on May 30, 1966. Each insecticide was applied in 25 gallons of water per acre using a hand-operated stainless steel sprayer equipped with a No. 8002 fan nozzle and using a pressure of 40 psi. Each plot was four rows wide and 25 feet long. Application rates for DDT were 2, 8, and 16 lb/acre and for endrin, 1, 2, and 4 lb/acre. Each experimental plot plus a check were replicated three times. The soil plots were disced immediately following application of each insecticide.

The peanuts (Star variety) and soybeans (Lee variety) were planted on May 30, 1966, and harvested October 29, 1966. Climatological conditions during this period are shown in Table 1. Because of the low amount of precipitation, the crops were irrigated periodically starting on June 20, 1966.

TABLE 1.—*Climatological data for the experimental area during the 1966 growing season*

Month	Temperature (°F)			Rainfall (Inches)
	Average Maximum	Average Minimum	Degree Days [1]	
June	90.1	70.5	1	0.47
July	95.9	73.7	0	0.08
August	92.2	72.0	1	0
September	87.0	65.9	31	4.10
October	79.9	53.8	361	2.72

[1] Monthly degree-day totals are the sums of negative departures of average daily temperatures from 65 F.

SAMPLING

The following samples of soil and crops were taken for residue analysis:

Planting soil samples—Soil samples taken after applications of DDT and endrin and on the same day the crops were planted.

Peanuts and Soybeans—Seed samples taken from crops grown in DDT- and endrin-treated soils.

Harvest soil samples—Soil samples taken on the same day the peanuts and soybeans were harvested.

Soil samples consisting of 20 cores, 1 x 6 inches, were randomly taken from each plot and stored in a freezer until analyzed. The peanuts and soybeans were shelled by hand and held in a sealed container until time of analysis.

EXTRACTION OF DDT AND ENDRIN FROM SOIL

Twenty-five grams of soil, as collected from the field, were placed in a quart jar and 100 ml of a 1:1 hexane-acetone mixture added. The jar was sealed and shaken on a flat-bed shaker at high speed for 30 minutes. The solvent was then decanted from the soil through Whatman No. 1 filter paper into a 500-ml Erlenmeyer flask. After repeating the extraction twice, the three filtrates were combined and washed three times with 100-ml portions of distilled water. The water layers were discarded. Anhydrous sodium sulfate was added to the hexane extract to remove any remaining water. This organic extract was then concentrated to a standard volume before being analyzed.

EXTRACTION OF DDT AND ENDRIN FROM PEANUTS

Fifty grams of shelled peanuts were placed in a quart Waring blendor jar containing 100 ml of a 1:1 mixture of hexane and methanol. After homogenizing for 2 minutes, the solvent was decanted into a 500-ml flask. The peanut residue was re-homogenized in 100 ml of 4:1 hexane-methanol and the homogenates filtered through cheese cloth into the first extract. The extract was then reduced to an oily residue using a rotary evaporator. Twenty-five milliliters of hexane was added to the flask to dissolve the residues, and a 5-ml aliquot was transferred to a 125-ml separatory funnel. An additional 20 ml of hexane was added to the funnel and the hexane solution extracted with 10 ml of hexane-saturated dimethylformamide. Two additional extractions of the hexane were made using 10-ml portions of dimethylformamide. The combined dimethylformamide layers were extracted with 10 ml of fresh dimethylformamide-saturated hexane. All of the dimethylformamide extracts were combined in a 500-ml separatory funnel, and 200 ml of a 2% (w/v) aqueous sodium sulfate solution was added. The funnel was shaken vigorously for 2 minutes and allowed to stand to permit the hexane dissolved in the dimethylformamide to separate. After 20 minutes, the lower dimethylformamide layer was discarded and the hexane drained into a 10-ml graduate cylinder. An aliquot of the hexane was analyzed for residues of endrin.

EXTRACTION OF DDT AND ENDRIN FROM SOYBEANS

Fifty grams of soybeans were homogenized in 50 ml of isopropanol for 3 minutes. The blending process was stopped and 100 ml of benzene added to the mixture. Homogenization was continued for an additional 3 minutes, and the homogenate was filtered through cheese cloth and Curtin No. 7783 filter paper into a 500-ml separatory funnel. Three 50-ml portions of water were then used to wash the filtrate. Anhydrous sodium sulfate was added to the benzene extract to remove the water. This dried extract was then concentrated to an oily residue which was then taken up in 50 ml of hexane. Five milliliters of the hexane solution was added to the top of a ready column which was prepared as follows: [A slurry of alumina (acid washed, Brochman activity 1, 80-200 mesh, Fisher) in hexane was added to a chromatographic column, 13 mm x 30 cm until the alumina had settled to a height of 5 cm. The column was then washed

with 50 ml of hexane]. The insecticide was eluted from the column with 100 ml of 6% ether in hexane. Concentration of the eluate to a constant volume was accomplished before aliquots were removed for analysis.

GAS CHROMATOGRAPHY

Two Barber-Colman Series 5000 Gas Chromatographs equipped with electron capture detectors were used to quantitate residues of DDT and endrin. The operating parameters for the two instruments were as follows:

	Instrument A	*Instrument B*
Column	6′ x 4 mm	6′ x 4 mm
Support	1% SE-304 5% QF-1 on 60/80 Chromosorb G	10% DC-200 on 80/90 Anakrom ABS
Carrier Gas	N_2 at 80 ml/min	N_2 at 50 ml/min
Inlet Pressure	35 psi	26 psi
Voltage	18	21
Sensitivity Setting	1000	1000
Attenuator Setting	2	5
Temperature:		
Column	205 C	220 C
Detector	215 C	225 C
Inlet	230 C	240 C

A minimum of two injections from a single sample were made into both instruments. The identity and concentration of the pesticide residue was considered valid only when verified by the two chromatographic systems.

Results

Efficiencies of the extraction and detection methods utilized in this study were established by adding known amounts of DDT or endrin to the soil or crop samples and following the procedures given above. The substrate (soil, peanut, or soybean) was added to a blender jar, the pesticide added at the 0.10 ppm level and the percentage recovery of the material determined. Results obtained in these experiments are shown in Table 2. Since *o,p*-DDT and *p,p′*-DDE are commonly found in crops treated with DDT, these analogs were included in the study.

In all instances, 80% or more of the added insecticide survived the cleanup and extraction methods and could be detected. Relatively poor recoveries, 80-86%, were obtained from soybeans containing endrin. However, reproducibility of results was good, and the procedures were used without correcting for loss of residues. Levels of residues in the crops were expressed on a whole-nut or whole-bean basis.

Peanuts and soybeans grown in soils which had been treated at planting with DDT at three application rates contained residues of DDT when harvested (Table 3). "Total DDT" residues were greater in the peanuts than in soybeans, the levels being 0.09, 0.11, and 0.17 ppm for treatment rates of 2, 8, and 16 lb/acre, respectively. Although the residues increased somewhat as the rates of DDT were increased, the levels of residues in the peanuts were not in proportion to the amounts of residues found in the soil. The DDT residues in nuts grown in soils treated at 16 lb/acre were less than twice the magnitude of residues in nuts grown in soils treated at 2 lb/acre. Similarly, the DDT residues in soybeans were not significantly increased by application rates of DDT of 2, 8, or 16 lb/acre. Residues in soybeans grown in soils treated with these three rates of DDT were 0.03, 0.07, and 0.09 ppm, respectively. These values were less in proportion to the amount in the soil than were the values found in peanuts, suggesting that the lower uptake of DDT by soybeans is a characteristic of the plant.

TABLE 2.—*Recoveries of DDT and endrin from soil and from peanuts and soybeans*

Substrate	Pesticide	Number of Samples	Range (%)	Average (%)	Standard Deviation
Soil	*p,p′*-DDE	4	90-96	93	2
	o,p -DDT	4	94-101	97	3
	p,p′-DDT	4	86-101	93	7
	Endrin	4	87-103	92	7
Peanuts	*p,p′*-DDE	4	87-93	90	3
	o,p -DDT	4	92-102	96	5
	p,p′-DDT	4	81-94	88	6
	Endrin	4	93-99	96	3
Soybeans	*p,p′*-DDE	4	93-104	99	5
	o,p -DDT	4	90-97	93	3
	p,p′-DDT	4	82-91	85	4
	Endrin	4	80-86	83	3

Endrin applied to the soil at rates of 1, 2, and 4 lb/acre when the peanuts and soybeans were planted resulted in detectable residues in the mature seeds of both crops at the two higher application rates. Levels of residues in peanuts grown in soil treated with endrin at 2 and 4 lb/acre were .07 and .1 ppm, respectively, while the corresponding values for soybeans were .02 and .03 ppm. Residues of endrin were also detected at the .02 ppm level in peanuts grown in soils treated with 1 lb/acre.

The persistence of DDT and endrin in the soil was estimated by analyzing soil taken at the time of crop harvest. Slightly more than 5 months had elapsed between insecticide application and collection of samples when crops were harvested. These experiments showed that endrin dissipated from the soil at a faster rate than DDT. For example, it was found that 2.08 ppm endrin residues at planting (Table 4) had declined to .60 ppm at harvest, whereas total DDT residues dropped from 7.26 ppm to only 5.75 ppm during the same time interval (Table 3). A decline in the residual content of the soil was not as apparent in the check or control soils. Very little decrease was noted and might be interpreted to mean that

"weathered" residues are more persistent in the soil than those which have recently been added.

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TABLE 3.—*Levels of DDT in soils at planting and at harvest, and in peanuts and soybeans*

Rate of Application (lb/acre)	Residues in ppm											
	Planting [1]				Harvest [2]				Crops [1 3]			
	p,p'-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT
	PEANUT SOILS								PEANUTS			
0	.14	.16	.67	.97	.18	.15	.53	.86	.00	.02	.02	.04
2	.28	.33	1.73	2.34	.33	.25	.94	1.52	.04	.02	.03	.09
8	.54	.80	3.68	5.02	.72	.51	2.61	3.84	.04	.03	.04	.11
16	.39	1.31	5.56	7.26	.63	1.28	3.84	5.75	.07	.04	.07	.17
LSD (05)	.15	.11	1.09	1.16	—	—	—	—	ns	ns	ns	ns
(01)	.25	.18	1.81	1.93	—	—	—	—	ns	ns	ns	ns
CV (%)	16	6	13	11	—	—	—	—	20	—	—	8
	SOYBEAN SOILS								SOYBEANS			
0	.09	.05	1.02	1.16	.05	.08	.46	.59	.00	.00	.01	.01
2	.18	.45	1.08	1.71	.07	.23	.93	1.23	.01	.00	.02	.03
8	.33	.90	3.55	4.78	.18	.74	2.42	3.34	.01	.01	.05	.07
16	.37	1.40	6.20	8.30	.39	1.21	3.66	5.26	.02	.01	.06	.09
LSD (05)	.10	.14	.53	.99	—	—	—	—	ns	ns	ns	ns
(01)	.17	.24	.88	1.64	—	—	—	—	ns	ns	ns	ns
CV (%)	16	7	7	9	—	—	—	—	60	130	24	37

[1] Samples from three field replications for each treatment rate analyzed separately.
[2] Soils from three field replications were composited before analysis.
[3] PPM expressed on a whole-nut or whole-bean basis.

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = not significant

TABLE 4.—*Levels of endrin in soil at planting and at harvest and in peanut seeds and soybean seeds*

Rate of Application (lb/acre)	Endrin Residues in ppm					
	Peanut Soils		Peanuts [1 3]	Soybean Soils		Soybeans [1 3]
	At Planting [1]	At Harvest [2]		At Planting [1]	At Harvest [2]	
0	.15	.13	.00	.18	.12	.00
1	.32	.23	.02	.47	.17	.00
2	.90	.51	.07	1.11	.49	.02
4	2.08	.60	.10	1.49	.48	.03
LSD (05)	.45	—	.03	.23	—	ns
(01)	.75	—	.05	.38	—	ns
CV (%)	18	—	22	10	—	—

[1] Samples from three field replications for each treatment rate analyzed separately.
[2] Soils from three field replications were composited before analysis.
[3] PPM expressed on a whole-nut or whole-bean basis.

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = not signficant

Residues of Dieldrin and DDT in Peanuts and Turnip Greens Grown in Soil Containing These Compounds

Roderick W. Young[1]

ABSTRACT

Peanuts and turnip greens grown in soils treated with 2, 8, and 16 lb/acre DDT and 1, 2, and 4 lb/acre dieldrin were analyzed to determine to what extent residues present in the soils were taken up by these crops. The two crops were grown in different areas of Virginia. The data indicate that in areas with high temperatures residues in the soil tend to disappear at a faster rate, although other factors such as rainfall and soil type may also influence the removal of residues from the soil. Higher application rates resulted in higher levels of dieldrin, and DDT and its analogs DDE, o,p-DDT, and p,p' DDT in soil, peanut hulls, peanut forage, and turnip greens, while the peanuts contained only traces of the residues for all treatments.

Introduction

Pesticides, principally the chlorinated hydrocarbons, have been used extensively and found to be persistent in the environment as indicated by various monitoring programs of food crops. Although data from these programs show persistence of pesticides, little information is available from controlled experiments to determine the conditions that result in significant levels of residues in food crops. Heptachlor and its epoxide have been found in levels above the tolerance in alfalfa hay and in milk in Virginia and other southern States. In some cases use of byproducts of peanuts, such as peanut vines and hulls, as feed supplements for milk cows has been impossible because of DDT, dieldrin, heptachlor, and heptachlor epoxide contamination.

This laboratory has investigated the levels of DDT and dieldrin resulting in crops grown on soils treated with different levels of these compounds. These pesticides were selected because they represent typical chlorinated hydrocarbons used in commercial growing areas in Virginia. The products selected for study were peanuts and turnip greens. Although DDT and dieldrin may not normally be applied to the crops under study, it is necessary to determine if residues from the application of these pesticides to the area are taken up by these crops. This study represents the first controlled experiment to be conducted in Virginia to determine the application rates that will assure production of a crop having residues below the tolerance level.

To provide ideal growing conditions, the crops were grown at different locations in soils best suited for each. The peanuts were grown at the Holland Station on a sandy loam soil, and the turnip greens were grown at the Horticulture Farm at the Blacksburg Station on a silt-loam soil. A randomized block design for one crop and two pesticides was used at each location.

Materials and Methods

SOIL TREATMENT

The experimental area at each location was marked into 21 plots. There were three replicates for each of the three treatment levels of DDT and dieldrin and for the common check plot. The plots were fertilized at normal rates, plowed, and disced. DDT and dieldrin were applied to the prepared plots with a power sprayer and disced into the soil on April 20, 1966 (turnip green plots), and May 9, 1966 (peanut plots). The pesticides were applied at rates of 2, 8, and 16 lb/acre for DDT and 1, 2, and 4 lb/acre for dieldrin. The turnip greens were planted on May 1 and the peanuts on May 9.

SAMPLING

The soil samples were taken prior to the application of the pesticides, just after the incorporation of the pesti-

[1] Department of Biochemistry and Nutrition, Virginia Polytechnic Institute, Blacksburg, Va. 24061.

cides into the soil (at planting), and when the crops were harvested.

Twenty 1-inch soil cores were taken from each plot at 6-inch depths, mixed, and transported to the residue laboratory in Blacksburg. The samples were cleaned of plant material and held in the freezer until analysis.

The turnip greens (approximately 6 lb/plot) were harvested June 10, 1966, from the two middle rows of each plot (6 rows/plot) starting 4 feet from either end. The samples were taken to the laboratory, cut up with a Hobart cutter with dry ice (to prevent loss of residue due to heating and mushing), mixed, divided into three equal parts, and frozen.

The peanuts were harvested October 20, 1966, in the same manner as the turnip greens. The tops (hay) were cut from 20 plants, and the peanuts were removed from the plants with electric hedge clippers. The hedge clippers were cleaned after each sample was taken. The samples were placed in paper bags and taken to the laboratory in Blacksburg; the hay was dried at 50 C in a force draft oven, ground in a Wiley Mill, mixed, and stored in a freezer.

The peanuts were shelled by hand, and the nuts and shells were ground in a Waring blendor, mixed, and stored in the freezer at −20 C.

EXTRACTION OF DDT AND DIELDRIN FROM SOIL

In order to obtain uniform extraction of residues, the moisture content of soil samples was adjusted to 12% before extraction. All solvents used for extractions were redistilled in glass.

Soil samples weighing 50 g each were taken for analysis, adjusted to contain 12% moisture, and mixed in a 500-ml Erlenmeyer flask with just enough distilled water (approximately 10 ml) to make a slurry. Each sample was shaken vigorously for 20 minutes with 125 ml of 3:1 hexane-isopropyl alcohol on a wrist-action shaker and allowed to settle for 10 minutes. The hexane layer was decanted into a 500-ml separatory funnel. The extraction was repeated twice more as given above. The hexane extract was then washed three times with 200 ml of water, run through a 25 mm x 80 mm column of granular anhydrous Na_2SO_4, and evaporated to dryness in an air-flow evaporator, 35-40 C. The residue was taken up in 10 ml of petroleum ether and run through a 25 mm x 200 mm Florisil column with a 300-ml reservoir. The column consisted of a layer of glass wool at the bottom, covered with a ½-inch layer of granular anhydrous Na_2SO_4, with a 200-mm layer of Florisil (5% water) and topped with a ½-inch layer of granular anhydrous Na_2SO_4. The column packing was moistened with 35-40 ml of petroleum ether before the sample was added. The sample was poured onto the column and permitted to percolate through at a rate of about 5 ml/min. After two successive rinsings (5 ml each) of the beaker were poured onto the column, the sample was separated into two fractions by eluting it from the column using two solvent mixtures. Two hundred milliliters of 6% purified diethyl ether in petroleum ether was used to elute aldrin, chlordane, heptachlor, and DDT products; beakers were changed, and 200 ml of 15% purified diethyl ether in petroleum ether was used to elute endrin, dieldrin, heptachlor epoxide, and other residues from the column. Each of the above two fractions was evaporated to dryness in the air-flow evaporator and made up to the desired volume in 15-ml centrifuge tubes with hexane. The samples were then injected into the gas-liquid chromatograph at the optimum level for analysis.

EXTRACTION OF DDT AND DIELDRIN FROM PEANUTS, PEANUT HULLS, PEANUT HAY, AND TURNIP GREENS

Samples of ground peanuts or hulls, weighing 10 g each, were blended in an Omni-Mixer for 2 minutes with 15 ml of water and 45 ml of ethanol. One hundred milliliters of hexane was added to each sample, and the mixture was blended for an additional 2 minutes. The sample was than transferred to a 250-ml centrifuge tube and centrifuged for 5 minutes at approximately 1500 rpm. The hexane layer (top) was siphoned into a separatory funnel. An additional 75 ml of hexane was added to the centrifuge tube, which was stoppered, shaken vigorously, and centrifuged; the hexane layer was siphoned off as above. The hexane was washed twice with two 50-ml portions of distilled water, the water discarded, and the hexane poured through a 2-inch column (1-inch diameter) of granular anhydrous Na_2SO_4 into a 400-ml beaker, followed by a 10-ml hexane rinse. The hexane extract was evaporated just to dryness on an air-flow evaporator at 35-40 C, taken up in 10 ml of hexane, and triple partitioned with acetonitrile-hexane. The acetonitrile was collected in a 500-ml separatory funnel containing 200 ml of 2% Na_2SO_4 in water. One hundred milliliters of petroleum ether was added to the above sample, which was shaken and allowed to settle for 10 minutes. The aqueous phase was discarded and the sample washed with two additional 100-ml portions of 2% Na_2SO_4 water solution as described above. The petroleum ether layer was drained through a 50 mm x 25 mm granular anhydrous Na_2SO_4 column and evaporated to dryness. The sample was then taken up in 5 ml of hexane, 50 µl of dye (7 mg of band C violet, No. 2 dye, Pylam Products, 799 Greenwich Street, New York 14, New York) added and poured onto a silicic acid column, 25 mm x 135 mm, composed of 4 layers: glass wool, a ½-inch layer of granular anhydrous Na_2SO_4, a 1-inch layer of silicic acid mixture (2 parts silicic acid, 2 parts Super-Cel, and 1 part granular anhydrous Na_2SO_4 by weight), and topped with a ½-inch layer of granular anhydrous Na_2SO_4. The sample beaker was

rinsed twice with two 5-ml portions of hexane, allowing each rinsing to go to dryness on the column before applying the next one to the column. The sample was then eluted from the column with 0.75% nitromethane in hexane solution. When the dye had moved halfway down the column, the beaker was removed from under the column labeled A and replaced by a second beaker labeled B to obtain the second part of the eluted sample, which included the dye. After the dye was removed from the column, an additional 10 ml of the above solution was added to the column. Beakers A and B were evaporated almost to dryness, made up to the desired volume with hexane in graduated centrifuge tubes, and injected onto the gas chromatographic column.

A 10-g sample of the turnip greens was blended with 50 ml of ethanol for 2 minutes in an Omni-Mixer. One hundred milliliters of hexane was added and the sample blended for an additional 2 minutes. The sample was centrifuged at approximately 1500 rpm for 10 minutes in a 250-ml centrifuge tube and the hexane layer siphoned into a beaker. An additional 75 ml of hexane was added to the centrifuge tube which was stoppered, shaken vigorously, and centrifuged; the hexane layer was siphoned off. The sample was then evaporated to dryness on the air-flow evaporator, 35-40 C, and taken up in 10 ml of methylene chloride. To remove the pigments and some waxes, the sample was run through a No. 5 column. The No. 5 column was composed of a homogeneous mixture by weight: 8 parts granular anhydrous Na_2SO_4, 8 parts Celite 545, 2 parts Attapulgus clay, 3 parts activated carbon, and 6 parts alumina. The No. 5 column was prepared by pouring 1 inch of the mixture into a 30-ml coarse glass-fitted Buchner funnel and covering the mixture with a ⅛-inch layer of granular anhydrous Na_2SO_4. The sample was poured gently on the column and the filtrate caught in a beaker. When the sample liquid had sunk in the column, two 10-ml rinsings of the beaker were poured onto the column one at a time. An additional 40 ml of methylene chloride was required to elute the sample from the column. (The column was not allowed to go to dryness until the 40 ml of methylene chloride was used.) The sample was evaporated on the air-flow evaporator, 35-40 C, taken up in 2-3 ml of hexane and evaporated just to dryness to remove any traces of methylene chloride. The samples were taken up in hexane and stored under refrigeration in 15-ml glass-stoppered graduated centrifuge tubes until they could be analyzed in the gas chromatographic units.

GAS CHROMATOGRAPHY

A MicroTek 200 gas chromatograph with a Ni^{63} electron capture detector was used for analysis. The operating conditions were as follows:

Column:	Glass, 180 cm x 5 mm I.D., packed with 4% SE-30 + 6% QF-1 on 80-100 mesh gas Chrom Q (Applied Science Labs., State College, Pa.), preconditioned 48 hours at 230 C.
Temperatures:	Inlet 220 C Column 200 C Detector 275 C
Carrier Gas:	N_2 at 100 ml/min, tank pressures at 40 lb

Results and Discussion

Data in Table 1 show the vast differences in climate between the two experimental areas. The Blacksburg Station, with an elevation of 2500 feet, had a total of 1440 monthly degree days in the 7-month growing period while the Holland Station, 30 feet above sea level, had only 652 monthly degree days in the same period.

To calculate the recoveries as shown in Table 2, control samples were spiked with known amounts of DDT and dieldrin (1 mg of pesticide per sample). Samples were made up to the desired volume to give approximately 10 ng/μl of sample injected onto the GLC column for analysis. From four to eight analyses were determined on each level of the standard curve. The standard deviations ranged from 1 to 6.

Data show that DDT and dieldrin decreased at a faster rate at Holland Station where higher average temperatures occurred (Tables 1, 3, 4, and 7). However, rainfall and soil type may also have been factors contributing to the more rapid disappearance of residues. The results of the soil analyses (Tables 3 and 4) show such great variations, especially at the lower application levels, no conclusion can be made on the rate of residue disappearance. In some cases levels of DDT and its metabolites increased between planting and harvest periods; the values were significant at the 1% level for the planting and harvest periods with the exception of *p,p'*-DDE which was at the 5% level. No explanation for this increase can be given.

The data in Table 5 indicate that the uptake of DDT and its metabolites by peanut hulls and dried peanut forage was significant at the 1% level with the exception of *p,p'*-DDE which was only at the 5% level. The amount of residue taken up by peanuts was at or below 0.05 ppm for all treatments. The F-values for the uptake of DDT in turnip greens (Table 6) were at the 1% level for *p,p'*-DDT and total DDT while the F-values for *p,p'*-DDE and *o,p*-DDT were not significant.

Table 7 shows the results of analyses of dieldrin residues recovered from the soils and crops at the two locations. The levels resulting from the increased application rates on the peanut soils at planting time were significant only at the 5% level while the harvest results were at the 1% level. The amounts of dieldrin found in the turnip

TABLE 1.—*Climatological data for the experimental areas during the 1966 growing season*

Month	Temperature (°F)			Rainfall (Inches)
	Average Maximum	Average Minimum	Degree Days[1]	
BLACKSBURG STATION				
April	58.5	39.2	369	2.68
May	72.0	48.2	320	3.15
June	81.8	51.8	93	0.39
July	87.4	59.2	2	5.00
August	78.5	57.6	26	4.61
September	71.0	48.5	152	5.09
October	63.0	35.8	478	3.66
HOLLAND STATION				
April	72.5	46.1	217	1.39
May	73.6	49.2	151	2.81
June	82.3	58.2	34	4.13
July	85.3	67.1	0	4.55
August	84.3	65.2	0	9.37
September	77.5	53.4	23	3.00
October	71.1	44.2	227	1.58

[1] Degree-day totals are the sums of the negative departures of average daily temperature from 65 F.

TABLE 2.—*Recoveries of DDT and dieldrin from soil, from vegetable oil (for peanuts), peanut hulls, peanut dried forage, and turnip greens*

Soil or plant part	Pesticide	Number of Samples	Range (%)	Average (%)	Standard Deviation
Soil	*p,p'*-DDE	4	85- 95	90	6
	o,p-DDT	4	85-101	97	2
	p,p'-DDT	4	84-105	92	6
	Dieldrin	4	80- 92	88	5
Vegetable oil (for peanuts)	*p,p'*-DDE	8	80- 95	86	5
	o,p-DDT	8	90- 98	93	3
	p,p'-DDT	8	95- 98	96	1
	Dieldrin	8	84-101	88	6
Peanut Hulls	*p,p'*-DDE	5	85- 90	88	2
	o,p-DDT	5	86- 91	89	2
	p,p'-DDT	5	85- 92	89	5
	Dieldrin	5	82- 94	88	5
Dried Peanut Forage	*p,p'*-DDE	5	81- 90	86	3
	o,p-DDT	5	81- 92	86	4
	p,p'-DDT	5	80- 94	85	5
	Dieldrin	5	79- 89	84	4
Turnip Greens	*p,p'*-DDE	5	80- 89	85	4
	o,p-DDT	5	81- 94	88	5
	p,p'-DDT	5	75- 92	87	4
	Dieldrin	5	81- 91	86	4

TABLE 3.—*Levels of p,p'-DDE, o,p-DDT, p,p'-DDT, and total DDT in soil at planting and at harvest (peanuts grown at Holland Station)*

Rate of Application (lb/acre)	Residues in ppm							
	Planting soil				Harvest soil			
	p,p'-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT
0	0.03	0.05	0.28	0.36	0.05	0.17	0.30	0.52
2	0.15	0.47	1.05	1.67	0.16	0.32	0.62	1.10
8	0.13	0.12	1.95	2.20	0.18	0.59	1.26	2.03
16	0.14	1.59	8.48	10.21	0.33	1.14	3.97	5.44
LSD (05)	0.20	0.26	1.12	1.28	0.14	0.23	0.47	0.75
(01)	0.31	0.41	1.64	1.94	0.21	0.35	0.71	1.19
CV (%)	21	12	12	10	39	17	15	16
F-value	(1)	(1)	(1)	(1)	(2)	(1)	(1)	(1)

[1] F-value at 1% level
[2] F-value at 5% level

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

TABLE 4.—*Levels of p,p'-DDE, o,p-DDT, p,p'-DDT, and total DDT in soil at planting and at harvest (turnip greens grown at Blacksburg Station)*

Rate of Application (lb/acre)	Residues in ppm							
	Planting soil				Harvest soil			
	p,p'-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT	*p,p'*-DDE	*o,p*-DDT	*p,p'*-DDT	Total DDT
0	0.42	0.38	2.03	2.83	0.34	0.26	1.35	1.95
2	0.45	0.69	1.84	2.98	0.46	0.89	2.18	3.53
8	0.44	0.78	3.14	4.36	0.41	0.64	4.69	5.74
16	0.61	2.70	12.18	15.49	0.84	2.28	10.79	13.91
LSD (05)	0.05	0.26	2.03	2.09	0.43	0.79	3.14	4.00
(01)	0.07	0.39	3.07	3.17	0.65	1.20	4.78	6.06
CV (%)	21	24	33	28	42	39	33	32
F-value	(1)	(2)	(2)	(2)	(1)	(2)	(2)	(2)

[1] F-value at 5% level
[2] F-value at 1% level

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

TABLE 5.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT*, *and total DDT in hulls, nuts, and dried forage of peanuts*

Rate of Application (lb/acre)	Residues in ppm											
	Hulls				Nuts [1]				Dried Forage			
	p,p′-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT	*p,p′*-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT	*p,p′*-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT
0	0.06	0.11	0.34	0.51	0.01	0.01	0.01	0.01	0.07	0.18	0.37	0.62
2	0.06	0.13	0.36	0.55	0.01	0.01	0.01	0.01	0.08	0.23	0.48	0.79
8	0.10	0.19	0.78	1.07	0.05	0.05	0.05	0.05	0.08	0.26	0.58	0.92
16	0.19	1.00	2.04	3.23	0.05	0.05	0.05	0.05	0.21	0.74	1.51	2.46
LSD (05)	0.07	0.15	0.20	0.27	ns	ns	ns	ns	0.07	0.09	0.14	0.27
(01)	ns	0.23	0.30	6.39	ns	ns	ns	ns	ns	0.14	0.22	0.41
CV (%)	38	21	11	10	ns	ns	ns	ns	34	13	10	11
F-value	(2)	(3)	(3)	(3)	ns	ns	ns	ns	(2)	(3)	(3)	(3)

[1] PPM expressed on a whole-nut basis
[2] F-value at 5% level
[3] F-value at 1% level
NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = not significant

TABLE 6.—*Levels of* p,p′-*DDE*, o,p-*DDT*, p,p′-*DDT*, *and total DDT in turnip greens*

Rate of Application (lb/acre)	Residues in ppm			
	Turnip Greens			
	p,p′-DDE	*o,p*-DDT	*p,p′*-DDT	Total DDT
0	0.01	0.03	0.06	0.10
2	0.01	0.05	0.07	0.13
8	0.04	0.06	0.09	0.19
16	0.02	0.08	0.13	0.23
LSD (05)	ns	0.02	0.02	0.03
(01)	ns	0.03	0.03	0.05
CV (%)	87	18	11	10
F-Value	ns	ns	(1)	(1)

[1] F-value at 1% level
NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation
ns = not significant

green soils were significant at the 1% level. The uptake of dieldrin by the hulls, dried peanut hay, and turnip greens was at the 1% level while the uptake by the peanut was only at the 5% level. The level of dieldrin in the soils decreased about 50% between the planting and harvest period.

In Tables 3, 4, 5, 6, and 7 the CV (%) values are relatively high, from 10 to 87% with an average of 25% for 36 observations.

The relatively high CV (%) values indicate either an inadequate sampling or an unknown factor in the analysis of the materials under study. The recoveries obtained from the spiked samples were fairly constant but not as high as desirable.

The climatological data demonstrate the wide variation in conditions found in Virginia. Although factors such as rainfall and soil type may influence the disappearance of residues from the soil, the data indicate that the higher temperatures are primarily responsible for the removal of residues at a faster rate.

Residues of dieldrin and DDT and its analogs *p,p′*-DDE, *o,p*-DDT, and *p,p′*-DDT were found to increase in the soil, peanut hulls, peanut forage, and turnip greens with higher applications of the pesticides. Only trace amounts were found in the peanut meats. While levels of DDT and dieldrin found in the peanut hulls and forage and levels of dieldrin in turnip greens would be considered objectionable, amounts of both pesticides found in peanut meats were insignificant.

Acknowledgments

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TABLE 7.—*Levels of dieldrin in soil at planting and at harvest, in hulls, nuts, and dried forage of peanuts, and in turnip greens*

Rate of Application (lb/acre)	Residues in ppm							
	Soil from Peanut Plots (Holland Station)		Soil from Turnip Green Plots (Blacksburg Station)		Peanuts			Turnip Greens
	At Planting	At Harvest	At Planting	At Harvest	Hulls	Nuts [1]	Dried Hay	
0	0.03	0.04	0.03	0.06	0.09	0.01	0.26	0.02
1	0.52	0.22	0.55	0.26	0.14	0.13	0.32	0.03
2	0.80	0.34	0.86	0.61	0.22	0.23	0.45	0.04
4	1.42	0.74	2.60	1.49	0.73	0.35	0.77	0.08
LSD (05)	0.23	0.19	0.31	0.39	0.21	0.16	0.22	0.02
(01)	0.34	0.28	0.47	0.59	0.32	0.25	0.34	0.03
CV (%)	18	28	16	33	36	51	26	23
F-value	[2]	[3]	[3]	[3]	[3]	[2]	[3]	[3]

[1] PPM expressed on a whole-nut basis
[2] F-value at 5% level
[3] F-value at 1% level

NOTE: LSD = Least Significant Differences
CV = Coefficients of Variation

GENERAL SUMMARY AND CONCLUSIONS

It is apparent from the results obtained in these cooperative studies that it is very difficult to incorporate a predetermined, homogeneous mixture of a pesticide to a 6-inch depth in soil plots of the size normally employed in field experiments. Actual values varied on an average of at least ±20% of theoretical in the various experiments of this cooperative study.

In most cases the following quantities of pesticides were incorporated in the top 6 inches of soil: DDT at 2, 8, and 16 lb/acre; endrin and dieldrin at 1, 2, and 4 lb/acre. Assuming a standard soil density of 2×10^6 lb/acre in the top 6 inches, the pesticide concentrations were calculated to be: DDT—1, 4, and 8 ppm; endrin and dieldrin—0.5, 1, and 2 ppm.

Peanuts: The most significant pesticide residues detected in the entire cooperative study involving possible uptake from the soil were found to be "total DDT" and dieldrin in peanut meats, hulls, and forage. Considerably more than 1.0 ppm total DDT residue was found in the peanut hulls and dried forage, definitely constituting an excessive residue potential in milk if fed to dairy cattle for any length of time. Total DDT residues detected in peanut meats were found to be from 0.04 to 0.13 ppm (based on whole nut) taken from plants grown in the soil plots containing the highest DDT contamination. Dieldrin residues were detected at 0.35 to 0.83 ppm in peanut meats, hulls, and forage. Dieldrin residues of this magnitude would be illegal in peanut meats and also constitute a possible hazard in milk if fed to dairy cows over an extended period of time.

Soybeans: The level of total DDT in soybeans varied considerably in the three laboratories involved, ranging from less than 0.01 to 0.15 ppm in beans taken from plants grown in soils previously treated with the highest rate of this pesticide. Endrin residues from 0.02 to 0.11 ppm were found in soybeans grown in soil treated with as much as 8 lb/acre of this pesticide. It would appear from these studies that soybeans may present a possible low-level residue problem when grown in soils containing relatively high levels of such pesticides as DDT and endrin.

Turnip Greens: Total DDT residues detected in turnip tops, peeled turnip roots, or root peels were found to be less than 0.13 ppm, regardless of the level of DDT in the soil or the location of the level of DDT in the soil or the location of the experiment. Levels of endrin were found to be insignificant in the turnip tops, but 0.12 ppm was detected in the peels of the turnip roots. Turnip tops contained 0.06 ppm dieldrin when grown in soil fortified with as much as 4 lb/acre dieldrin at planting time. Although DDT residues of this magnitude pose no human health problem there is always the possibility of illegal residues appearing in milk if cows were fed this type of feed over an extended period of time. Since the tolerance for endrin and dieldrin is zero in turnip greens, any detectable residue would be illegal.

Tobacco: Insignificantly low residues of total DDT and endrin (0.02 and 0.04 ppm, respectively) were found in the green leaves of tobacco. Since tobacco is not a source of food, there appears to be no pesticide residue hazard to man under the conditions outlined for these experiments.

In general, there was satisfactory agreement between residue results determined by the coordinating centralized laboratory in Florida and those obtained by two or more cooperating laboratories on duplicate field samples. This observation was made by comparing the results obtained for the analyses of total DDT, dieldrin, and endrin in peanut meats, soybeans, turnip greens, and tobacco. Most of the differences in data obtained from two or more laboratories involving the same pesticide and crop were usually within the experimental variability that might be expected when comparing analytical data from samples selected from two or more field replications of the same experiment.

C. H. Van Middelem
Chairman, S-58 Technical Committee

See Appendix for chemical names of compounds mentioned in these papers.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Organochlorine Insecticide Residues in Starlings

William E. Martin[1]

ABSTRACT

As part of the National Pesticide Monitoring Program, starlings (Sturnus vulgaris) *were collected from 128 sampling sites throughout the contiguous United States. In most cases, three collections were made at each sampling site. Residue analyses for the persistent organochlorine insecticides were made at a private laboratory under contract with the Bureau of Sport Fisheries and Wildlife. DDT and its metabolites and dieldrin were found in all samples. Other residues, in order of frequency, were heptachlor epoxide, lindane, and BHC. Higher averaged residues of DDT and its metabolites and/or dieldrin were found in the southeastern United States; southern New Mexico, Arizona and California; eastern Utah; and the Willamette River drainage of Oregon.*

Introduction

A stated objective of the National Pesticide Monitoring Program, coordinated by the Federal Committee on Pest Control, is to develop a continuing nationwide assessment of the general levels of pesticide residues in the environment (2). This report contains data collected for the purpose of establishing a "baseline residue index" of persistent organochlorine insecticides in starlings *(Sturnus vulgaris)* as a step toward accomplishing a portion of the program goal. Starlings represent one of three substrata sampled by the Bureau of Sport Fisheries and Wildlife; the other two are waterfowl and fresh-water fish.

Starlings were selected to be sampled, because they are a terrestrial avian species found year-round throughout most of the contiguous 48 States; they are generally regarded as expendable; and their omnivorous feeding habits can be expected to reflect pesticide intake from insects, fruits, grain, crops, and miscellaneous other foods.

Data presented in this report result from three starling collections taken at approximately 128 sites during August/September and November 1967, and January/February 1968.

Sampling Sites and Procedures

Sampling sites were selected randomly. The 48 contiguous States were divided into blocks of 5 degrees latitude (24° to 49°) and longitude (64° to 124°). The five north to south rows were designated by numbers 1 through 5. The 12 each to west columns were lettered A through L. This delineated 44 sampling blocks, each containing at least a portion of one of the 48 States. Within each block, up to four sampling sites were randomly selected and numbered consecutively. (Four blocks contained no sampling sites.) Thus, each location was uniquely identified by a row number and a column letter to designate a five by five degree block and, within each block, a specific sampling site number; e.g., 1-A-1 designates a specific site near Tacoma, Wash. (see Fig. 1). There were 139 sampling sites initially selected.

Where sufficient starlings were not present to permit sampling, movement of a site within the same five degree block was permitted. In three such instances the original sites were located near block lines, making it necessary to relocate those sites in an adjoining block in order to obtain birds.

Collections were taken three times during a 15-month period:

[1] Division of Wildlife Services, Bureau of Sport Fisheries and Wildlife, U. S. Department of the Interior, Washington, D.C. 20240.

August 28 to September 7, 1967—designated S (summer)
January 29 to February 9, 1968—designated W (winter)
November 18 to November 29, 1968—designated F (fall)

Collection period designators are placed after the sampling site numbers to clearly establish when and where the collections were made; e.g., 1-A-1-W identifies the winter collection near Tacoma, Wash.

The summer collection was expected to reflect residues resulting from direct exposure to crops during growing-season pesticide treatments at a time when birds were dispersed. The winter collection was selected to represent a time when birds had flocked and when direct contact with pesticides would be minimal and might reflect a more stabilized residue level. The fall collection was chosen as a midpoint between summer and winter for consideration as a future single sampling period when it became apparent that biannual collections would not be economically feasible.

Each sample normally consisted of a "pool" of 10 birds collected at each site. Pools of less than 10 birds are indicated in Table 5. Birds were taken either by trapping or shooting. The 10 pooled birds were placed together in a polyethylene bag and frozen immediately after collection. The samples were kept frozen until laboratory analysis.

Analytical Procedures

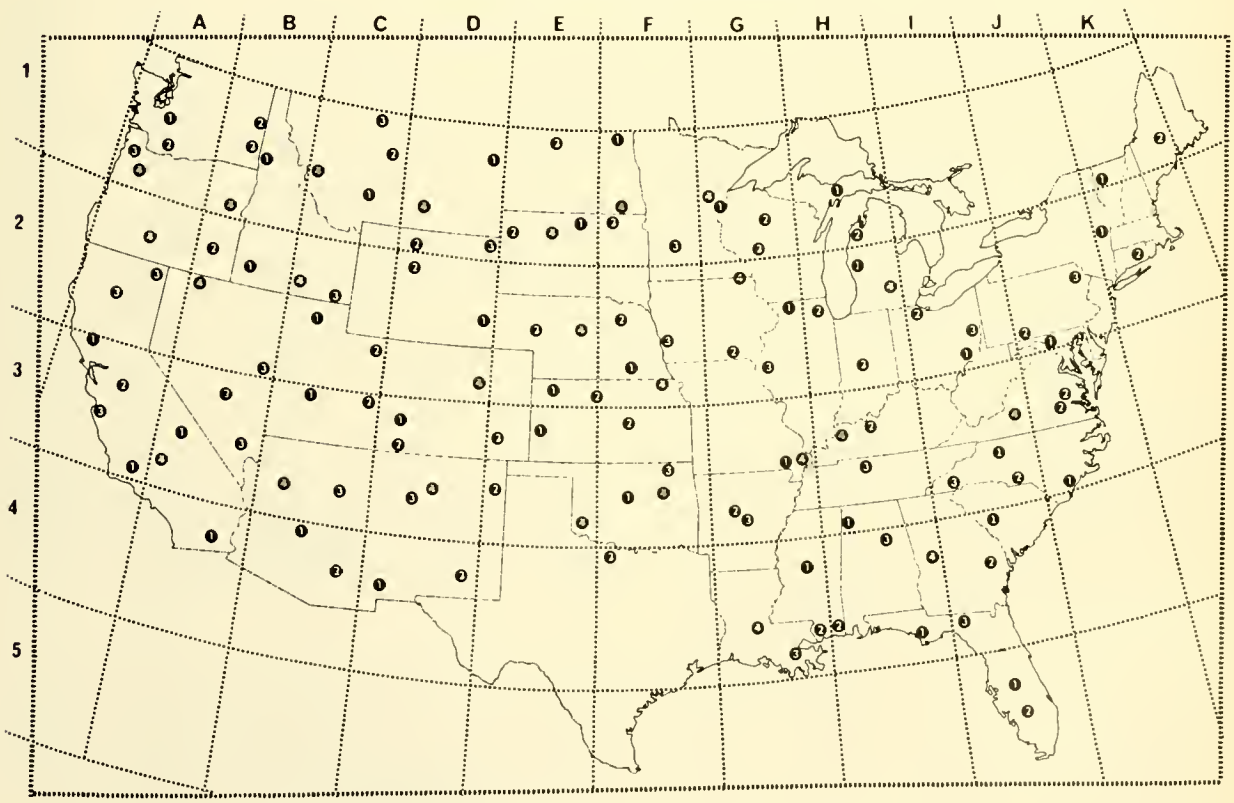
All residue analyses were done by the Wisconsin Alumni Research Foundation* under contract with the Bureau of Sport Fisheries and Wildlife.

The birds were prepared by skinning and then removing the beak, feet, and wings at the first joint out from the body. The removed parts were discarded, and analyses were made on the remaining whole body. Residues of the persistent organochlorine insecticides and their metabolites were determined by gas chromatography, and identification confirmations were made by thin layer chromatography on 5% of the total collection.

Analytical methodology followed procedures outlined in the Food and Drug Administration's *Pesticide Analytical Manual* (*1*) with minor modifications. Each 10-bird pool was ground in a Hobart food chopper. A sample weighing approximately 20 g was taken and partially de-

* Mention of this commercial laboratory is for identification only and does not constitute endorsement by the U.S. Department of the Interior.

FIGURE 1.—*Starling monitoring sites.*



hydrated in a 40 C oven for 48-72 hours. The sample was then ground with approximately 50 g of Na_2SO_4 and placed in a 33 mm x 94 mm Whatman extraction thimble and extracted 8 hours on a Soxhlet extractor using ethyl ether and petroleum ether (70:170). The extract was then concentrated to 10-15 ml on a steam bath and made to appropriate volume (50-100 ml). Cleanup was accomplished as outlined in the FDA *Pesticide Analytical Manual* Sect. 211.15. Where additional cleanup was necessary, methods in Sect. 211.14 and 211.16 were used. Determination was made using a Model 5360 Barber-Colman gas chromatograph with a Sr-90 electron capture detector. Instrument conditions were:

Column:	Glass, 4' x 4 mm, packed with 5% DC-200 on Chromport XXX 70/90 mesh	
Temperatures:	Inlet	230 C
	Column	190 - 210 C
	Detector	240 C
Carrier Gas:	N_2 at 70-90 ml/min	

Lipid content was calculated by placing an aliquot of the extract in a tared beaker, reducing it to dryness on a steam bath, placing it in a 40 C oven for 2-4 hours, and weighing the end result.

Results and Discussion

SAMPLE DESIGN AND COLLECTION

Starlings were unexpectedly difficult to collect in some areas. The sampling design did not fit availability of birds in Texas in particular, where no collections were made at eight originally selected sites. Personnel in other areas reported that, even with the latitude provided for moving sampling sites a considerable distance, birds in some locations were either not available or were so dispersed that collection of a 10-bird pool was extremely difficult.

Collections were made at 128 of the planned 139 sampling sites (92%). A total of 360 pool samples were collected of a planned 417 (86%). States and counties in which samples were taken are indicated in Table 1.

Some deviation from the designated collection periods was unavoidable; however, every effort was made to obtain these samples as close to the designated time as possible. Hopefully, a thorough analysis of variation between data from different collection periods contained in this report will guide the future selection of an appropriate single sampling period for further monitoring. Future planning will include consideration of relocating some sampling sites to areas of higher or more concentrated bird populations without losing the benefits of the present baseline data.

RESIDUE LEVELS IN STARLINGS

Results of residue analysis for persistent organochlorine insecticides are shown in Table 5. These results are reported as ppm ($\mu g/g$) wet weight of prepared, whole starling. In keeping with the general policy of the *Pesticides Monitoring Journal*, data generally are presented in an unevaluated form. Efforts were made only to summarize some data; however, it appears from this summary that a thorough evaluation of the complete data and its possible implications will be a profitable endeavor.

DDT and its metabolites and dieldrin were found in all samples taken. Frequency of occurrence at various residue levels for 126 sample sites is indicated in Table 2. Sites in which only one collection was made are not included. The summary does include data from 20 sites at which collections were made in only two of the three sampling periods. As indicated in Table 2, most of the averaged residues found for DDT and metabolites occurred in the range of $<$1.0-3.0 ppm; and for dieldrin, in the range of $<$0.1-0.3 ppm.

Sampling sites having an averaged residue level greater than 3.0 ppm DDT and metabolites and/or greater than 0.3 ppm dieldrin are shown in Table 3. Higher averaged levels of these two pesticides were found in the Southeastern United States (DDT and dieldrin); southern New Mexico, Arizona, and California (DDT); eastern Utah (DDT); and the Willamette River drainage of Oregon (dieldrin). Spots of relatively high dieldrin residues in eastern Washington and Oregon (1-B-3 and 4) and in Illinois (2-G-3) suggest a need for more refined monitoring of these areas. A spot of relatively high DDT residue in Oklahoma (3-E-4) and the higher levels found in New Mexico (4-D-3) and Louisiana (4-G-4) indicate a possibility of finding relatively high residues in Texas, since patterns of land use are similar in areas bordering these States.

Recovery of heptachlor epoxide, lindane, and BHC appears to follow more of a seasonal than geographic distribution. High frequency of occurrence also seems to correlate with the frequency of highest lipid weight found in the winter and fall collection periods, as shown in Table 4.

Thin layer chromatography was used to confirm gas chromatography findings in 21 samples. Of 107 residues identified by gas chromatography, 80 were confirmed (75.7%). Five residues not found by gas chromatography were identified by the thin layer method.

TABLE 1.—*Sampling site locations by State and county*

State	Site Number	County
Alabama	3-H-1	Marion
	4-H-3	Talladega/Calhoun
Arizona	3-C-3	Navajo
	3-C-4	Yavapi
	4-C-1	Maricopa
	4-C-2	Graham
Arkansas	3-G-2	Logan/Faulkner/Yell
	3-G-3	Lonoke
California	2-A-1	Colusa/Napa
	2-A-2	Shasta
	2-A-3	Modoc
	3-A-1	Ventura
	3-A-2	Stanislaus
	3-A-3	Monterey
	3-B-1	Inyo
	3-B-4	Kern
	4-B-1	Imperial
Colorado	2-D-4	Adams
	3-D-1	Montrose
	3-D-2	La Plata/Rio Grande
	3-E-3	Otero
Connecticut	2-K-2	New London
Florida	4-H-1	Bay
	4-I-3	Madison
	5-I-1	Polk
	5-I-2	Highlands/Hardee
Georgia	4-H-4	Upson
	4-I-2	Screven/Wayne
Idaho	1-B-1	Nezperce
	2-B-1	Owyhee
	2-C-3	Franklin
	2-C-4	Cassia/Minidoka
Illinois	2-G-1	Stephenson
	2-G-3	Adams/McDonough/Sangamba
	2-H-2	McHenry/Kane
Indiana	2-H-3	Hendricks/Tippecanoe/Hamilton/ Brown
Iowa	2-F-3	Pottawattamie
	2-G-2	Davis/Van Buren
	2-G-4	Winneshiek/Allamaker
Kansas	2-E-1	Rawlins
	2-E-2	Smith
	3-E-1	Hamilton/Kearny
	2-F-4	Nemaha
	3-F-2	Marion
Kentucky	3-H-2	Ohio
	3-H-4	McLean
Louisiana	4-G-3	Jefferson
	4-G-4	Rapides
Maine	1-K-2	Penobscot
Maryland	2-J-1	Prince Georges
Michigan	1-H-2	Leelanau/Wexford/Grand Traverse
	2-H-1	Muskegon/Kent
	2-H-4	Ingham
	1-H-1	Marquette/Mackinac/Schoolcraft
Minnesota	1-F-2	Renville
	1-G-1	Pine
	1-G-4	Aitkin
Mississippi	4-G-1	Leake
	4-G-2	Harrison
	4-H-2	Jackson
Missouri	3-G-1	Butler/Stoddard/Mississippi
	3-G-4	Bollinger/Mississippi/Stoddard
Montana	1-C-1	Meagher/Park
	1-C-2	Fergus
	1-C-3	Hill
	1-C-4	Missoula/Ravalli
	1-D-1	Richland
	1-D-4	Yellowstone
Nebraska	2-E-3	Grant/Keith
	2-E-4	Brown/Lincoln
	2-F-1	Saline/Adams/Clay
	2-F-2	Boone/Holt/Antelope
Nevada	2-B-3	White Pine
	2-B-4	Humboldt
	3-B-2	Nye
	3-B-3	Clark
New Mexico	3-D-3	Bernalillo
	3-D-4	Santa Fe/Torrance
	4-D-1	Luna
	4-D-3	Chaves
	3-E-2	Quay
New York	2-K-1	Rennselaer
North Carolina	3-I-1	Wilkes
	3-I-2	Union
	3-I-3	Macon
	3-J-1	Pender/Brunswick
North Dakota	1-E-3	Ward
	1-F-1	Cavalier/Pembina/Walsh
	1-F-4	Sargent/Dickey
Ohio	2-I-1	Noble/Washington
	2-I-2	Wood/Sanovsky
	2-I-3	Jefferson
Oklahoma	3-E-4	Greer
	3-F-1	Canadian
	3-F-3	Nowata
	3-F-4	Okmulgee
Oregon	1-A-3	Yamhill
	1-A-4	Lane
	2-A-4	Klamath
	1-B-4	Baker
	2-B-2	Harney
Pensylvania	2-J-2	Somerset
	2-J-3	Wyoming
South Carolina	4-I-1	Aiken
South Dakota	1-E-1	Edmunds/Potter
	1-E-2	Harding/Butte
	1-E-4	Corson/Stanley
	1-F-3	Brown
Tennessee	3-H-4	Davidson
Texas	4-F-3	Clay
Utah	2-C-1	Weber
	2-C-2	Uintah
	3-C-1	Sevier/Millard
	3-C-2	Grand
Vermont	1-K-1	Addison
Virginia	3-I-4	Campbell/Floyd
	3-J-2	Prince George/Rockingham/Chesterfield
	3-J-3	Henrico/Surrey/Caroline
Washington	1-A-1	Pierce
	1-A-2	Yakima
	1-B-2	Spokane
	1-B-3	Whitman
Wisconsin	1-G-2	Sawyer/Marathon/Clark
	1-G-3	Trempeleau
Wyoming	1-D-2	Big Horn
	1-D-3	Crook
	2-D-1	Goshen
	2-D-2	Washakie

TABLE 2.—*Distribution of average residues of DDT and metabolites and dieldrin by frequency of occurrence in different quantitative ranges*

DDT and Metabolites		Dieldrin	
Range (ppm)	Frequency of Occurrence (sites)	Range (ppm)	Frequency of Occurrence (sites)
≤1.0	76	≤0.1	65
>1.0 and ≤2.0	25	>0.1 and ≤0.2	40
>2.0 and ≤3.0	12	>0.2 and ≤0.3	11
>3.0 and ≤4.0	3	>0.3 and ≤0.4	2
>4.0 and ≤5.0	3	>0.4 and ≤0.5	3
>5.0 and ≤10.0	5	>0.5 and ≤1.0	4
>10.0 and ≤15.0	0	>1.0 and ≤1.5	1
>15.0 and ≤20.0	1	>1.5 and ≤2.0	0
>20.0 and ≤25.0	1	>2.0 and ≤2.5	0
	126		126

TABLE 3.—*Average residue levels for DDT and metabolites >3.0 ppm and for dieldrin >0.3 ppm*

Sampling Site	DDT and Metabolites	Dieldrin
1-A-3		0.528
1-A-4		0.492
1-B-3		0.587
1-B-4		0.418
3-B-4	4.376	
4-B-1	3.450	
2-C-2	9.551	
3-C-2	3.163	
4-C-1	23.902	
4-D-3	19.680	
3-E-4	4.948	
2-G-3		0.657
3-G-1		0.403
3-G-3	5.950	0.317
4-G-1	8.128	
4-G-2		0.970
4-G-4	4.220	
4-H-4	3.510	
3-I-1		1.385
4-I-1	5.483	
4-I-3	5.668	
3-J-1		0.333

TABLE 4.—*Frequency of occurrence of residues of heptachlor epoxide, lindane, and BHC by collection period*

Collection Period	Frequency of Residues by Site [1]			Occurrence of Highest Lipid Wgt. by Site
	Heptachlor epoxide	Lindane	BHC	
S	43	4	0	1
F	31	17	4	25
W	94	84	45	80
Total				106

[1] 106 sites sampled three times each.

Conclusions

The basic conclusion is that DDT, dieldrin, and other persistent organochlorine insecticides are consistently found as residues in starlings, making them a valid substrate for monitoring. With modification of study design, monitoring of starlings should provide data on the relative status of pesticide residues in a terrestrial avian species. Experience gained in this study should be valuable for establishing areas in which starlings can be used in monitoring for other environmental contaminants, e.g., arsenic, mercury, lead, and synthetic industrial chemicals.

Data are presented for the purpose of establishing general baseline residue levels to develop a long term monitoring program. Specific residue figures are as valid, reliable, and accurate as the study design and methods described for collection and analysis allow. Use of specific residue figures out of context or beyond the limitations of this study could be misleading.

TABLE 5.—*Pesticide residue levels in starlings*

Identification Number	Wet Weight (grams)	Lipid Weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
1-A-1-S	19.99	0.310	0.220	0.024	0.048	0.292	0.190	0.065	—	—
-W	20.05	0.510	0.670	0.014	0.031	0.715	0.400	0.110	0.011	—
-F	19.74	0.294	0.500	<0.015	<0.015	0.530	0.080	—	—	—
Average	19.92	0.371	0.463	0.018	0.031	0.512	0.223			
1-A-2-S	20.00	0.346	3.590	<0.013	0.044	3.647	0.039	—	—	—
-W	20.02	0.633	2.070	0.033	<0.013	2.116	0.110	<0.010	0.320	—
-F	19.51	0.548	1.680	<0.015	0.021	1.716	0.190	—	—	—
Average	19.85	0.509	2.448	0.020	0.026	2.493	0.113			
1-A-3-S	20.00	0.645	0.490	<0.013	<0.013	0.516	0.034	—	—	—
-W	19.99	1.878	3.320	0.390	0.066	3.776	0.930	0.210	—	—
-F	20.66	1.329	2.720	0.030	0.039	2.789	0.620	—	—	—
Average	20.22	1.284	2.177	0.144	0.039	2.360	0.528			
1-A-4-S	20.00	0.652	0.580	<0.013	<0.013	0.606	0.017	—	—	—
-W	19.99	1.170	2.660	0.120	0.056	2.836	0.940	0.060	—	—
-F	20.31	0.759	0.990	0.190	0.089	1.269	0.520	—	—	—
Average	20.10	0.858	1.410	0.108	0.053	1.570	0.492			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet weight (grams)	Lipid weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
2-A-1-S	20.00	0.471	1.190	<0.013	0.013	1.216	<0.010	—	—	—
-W	20.06	1.666	2.260	<0.013	0.026	2.299	0.190	0.027	0.027	—
-F	19.99	0.834	1.280	<0.015	0.016	1.311	0.056	—	—	—
Average	20.02	0.990	1.577	0.013	0.018	1.608	0.085			
2-A-2-S	20.00	0.525	0.360	<0.013	<0.013	0.386	>0.010	—	—	—
W-	20.04	0.978	0.370	<0.013	0.016	0.399	0.021	—	0.031	—
-F	20.20	0.851	0.200	<0.015	0.020	0.235	0.043	—	—	—
Average	20.08	0.785	0.310	0.013	0.016	0.340	0.025			
2-A-3-S	20.00	0.763	0.760	<0.013	<0.013	0.786	<0.010	—	—	—
-W	19.94	2.240	0.710	<0.013	0.038	0.761	0.380	0.120	0.033	—
-F	20.01	1.928	0.550	<0.015	<0.015	0.580	0.022	—	—	—
Average	19.98	1.644	0.674	0.013	0.023	0.709	0.137			
2-A-4-S	20.00	0.725	0.130	<0.013	<0.013	0.156	<0.010	0.029	—	—
-W	19.99	1.786	0.460	<0.013	<0.013	0.486	<0.010	0.016	0.014	—
-F	20.43	1.281	0.410	<0.015	<0.015	0.440	0.037	—	—	—
Average	20.14	1.264	0.333	0.013	0.013	0.360	0.019			
3-A-1-S	20.00	0.615	2.270	<0.013	0.094	2.377	0.033	—	—	—
-W	20.00	3.085	1.310	<0.013	0.026	1.349	0.025	0.018	<0.010	—
-F	20.15	0.833	1.940	<0.015	0.028	1.983	0.031	—	—	—
Average	20.05	1.511	1.840	0.013	0.049	1.903	0.030			
3-A-2-S	20.00	0.662	2.930	<0.013	0.025	2.968	0.075	—	—	—
-W	19.97	1.164	1.560	<0.013	0.026	1.599	0.120	0.014	0.014	—
-F	19.72	1.235	1.380	<0.015	0.035	1.430	0.063	—	—	—
Average	19.90	1.020	1.957	0.013	0.029	1.999	0.086			
3-A-3-S	20.00	0.664	4.450	<0.013	0.015	4.478	0.055	—	—	—
-W	20.00	1.188	2.730	0.019	0.031	2.780	0.190	0.016	0.015	—
-F	20.26	1.041	1.540	0.015	0.017	1.572	0.074	—	—	—
Average	20.09	0.964	2.907	0.016	0.021	2.943	0.106			
1-B-1-S	20.00	0.655	1.430	0.013	0.020	1.463	0.014	—	—	—
-W	19.97	1.522	0.680	0.031	<0.013	0.724	0.280	0.012	1.250	—
-F	19.69	1.262	0.350	0.033	0.160	0.543	0.051	—	—	—
Average	19.89	1.146	0.820	0.026	0.064	0.910	0.115			
1-B-2-S	20.00	0.648	0.310	0.013	0.034	0.357	<0.010	—	—	—
-W	20.02	1.859	1.220	0.018	0.049	1.287	0.580	0.045	1.170	—
-F	20.11	1.841	0.250	<0.015	0.016	0.281	0.120	—	—	—
Average	20.04	1.449	0.593	0.015	0.033	0.602	0.237			
1-B-3-S	20.00	0.888	1.810	<0.013	0.014	1.837	<0.010	—	—	—
-W	19.99	1.309	0.680	<0.013	<0.013	0.706	1.090	0.063	0.260	—
-F	20.21	1.082	0.700	<0.015	<0.015	0.730	0.660	—	—	—
Average	20.07	1.093	1.063	0.013	0.014	1.091	0.587			
1-B-4-S	20.00	0.644	0.460	<0.013	0.034	0.507	0.038	—	—	—
-W	20.00	2.712	0.730	0.052	0.038	0.820	1.180	0.053	—	—
-F	20.06	1.996	0.370	0.031	0.056	0.457	0.035	—	—	—
Average	20.02	1.784	0.520	0.032	0.043	0.595	0.418			
2-B-1-S	20.00	0.705	1.340	<0.013	0.014	1.367	0.019	—	—	—
-W	20.03	1.256	1.000	<0.013	0.014	1.027	0.062	0.051	0.019	—
-F	20.31	1.379	0.850	0.022	0.038	0.910	0.170	—	—	0.007
Average	20.11	1.113	1.063	0.016	0.022	1.101	0.084			
2-B-2-S	20.00	0.826	4.730	0.019	<0.013	4.762	0.018	—	—	—
-W	20.02	1.931	0.460	<0.013	0.017	0.490	0.037	0.017	0.025	—
-F	20.35	0.944	0.770	<0.015	0.015	0.800	0.041	—	0.020	—
Average	20.12	1.234	1.987	0.015	0.015	2.017	0.032			
2-B-3-S	20.00	0.753	0.210	0.076	0.150	0.436	0.069	0.028	—	—
-W	19.95	1.363	0.460	0.034	0.047	0.541	0.250	0.030	0.012	—
-F	20.74	1.563	0.420	<0.015	0.015	0.450	0.066	—	—	—
Average	20.23	1.226	0.363	0.042	0.071	0.476	0.122			
2-B-4-S	20.00	0.783	0.440	<0.013	<0.013	0.466	0.023	0.054	—	—
-W	20.07	1.205	0.800	<0.013	0.014	0.827	0.037	0.017	0.016	—
-F	19.86	1.425	0.710	0.019	0.036	0.765	0.088	—	—	—
Average	19.98	1.138	0.650	0.015	0.021	0.686	0.049			
3-B-1-S	20.00	0.691	0.820	<0.013	0.014	0.847	<0.010	—	—	—
-W	20.02	1.686	1.560	<0.013	0.025	1.598	0.250	0.022	0.020	—
-F	19.40	1.632	0.320	<0.015	0.016	0.351	0.090	—	—	—
Average	19.80	1.336	0.900	0.013	0.018	0.932	0.117			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet weight (grams)	Lipid weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
3-B-2-S	20.00	0.780	0.470	0.013	0.036	0.519	0.018	—	—	—
-W	19.99	1.328	0.170	<0.013	0.016	0.199	0.150	0.100	0.010	—
-F	19.80	1.503	0.540	<0.015	0.016	0.571	0.140	—	—	—
Average	19.93	1.204	0.393	0.013	0.023	0.430	0.103			
3-B-3-S	20.00	0.719	1.860	0.068	0.560	2.488	0.210	—	—	—
-W	19.97	0.860	0.660	0.067	0.200	0.927	0.110	0.100	0.016	—
-F	21.03	1.208	0.390	0.065	0.120	0.575	0.071	0.090	0.012	0.012
Average	20.00	0.929	0.970	0.067	0.293	1.330	0.130			
3-B-4-S	20.00	0.834	3.240	<0.013	<0.013	3.266	0.038	—	—	—
-W	20.00	1.229	7.730	0.047	0.034	7.811	0.370	0.063	0.016	—
-F	20.12	0.971	2.020	<0.015	<0.015	2.050	0.075	—	—	—
Average	20.04	1.011	4.330	0.025	0.021	4.376	0.161			
4-B-1-S	20.00	0.785	6.740	<0.013	0.036	6.789	0.160	—	—	—
-W	20.00	1.040	0.480	0.016	0.026	0.522	0.300	0.036	<0.010	—
-F	20.44	1.072	3.010	<0.015	<0.015	3.040	0.042	0.045	—	—
Average	20.15	0.966	3.410	0.014	0.026	3.450	0.167			
1-C-1-S	20.00	0.610	0.110	<0.013	<0.013	0.136	0.019	—	—	—
-W	20.08	1.874	0.230	<0.013	0.014	0.257	<0.010	0.022	<0.010	—
-F	21.33	2.328	0.250	0.050	0.031	0.331	<0.015	0.130	—	—
Average	20.47	1.604	0.197	0.025	0.019	0.241	0.015			
1-C-2-S	20.00	0.624	0.100	<0.013	0.016	0.129	0.063	—	—	—
-W	20.02	1.867	0.150	0.036	0.051	0.237	0.250	0.049	0.011	—
-F	19.47	2.319	0.150	0.059	0.063	0.272	<0.015	0.066	—	—
Average	19.83	1.603	0.133	0.036	0.043	0.213	0.109			
1-C-3-S	20.00	0.805	0.046	—	—	0.046	<0.010	—	—	—
-W	20.00	1.576	0.068	<0.013	<0.013	0.094	0.180	—	<0.010	—
Average	20.00	1.190	0.057	0.013	0.013	0.070	0.095			
1-C-4-S	20.00	0.661	0.420	<0.013	<0.013	0.446	<0.010	—	—	—
-W	20.01	1.439	1.430	<0.013	0.025	1.468	0.050	0.018	0.020	—
Average	20.00	1.050	0.925	0.013	0.019	0.957	0.030			
2-C-1-S	20.00	0.649	1.290	0.026	0.095	1.411	0.014	—	—	—
-W	20.38	1.982	0.810	0.019	0.048	0.877	<0.010	0.036	0.016	<0.010
-F	20.01	1.550	0.390	<0.015	0.031	0.436	<0.015	—	—	—
Average	20.13	1.394	0.830	0.020	0.058	0.908	0.013			
2-C-2-S	20.00	0.777	28.000	—	<0.013	28.000	0.022	—	—	—
-W	20.01	1.631	0.410	0.028	<0.013	0.451	0.240	0.066	<0.010	<0.010
-F	20.02	2.195	0.150	<0.015	0.025	0.190	0.031	0.056	—	—
Average	20.01	1.534	9.520	0.020	0.019	9.551	0.098			
2-C-3-S	20.00	0.613	0.290	<0.013	0.020	0.323	<0.010	—	—	—
-W	20.02	1.405	3.120	<0.013	0.026	3.159	0.069	0.040	0.031	—
-F	20.13	1.104	0.380	<0.015	0.022	0.417	0.042	0.020	—	—
Average	20.05	1.041	1.263	0.013	0.023	1.300	0.040			
2-C-4-S	20.00	0.295	0.590	<0.013	0.020	0.623	0.017	—	—	—
-W	20.05	1.598	6.650	0.120	0.160	6.930	0.350	0.026	<0.010	—
-F	20.28	1.805	0.550	<0.015	0.018	0.583	0.031	—	—	—
Average	20.11	1.233	2.596	0.046	0.066	2.710	0.133			
3-C-1-S	20.00	0.338	3.170	<0.013	<0.013	3.196	0.210	—	—	—
-W	20.01	1.049	0.710	<0.013	0.022	0.745	0.062	0.020	0.011	<0.010
-F	20.00	1.263	0.750	0.016	0.023	0.789	0.045	0.017	—	—
Average	20.00	0.883	1.543	0.014	0.019	1.577	0.106			
3-C-2-S	20.00	0.262	7.580	<0.013	0.018	7.611	0.031	—	—	—
-W	20.20	1.229	1.530	0.015	<0.013	1.558	0.280	0.310	0.020	—
-F	20.00	1.654	0.260	0.021	0.039	0.320	0.042	—	—	0.019
Average	20.07	1.048	3.123	0.016	0.023	3.163	0.177			
3-C-3-S	20.00	0.283	0.960	0.013	0.046	1.019	<0.010	—	—	—
-W	20.15	0.986	0.600	0.019	0.014	0.633	0.047	0.025	<0.010	<0.010
Average	20.07	0.635	0.780	0.016	0.030	0.826	0.029			
3-C-4-S	20.00	0.273	1.440	<0.013	0.016	1.469	0.130	—	—	—
-W	20.09	1.212	4.360	0.028	0.022	4.410	0.250	0.026	<0.010	<0.010
-F	20.01	0.704	0.086	<0.015	0.027	0.128	0.016	<0.015	—	—
Average	20.07	0.396	1.962	0.019	0.022	2.002	0.132			
4-C-1-S	20.00	0.301	26.600	0.110	0.054	26.764	0.081	—	—	—
-W	20.02	0.865	23.408	0.056	0.026	23.482	0.140	0.014	<0.010	—
[illegible]	20.01	0.701	21.408	—	0.062	21.462	0.097	—	—	—
[illegible]	20.01	0.622	23.800	0.083	0.047	23.902	0.106			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet Weight (grams)	Lipid Weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
4-C-2-S	20.00	0.360	2.240	<0.013	0.016	2.269	0.015	—	—	—
-W	19.99	0.833	2.110	0.038	0.015	2.163	0.066	0.010	<0.010	—
-F	20.03	0.741	1.610	<0.015	0.029	1.654	<0.015	—	—	—
Average	20.01	0.644	1.987	0.022	0.020	2.028	0.032			
1-D-1-S	20.00	0.309	0.049	<0.013	0.014	0.076	<0.010	—	—	—
-W	20.01	1.577	0.058	<0.013	<0.013	0.084	<0.010	—	<0.010	—
-F	20.21	1.104	0.062	<0.015	0.015	0.092	0.019	—	—	—
Average	20.08	0.997	0.057	0.013	0.014	0.084	0.013			
1-D-2-S	20.00	0.381	0.270	<0.013	0.029	0.312	0.021	—	—	—
-W	19.98	1.794	0.059	<0.013	<0.013	0.085	<0.010	0.024	<0.010	<0.010
-F	20.02	1.049	0.047	<0.015	0.016	0.078	0.017	—	—	—
Average	20.00	0.940	0.126	0.013	0.019	0.158	0.016			
1-D-3-S	20.03	0.689	0.031	<0.013	0.014	0.058	<0.010	—	—	—
-W [6]	20.38	1.425	0.480	<0.013	0.031	0.524	<0.010	0.022	0.011	<0.010
-F [1]	19.99	1.775	0.130	—	0.025	0.155	<0.015	—	—	—
Average	20.13	1.296	0.214	0.013	0.023	0.245	0.012			
1-D-4-S	20.00	0.349	0.200	<0.013	<0.013	0.226	0.140	—	—	—
-W	19.97	0.869	0.051	<0.013	<0.013	0.077	0.018	<0.010	<0.010	—
-F	20.22	1.247	0.110	<0.015	<0.015	0.140	0.059	—	—	—
Average	20.06	0.822	0.120	0.013	0.013	0.147	0.072			
2-D-1-S	20.06	0.719	0.450	<0.013	0.020	0.483	0.026	—	—	—
-W	20.28	1.190	0.480	<0.013	0.022	0.515	0.046	0.020	0.010	<0.010
-F	20.02	1.074	0.230	<0.015	0.025	0.270	0.016	—	—	—
Average	20.12	0.994	0.387	0.013	0.022	0.422	0.029			
2-D-2-S	20.00	0.793	0.150	0.033	0.068	0.251	0.096	—	—	—
-W	19.99	1.391	0.096	<0.013	0.018	0.127	0.190	0.043	0.010	<0.010
-F	20.00	1.089	0.050	—	0.025	0.075	0.048	0.032	—	—
Average	20.00	1.091	0.099	0.023	0.034	0.151	0.111			
2-D-4-S	20.00	3.411	1.130	<0.013	0.046	1.189	0.081	—	—	—
-W	20.12	1.867	0.470	<0.013	0.026	0.509	0.270	0.013	<0.010	<0.010
-F	20.00	1.143	0.420	<0.015	0.038	0.473	0.031	0.041	—	—
Average	20.04	2.140	0.673	0.013	0.037	0.724	0.127			
3-D-1-S	20.00	0.574	2.170	<0.013	<0.013	2.196	0.050	—	—	—
-W	19.91	0.961	1.260	<0.013	0.013	1.286	0.041	0.011	<0.010	<0.010
-F	20.02	1.564	0.180	<0.015	0.019	0.214	0.057	<0.015	—	0.008
Average	19.98	1.033	1.203	0.013	0.014	1.232	0.049			
3-D-2-W	19.44	1.316	0.860	0.019	0.018	0.897	0.220	0.013	0.011	<0.010
3-D-3-S	20.00	0.805	0.900	0.098	0.014	1.012	0.030	—	—	—
-W	19.96	0.960	0.580	0.490	1.250	2.320	0.200	0.063	<0.010	<0.010
-F	20.03	0.930	0.350	<0.015	0.027	0.392	0.019	<0.015	—	—
Average	20.00	0.898	0.610	0.201	0.430	1.241	0.083			
3-D-4-S	20.00	0.432	2.090	<0.013	0.019	2.122	0.030	0.014	—	—
-W	19.96	1.648	0.690	<0.013	0.018	0.721	0.390	0.021	<0.010	0.024
-F	20.01	0.940	0.420	<0.015	0.031	0.461	0.028	<0.015	—	—
Average	19.99	1.070	1.067	0.013	0.023	1.101	0.149			
4-D-1-W	20.16	1.129	3.260	0.019	<0.013	3.292	0.047	0.011	<0.010	<0.010
-F	19.92	0.832	0.530	<0.015	0.023	0.568	0.022	—	—	—
Average	20.04	0.980	1.895	0.017	0.018	1.930	0.034			
4-D-3-S	20.00	0.767	0.098	<0.013	<0.013	0.124	0.017	0.016	—	—
-W	19.89	0.845	48.200	0.046	<0.013	48.259	0.069	0.016	0.031	0.033
-F [4]	20.05	0.956	10.600	—	0.028	10.628	0.052	0.024	—	—
Average	19.98	0.856	19.632	0.030	0.018	19.680	0.046			
1-E-1-W	20.04	1.829	0.190	<0.013	0.014	0.217	<0.010	<0.010	0.012	0.019
-F	20.03	1.521	0.200	<0.015	0.031	0.246	<0.015	—	—	—
Average	20.02	1.675	0.195	<0.014	0.022	0.231	0.012			
1-E-2-S	20.00	0.579	0.120	<0.013	<0.013	0.146	0.065	0.014	—	—
-W	20.08	1.568	0.130	—	0.026	0.156	0.130	0.016	<0.010	0.020
-F	19.97	1.385	0.060	<0.015	<0.015	0.090	<0.015	—	—	—
Average	20.02	1.177	0.103	0.013	0.018	0.131	0.070			
1-E-3-S	20.00	0.623	2.150	1.490	0.034	3.674	0.011	—	—	—
-W	20.49	1.729	0.470	0.071	0.040	0.581	0.410	0.085	0.018	0.016
-F	20.03	1.358	0.086	0.015	0.027	0.128	<0.015	—	—	—
Average	20.17	1.237	0.902	0.525	0.034	1.461	0.145			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet weight (grams)	Lipid weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
1-I-4-W [6]	20.06	1.451	0.280	0.022	0.034	0.336	0.240	0.081	<0.010	<0.010
-F	20.15	1.285	3.570	<0.015	0.027	3.612	0.020	—	—	—
Average	20.10	1.368	1.925	0.018	0.030	1.974	0.080			
2-E-1-S [5]	20.00	0.566	0.240	<0.013	<0.013	0.266	0.017	—	—	—
-W	20.03	1.659	0.160	<0.013	<0.013	0.186	0.310	<0.010	<0.010	<0.010
-F	20.01	1.136	0.100	<0.015	0.031	0.146	<0.015	—	—	—
Average	20.01	1.120	0.167	0.013	0.019	0.199	0.114			
2-F-2-S	20.00	0.553	0.330	<0.013	0.014	0.357	0.031	—	0.029	—
-W	19.99	1.468	0.810	<0.013	0.013	0.836	0.230	0.160	0.013	0.010
-F	20.00	1.155	0.240	<0.015	0.046	0.301	<0.015	<0.015	—	—
Average	20.00	1.058	0.460	0.013	0.024	0.505	0.092			
2-F-3-S	20.00	0.829	0.400	<0.013	0.026	0.439	0.280	0.320	—	—
-W	20.03	1.572	0.490	0.085	0.064	0.639	0.550	0.022	0.011	0.016
-F	20.20	1.185	0.180	<0.015	<0.015	0.210	<0.015	—	—	—
Average	20.01	1.195	0.357	0.038	0.035	0.429	0.281			
2-E-4-S	20.00	0.769	0.530	0.021	0.015	0.566	0.230	0.130	<0.010	—
-W [7]	20.01	1.139	0.043	<0.013	0.022	0.078	<0.010	<0.010	<0.010	<0.010
-F	20.15	0.910	0.055	<0.015	<0.015	0.085	<0.015	—	—	—
Average	20.05	0.939	0.209	0.016	0.017	0.243	0.085			
3-E-1-S	20.00	0.521	0.110	<0.013	<0.013	0.136	0.075	<0.010	—	—
-W	20.06	1.655	0.160	<0.013	<0.013	0.186	0.210	0.024	0.014	<0.010
-F	20.01	1.093	0.210	0.016	0.120	0.346	0.019	—	—	—
Average	20.02	0.090	0.160	0.014	0.045	0.222	0.102			
3-E-2-W	20.15	1.148	1.230	<0.013	0.014	1.257	0.200	—	0.016	<0.010
-F	20.01	0.887	0.560	0.023	0.031	0.614	0.099	<0.015	—	—
Average	20.08	1.017	0.895	0.018	0.022	0.935	0.150			
3-E-3-S	20.00	0.650	0.650	<0.013	0.015	0.678	0.035	<0.010	0.035	—
-W	20.29	1.396	0.330	0.081	0.230	0.641	0.160	0.023	0.015	<0.010
-F	20.01	1.231	0.340	<0.015	0.044	0.399	0.041	<0.015	—	—
Average	20.10	1.092	0.440	0.036	0.096	0.572	0.079			
3-E-4-S	20.00	0.705	6.090	<0.013	0.015	6.118	0.089	—	—	—
-W	20.00	1.131	6.980	0.088	0.017	7.085	0.088	<0.010	<0.010	<0.010
-F	20.04	0.464	1.590	<0.015	0.037	1.642	0.031	<0.015	—	—
Average	20.01	0.767	4.886	0.038	0.023	4.948	0.069			
1-F-1-S	20.00	0.508	0.270	<0.013	<0.013	0.296	<0.010	—	—	—
-W	19.84	2.005	0.260	<0.013	<0.013	0.286	0.470	0.012	—	0.022
-F	20.23	2.163	0.560	0.027	0.022	0.609	0.015	—	—	—
Average	20.02	1.559	0.363	0.017	0.015	0.397	0.165			
1-F-2-S	20.00	0.608	0.093	<0.013	0.018	0.124	0.061	—	<0.010	—
-W [8]	19.98	2.069	0.140	<0.013	0.022	0.175	0.550	0.120	0.018	0.016
-F	20.29	1.880	0.220	0.017	0.069	0.306	0.140	—	—	—
Average	20.09	1.519	0.151	0.014	0.036	0.202	0.250			
1-F-3-S	20.00	0.407	0.043	<0.013	<0.013	0.069	0.014	—	—	—
-W	20.09	2.381	0.150	0.016	—	0.166	0.560	0.012	<0.010	0.016
-F	20.02	1.326	0.140	<0.015	0.024	0.179	<0.015	—	—	—
Average	20.04	1.371	0.111	0.014	0.018	0.138	0.196			
1-F-4-S	20.00	0.618	0.048	<0.013	<0.013	0.074	<0.013	—	—	—
-F	20.06	2.199	0.098	<0.015	<0.015	0.128	<0.015	—	—	—
Average	20.03	1.408	0.073	0.014	0.014	0.101	0.014			
2-F-1-S	20.00	0.651	0.420	<0.013	<0.013	0.446	0.027	—	—	—
-W	20.11	1.753	0.210	<0.013	0.013	0.236	0.180	0.019	0.011	0.012
-F	20.05	1.169	0.100	<0.015	<0.015	0.130	0.046	—	—	—
Average	20.05	1.191	0.243	0.013	0.013	0.270	0.084			
2-F-2-S	20.00	0.786	0.034	<0.013	<0.013	0.060	<0.010	—	—	—
-W	20.02	0.917	0.150	<0.013	<0.013	0.176	0.330	0.028	<0.010	<0.010
-F	20.04	1.313	0.130	<0.015	0.024	0.169	0.067	—	—	—
Average	20.02	1.005	0.105	0.013	0.016	0.135	0.136			
2-F-3-S	20.02	1.415	0.310	<0.013	0.037	0.360	0.035	<0.013	—	—
-W	19.99	2.013	0.440	<0.013	0.018	0.471	0.270	0.110	<0.010	<0.010
-F	19.72	1.451	0.210	0.018	0.041	0.269	0.110	—	—	—
Average	19.93	1.626	0.320	0.014	0.032	0.367	0.138			
2-F-4-S [9]	20.00	0.652	0.280	<0.013	<0.013	0.306	0.025	—	—	—
-W	20.46	1.950	0.190	<0.013	0.021	0.224	0.320	0.024	0.011	<0.010
-F	20.03	1.443	0.660	<0.015	0.039	0.714	0.056	0.048	—	—
Average	20.16	1.348	0.377	0.013	0.024	0.415	0.134			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet Weight (grams)	Lipid Weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
3-F-1-S	20.00	0.921	0.690	<0.013	0.026	0.729	0.018	—	—	—
-W	20.28	2.563	0.280	<0.013	0.026	0.319	<0.010	0.025	0.017	<0.010
-F	20.00	0.862	0.280	<0.015	0.044	0.339	0.041	—	—	—
Average	20.09	1.449	0.417	0.013	0.032	0.462	0.023			
3-F-2-S	20.00	0.606	0.700	<0.013	0.029	0.742	0.034	—	—	—
-W	20.07	1.655	0.210	<0.013	<0.013	0.236	0.310	0.018	0.031	0.027
-F	20.03	0.827	0.410	—	0.019	0.429	0.062	0.120	—	—
Average	20.03	1.029	0.440	0.013	0.020	0.469	0.135			
3-F-3-S [7]	20.00	0.799	0.710	<0.013	0.031	0.754	<0.010	—	—	—
-W	20.00	2.270	0.540	0.019	<0.013	0.572	<0.010	0.036	<0.010	<0.010
-F	20.04	1.085	0.440	<0.015	0.044	0.499	0.017	—	—	—
Average	20.01	1.385	0.592	0.016	0.029	0.609	0.012			
3-F-4-S	20.00	0.772	1.340	<0.013	0.019	1.372	<0.010	—	—	—
-W	19.33	2.236	2.030	0.016	0.019	2.065	0.410	0.018	0.021	0.011
-F	20.01	0.988	0.470	—	0.025	0.495	<0.015	—	—	—
Average	19.78	1.332	1.280	0.014	0.020	1.312	0.145			
4-F-3-W	20.00	1.580	0.640	<0.013	0.014	0.667	0.034	0.013	<0.010	<0.010
1-G-1-S	20.00	0.683	0.340	<0.013	0.014	0.367	0.150	—	—	—
-W [5]	19.98	2.058	0.160	0.019	0.031	0.210	0.360	0.023	0.015	—
-F	20.05	2.091	0.210	0.015	0.024	0.249	<0.015	—	—	—
Average	20.01	1.611	0.237	0.016	0.023	0.275	0.175			
1-G-2-S [7]	20.00	0.802	0.140	<0.013	<0.013	0.166	0.013	—	—	—
-W [3]	20.15	1.884	0.720	0.099	0.071	0.890	0.370	0.029	0.017	—
-F	20.01	2.184	0.200	0.019	0.024	0.243	<0.015	—	—	—
Average	20.05	1.610	0.353	0.044	0.036	0.433	0.133			
1-G-3-S	20.00	0.536	0.092	<0.013	<0.013	0.118	<0.010	—	—	—
-W [6]	20.09	2.641	0.380	0.019	0.031	0.430	<0.010	0.024	0.018	<0.010
-F	20.21	1.929	0.230	0.019	0.054	0.303	0.023	—	—	—
Average	20.10	1.702	0.234	0.017	0.033	0.284	0.013			
1-G-4-S [6]	20.02	0.665	0.037	<0.013	<0.013	0.063	<0.010	0.042	—	—
-F	20.01	1.965	0.270	0.019	0.031	0.320	0.054	—	—	—
Average	20.01	1.315	0.153	0.016	0.022	0.192	0.032			
2-G-1-S	20.00	0.812	0.690	<0.013	<0.013	0.716	<0.010	<0.013	—	—
-W	19.90	1.891	0.870	0.015	<0.013	0.898	0.580	0.082	0.033	0.013
-F	20.27	1.533	0.350	0.015	0.039	0.404	0.250	0.170	—	—
Average	20.06	1.412	0.637	0.013	0.020	0.673	0.280			
2-G-2-W	20.02	1.511	0.240	<0.013	<0.013	0.266	0.430	0.087	0.015	0.015
-F	20.07	1.760	0.180	<0.015	0.031	0.216	0.081	0.030	—	—
Average	20.04	1.635	0.210	0.014	0.022	0.241	0.256			
2-G-3-S	20.00	0.798	0.250	<0.013	<0.013	0.276	0.280	0.044	—	—
-W	19.88	2.018	0.550	0.016	0.029	0.595	0.940	0.200	0.018	0.014
-F	20.23	1.525	0.630	0.027	0.069	0.726	0.750	0.033	—	—
Average	20.04	1.447	0.477	0.019	0.037	0.532	0.657			
2-G-4-W	19.98	2.191	0.120	0.025	0.018	0.163	<0.010	0.031	0.013	0.011
-F	20.04	1.225	0.120	0.015	0.031	0.166	0.054	0.046	0.046	—
Average	20.01	1.708	0.120	0.020	0.024	0.164	0.032			
3-G-1-S	20.01	0.539	0.390	<0.013	0.013	0.416	0.350	0.016	—	—
-W	20.00	2.086	1.390	0.049	0.018	1.457	0.590	0.049	0.340	—
-F	20.03	1.063	0.640	0.024	0.039	0.703	0.270	0.081	—	—
Average	20.01	1.229	0.806	0.029	0.023	0.858	0.403			
3-G-2-S	20.02	0.868	1.560	<0.013	0.021	1.584	<0.010	—	—	—
-W	20.02	1.849	0.780	0.026	0.039	0.845	0.240	—	—	—
-F	20.32	0.866	0.420	<0.015	0.016	0.451	0.039	—	—	—
Average	20.12	1.194	0.920	0.017	0.025	0.952	0.096			
3-G-3-S	20.01	0.777	4.840	0.062	0.031	4.933	0.310	0.042	—	—
-W	20.02	1.704	11.000	0.260	0.044	11.304	0.540	—	—	0.044
-F	19.57	0.932	1.550	0.024	0.040	1.614	0.100	—	0.009	—
Average	19.87	1.138	5.796	0.115	0.038	5.950	0.317			
3-G-4-S	20.00	0.850	0.480	<0.013	0.013	0.506	0.020	0.016	—	—
-W	20.04	4.498	1.350	0.097	0.034	1.481	0.550	0.070	0.016	<0.010
-F	20.01	0.919	0.270	0.015	0.024	0.309	0.051	0.034	—	—
Average	20.01	2.089	0.700	0.042	0.024	0.765	0.207			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet weight (grams)	Lipid weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
4-G-1-S	20.01	0.722	9.760	0.060	<0.025	9.845	0.090	0.031	—	—
-W	20.05	1.298	8.420	0.044	0.026	8.490	0.180	—	—	—
-F	20.15	0.698	6.010	0.023	0.015	6.048	0.067	—	—	—
Average	20.07	0.906	8.063	0.042	0.022	8.128	0.112			
4-G-2-W	20.00	0.902	1.180	0.017	0.034	1.231	0.670	0.130	<0.010	—
-F	20.65	0.614	1.820	<0.015	0.085	1.930	1.270	—	—	—
Average	20.32	0.758	1.500	0.016	0.054	1.580	0.970			
4-G-3-W	20.01	1.609	0.370	0.024	0.034	0.428	0.260	0.120	0.011	—
-F	21.27	0.748	1.380	0.018	0.036	1.434	0.026	0.120	0.011	—
Average	20.14	1.178	0.875	0.021	0.035	0.931	0.143			
4-G-4-S	20.00	0.789	2.580	<0.025	<0.025	2.630	<0.013	—	—	—
-W	20.04	1.766	6.640	0.049	0.031	6.720	0.350	0.094	—	0.017
-F	21.40	1.144	3.180	0.027	0.043	3.250	0.043	—	0.006	—
Average	20.48	1.233	4.133	0.034	0.033	4.200	0.135			
1-H-1-S	20.00	0.584	0.120	<0.025	<0.025	0.170	<0.013	—	—	—
-W	19.98	0.941	1.800	0.063	0.250	2.113	0.170	0.053	—	—
Average	19.99	0.762	0.960	0.044	0.137	1.141	0.091			
1-H-2-S	20.00	0.603	0.360	<0.013	<0.013	0.386	<0.013	<0.013	—	—
-W [7]	20.12	1.339	0.930	0.026	0.078	1.034	0.190	0.039	0.010	<0.010
-F	20.02	2.939	1.210	0.036	0.110	1.356	<0.015	0.045	0.022	—
Average	20.05	1.627	0.833	0.025	0.067	0.925	0.073			
2-H-1-S	20.01	0.717	0.610	<0.025	<0.025	0.660	0.025	0.025	—	—
-W	20.02	1.859	1.610	0.230	0.890	2.730	0.390	0.098	—	—
-F	20.02	1.372	0.790	0.062	0.190	1.042	0.022	0.066	0.024	—
Average	20.02	1.316	1.003	0.106	0.368	1.477	0.096			
2-H-2-S	20.00	0.682	0.750	0.025	0.054	0.829	0.078	0.063	—	—
-W	19.98	2.064	1.420	0.064	0.140	1.624	0.470	0.088	0.015	<0.010
-F	20.02	1.093	0.770	0.019	0.055	0.844	0.074	0.066	<0.010	—
Average	20.00	1.280	0.980	0.036	0.083	1.099	0.208			
2-H-3-S	20.01	0.428	0.140	<0.013	0.019	0.172	0.047	0.025	—	—
-W	20.02	1.219	1.370	0.021	0.026	1.417	0.050	0.032	—	—
-F	20.02	1.223	0.570	0.022	0.039	0.631	0.071	0.045	<0.010	—
Average	20.02	0.957	0.693	0.018	0.028	0.740	0.056			
2-H-4-S	20.02	0.831	0.720	<0.013	<0.013	0.746	0.013	0.036	—	—
-W	20.03	1.735	1.370	0.022	0.075	1.467	0.260	0.024	0.012	—
-F	20.06	1.274	0.850	0.015	0.039	0.904	0.028	0.030	<0.010	—
Average	20.04	1.280	0.980	0.016	0.042	1.039	0.100			
3-H-1-S	20.01	0.607	2.220	<0.013	0.019	2.242	0.066	0.140	—	—
-W	20.01	1.307	2.190	0.076	0.034	2.300	0.170	0.120	—	—
-F	19.58	1.092	1.750	0.018	0.057	1.835	0.050	—	—	—
Average	19.87	1.002	2.053	0.036	0.037	2.125	0.095			
3-H-2-S	20.01	0.931	0.230	<0.013	<0.013	0.256	<0.013	<0.013	—	—
-W	19.99	1.773	0.320	<0.013	0.016	0.349	<0.010	—	—	—
-F	19.67	1.024	0.260	0.029	0.042	0.331	0.140	—	—	—
Average	19.89	1.242	0.270	0.018	0.024	0.312	0.054			
3-H-3-S	20.01	0.830	0.470	0.034	0.100	0.604	0.081	0.031	—	—
-W	20.00	1.821	0.620	0.031	0.044	0.695	0.560	0.130	—	—
-F	19.70	0.859	0.300	0.038	0.056	0.394	0.093	—	0.006	—
Average	19.90	1.170	0.463	0.034	0.067	0.564	0.245			
3-H-4-S	20.01	0.787	0.250	<0.013	<0.013	0.276	0.025	—	—	—
-W	20.07	2.042	6.950	0.100	0.280	7.330	<0.010	0.034	—	—
-F	20.54	1.422	0.880	0.024	0.040	0.944	0.028	—	—	—
Average	20.21	1.417	2.693	0.046	0.111	2.850	0.021			
4-H-1-S	20.01	0.870	1.690	<0.025	0.031	1.746	0.190	0.310	—	—
-W	20.00	0.975	0.810	0.018	0.022	0.850	0.130	0.190	—	—
-F	20.31	0.878	1.050	<0.015	0.048	1.113	0.084	—	—	—
Average	20.11	0.908	1.183	0.019	0.034	1.236	0.135			
4-H-2-S [8]	20.00	0.771	0.940	0.031	0.210	1.181	0.480	0.440	—	—
-F	20.75	1.156	0.640	0.018	0.052	0.710	0.087	—	<0.005	—
Average	20.37	0.963	0.790	0.024	0.131	0.945	0.283			
4-H-3-S	20.01	0.786	1.640	0.091	0.200	1.931	0.031	0.047	—	—
-W [9]	20.00	1.258	3.280	0.059	0.100	3.439	0.180	—	—	—
-F	20.58	0.916	1.340	0.021	0.310	1.671	0.068	—	—	—
Average	20.20	0.986	2.086	0.057	0.203	2.347	0.093			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification number	Wet Weight (grams)	Lipid Weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
4-H-4-S	20.00	0.695	1.210	<0.025	0.038	1.273	0.160	0.031	—	—
-W	20.01	1.292	5.150	0.044	0.050	5.244	0.062	—	—	—
-F	20.27	1.136	3.970	<0.015	0.028	4.013	0.097	—	—	—
Average	20.09	1.041	3.443	0.028	0.039	3.510	0.106			
2-I-1-S	20.01	0.850	0.110	<0.013	0.014	0.137	0.025	<0.025	—	—
-W	20.07	1.620	0.370	0.073	0.085	0.528	0.140	0.019	<0.010	—
-F	20.02	1.287	0.230	0.022	0.031	0.283	0.016	0.016	<0.010	—
Average	20.03	1.252	0.237	0.036	0.043	0.316	0.060			
2-I-2-S	20.00	0.406	2.220	0.031	0.028	2.279	0.076	0.016	—	—
-W	19.99	2.310	0.630	0.052	0.080	0.762	0.460	0.057	—	—
-F	20.03	0.901	0.300	0.022	0.062	0.384	0.045	0.030	<0.010	—
Average	20.01	1.206	1.050	0.035	0.057	1.141	0.193			
2-I-3-S	20.01	0.735	0.210	<0.013	<0.013	0.236	0.025	0.027	—	—
-W	20.07	1.606	0.150	0.021	0.026	0.197	0.260	0.039	<0.010	—
-F	20.01	1.171	0.320	0.022	0.039	0.381	0.016	0.016	<0.010	—
Average	20.03	1.171	0.227	0.019	0.026	0.271	0.100			
3-I-1-S	20.01	0.553	0.800	<0.025	0.037	0.862	2.730	—	—	—
-F	20.42	0.999	0.270	<0.015	0.021	0.306	0.045	—	—	—
Average	20.21	0.776	0.535	0.020	0.029	0.584	1.385			
3-I-2-S	20.01	0.703	1.480	<0.025	0.069	1.574	0.550	—	—	—
-F	20.78	0.851	1.120	<0.015	0.055	1.190	0.034	—	—	—
Average	20.39	0.777	1.300	0.020	0.062	1.382	0.242			
3-I-3-S	20.01	0.493	0.470	<0.025	<0.025	0.520	<0.013	—	—	—
-W	20.00	0.962	0.760	<0.013	0.019	0.792	<0.010	0.030	—	—
-F	19.79	0.800	0.200	<0.015	<0.015	0.230	0.047	—	—	—
Average	19.93	0.752	0.476	0.017	0.019	0.514	0.023			
3-I-4-S	20.01	0.527	0.310	<0.013	<0.014	0.337	<0.013	0.044	—	—
-W	20.01	1.639	0.150	<0.013	0.016	0.179	<0.010	0.067	<0.010	<0.010
-F	20.05	0.849	0.700	<0.015	0.029	0.744	0.150	—	—	—
Average	20.02	1.005	0.386	0.013	0.021	0.420	0.024			
4-I-1-S	20.01	0.711	7.030	0.027	0.031	7.088	0.052	0.028	—	—
-W	20.03	1.329	3.900	0.023	0.031	3.954	0.062	0.027	0.017	0.012
-F	20.98	0.927	5.360	<0.015	0.027	5.407	0.057	—	—	—
Average	20.34	0.989	5.430	0.022	0.030	5.483	0.057			
4-I-2-S	20.01	0.957	4.690	0.047	0.016	4.753	0.028	0.016	—	—
-W	20.01	1.094	0.760	<0.013	0.044	0.817	0.030	—	0.011	—
-F	19.95	1.039	1.270	<0.015	0.041	1.326	0.022	—	—	—
Average	19.99	1.030	2.240	0.025	0.034	2.299	0.027			
4-I-3-W	20.00	0.959	3.600	<0.013	0.034	3.647	0.038	0.039	0.015	—
-F	19.95	0.676	7.640	<0.015	0.035	7.690	0.073	—	—	—
Average	19.98	0.817	5.620	0.014	0.034	5.668	0.055			
5-I-1-S [7]	20.02	0.729	2.150	0.028	0.350	2.528	0.081	0.039	—	—
-W	19.98	0.995	2.260	0.100	0.031	2.391	<0.010	0.040	<0.010	—
-F	19.83	0.855	1.340	<0.015	0.063	1.418	0.170	—	—	—
Average	19.94	0.860	1.917	0.048	0.148	2.112	0.087			
5-I-2-S [2]	20.00	0.902	0.460	<0.013	0.013	0.486	0.019	0.044	—	—
-W	20.01	0.658	0.780	<0.013	0.130	0.923	0.035	—	—	—
-F	19.96	0.977	1.470	<0.015	0.071	1.556	0.120	—	—	—
Average	19.99	0.846	0.903	0.013	0.071	0.988	0.058			
2-J-1-W	20.01	1.236	0.760	0.051	0.120	0.931	0.360	0.170	—	—
-F	19.22	0.631	0.260	<0.015	0.100	0.375	0.073	—	—	—
Average	19.61	0.933	0.510	0.033	0.110	0.653	0.144			
2-J-2-S	20.00	0.670	0.530	<0.013	0.016	0.559	0.016	0.016	—	—
-W	20.01	1.614	0.760	0.021	0.037	0.818	<0.010	—	—	—
-F	19.90	1.352	0.230	0.019	0.031	0.280	0.024	—	—	—
Average	19.97	1.212	0.507	0.018	0.028	0.552	0.017			
2-J-3-S	20.01	0.877	0.500	<0.013	0.026	0.539	0.039	—	—	—
-W	19.98	1.697	0.760	0.014	0.025	0.799	0.460	0.099	0.012	—
-F	21.23	1.619	1.140	0.018	0.052	1.210	0.082	—	<0.005	—
Average	20.07	1.398	0.800	0.015	0.034	0.849	0.194			
3-J-1-S	20.01	0.784	2.160	<0.013	0.019	2.192	0.110	0.053	—	—
-W	19.99	1.414	1.590	0.017	0.046	1.653	0.770	0.046	<0.010	—
-F	19.98	1.077	0.510	0.041	0.046	0.597	0.120	—	—	—
Average	19.99	1.092	1.420	0.024	0.037	1.481	0.333			

TABLE 5.—*Pesticide residue levels in starlings*—Continued

Identification Number	Wet Weight (grams)	Lipid Weight (grams)	Residues in ppm (μg/g)							
			DDE	DDD	DDT	DDT and Metabolites	Dieldrin	Heptachlor epoxide	Lindane	BHC
3-J-2-S	20.01	0.692	0.410	<0.013	0.019	0.442	0.014	0.041	—	—
-W	20.07	2.212	0.150	0.190	0.290	0.630	<0.010	0.069	0.016	<0.010
-F	19.88	1.242	0.540	<0.015	0.025	0.580	0.021	—	—	—
Average	19.99	1.382	0.367	0.073	0.111	0.551	0.015			
3-J-3-S	20.01	0.571	0.250	<0.013	0.013	0.286	0.014	0.062	—	—
-W	20.01	2.039	0.160	<0.013	0.019	0.192	<0.010	0.110	<0.010	<0.010
-F	19.38	0.570	0.580	<0.015	0.088	0.581	0.140	—	—	—
Average	20.80	1.060	0.330	0.013	0.040	0.353	0.055			
1-K-1-S [4]	20.01	0.635	0.150	<0.013	<0.013	<0.176	<0.010	0.016	—	—
-F	19.33	2.094	0.290	0.024	0.065	0.379	0.033	—	0.005	—
Average	19.67	1.364	0.220	<0.018	0.039	0.277	0.021			
1-K-2-S	20.01	0.636	0.310	<0.013	<0.013	0.336	<0.010	<0.013	—	—
-W	20.00	1.390	0.300	0.026	0.059	0.385	<0.010	—	0.013	—
-F	19.89	2.071	0.420	0.043	0.082	0.545	0.054	—	0.006	—
Average	19.97	1.366	0.343	0.027	0.051	0.422	0.025			
2-K-1-S [6]	20.00	0.526	0.440	<0.013	0.019	0.472	0.010	0.026	—	—
-W	19.99	1.783	0.560	0.025	0.075	0.660	0.010	0.096	—	—
-F	20.78	2.247	0.850	0.041	0.067	0.958	0.015	—	0.075	—
Average	20.26	1.519	0.617	0.026	0.054	0.697	0.012			
2-K-2-S	20.02	0.493	0.620	<0.013	0.028	0.661	0.010	—	—	—
-W	20.02	1.631	0.410	0.016	0.029	0.455	<0.010	0.027	0.012	—
-F	19.91	1.158	0.290	<0.015	0.044	0.349	0.019	—	0.005	—
Average	19.98	1.094	0.440	0.015	0.034	0.488	0.013			

[1] 3 birds.
[2] 4 birds.
[3] 5 birds.
[4] 6 birds.
[5] 7 birds.
[6] 8 birds.
[7] 9 birds.
[8] 12 birds.

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See Appendix for chemical names of compounds mentioned in this paper.

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Nationwide Residues of Organochlorine Pesticides in Wings of Mallards and Black Ducks

Robert G. Heath[1]

ABSTRACT

Nationwide monitoring of organochlorine pesticides in wings of more than 24,000 mallards and black ducks bagged during the 1965 and 1966 hunting seasons showed DDE to be the predominant residue, followed in order by DDT, DDD, dieldrin, and heptachlor epoxide. Residues were generally highest in wings from the Atlantic and Pacific Flyways, and lowest in the Central Flyway. DDE was reported for every State and was notably high in wings from New Jersey, Massachusetts, Connecticut, Rhode Island, New York, Pennsylvania, Alabama, California, and Utah. Dieldrin residues were prevalent in wings from Arkansas, Texas, Utah, California, and several States in the Atlantic Flyway.

Introduction

Nationwide monitoring of organochlorine pesticides in wings of wild mallards and black ducks was initiated by the Bureau of Sport Fisheries and Wildlife in late 1965 as a segment of the National Pesticide Monitoring Program. Findings reported here are based on chemical analyses of wings from more than 24,000 ducks bagged during the 1965 and 1966 hunting seasons. The data provide base readings from which future trends in residue levels can be measured, and they permit geographic comparisons of residues. Wing monitoring is scheduled hereafter at 2- to 3-year intervals. A full description of the Bureau's monitoring commitments has been given by Johnson, Carver, and Dustman (*5*).

The decision to monitor mallard and black duck wings was based on several factors: (a) The combined range of the two species covers the continental United States, the mallard being relatively abundant in all but the Eastern States where the black duck predominates; (b) Wings were readily available as a byproduct of an established nationwide survey of waterfowl productivity wherein each fall cooperating hunters mail the Bureau tens of thousands of duck wings for biological examination; and (c) Dindal and Peterle (*3*), using DDT, ring-labeled with chlorine-36, to study DDT dispersion in a marsh ecosystem, found highly significant correlations in 104 captive mallards and scaup ducks between DDT residues in wings and those in breast skin, kidney, breast muscle, uropygial gland, adrenal gland, pancreas, brain, gonads, liver, and thyroid. The average level in the wings was essentially equal to the median level in the above body parts; it was approximately twice that in breast muscle and about one-eighth that in the uropgial gland.

The monitoring methodology was successfully tested in early 1965 with wings from mallards and black ducks taken in New York and Pennsylvania during the fall of 1964, as reported by Heath and Prouty (*4*). Findings based on analyses of 36 "pools" of wings, each pool composed of 25 defeathered wings chopped and blended into an homogenate, indicated that organochlorine residues were present in all pools and that levels of DDE tended to be higher in wings of adults than in those of immature birds. Wings were analyzed in pools rather than individually to increase the precision of estimates of *average* residue levels from a fixed number of analyses. Variability of residue levels among replicated pools indicated that pool size should not be reduced from 25 wings.

Methods

Wings from the 1965 and 1966 hunting seasons were mailed by selected hunters throughout the United States to one of four regional collecting points and held in frozen storage for examination in early 1966 and 1967. During examination mallard wings from most States and

[1] Patuxent Wildlife Research Center, Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, Laurel, Md. 20810.

black duck wings from Eastern States were first segregated into State groups of immature and adult wings, and each group was then systematically sorted into pools of 25 wings each. A random sample of these pools, roughly proportional in number to a State's mallard or black duck harvest, was selected for pesticidal analysis. Pools not selected were discarded. Each selected pool was enclosed with an individually numbered tag in a plastic bag, packaged in dry ice, and shipped to the analytical laboratory. Records associating pool number with pool description (State and age) were retained by the investigators; thus, pools were identified only by number during chemical analysis.

Wings were analyzed in 1966 by the Hazleton Laboratories, Falls Church, Va., and in 1967 by the Wisconsin Alumni Research Foundation, Madison, Wis. Laboratory selection was by bid. Prior to selection both laboratories satisfactorily analyzed material treated with known amounts of the pesticides expected in monitoring; recovery rates generally exceeded 84%.

Preparatory to analysis, wings were trimmed of flight feathers with a band saw and chopped and blended into 25-wing homogenates with a Hobart food cutter. Residues were measured to a limit of sensitivity of 0.05 ppm (wet weight). Analytical procedures (*1*) were as follows:

Hazleton Laboratories. A 20-g aliquot of the homogenate was dried by grinding with anhydrous sodium sulfate; extracted by shaking and centrifuging three times with petroleum ether (one 100-ml portion and two 50-ml portions); cleaned by acetonitrile-petroleum ether partitioning and elution through a Florisil column in two fractions, the first containing 6% ethyl ether and 94% petroleum ether, and the second containing 15% ethyl ether and 85% petroleum ether. The two fractions were analyzed separately by electron capture gas chromatography using a Chromalab Model A-110 gas chromatograph with a radium-226 detector (Glowall Corporation). The operating parameters were:

Column:	Glass, 6′ x ¼″ OD, packed with 10% DC-200 on 100/120 mesh Gaschrom Q
Carrier Gas:	N_2 at 120 ml/min
Temperatures:	Inlet 225 C Column 205 C Detector 250 C

WARF Institute. A 40-g aliquot of the homogenate was air-dried 96-120 hours at 40 C; extracted in Soxhlet for 8 hours with 70 ml ethyl ether and 170 ml petroleum ether; cleaned and separated by elution through a Florisil column in two fractions, the first containing 5% ethyl ether and 95% petroleum ether, and the second containing 15% ethyl ether and 85% petroleum ether. The two fractions were analyzed separately by electron capture gas chromatography using a Barber-Colman Pesticide Analyzer Model 5360 with a strontium-90 detector. The operating parameters were:

Column:	Glass, 4′ x 4 mm OD, packed with 5% DC-200 on 70/90 mesh Chromport XXX
Carrier Gas:	N_2 at 70-90 ml/min
Temperatures:	Inlet 230 C Column 200 C Detector 240 C

Table 1 lists, by State of collection, the average residue levels of DDE, DDT, DDD, and dieldrin in the wings of adult and immature birds in late 1965 and 1966. The 2-year range in levels and the number of pools in each set are also presented. Table 2 lists the 2-year average levels and standard errors of these chemicals, derived by combining both years' data. The 2-year averages are intended as reference points for detection of trends in future levels. Other chemicals were detected in no more than trace amounts and are discussed in text only.

States are listed in both tables in north-to-south order within each of the four continental waterfowl flyways: Atlantic, Mississippi, Central, and Pacific. Geographic rather than alphabetical listing was used to facilitate geographic comparisons. States were stratified (*2*) by flyways since a majority of mallards and black ducks remain within a given flyway during migration. Essentially, then, we are monitoring flyway as well as State populations, the wings from each State being a sample of that part of a flyway population frequenting the State during its hunting season. Table 3 gives the 2-year flyway means and standard errors for the subject pesticides, derived by weighting (*2*) each State statistic by the estimated total bag in that State of the respective species and age group.

Results

DDE proved to be the predominant residue throughout the survey. Measurable amounts of this stable metabolite of DDT were reported in nearly all pools of adult wings and in most pools of immature wings. Residues of DDE were generally from two to five times higher than those of DDT which, in turn, tended to be higher than those of DDD. Dieldrin was found in wings from more than 30 States, although aldrin, which converts to dieldrin, was not detected. Heptachlor epoxide was reported at trace levels from one-third of the States; heptachlor was not detected. Lindane was found in wings from only two States, and endrin was not detected.

Pronounced State and regional differences in average levels of DDE were apparent. Some of the highest levels were encountered in adult black ducks from a contigu-

ous group of Atlantic Flyway States that included New Hampshire, Massachusetts, Rhode Island, Connecticut, New York, Pennsylvania, New Jersey, and Delaware. DDE averages ranged from 0.88 ppm in New Hampshire to 2.10 ppm in New Jersey. Mallards from the three States sampled in this group—New York, Pennsylvania, and New Jersey—exhibited similarly high residues. Elsewhere, only Alabama, California, and Utah showed comparable levels of DDE. Adult mallards from Alabama had the highest average level in the survey (2.17 ppm), adult black ducks from New Jersey the second highest level (2.10 ppm), and adult mallards from California the second highest level among mallards (1.45 ppm).

In contrast, DDE averaged below 0.14 ppm in both adult and immature mallards from Illinois and Missouri in the Mississippi Flyway and from North Dakota, South Dakota, eastern Montana, Nebraska, Kansas, and Oklahoma in the Central Flyway.

DDT and DDD residues in a given set of pools tended to parallel those of DDE, but at lower levels. Nationwide, DDT exceeded 0.50 ppm in only five sets of pools (immature black ducks from New Jersey were high at 1.72 ppm DDT), and DDD averages failed to exceed 0.50 ppm.

Comparison of average DDE residues in flyway populations (Table 3) shows that levels in black ducks, in the Atlantic Flyway, were the highest in the survey. Among mallards, averages were similarly high in the Atlantic and Pacific Flyways, and about one-third as high in the Mississippi and one-fourth as high in the Central as in either coastal flyway. Average levels of DDT and DDD were highest in the Atlantic Flyway and were usually too low to be quantified in the Mississippi and Central Flyways.

Dieldrin was detected most frequently in the Atlantic Flyway in both mallards and black ducks: wings from only Maine and the combined States of Georgia and Florida failed to show residues. Dieldrin also was prevalent in wings from Arkansas, Texas, Utah, and California; otherwise it was either undetected or present in little more than trace amounts. State averages rarely exceeded 0.25 ppm.

Residue levels of DDE tended to be higher in wings of adults than in those of immature birds, a difference not apparent with DDT, DDD, or dieldrin. This phenomenon, first observed in trial monitoring (*4*), suggests that equilibrium between chemical storage and elimination, in at least the wing, is less readily attained with DDE than with the other chemicals.

Heptachlor epoxide was reported in at least one pool from each of 16 States, nine of them in the Atlantic Flyway. Residues were most prevalent in both mallard and black duck wings from New York and Connecticut where levels averaged about 0.06 ppm. Traces of heptachlor epoxide were also recorded for New Hampshire, Massachusetts, Rhode Island, Pennsylvania, Maryland, Virginia, and North Carolina in the Atlanta Flyway; Ohio, Wisconsin, and Iowa in the Mississippi Flyway; Nebraska in the Central Flyway; and Washington, Oregon, and western Montana in the Pacific Flyway.

Lindane at trace levels was recorded in wings from Washington and Michigan; otherwise, it was not reported. Lindane is recommended by the U. S. Department of Agriculture primarily to control aphids in apple and pear orchards (*7*), which could explain the residues associated with these two orchard States.

Analysis of the ground wing material showed that the homogenates contained approximately 11% lipid material and 36% moisture. (Precise percentages of moisture and lipid content for specific sets of pools are available upon request.)

Discussion

While agricultural uses of pesticides probably accounted for much of the residue material detected in wing monitoring, other sources of contamination should be considered. Sewage from population centers may contribute significant amounts of pesticides to some aquatic environments. Similarly, industrial effluents from pesticide manufacturing plants have been known to contain substantial residues of pesticides lost in chemical processing. It is well known that in some States, vast quantities of DDT have been applied to coastal marshes over the past 2 decades in mosquito control programs. The practice has been especially notable in those States extending from Massachusetts to Delaware.

Because of persistence and a tendency to accumulate in many organisms, substantial residues of DDT, and especially the metabolite DDE, are now present in marsh soils and fauna. Woodwell, Wurster, and Isaaeson (*6*) report that residues of DDT and its metabolites averaged more than 13 lb/acre in the soil of an extensive salt marsh on the south shore of Long Island, and that within the marsh, residues increased with trophic levels from 0.04 ppm in plankton to 75 ppm in a ring-billed gull. DDE residues were exceptionally high in wings of both mallards and black ducks from New Jersey, where for many years coastal marshes have been treated with repeated aerial applications of DDT. A number of States are now using chemicals less persistent than DDT in mosquito control work.

Summary and Conclusions

The findings from 2 years of monitoring indicate that duck wings can function as sensitive detectors of environ-

mental DDT and the metabolites DDE and DDD, as well as dieldrin and undoubtedly other organochlorine compounds. Despite some variation due to sampling and analytical processes, residue statistics were sufficiently precise to show differences in levels between flyways, various groups of States, and frequently between individual States. In some instances adjacent States, undoubtedly frequented by many of the same ducks, showed clear differences in residue levels, suggesting rapid assimilation of pesticides into the wing, probably through the diet. The precision with which monitoring will detect trends in wing residue levels will vary from State to State depending upon numbers of wings sampled and the variability in residue concentration within a State's waterfowl habitat.

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See Appendix for chemical names of compounds mentioned in this paper.

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TABLE 1.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in pools of 25 wings of mallards or black ducks: fall, 1965 and 1966*

State	Age	Number of Pools		Residues in ppm (wet weight)											
				DDE			DDT			DDD			Dieldrin		
				Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range
		1965	1966	1965	1966		1965	1966		1965	1966		1965	1966	
BLACK DUCKS, ATLANTIC FLYWAY															
Maine	Ad.	4	4	0.46	0.49	0.32-0.82	0.08	0.06	n -0.17	0.06	0.06	n -0.16	n	n	—
	Imm.	4	4	0.16	0.42	0.11-0.88	0.05	0.17	n -0.41	T	T	n -0.11	n	n	—
Vt.	Ad.	3	3	1.07	0.42	0.18-2.10	0.12	0.08	n -0.21	0.11	0.05	n -0.15	n	n	—
	Imm.	3	3	0.20	0.16	0.12-0.20	0.05	T	n -0.10	0.05	n	n -0.10	0.45	n	n -1.30
N. H.	Ad.	3	3	1.06	0.70	0.48-2.17	0.27	0.06	n -0.46	0.12	n	n -0.20	0.20	n	n -0.55
	Imm.	3	3	0.21	0.28	0.14-0.43	0.17	0.08	n -0.32	n	n	—	0.06	n	n -0.10
Mass.	Ad.	4	4	1.73	1.65	1.28-2.67	0.38	0.18	n -0.52	0.21	0.12	n -0.28	0.17	T	n -0.38
	Imm.	4	4	0.63	1.42	0.29-2.40	0.37	0.37	n -0.89	0.21	0.14	n -0.34	0.18	0.06	n -0.24
Conn.	Ad.	3	3	1.62	1.39	0.77-2.62	0.78	0.26	n -0.90	0.67	0.17	n -0.72	0.11	n	n -0.18
	Imm.	3	3	0.73	0.43	0.30-1.00	0.32	0.12	n -0.42	0.22	0.09	n -0.29	1.04	n	n -2.97
R. I.	Ad.	3	3	0.77	1.11	0.56-1.50	0.23	0.11	n -0.34	0.19	0.05	n -0.27	0.31	0.10	n -0.43
	Imm.	3	3	0.29	0.96	0.27-1.00	0.26	0.14	n -0.36	0.08	0.08	n -0.13	0.14	0.11	n -0.23
N. Y.	Ad.	4	4	1.36	1.12	0.78-1.58	0.45	T	n -0.50	0.19	0.07	n -0.24	0.05	T	n -0.15
	Imm.	4	4	0.38	1.18	0.20-1.50	0.25	0.46	n -0.94	0.13	0.11	n -0.28	0.10	0.05	n -0.17
Pa.	Ad.	3	3	1.78	0.50	0.33-3.60	0.16	n	n -0.18	0.11	n	n -0.14	0.05	n	n -0.10
	Imm.	3	3	0.55	0.15	0.10-0.82	0.18	0.05	n -0.24	0.10	n	n -0.20	0.06	n	n -0.13
N. J.	Ad.	5	5	1.94	2.26	1.32-3.45	0.78	0.77	0.45-1.31	0.18	0.13	n -0.25	0.05	n	n -0.08
	Imm.	5	5	1.58	1.86	0.94-4.10	1.63	1.80	0.40-4.90	0.26	0.17	0.08-0.42	T	T	n -0.11
Del	Ad.	3	3	0.59	1.17	0.50-1.50	0.14	0.07	n -0.19	0.08	T	n -0.13	n	0.08	n -0.19
	Imm.	3	3	0.10	0.47	n -0.72	0.06	0.13	n -0.35	0.06	T	n -0.11	n	n	—

TABLE 1.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in pools of 25 wings of mallards or black ducks: fall, 1965 and 1966*—Continued

State	Age	Number of Pools		Residues in ppm (wet weight)											
				DDE			DDT			DDD			Dieldrin		
				Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range
		1965	1966	1965	1966		1965	1966		1965	1966		1965	1966	
BLACK DUCKS, ATLANTIC FLYWAY—Continued															
Md.	Ad.	3	3	0.22	0.43	0.13-0.51	0.13	0.06	n -0.14	0.11	T	n -0.13	T	n	n -0.06
	Imm.	3	3	0.15	0.56	0.12-1.30	n	0.16	n -0.37	n	n	—	0.05	n	n -0.07
Va.	Ad.	3	3	0.25	0.54	0.20-0.72	T	n	n -0.06	0.05	0.05	n -0.12	0.20	n	n -0.43
	Imm.	3	3	0.28	0.19	0.09-0.42	0.07	n	n -0.18	T	n	n -0.09	0.39	n	n -0.78
N. C.	Ad.	1	2	0.48	0.48	0.31-0.66	0.12	0.07	n -0.12	0.11	n	n -0.11	n	n	—
	Imm.	2	1	0.41	0.18	0.18-0.45	0.12	n	n -0.18	0.13	n	n -0.16	0.08	n	n -0.11
S. C.	Ad.	2	2	0.21	0.38	0.18-0.53	0.10	n	n -0.10	n	n	—	n	0.05	n -0.07
	Imm.	2	2	0.64	0.38	0.38-0.69	0.21	0.20	0.19-0.21	0.05	n	n -0.09	0.16	n	n -0.16
MALLARDS, ATLANTIC FLYWAY															
N. Y.	Ad.	3	3	1.70	0.78	0.52-2.15	1.24	n	n -2.98	0.26	n	n -0.30	0.06	n	n -0.11
	Imm.	3	3	0.45	0.35	0.21-0.61	0.32	0.19	n -0.42	0.23	n	n -0.30	0.05	n	n -0.08
Pa.	Ad.	3	3	0.39	1.16	0.37-1.50	0.20	0.14	n -0.25	0.09	0.05	n -0.14	n	0.09	n -0.16
	Imm.	3	3	1.71	0.65	0.14-4.49	0.64	0.05	n -1.59	0.14	0.07	n -0.18	n	0.08	n -0.12
N. J.	Ad.	3	3	1.00	1.85	0.40-2.60	0.46	0.55	0.05-1.20	0.08	0.17	n -0.22	T	n	n -0.06
	Imm.	3	3	0.59	0.54	0.33-0.70	0.33	0.37	n -0.75	0.12	0.10	0.08-0.17	n	n	—
Md.	Ad.	3	2	0.26	0.70	0.20-0.84	0.05	n	n -0.12	0.05	n	n -0.10	n	0.10	n -0.17
	Imm.	3	3	0.42	0.17	0.14-0.46	0.19	n	n -0.21	0.20	n	n -0.32	0.07	T	n -0.18
Va.	Ad.	3	3	0.24	0.36	0.19-0.59	0.06	T	n -0.10	0.06	n	n -0.08	0.08	T	n -0.11
	Imm.	3	3	0.16	0.20	0.07-0.28	0.08	n	n -0.14	0.11	n	n -0.19	n	n	—
S. C.	Ad.	3	3	0.17	0.56	0.13-1.00	T	0.09	n -0.23	n	n	—	T	0.07	n -0.16
	Imm.	3	3	0.10	0.36	0.05-0.76	0.05	0.19	n -0.47	n	n	—	0.05	n	n -0.08
Ga. and Fla.	Ad.	2	2	0.53	0.52	0.35-0.70	0.13	0.05	n -0.15	0.08	n	n -0.10	n	n	—
	Imm.	2	3	1.18	0.13	0.11-1.81	0.24	n	n -0.29	n	n	—	n	n	—
MALLARDS, MISSISSIPPI FLYWAY															
Minn.	Ad.	7	6	0.25	0.22	0.08-0.52	n	T	n -0.10	n	n	—	n	n	—
	Imm.	6	6	0.10	0.07	n -0.22	T	n	n -0.10	n	n	—	n	n	—
Wis.	Ad.	3	5	0.50	0.14	0.08-0.81	0.28	n	n -0.68	0.21	n	n -0.60	n	T	n -0.05
	Imm.	4	5	0.14	T	n -0.19	T	n	n -0.09	n	n	—	0.08	n	n -0.20
Mich.	Ad.	2	3	0.29	0.18	0.10-0.48	0.11	T	n -0.20	0.07	n	n -0.11	n	n	—
	Imm.	4	3	0.13	0.11	0.09-0.19	n	0.07	n -0.16	n	n	—	n	n	—
Iowa	Ad.	5	5	0.32	0.12	0.06-0.92	0.06	n	n -0.24	T	n	n -0.14	n	n	—
	Imm.	5	5	0.14	T	n -0.39	n	n	—	n	n	—	n	n	—
Ill.	Ad.	7	6	0.10	0.08	n -0.27	n	n	—	n	n	—	n	T	n -0.06
	Imm.	6	6	0.05	0.18	n -0.49	n	n	—	n	n	—	T	n	n -0.07
Ind.	Ad.	4	3	0.23	0.09	0.06-0.29	0.05	n	n -0.12	T	T	n -0.08	n	n	—
	Imm.	4	3	0.15	0.09	n -0.20	0.08	n	n -0.15	T	0.08	n -0.19	n	n	—
Ohio	Ad.	3	3	0.18	0.30	0.15-0.31	n	0.11	n -0.17	0.05	0.16	n -0.31	n	n	—
	Imm.	4	3	0.11	0.45	0.09-1.01	0.06	0.14	n -0.25	0.07	n	n -.013	T	n	n -0.08
Mo.	Ad.	6	5	0.23	n	n -0.72	T	n	n -0.12	n	n	—	n	n	—
	Imm.	5	5	T	T	n -0.12	n	n	—	n	n	—	n	n	—
Ky.	Ad.	3	3	0.30	0.30	0.13-0.62	0.08	0.09	n -0.23	T	0.06	n -0.10	n	n	—
	Imm.	3	3	0.13	0.09	0.06-0.16	0.05	n	n -0.10	0.05	n	n -0.10	n	n	—
Ark.	Ad.	7	6	0.19	0.21	0.08-0.31	0.06	0.07	n -0.15	T	n	n -0.05	0.11	0.06	n -0.34
	Imm.	6	6	0.15	0.09	0.05-0.29	0.06	0.06	n -0.15	n	T	n -0.06	0.08	0.12	n -0.31
Tenn.	Ad.	5	4	0.38	0.27	0.11-1.10	0.06	0.05	n -0.12	T	n	n -0.09	n	0.11	n -0.39
	Imm.	4	4	0.13	0.16	0.05-0.30	T	0.06	n -0.12	T	n	n -0.09	0.06	n	n -0.16
La.	Ad.	5	6	0.22	0.11	0.05-0.26	0.06	0.06	n -0.11	n	n	—	T	n	n -0.05
	Imm.	5	6	0.07	0.15	n -0.34	T	0.09	n -0.22	n	T	n -0.06	T	0.12	n -0.19

TABLE 1.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in pools of 25 wings of mallards or black ducks: fall, 1965 and 1966*—Continued

State	Age	Number of Pools		Residues in ppm (wet weight)											
				DDE			DDT			DDD			Dieldrin		
				Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range	Pool Means		2-Year Range
		1965	1966	1965	1966		1965	1966		1965	1966		1965	1966	
MALLARDS, MISSISSIPPI FLYWAY—Continued															
Miss.	Ad.	3	3	0.73	0.28	0.21-0.96	0.20	0.12	0.08-0.27	0.06	n	n -0.08	n	T	n -0.05
	Imm.	3	3	0.22	0.23	0.07-0.50	0.11	0.12	n -0.16	n	n	—	n	T	n -0.06
Ala.	Ad.	2	3	0.88	3.03	0.54-5.31	0.23	0.26	0.13-0.45	0.10	0.27	n -0.49	0.14	n	n -0.14
	Imm.	3	3	0.68	2.21	0.42-3.23	0.35	0.44	0.15-0.69	0.14	0.84	0.06-2.03	n	n	—
MALLARDS, CENTRAL FLYWAY															
Mont. (eastern)	Ad.	8	4	0.08	0.12	0.05-0.16	n	n	—	n	n	—	T	T	n -0.16
	Imm.	8	4	0.10	0.07	n -0.29	T	0.06	n -0.15	n	0.06	n -0.19	T	n	n -0.16
N. Dak.	Ad.	8	8	0.12	0.11	0.05-0.43	n	n	—	n	n	—	n	n	—
	Imm.	8	8	T	n	n -0.05	n	n	—	n	n	—	n	n	—
S. Dak.	Ad.	7	8	0.09	0.12	n -0.20	n	T	n -0.10	n	n	—	n	n	—
	Imm.	6	8	T	0.08	n -0.34	n	n	—	n	n	—	n	n	—
Wyo. (eastern)	Ad.	1	3	0.05	0.20	0.05-0.45	n	0.12	n -0.32	n	T	n -0.05	n	n	—
	Imm.	2	3	n	0.09	n -0.10	n	n	—	n	n	—	n	n	—
Nebr.	Ad.	6	7	0.10	0.09	0.05-0.17	n	n	—	n	n	—	n	n	—
	Imm.	6	7	T	T	n -0.10	n	T	n -0.09	n	n	—	n	n	—
Colo. (eastern)	Ad.	10	4	0.33	0.24	0.17-0.85	0.24	0.25	n -1.20	0.05	0.07	n -0.18	n	n	—
	Imm.	10	4	0.31	0.17	0.05-0.69	0.20	0.55	n -0.81	T	T	n -0.11	n	n	—
Kans.	Ad.	7	6	0.08	0.08	n -0.12	n	n	—	n	n	—	n	n	—
	Imm.	7	6	0.15	T	n -0.91	n	T	n -0.09	n	n	—	n	n	—
N. Mex. (eastern)	Ad.	3	3	0.31	1.17	0.22-2.44	n	0.11	n -0.19	n	n	—	n	T	n -0.06
	Imm.	3	3	0.39	0.63	0.20-1.35	n	0.12	n -0.22	n	n	—	n	n	—
Okla.	Ad.	5	4	0.12	0.10	0.07-0.20	n	n	—	n	n	—	n	n	—
	Imm.	3	4	n	0.07	n -0.12	n	n	—	n	n	—	n	n	—
Tex.	Ad.	6	9	0.19	0.45	0.12-1.14	0.10	0.07	n -0.36	n	T	n -0.17	0.06	0.10	n -0.53
	Imm.	4	9	0.10	0.34	n -0.74	0.08	0.14	n -0.74	n	T	n -0.10	n	0.09	n -0.28
MALLARDS, PACIFIC FLYWAY															
Wash.	Ad.	13	11	0.27	0.70	0.06-2.75	0.05	0.09	n -0.38	T	T	n -0.14	n	T	n -0.10
	Imm.	13	11	0.42	0.31	0.10-1.36	0.18	0.06	n -0.72	T	n	n -0.08	T	T	n -0.07
Oreg.	Ad.	7	7	0.36	0.35	0.12-0.59	0.06	T	n -0.17	T	n	n -0.12	n	T	n -0.09
	Imm.	7	7	0.27	0.32	0.08-1.56	0.05	0.13	n -0.42	n	n	—	n	n	—
Idaho	Ad.	9	9	0.64	0.37	0.06-2.77	0.28	0.05	n -1.00	0.08	T	n -0.36	n	T	n -0.09
	Imm.	9	9	0.21	0.52	n -1.50	0.06	0.06	n -0.20	n	n	—	n	n	—
Mont. (western)	Ad.	4	4	0.13	0.20	0.08-0.34	n	T	n -0.07	n	n	—	n	T	n -0.06
	Imm.	4	4	0.16	0.04	n -0.30	0.09	n	n -0.30	T	n	n -0.10	n	n	—
Wyo. (western)	Ad.	2	3	T	0.09	n -0.10	n	n	—	n	n	—	n	n	—
	Imm.	3	3	0.05	0.07	n -0.11	n	n	—	n	n	—	n	n	—
Calif	Ad.	11	11	1.41	1.49	0.20-3.50	0.32	0.20	n -1.67	0.06	n	n -0.21	T	T	n -0.08
	Imm.	11	11	0.96	1.30	0.29-4.11	0.08	0.22	n -0.38	0.17	n	n -0.60	0.06	0.18	n -0.94
Nev.	Ad.	2	3	0.32	0.17	0.08-0.37	n	T	n -0.09	n	T	n -0.08	n	n	—
	Imm.	3	3	0.11	0.67	0.06-1.56	T	T	n -0.08	n	n	—	n	n	—
Utah	Ad.	6	5	0.66	1.26	0.39-1.41	0.20	0.13	n -0.54	T	T	n -0.12	T	0.06	n -0.16
	Imm.	6	5	0.86	0.68	0.37-1.30	0.25	0.09	n -0.76	0.07	0.05	n -0.16	0.08	0.09	n -0.28
Colo. (western)	Ad.	3	3	1.15	0.22	0.11-3.20	0.68	n	n -1.94	0.12	n	n -0.33	n	n	—
	Imm.	3	3	0.24	0.10	0.10-0.34	n	n	—	n	n	—	T	n	n -0.09
Ariz. and N. Mex. (western)	Ad.	1	3	0.12	0.34	n -0.73	0.09	T	n -0.09	n	n	—	0.12	n	n -0.12
	Imm.	2	3	0.42	0.63	0.11-0.98	0.45	0.10	n -0.88	0.43	n	n -0.85	n	n	—

NOTE: Means were computed by assigning the trace value 0.02 ppm to pool residues below the limit of sensitivity (0.05 ppm).
T = Residues reported, but mean level probably a trace (below 0.05 ppm).
n = Residues not detectable at 0.05 ppm limit of sensitivity.

TABLE 2.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in wings of mallards or black ducks: 1965-1966*

[Estimates are 2-year means and standard errors for pools of 25 wings each]

State	Age	Total Pools 1965 + 1966	Residues in ppm (wet weight)							
			DDE		DDT		DDD		Dieldrin	
			2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error
BLACK DUCKS, ATLANTIC FLYWAY										
Maine	Ad.	8	0.48	.064	0.07	.023	0.06	.021	[1](0.02)	[1](.006)
	Imm.	8	0.29	.099	0.11	.048	(0.04)	.015	(0.02)	(.006)
Vt.	Ad.	6	0.75	.279	0.10	.033	0.08	.025	(0.02)	(.008)
	Imm.	6	0.18	.013	(0.04)	(.018)	(0.03)	.017	0.23	.217
N. H.	Ad.	6	0.88	.262	0.17	.072	0.07	.034	0.10	.092
	Imm.	6	0.25	.043	0.13	.050	(0.02)	(.008)	(0.04)	(.017)
Mass.	Ad.	8	1.69	.166	0.28	.065	0.18	.039	0.10	.045
	Imm.	8	1.03	.239	0.23	.109	0.18	.037	0.12	.030
Conn.	Ad.	6	1.51	.311	0.52	.135	0.42	.120	0.06	.029
	Imm.	6	0.58	.175	0.22	.061	0.16	.042	0.53	.491
R. I.	Ad.	6	0.94	.156	0.17	.059	0.12	.042	0.21	.061
	Imm.	6	0.63	.151	0.19	.053	0.08	.018	0.12	.035
N. Y.	Ad.	8	1.24	.092	0.24	0.82	0.13	.036	0.05	.021
	Imm.	8	0.78	.165	0.36	.103	0.12	.038	0.08	.022
Pa.	Ad.	6	1.14	.511	0.09	.033	0.06	.025	(0.03)	(.016)
	Imm.	6	0.35	.134	0.11	.039	0.06	.033	(0.04)	(.021)
N. J.	Ad.	10	2.10	.228	0.78	.103	0.15	.103	(0.03)	(.010)
	Imm.	10	1.75	.303	1.72	.402	0.21	.402	(0.03)	(.012)
Del.	Ad.	6	0.88	.171	0.11	.033	0.07	.034	0.05	.032
	Imm.	6	0.29	.102	0.10	.057	0.05	.019	(0.02)	(.008)
Md.	Ad.	6	0.33	.056	0.10	.026	0.07	.029	(0.03)	(.010)
	Imm.	6	0.36	.190	0.09	.059	(0.02)	(.008)	0.05	.013
Va.	Ad.	6	0.40	.077	(0.03)	(.012)	0.05	.025	0.11	.017
	Imm.	6	0.24	.054	0.05	.031	(0.03)	(.015)	0.21	.133
N. C.	Ad.	3	0.48	.101	0.09	.040	0.05	.037	(0.02)	(.017)
	Imm.	3	0.33	.080	0.09	.053	0.09	.046	0.06	.032
S. C.	Ad.	4	0.30	.081	0.10	.031	(0.02)	(.013)	(0.03)	(.017)
	Imm.	4	0.51	.078	0.21	.005	(0.04)	(.022)	0.07	.053
MALLARDS, ATLANTIC FLYWAY										
N. Y.	Ad.	6	1.24	.237	0.63	.478	0.14	.058	T	—
	Imm.	6	0.40	.059	0.24	.062	0.12	.056	T	—
Pa.	Ad.	6	0.78	.189	0.17	.035	0.07	.023	0.05	.027
	Imm.	6	1.18	.682	0.35	.251	0.11	.033	0.05	.022
N. J.	Ad.	6	1.08	.383	0.51	.195	0.13	.034	T	—
	Imm.	6	0.57	.060	0.35	.108	0.11	.013	n	—
Md.	Ad.	5	0.44	.118	0.05	.025	0.05	.020	0.05	.034
	Imm.	6	0.30	.058	0.11	.039	0.11	.053	0.05	.030
Va.	Ad.	6	0.30	.061	0.05	.017	(0.04)	(.016)	0.06	.018
	Imm.	6	0.18	.030	(0.04)	(.026)	0.07	.034	n	—
S. C.	Ad.	6	0.37	.133	0.07	.038	(0.02)	(.008)	0.05	.026
	Imm.	6	0.23	.109	0.12	.072	(0.02)	(.008)	T	—
Ga. and Fla.	Ad.	4	0.53	.079	0.09	.029	0.05	.024	n	—
	Imm.	5	0.66	.325	0.11	.057	(0.02)	(.010)	n	—

TABLE 2.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in wings of mallards or black ducks: 1965-1966*—Continued

[Estimates are 2-year means and standard errors for pools of 25 wings each]

State	Age	Total Pools 1965 + 1966	Residues in ppm (wet weight)							
			DDE		DDT		DDD		Dieldrin	
			2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error
MALLARDS, MISSISSIPPI FLYWAY										
Minn.	Ad.	13	0.24	.039	(0.03)	(.053)	n	—	n	—
	Imm.	12	0.08	.019	T	—	n	—	n	—
Wis.	Ad.	8	0.28	.096	0.12	.084	0.09	.075	T	—
	Imm.	9	0.08	.021	T	—	n	—	0.05	.023
Mich.	Ad.	5	0.22	.067	0.06	.039	T	—	n	—
	Imm.	7	0.12	.013	T	—	n	—	n	—
Iowa	Ad.	10	0.22	.080	0.09	.024	T	—	n	—
	Imm.	10	0.09	.037	n	—	n	—	n	—
Ill.	Ad.	13	0.09	.020	(0.02)	(.004)	n	—	T	—
	Imm.	12	0.12	.037	n	—	n	—	T	—
Ind.	Ad.	7	0.17	.034	0.06	.017	T	—	T	—
	Imm.	7	0.12	.024	T	—	0.05	.027	T	—
Ohio	Ad.	6	0.24	.028	0.06	.028	0.11	.044	n	—
	Imm.	7	0.26	.127	0.11	.032	0.05	.022	T	—
Mo.	Ad.	11	0.13	.065	(0.03)	(.011)	n	—	n	—
	Imm.	10	(0.04)	.012	n	—	n	—	n	—
Ky.	Ad.	6	0.30	.080	0.08	.039	0.05	.018	n	—
	Imm.	6	0.11	.018	T	—	T	—	n	—
Ark.	Ad.	13	0.20	.021	0.06	.015	T	—	0.08	.028
	Imm.	12	0.12	.024	0.06	.017	T	—	0.10	.021
Tenn.	Ad.	9	0.33	.099	0.05	.018	T	—	0.06	.043
	Imm.	8	0.15	.031	0.05	.018	T	—	T	—
La.	Ad.	11	0.18	.018	(0.04)	(.014)	n	—	T	—
	Imm.	11	0.11	.029	0.06	.025	T	—	0.07	.019
Miss.	Ad.	6	0.51	.137	0.16	.026	T	—	T	—
	Imm.	6	0.23	.060	0.11	.027	n	—	T	—
Ala.	Ad.	5	2.17	.922	0.24	.061	0.20	.084	0.05	.035
	Imm.	6	1.45	.525	0.40	.078	0.49	.312	n	—
MALLARDS, CENTRAL FLYWAY										
Mont. (eastern)	Ad.	12	0.09	.010	n	—	n	—	T	—
	Imm.	12	0.09	.026	T	—	T	—	T	—
N. Dak.	Ad.	16	0.12	.022	n	—	n	—	n	—
	Imm.	16	(0.03)	(.003)	n	—	n	—	n	—
S. Dak.	Ad.	15	0.11	.014	T	—	n	—	n	—
	Imm.	14	0.06	.025	n	—	n	—	n	—
Wyo. (eastern)	Ad.	4	0.16	.097	0.10	.080	T	—	n	—
	Imm.	5	0.06	.017	n	—	n	—	n	—
Nebr.	Ad.	13	0.10	.009	n	—	n	—	n	—
	Imm.	13	(0.04)	(.009)	T	—	n	—	n	—
Colo. (eastern)	Ad.	14	0.30	.048	0.24	.093	0.05	.016	n	—
	Imm.	14	0.27	.041	0.22	.067	T	—	n	—
Kans.	Ad.	13	0.08	.009	n	—	n	—	n	—
	Imm.	13	0.09	.070	T	—	n	—	n	—
N. Mex. (eastern)	Ad.	6	0.74	.349	0.06	.033	n	—	T	—
	Imm.	6	0.51	.185	0.07	.035	n	—	n	—
Okla.	Ad.	9	0.11	.016	n	—	n	—	n	—
	Imm.	7	0.05	.017	n	—	n	—	n	—
Tex.	Ad.	15	0.35	.072	0.08	.025	T	—	0.08	.037
	Imm.	13	0.27	.071	0.12	.057	T	—	0.07	.025

TABLE 2.—*Nationwide residue levels of DDE, DDT, DDD, and dieldrin in wings of mallards or black ducks: 1965-1966*—Continued

[Estimates are 2-year means and standard errors for pools of 25 wings each]

State	Age	Total Pools 1965 + 1966	Residues in ppm (wet weight)							
			DDE		DDT		DDD		Dieldrin	
			2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error
MALLARDS, PACIFIC FLYWAY										
Wash.	Ad.	24	0.47	.125	0.07	.017	T	—	T	—
	Imm.	24	0.37	.063	0.12	.037	T	—	T	—
Oreg.	Ad.	14	0.36	.038	0.07	.017	T	—	T	—
	Imm.	14	0.30	.113	0.09	.030	n	—	n	—
Idaho	Ad.	18	0.51	.140	0.17	.060	0.05	.020	T	—
	Imm.	18	0.37	.084	0.05	.014	n	—	n	—
Mont. (western)	Ad.	8	0.17	.031	(0.03)	(.009)	n	—	T	—
	Imm.	8	0.10	.040	0.06	.037	T	—	n	—
Wyo. (western)	Ad.	5	0.07	.015	(0.02)	(.010)	n	—	n	—
	Imm.	6	0.06	.022	(0.02)	(.008)	n	—	n	—
Calif.	Ad.	22	1.45	.174	0.26	.070	T	—	T	—
	Imm.	22	1.13	.210	0.15	.025	0.10	.033	0.12	.046
Nev.	Ad.	5	0.23	.047	(0.03)	(.020)	T	—	n	—
	Imm.	6	0.39	.237	(0.04)	(.015)	n	—	n	—
Utah	Ad.	11	0.93	.102	0.17	.046	T	—	0.05	.019
	Imm.	11	0.78	.079	0.18	.066	0.06	.018	0.08	.030
Colo. (western)	Ad.	6	0.69	.504	0.35	.320	0.07	.003	n	—
	Imm.	6	0.17	.040	(0.02)	(.008)	n	—	T	—
Ariz. and N. Mex.	Ad.	4	0.31	.146	0.05	.022	n	—	0.05	.030
	Imm.	5	0.55	.156	0.24	.167	0.19	.170	n	—

[1] Parenthesized trace values were estimated numerically to compute average flyway levels; corresponding standard errors are maximized estimates.

NOTE: Means were computed by assigning the trace value 0.02 ppm to pool residues below the limit of sensitivity (0.05 ppm).
T = Residues reported but mean level probably a trace (below 0.05 ppm).
n = Residues not detectable at 0.05 ppm limit of sensitivity.

TABLE 3.—*Residues of DDE, DDT, DDD, and dieldrin, by waterfowl flyways, in pools of 25 wings of mallards or black ducks: 1965-1966*

[Estimates are 2-year means and standard errors weighted by each State's total bag of the given species and age group.]

Species	Flyway	Age	Number of Pools	Residues in ppm (wet weight)							
				DDE		DDT		DDD		Dieldrin	
				2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error	2-Year Mean	Standard Error
Black duck	Atlantic	Ad.	89	1.23	.078	0.33	.031	0.12	.029	0.05	.008
		Imm.	89	0.75	.071	0.46	.076	0.11	.073	0.11	.034
Mallard	Atlantic	Ad.	39	0.72	.078	0.25	.095	0.07	.013	T	—
		Imm.	41	0.60	.183	0.24	.071	0.10	.022	T	—
Mallard	Mississippi	Ad.	123	0.25	.024	0.06	.011	T	—	T	—
		Imm.	123	0.12	.011	T	—	T	—	T	—
Mallard	Central	Ad.	117	0.17	.017	T	—	T	—	T	—
		Imm.	113	0.09	.014	T	—	T	—	T	—
Mallard	Pacific	Ad.	117	0.70	.063	0.14	.022	T	—	T	—
		Imm.	120	0.59	.068	0.11	.015	0.05	—	0.05	—

NOTE: Means were computed by assigning the trace value 0.02 ppm to pool residues below the limit of sensitivity (0.05 ppm).
T = Residues reported, but mean level probably a trace (below 0.05 ppm).

PESTICIDES IN WATER

Pesticides in Selected Western Streams—A Progress Report [1]

Douglas B. Manigold and Jean A. Schulze

ABSTRACT

This paper presents data from the U. S. Geological Survey program for monitoring pesticides in the streams of the Western United States and covers the period October 1966 - September 1968. Data from the first year's study beginning in October 1965 were published in an earlier issue of this Journal (2). *The original network of 11 monthly sampling stations, established in October 1965, was increased to 20 in October 1967. Compounds determined include the common cholorinated insecticides and herbicides. All of these pesticides were detected at one time or another; DDT was the most frequently occurring insecticide, and 2,4-D the most common herbicide. The amounts observed were small; the maximum concentrations of DDT and 2,4-D were 0.12 and 0.35 μg/liter, respectively. Concentrations were highest in the water samples that contained appreciable amounts of suspended sediment. Data obtained thus far in the operation of the network have been insufficient to show real correlation with discharge or season of the year.*

Introduction

In the September 1967 issue of this Journal, Brown and Nishioka (*2*) reported on data obtained by the U. S. Geological Survey during the first year of operation of a pesticides monitoring network, which is part of a program for continuous surveillance of pesticides in surface waters proposed for joint operation by the Federal Water Pollution Control Administration and the Geological Survey of the U. S. Department of Interior (*5*). This paper presents data from this study for the period October 1966-September 1968. Beginning in October 1965, the Geological Survey obtained pesticide data for 11 streams in the Western United States. The study was expanded in October 1967 to include a total of 20 sites. Pesticides selected for routine analysis were chosen mainly from the primary list of compounds established in March 1964 by the Subcommittee on Monitoring, Federal Committee on Pest Control, and include the chlorinated insecticides aldrin, DDD, DDE, DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, and lindane; and the chlorinated herbicides, 2,4-D, 2,4,5-T; and silvex.

Analytical work for the program, from its initiation until June 1967, was performed in the Geological Survey laboratory in Sacramento, Calif. During an interim period, August 1967 to January 1968, samples were analyzed in Menlo Park, Calif., and in February 1968 the program was transferred to the Survey Laboratory at Austin, Tex.

Data Collection Sites

Each of the 20 sampling stations is a designated or operated U. S. Geological Survey irrigation-network location where inorganic water quality and stream discharge data are obtained (*8*). These stations are listed in Table 1 and their locations shown on Fig. 1. The original 11 stations are indicated by underlined numbers on the map. Historical hydrologic data for all 20 stations are available in annual reports of the U. S. Geological Survey entitled "Quality of Surface Waters for Irrigation, Western United States." These reports give inorganic water quality data, drainage area, and stream discharge figures. The latest report, released in 1967, contains data for the period from October 1, 1962 to September 30, 1963 (*8*).

Sampling Procedures

In these studies samples are collected in 1-quart Boston Round glass bottles sealed with a Teflon-lined screw cap. The narrow-mouthed bottles make possible the collection of depth-integrated samples. Earlier, wide-mouth bottles were used which filled almost instantly when lowered into a stream and made a depth-integrated sample

[1] Water Resources Division, U.S. Geological Survey, Austin, Tex. 78701 (Publication authorized by the Director, U.S. Geological Survey.)

practically impossible. Two bottles are collected at each station, one being used for insecticide analysis and the other for herbicides. A duo-pak container is used for mailing the samples, with the bottles protected by a form-fitting expanded polystyrene case placed in a corrugated cardboard carton. The package is compact and light-weight, and no breakage has occurred. The samples are transported by airmail because herbicides, particularly 2,4-D, can decompose quite rapidly (*4*). The average time from sampling to receipt of the sample at the laboratory is 3 days.

TABLE 1.—*Pesticide monitoring stations in Western United States*

Irrigation network no.[1]	Geological Survey station ident. no.	Stream and location	Inorganic analysis started (Date)
4	6-8070	Missouri River at Nebraska City, Nebr.	1-4-51
5	6-2145	Yellowstone River near Billings, Mont.	12-15-50
15	6-4760	James River at Huron, S. Dak.	8-56
18	6-7660	Platte River at Brady, Nebr.	2-28-51
24	7-1305	Arkansas River below John Martin Reservoir, Colo.	1-10-51
27	7-2505	Arkansas River at Van Buren,Ark.	10-1-45
30	7-2450	Canadian River near Whitefield, Okla.	9-1-46
37	8-1140	Brazos River at Richmond, Tex.	9-1-45
40	8-1620	Colorado River at Wharton, Tex.	4-11-44
52	8-4692	Rio Grande below Anzalduas Dam, Tex.	1944
54	8-3965	Pecos River near Artesia, N.Mex.	7-1-37
63	9-5255	Colorado River (Yuma Main Canal) below Colorado River Siphon, at Yuma, Ariz.	10-42
66	9-3150	Green River at Green River, Utah	10-28
71	9-5195	Gila River below Gillespie Dam, Ariz.	12-1-50
79	10-3350	Humboldt River near Rye Patch, Nev.	12-10-51
86a	11-4255	Sacramento River at Verona, Calif.	
88a	11-4070	Feather River at Oroville, Calif.	10-53
94	12-5105	Yakima River at Kiona, Wash.	12-30-52
97	13-1545	Snake River at King Hill, Idaho	3-27-51
102	14-1057	Columbia River near The Dalles, Oreg.	12-1-50

[1] Number refers to list of irrigation-quality network stations (U.S. Geological Survey, 1967, p. 2).

Analytical Procedures

Upon receipt of the sample, one bottle is designated for insecticide analysis and the other for herbicide analysis. The herbicide sample is acidified with high-purity concentrated sulfuric acid until the pH is 2 or less and then refrigerated at about 5 C to inhibit biological degradation of the herbicides. The insecticide sample is stored at room temperature until extracted and analyzed, usually within 7 days after receipt or a total time of 8-10 days from the date of sampling. Each sample is analyzed as received, with no separation of water and sediment for individual analysis.

Insecticide samples are analyzed in groups of eight including a distilled water blank, basically by the method of Lamar *et al.* (*6*), which is summarized below. The entire sample (800-900 ml) is extracted with Nanograde hexane, and the extracts are dried over anhydrous sodium sulfate for 1 hour. The hexane is evaporated to 2-3 ml in a Kuderna-Danish concentrator apparatus.

The next step deviates from the procedure originally published by Lamar *et al.* (*6*) to allow use of a sample cleanup procedure which was developed by Law (*Written communication, 1968*). The extract is further concentrated to 0.5 ml by use of a heat lamp and a gentle stream of nitrogen directed over the liquid. This concentrate is then transferred quantitatively to a disposable pipette packed with a small plug of hexane-washed glass wool supporting 3.0 cm of deactivated alumina and 0.5 cm of anhydrous sodium sulfate. The extract is then eluted with 4.5 ml of hexane and collected in a 5 ml graduated concentrator tube. This eluate is reduced in volume to 0.5 ml by the heat lamp and nitrogen and brought to 1.0 ml by rinsing the sides of the concentrator tube with hexane. The cleanup step is used routinely on all samples and has greatly reduced time lost due to gas chromatograph maintenance. In addition, the cleanup procedure increases the sensitivity of the method by approximately five times. Occasionally this cleanup column has been used to separate DDE and dieldrin occurring together. Almost all the DDE is eluted in the first milliliter, and dieldrin is retained on the column until the third milliliter is eluted.

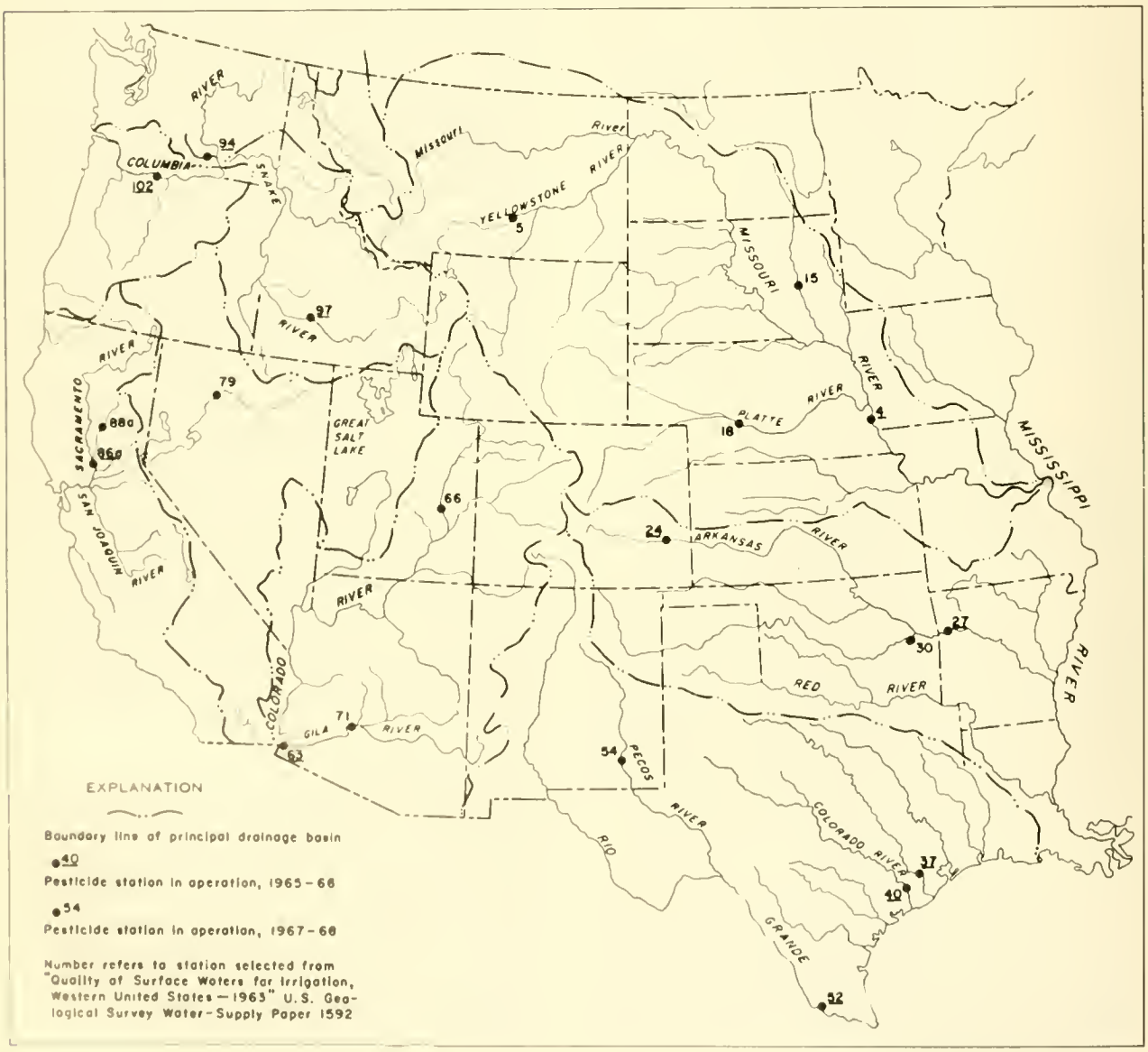
Insecticides are analyzed on both a Varian Aerograph Model 600 chromatograph with a Model 328 isothermal temperature controller and a dual column Aerograph Model 200. Columns used are ⅛″ x 5′ pyrex glass, packed with 60/80 mesh Gas-Chrom Q coated with either 3-5% DC-200 or 3-5% QF-1. Five-microliter aliquots are injected into both columns, and if the presence of an insecticide cannot be definitely confirmed on both columns, it is not reported. Because some noninsecticidal compounds possibly have the same retention

time on one column as the insecticide of interest, the lowest value is reported. Occasionally a mixed DC-200—QF-1 column as described by Burke and Holswade (*3*) is used to confirm the identity of pesticides when separation is difficult, as in the case of DDE and dieldrin on the DC-200 column.

Recovery data range from 89% to 121% using emulsifiable concentrates added to water solutions. Routine recovery checks of the entire procedure are conducted by adding hexane solutions of standard insecticides to distilled water in regular sample bottles. The alumina cleanup step is frequently checked by putting 1 ml of insecticide standard in hexane through the column and eluting in 0.5 ml increments. This tests column resolution for DDE and dieldrin as well as total recovery. Recoveries range from 75% to 98% for the entire procedure and from 85% to 105% for the column performance. No data corrections are made to compensate for recovery losses because most of the values are only a little above the lower limits of sensitivity, but corrections are made for the reagent blank when necessary. Standard solutions of insecticides are injected at the beginning of each analysis and periodically thereafter to correct for fluctuations in instrument response.

Herbicide sample extractions are also done in groups of eight using the method of Goerlitz and Lamar (*4*) with minor modifications. Each sample (800-900 ml) is ex-

FIGURE 1.—*Pesticide monitoring stations in Western United States*



tracted with ethyl ether. The extract is saponified using potassium hydroxide. This basic solution is subjected to a cleanup extraction using ether to remove organic contamination that may have been present in the original sample. After the cleanup extraction the solution is acidified and the phenoxy acid herbicides are extracted with ether. The extract is allowed to dry over acid sodium sulfate, the ether is evaporated, and the herbicides are esterified with boron trifluoride-methanol reagent. After esterification the samples are passed through a cleanup column using Florisil as the adsorbent. The herbicide methyl esters are eluted with benzene to obtain a final volume of 2.0 ml. Spiked samples are used to check the entire extraction and cleanup procedures; recovery ranges from 85% to 110%. Herbicides are analyzed on a dual column Aerograph Model 200 chromatograph. Columns used are packed similarly to those used for insecticides, except for the addition of 0.5% Carbowax 20M. Using these procedures, pesticide concentrations as low as 0.005 μg/liter can be routinely determined in most waters. An exception is 2,4-D, which is detectable in concentrations of about 0.020 μg/liter.

Discussion of Results

Results from analyses of water samples for the 2-year period, October 1966 to September 1968, are given in Table 2. No samples were analyzed for July 1967.

Each pesticide of interest was detected at one time or another during this investigation. Every river sampled contained pesticides at least one time. There were streams that showed only insecticides and no herbicides, such as the Gila River below Gillespie Dam, Ariz.; Platte River at Brady, Neb.; Colorado River at Yuma, Ariz.; Feather River at Oroville, Calif.; and Rio Grande below Anzalduas Dam, Tex. In the earlier months of the reporting period, herbicides were not found at any station. Beginning in August 1967, all three herbicides have been detected frequently.

Pesticide concentrations found were never in excess of the permissible limits established for public water supplies by the National Technical Advisory Committee to the Secretary of Interior (*7*). The highest concentration of insecticide observed was 0.12 μg/liter DDT in the January 1968 sample from Colorado River at Wharton, Tex. The criteria permits 42 μg/liter DDT in public water supplies. The highest concentration of herbicide found was 0.35 μg/liter, 2,4-D in James River at Huron, S. Dak., in July 1968. The established criteria permits 100 μg/liter for herbicides. There has been no conclusive pattern for the occurrence of pesticides. Data published previously (*2*) and Table 2 show no real correlation with discharge nor season of the year, although lack of data for July 1967 and irregular sampling at some stations limit the amount of information available.

Although samples usually contained little sediment, the highest insecticide concentrations found were in those samples which contained the most sediment. Streambed sediment samples have been found to contain much higher insecticide concentrations than those shown in Table 2 (*1*). Correlative studies of both streambed material and water would provide meaningful information on the fate and movement of pesticides in streams.

Data for the period October 1967 to September 1968, when all 20 stations were in operation, are summarized in Table 3 to show the number of occurrences of the various pesticides at each station. Insecticides occurring most frequently were DDT and its metabolites, DDD and DDE; 82% of all insecticide occurrences were due to these compounds. DDT was detected at least once at every station except Pecos River near Artesia, N. Mex. The most frequently detected herbicide was 2,4-D, which accounted for 50% of the herbicide occurrences.

See Appendix for chemical names of compounds mentioned in this paper.

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TABLE 2.—*Pesticide content of selected streams in Western United States*

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 4—USGS NO. 6-8070 MISSOURI RIVER AT NEBRASKA CITY, NEBR.														
10/13/66	1515	34,400	—	—	—	—	—	—	—	—	—	—	—	—
11/04/66	1000	36,600	—	—	—	—	—	—	—	—	—	—	—	—
12/15/66	1545	18,000	—	—	—	—	—	—	—	—	—	—	—	—
01/27/67	1330	14,800	—	—	—	—	—	—	—	—	—	—	—	—
02/16/67	1130	17,000	—	—	—	—	—	—	—	—	—	—	—	—
03/06/67	1200	35,100	—	—	—	—	.01	—	.01	—	—	—	—	—
04/19/67	1100	35,400	—	—	—	.01	—	—	.01	—	—	—	—	—
05/12/67	1140	40,900	—	—	.01	—	—	—	—	—	—	—	—	—
06/26/67	1100	72,200	—	—	—	—	.07	—	.04	.02	—	—	—	—
08/22/67	1030	38,500	—	—	—	—	—	—	—	—	—	—	—	—
09/20/67	1130	38,800	—	—	—	—	—	—	—	—	—			
10/11/67	1230	37,600	—	—	—	—	—	—	—	—	—	—	—	—
11/21/67	0930	36,800	—	—	—	—	—	—	—	—	—	—	—	—
12/13/67	1400	22,700	—	—	—	.01	—	—	—	—	—	.07	—	—
01/09/68	1430	11,000	—	—	—	—	—	—	—	—	—	—	—	—
02/14/68	1230	25,200	—	—	—	—	—	—	—	—	—	—	—	—
03/26/68	1100	37,100	—	—	—	—	—	—	—	—	—	—	—	—
04/18/68	0830	37,600	—	—	—	—	—	—	—	—	—	—	—	—
05/16/68	1430	38,200	.02	—	—	.09	.04	—	—	—	—	.12	—	—
06/21/68	1300	35,800	—	—	—	—	—	—	—	—	—	.08	—	—
07/24/68	1520	42,400	—	—	—	—	—	—	—	—	—	—	—	—
08/28/68	1420	37,600	—	—	—	—	—	—	—	—	—	—	—	—
09/24/68	1345	34,100	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 5—USGS NO. 6-2145 YELLOWSTONE RIVER NEAR BILLINGS, MONT.														
10/11/67	1445	5,350	—	—	—	—	—	—	—	—	—	—	—	—
11/14/67	1330	4,330	—	—	—	—	—	—	—	—	—	—	—	—
12/14/67	1330	2,720	—	—	—	—	—	—	—	—	—	—	—	—
01/08/68	1130	1,950	—	—	—	.01	—	—	—	—	—			
02/07/68	1600	3,910	—	—	—	—	—	—	—	—	—	—	—	—
03/13/68	1520	3,290	—	—	—	—	—	—	—	—	—	—	—	—
04/09/68	1235	3,730	—	—	—	—	—	—	—	—	—	—	—	—
05/13/68	1430	6,260	—	—	—	—	—	—	—	—	—	.02	—	—
06/11/68	1600	33,400	—	—	—	—	—	—	—	—	—	—	—	—
07/10/68	1200	24,200	—	—	—	—	—	—	—	—	—	—	—	—
08/09/68	0915	6,430	—	—	—	—	—	—	—	—	—	.07	—	—
09/09/68	0930	7,400	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 15—USGS NO. 6-4760 JAMES RIVER AT HURON, S. DAK. [* = no flow over dam]														
10/31/67	1330	*	—	—	—	.01	—	—	—	—	—	.07	—	—
11/27/67	1330	46	—	—	—	—	—	—	—	—	—	—	—	—
12/27/67	1545	8.0	—	—	—	—	—	—	—	—	—	—	—	—
01/25/68	1100	*	—	—	—	—	—	—	—	—	—	—	—	—
02/27/68	1600	4	—	—	—	—	—	—	—	—	—	—	—	—
03/26/68	1100	*	—	—	—	—	—	—	—	—	—	—	—	—
04/30/68	1350	211	—	—	—	—	—	—	—	—	—	.08	—	—
05/23/68	1400	211	—	—	—	—	—	—	—	—	—	—	—	—
06/28/68	0840	47	—	—	—	—	—	—	—	—	—	.11	—	—
07/22/68	1120	80	—	—	—	—	—	—	—	—	—	.35	—	—
08/30/68	0830	*	—	—	—	—	—	—	—	—	—	—	—	—
10/01/68	1400	6	—	—	—	—	—	—	—	—	—	.19	—	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 18—USGS NO. 6-7660 PLATTE RIVER AT BRADY, NEBR.														
10/18/67	1330	70.3	—	—	—	—	—	—	—	—	—			
11/13/67	1525	54.2	—	—	—	—	—	—	—	—	—	—	—	—
12/05/67	1510	54.2	—	—	—	—	—	—	—	—	—	—	—	—
01/03/68	1230	75.0	—	—	—	.01	.01	—	—	—	—	—	—	—
02/02/68	0945	58.4	—	—	—	—	—	—	—	—	—	—	—	—
03/05/68	1540	84.0	—	—	—	—	—	—	—	—	—	—	—	—
04/02/68	1535	54.2	—	—	—	—	—	—	—	—	—	—	—	—
05/07/68	1620	135	—	—	—	—	—	—	—	—	—	—	—	—
06/04/68	0935	47.4	—	—	—	—	—	—	—	—	—	—	—	—
07/02/68	1500	74.0	—	—	—	—	—	—	—	—	—	—	—	—
08/06/68	1435	24.4	—	—	—	—	—	—	—	—	—	—	—	—
09/06/68	—	198	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 24—USGS NO. 7-1305 ARKANSAS RIVER BELOW JOHN MARTIN RESERVOIR, COLO.														
10/22/66	1100	181	—	—	—	—	—	—	—	—	—	—	—	—
11/19/66	0930	23	—	—	—	—	—	—	—	—	—	—	—	—
12/17/66	1000	5.7	—	—	—	—	—	—	—	—	—	—	—	—
01/26/67	1530	4.3	—	—	—	—	—	—	—	—	—	—	—	—
02/24/67	2145	29	—	—	—	—	—	—	.01	—	—	—	—	—
03/28/67	0910	22	—	—	—	—	—	—	—	—	—	—	—	—
05/20/67	1115	630	—	—	—	—	—	—	—	—	—	—	—	—
06/20/67	0915	128	—	—	—	—	—	—	.02	—	—			
09/22/67	1215	540	—	—	—	—	—	—	—	—	—			
10/20/67	0800	348	—	—	—	.01	—	—	—	—	—	—	—	.02
11/21/67	0930	12	—	—	—	—	—	—	—	—	—	—	—	—
12/27/67	1135	2.8	—	—	—	.01	—	—	—	—	—	—	—	—
01/24/68	0900	2.3	—	—	—	—	—	—	—	—	—	—	—	—
02/16/68	0920	2.6	—	—	—	—	—	—	—	—	—	—	—	—
03/21/68	0930	2.6	—	—	—	—	—	—	—	—	—	—	—	—
04/23/68	0830	69	—	—	—	—	.01	—	—	—	—	—	—	—
05/17/68	1000	56	—	—	—	—	.01	—	—	—	—	.04	—	—
06/20/68	0630	322	—	—	—	—	.01	—	—	—	—	.24	—	—
07/30/68	0820	465	—	—	—	.04	.01	—	—	—	.01	—	—	.02
08/20/68	0935	810	—	—	—	—	—	—	—	—	—	—	—	—
09/27/68	0945	77	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 27—USGS NO. 7-2505 ARKANSAS RIVER AT VAN BUREN, ARK.														
10/21/66	0950	6,840	—	—	—	—	—	—	—	—	—	—	—	—
11/15/66	0945	2,660	—	—	—	—	—	—	—	—	—	—	—	—
12/15/66	1345	4,760	—	—	—	—	—	—	—	—	—	—	—	—
01/16/67	1320	2,040	—	—	—	—	—	—	—	—	—	—	—	—
02/14/67	1410	1,720	—	—	—	—	—	—	—	—	—	—	—	—
03/16/67	0925	2,620	—	—	—	—	—	—	.01	—	—	—	—	—
04/24/67	1530	22,700	—	—	.01	.01	—	—	.01	—	—	—	—	—
05/09/67	0740	21,600	—	.01	.01	—	—	—	.01	—	—	—	—	—
06/06/67	0725	10,700	—	—	—	—	—	—	—	—	—	—	—	—
08/28/67	0930	5,230	—	—	—	—	—	—	—	—	—	.06	—	—
09/14/67	1130	17,100	—	—	—	—	—	—	—	—	—	—	—	.02
10/10/67	1020	4,220	—	—	—	—	—	—	—	—	—	—	—	—
11/21/67	—	12,100	—	—	—	.01	—	—	—	—	—	—	—	.01
12/20/67	1130	22,500	—	—	—	.01	—	—	—	—	—	.13	—	.04
01/17/68	1025	11,200	—	—	—	—	—	—	—	—	—	—	—	—
02/13/68	1435	33,600	—	—	—	—	—	—	—	—	—	—	—	—
03/14/68	2100	49,000	—	—	—	—	—	—	—	—	—	—	—	.02
04/12/68	0900	52,600	—	—	—	—	—	—	—	—	—	.05	—	.02
05/07/68	1435	26,400	—	—	—	—	—	—	—	—	—	.03	—	—
06/12/68	1210	41,600	—	—	—	—	—	—	—	—	—	.03	—	.02
07/19/68	1125	17,900	—	—	—	—	—	—	—	—	—	—	—	.02
08/07/68	0815	26,100	—	—	—	—	—	—	—	—	—	.11	—	.04
09/05/68	1200	9,830	—	—	—	.01	—	—	—	—	—	—	—	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 30—USGS NO. 7-2450 CANADIAN RIVER NEAR WHITEFIELD, OKLA.														
12/13/67	1215	3,970	—	0.01	—	.01	—	—	—	—	—	—	—	.04
01/10/68	1345	10,200	—	—	—	.01	—	—	—	—	—			
02/20/68	1500	8,020	—	—	—	—	—	—	—	—	—	—	—	.03
03/20/68	1700	17,000	—	—	—	—	—	—	—	—	—	—	—	.02
04/11/68	1425	19,600	—	—	—	—	—	—	—	—	—	.06	—	.04
05/14/68	1225	1,970	—	—	—	—	—	—	—	—	—	.01	—	.03
07/12/68	0655	1,990	—	—	—	—	—	—	—	—	—	—	—	.03
09/18/68	1415	9,100	—	—	—	.01	—	—	—	—	—	—	—	.03
IRRIG. NETWORK NO. 37—USGS NO. 8-1140 BRAZOS RVER AT RICHMOND, TEX.														
11/07/66	1140	6,520	—	—	.01	.08	—	—	—	—	—	—	—	—
11/14/66	1415	1,390	—	—	—	—	—	—	—	—	—	—	.02	—
12/20/66	1430	1,310	—	—	—	.07	—	—	—	—	—	—	—	—
01/20/67	1200	1,010	—	—	—	—	—	—	—	—	—	—	—	—
02/20/67	1630	898	.01	—	—	—	—	—	.02	—	—	—	—	—
03/20/67	1115	410	.04	—	—	—	—	—	—	—	—	—	—	—
05/04/67	1330	1,880	—	.03	.01	.01	—	—	—	—	.02	—	—	—
06/08/67	1600	2,800	—	—	.06	.06	—	—	.02	—	—	—	—	—
08/23/67	0800	730	—	—	—	—	—	—	—	—	—	—	.02	.02
09/22/67	1050	1,980	—	—	—	—	—	—	—	—	—	.01	.02	.06
10/26/67	1400	1,000	—	.01	.01	.01	—	—	—	—	—	—	—	.02
12/08/67	1400	1,100	—	—	.01	.01	—	—	—	—	.01	—	—	—
01/10/68	1335	8,030	—	.01	.02	.04	—	—	—	—	—	—	—	—
02/16/68	1400	10,600	—	—	—	—	—	—	—	—	—	—	—	—
03/22/68	1430	16,000	—	.01	.01	.01	—	—	—	—	—	—	—	—
04/24/68	—	12,700	—	—	—	—	.01	—	—	—	—	.06	—	—
05/27/68	1335	29,700	—	—	.02	—	—	—	—	—	—	.07	—	—
07/03/68	1445	21,000	—	.01	.01	.02	—	—	—	—	—	.11	—	.01
07/30/68	1215	6,320	—	—	.01	—	—	.02	—	—	—			
09/01/68	1200	3,520	—	—	.01	.01	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 40—USGS NO. 8-1620 COLORADO RIVER AT WHARTON, TEX.														
10/06/66	1400	750	—	—	—	—	—	—	—	—	—	—	—	—
11/08/66	1050	935	—	—	—	—	—	—	—	—	—	—	—	—
12/14/66	1015	280	—	—	—	—	—	—	—	—	—	—	—	—
01/18/67	1415	270	—	—	—	—	—	—	.01	—	—	—	—	—
02/28/67	1600	295	—	—	—	—	—	—	—	—	—	—	—	—
03/28/67	1100	675	—	—	—	—	.01	—	—	—	—	—	—	—
05/02/67	1315	880	—	—	—	—	—	—	—	—	—	—	—	—
06/06/67	1500	1,260	—	.01	.01	.03	—	—	—	—	—	—	—	—
08/23/67	0910	1,320	—	—	—	—	—	—	—	—	—	—	—	—
09/19/67	1140	770	—	—	—	—	—	—	—	—	—	—	—	—
10/24/67	1445	984	—	—	—	.04	—	—	—	—	—	—	—	—
11/30/67	—	670	—	.01	—	.01	.01	.07	—	—	—			
01/09/68	1600	2,340	—	.04	.02	.12	—	—	—	—	—	—	—	—
02/14/68	1030	6,370	—	.01	.01	.03	—	—	—	—	—	—	.01	—
03/13/68	0715	7,600	—	.01	.01	.05	—	—	—	—	—	—	—	—
04/16/68	1425	8,020	—	—	.01	.04	—	—	—	—	—	.05	—	.01
05/23/68	1230	12,500	—	—	—	.09	—	—	—	—	—	—	—	—
07/02/68	1700	6,740	—	.01	—	.02	—	—	—	—	—	—	—	—
08/08/68	1650	1,570	—	.01	.01	.01	—	—	—	—	—	—	—	—
09/03/68	1420	1,420	—	—	—	—	—	—	—	—	—	—	—	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 52—USGS NO. 8-4692 RIO GRANDE BELOW ANZALDUAS DAM, TEX.														
10/13/66	1415	180	—	—	—	—	—	—	—	—	—	—	—	—
11/16/66	0830	865	—	—	—	—	—	—	—	—	—	—	—	—
12/19/66	0830	1,550	—	—	—	—	—	—	—	—	—	—	—	—
01/16/67	0830	862	—	—	—	—	—	—	—	—	—	—	—	—
02/15/67	0830	791	—	—	.01	—	—	—	.01	—	—	—	—	—
03/14/67	1500	1,570	—	—	.01	—	—	—	.01	—	—	—	—	—
04/17/67	2145	2,450	—	—	—	—	—	—	—	—	—	—	—	—
05/15/67	0930	4,380	—	—	—	—	—	—	—	—	—	—	—	—
06/15/67	1145	2,830	.02	.01	.01	—	—	—	.02	—	.01	—	—	—
08/21/67	1345	1,800	—	—	—	—	—	—	—	—	—	—	—	—
09/19/67	1600	3,810	—	—	—	—	—	—	—	—	—			
10/16/67	0830	16,800	—	.01	.02	.01	—	—	—	—	—	—	—	—
11/20/67	1430	3,600	—	—	.01	.01	—	—	—	—	—	—	—	—
12/11/67	1300	2,620	—	—	.01	.01	—	—	—	—	—	—	—	—
01/16/68	0850	2,280	—	—	—	—	—	—	—	—	—	—	—	—
02/14/68	1230	1,940	—	—	—	—	—	—	—	—	—	—	—	—
03/12/68	0915	2,300	—	—	—	—	—	—	—	—	—	—	—	—
04/15/68	0850	1,350	—	—	—	—	—	—	—	—	—	—	—	—
05/15/68	0830	1,880	—	—	.01	—	—	—	—	—	—	—	—	—
06/17/68	1330	3,270	—	—	—	—	—	—	—	—	—	—	—	—
07/16/68	0945	3,220	—	—	—	—	—	—	—	—	—	—	—	—
08/15/68	0715	621	—	—	—	—	—	—	—	—	—	—	—	—
09/23/68	0735	191	—	—	.01	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 54—USGS NO. 8-3965 PECOS RIVER NEAR ARTESIA, N. MEX.														
11/02/67	1115	25.5	—	—	—	—	—	—	—	—	—	—	—	—
12/12/67	1100	39.0	—	—	—	—	—	—	—	—	.01	—	—	—
01/23/68	1145	75.9	—	—	—	—	—	—	—	—	—	—	—	—
03/05/68	1020	47.0	—	—	—	—	—	—	—	—	—	—	—	—
04/03/68	1440	795.0	—	—	—	—	—	—	—	—	—	—	—	.05
04/29/68	1400	45.2	—	—	—	—	—	—	—	—	—	—	—	—
05/29/68	1145	9.38	—	—	—	—	—	—	—	—	—	—	—	—
07/01/68	1350	42.0	—	—	—	—	—	—	—	—	—	—	—	—
07/30/68	—	17.6	—	—	—	—	—	—	—	—	—	—	—	—
08/28/68	—	3.40	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 63—USGS NO. 9-5255 COLORADO RIVER (YUMA MAIN CANAL) AT YUMA, ARIZ.														
10/03/66	1430	326	—	—	—	—	—	—	—	—	—	—	—	—
11/03/66	1045	419	—	—	—	—	—	—	—	—	—	—	—	—
12/02/66	1030	232	—	—	—	—	—	—	—	—	—	—	—	—
01/09/67	1330	152	—	—	—	—	—	—	—	—	—	—	—	—
02/06/67	1000	124	.02	—	—	—	—	—	—	—	—	—	—	—
03/06/67	0940	92	—	—	—	—	—	—	.01	—	—	—	—	—
04/06/67	1330	274	—	—	—	—	—	—	—	—	—	—	—	—
05/04/67	0930	653	—	—	—	—	—	—	—	—	—	—	—	—
06/01/67	1045	512	.02	—	—	—	—	.01	—	—	—	—	—	—
08/18/67	0930	614	—	—	—	—	—	—	—	—	—	—	—	—
09/07/67	0930	200	—	—	—	—	—	—	—	—	—	—	—	—
10/05/67	0930	578	—	—	—	—	—	—	—	—	—	—	—	—
11/07/67	0930	476	—	—	—	.01	—	—	—	—	—	—	—	—
12/05/67	0945	186	—	—	—	—	—	—	—	—	—	—	—	—
01/08/68	1100	120	—	—	—	.01	—	—	—	—	—	—	—	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 63—USGS NO. 9-5255 COLORADO RIVER (YUMA MAIN CANAL) AT YUMA, ARIZ.—Continued														
02/06/68	0950	539	—	—	—	—	—	—	—	—	—	—	—	—
03/05/68	—	154	—	—	—	—	—	—	—	—	—	—	—	—
04/02/68	0930	232	—	—	—	—	—	—	—	—	—	—	—	—
05/07/68	0850	403	—	—	—	—	—	—	—	—	—	—	—	—
06/04/68	0935	666	—	—	—	—	—	—	—	—	—	—	—	—
07/02/68	0930	553	—	—	—	—	—	—	—	—	—	—	—	—
08/06/68	0930	275	—	—	—	—	—	—	—	—	—	—	—	—
09/03/68	1030	349	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 66—USGS NO. 9-3150 GREEN RIVER AT GREEN RIVER, UTAH [* = estimate (ized)]														
11/22/67	1315	3,840	—	—	—	.01	—	—	—	—	—	—	—	—
01/17/68	1215	*3,800	—	—	—	.01	—	—	—	—	—	—	—	—
02/27/68	1430	4,370	—	—	—	—	—	—	—	—	—	—	—	—
03/13/68	1145	4,760	—	—	—	—	—	—	—	—	—	—	—	—
04/26/68	1200	6,540	—	—	—	—	—	—	—	—	—	—	—	—
05/15/68	1300	12,200	—	—	—	—	—	—	—	—	—	—	—	—
06/14/68	1330	17,900	—	—	—	—	—	—	—	—	—	—	—	—
07/15/68	1500	6,700	—	—	—	—	—	—	—	—	—	—	—	—
08/12/68	1545	5,790	—	—	—	—	—	—	—	—	—	—	—	—
09/16/68	1430	4,030	—	—	—	—	—	—	—	—	—	.06	—	.07
IRRIG. NETWORK NO. 71—USGS NO. 9-5195 GILA RIVER BELOW GILLESPIE DAM, ARIZ.														
11/21/67	1100	20	—	.01	.03	03	.01	.01	—	—	.02	—	—	—
12/19/67	1500	360	—	.02	.03	.07	—	—	—	—	.02	—	—	—
01/23/68	1100	34	—	—	.01	.01	—	—	—	—	.02	—	—	—
02/15/68	1315	83	—	—	.03	—	—	—	—	—	—	—	—	—
03/21/68	0945	105	—	.01	.02	.01	—	—	—	—	.01	—	—	—
04/17/68	1205	34	—	—	—	—	.02	—	—	—	.01	—	—	—
05/13/68	1015	28	—	.02	.04	01	—	—	—	—	.01	—	—	—
06/18/68	1200	12	—	.01	.03	—	—	—	—	—	—	—	—	—
07/18/68	1030	8	—	—	.05	.03	—	—	—	—	—	—	—	—
08/21/68	1200	14	—	—	—	—	—	—	—	—	—	—	—	—
09/18/68	1315	6	—	.01	.03	.04	.01	—	—	—	.01	—	—	—
IRRIG. NETWORK NO. 79— USGS NO. 10-3350 HUMBOLDT RIVER NEAR RYE PATCH, NEV.														
10/17/67	—	198	—	—	—	—	—	—	—	—	—	—	.05	—
12/01/67	0830	0.50	—	—	—	—	—	—	—	—	—	—	—	—
01/02/68	0810	1.2	—	—	—	06	—	—	—	—	—	—	—	—
02/01/68	0800	1.0	—	—	—	—	—	—	—	—	—	—	—	—
03/01/68	0830	2.7	—	—	—	02	—	—	—	—	—	—	.02	—
04/01/68	1300	96	—	—	—	—	—	—	—	—	—	—	.03	—
04/30/68	—	315	—	—	—	—	—	—	—	—	—	—	.02	—
06/01/68	—	313	—	—	—	—	—	—	—	—	—	—	.01	—
07/01/68	0930	275	—	—	—	—	—	—	—	—	—	—	.21	—
08/01/68	0900	68	—	—	—	—	—	—	—	—	—	.08	.13	—
09/03/68	1000	89	—	—	—	—	—	—	—	—	—	—	.12	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 86a—USGS NO. 11-4255 SACRAMENTO RIVER AT VERONA, CALIF.														
10/21/66	1300	8,630	—	—	—	—	—	—	—	—	—	—	—	—
11/03/66	1105	8,610	—	.01	—	—	—	—	—	—	—	—	—	—
01/06/67	0920	18,100	—	—	—	—	—	—	—	—	—	—	—	—
02/02/67	0800	66,000	.01	—	—	—	—	—	.02	—	—	—	—	—
03/06/67	1030	21,300	—	—	—	—	—	—	—	—	—	—	—	—
06/06/67	0815	38,300	—	—	—	—	—	—	—	—	—	—	—	—
08/25/67	1045	12,500	—	—	—	—	—	—	—	—	—	—	—	—
09/08/67	0850	14,800	—	—	—	—	—	—	—	—	—	—	—	—
10/16/67	0850	13,100	—	—	—	.01	—	—	—	—	—	—	.01	.01
11/16/67	1030	11,100	—	—	—	.01	—	—	—	—	—	—	—	—
12/21/67	1110	12,100	—	—	—	.01	—	—	—	—	—	—	—	.03
01/19/68	1115	30,600	—	—	—	.01	—	—	—	—	—	—	—	—
02/29/68	0930	58,400	—	—	—	—	—	—	—	—	—	—	—	.01
04/15/68	1500	11,000	—	—	—	—	—	—	—	—	—			
05/10/68	0930	12,800	—	—	.01	.05	—	—	—	—	—	.03	—	—
06/13/68	1030	9,620	—	—	—	—	—	—	—	—	—	—	—	—
06/29/68	1530	7,800	—	—	—	—	—	—	—	—	—	—	—	—
07/22/68	1025	10,000	—	—	—	.02	—	—	—	—	—	—	—	—
09/26/68	1130	11,700	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 88a—USGS NO. 11-4070 FEATHER RIVER NEAR OROVILLE, CALIF.														
10/31/67	1500	2,450	—	—	—	.01	—	—	—	—	—			
11/30/67	1630	930	—	—	—	—	—	—	—	—	—	—	—	—
12/27/67	1520	618	—	—	—	—	—	—	—	—	—	—	—	—
01/01/68	1630	361	—	—	—	01	—	—	—	—	—	—	—	—
01/31/68	1555	352	—	—	—	—	—	—	—	—	—	—	—	—
03/09/68	1120	370	—	—	—	.01	—	—	—	—	—	—	—	—
04/02/68	1115	342	—	—	—	—	—	—	—	—	—	—	—	—
05/03/68	1030	370	—	—	—	—	—	—	—	—	—	—	—	—
06/06/68	1600	332	—	—	—	—	—	—	—	—	—	—	—	—
07/02/68	1015	342	—	—	—	—	—	—	—	—	—	—	—	—
08/01/68	1140	352	—	—	—	—	—	—	—	—	—	—	—	—
09/05/68	1215	323	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 94—USGS NO. 12-5105 YAKIMA RIVER AT KIONA, WASH.														
10/11/66	1100	1,550	.01	—	—	—	—	—	.01	—	.01	—	—	—
11/08/66	1135	1,970	—	—	—	—	—	—	—	—	—	—	—	—
12/06/66	1430	3,270	—	—	—	—	—	—	—	—	—	—	—	—
01/12/67	1130	2,650	—	.02	—	—	—	—	—	—	—	—	—	—
02/13/67	1845	4,350	—	—	.01	—	—	—	.01	—	—	—	—	—
03/21/67	1115	2,060	—	—	—	—	.01	—	.01	—	—	—	—	—
04/20/67	1535	2,020	—	.02	—	.02	.02	—	.01	—	—	—	—	—
05/26/67	1115	5,380	—	—	—	—	—	—	—	—	—	—	—	—
06/23/67	1325	10,200	—	—	.03	.03	.04	—	—	.04	—	—	—	—
08/22/67	1630	1,470	—	—	—	—	—	—	—	—	—	.18	—	—
09/29/67	1145	1,540	—	—	—	—	—	—	—	—	—	.30	—	.01
10/30/67	1640	4,440	—	.01	.01	.01	.01	—	—	—	—	—	—	—
11/29/67	1155	2,840	—	—	—	.01	.01	—	—	—	—	—	—	—
12/28/67	1235	10,100	—	.02	.02	.01	—	—	—	—	—	—	—	—
01/22/68	1215	7,790	—	—	.01	.01	—	—	—	—	—	—	—	—

TABLE 2.—*Pesticide content of selected streams in Western United States*—Continued

[— = not present; blank = data not obtainable]

Date	Time (24 hour)	Instantaneous Discharge (cfs)	Parts Per Billion (Micrograms per liter)											
			Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T
IRRIG. NETWORK NO. 94—USGS NO. 12-5105 YAKIMA RIVER AT KIONA, WASH.—Continued														
02/24/68	1225	13,300	—	.01	.01	.01	—	—	—	—	—	—	—	—
03/28/68	1725	3,380	—	—	—	.01	—	—	—	—	—	—	—	—
04/24/68	1153	1,300	—	—	—	.03	—	—	—	—	—	.05	—	—
05/29/68	1105	1,900	—	—	.01	.03	.01	—	—	—	—	.24	—	—
06/27/68	1400	1,420	—	.01	.02	.02	—	—	—	—	—	.33	—	—
07/18/68	1450	1,120	—	.02	.01	.02	.01	—	—	—	—	.21	—	—
08/26/68	0945	2,890	—	.01	.01	.02	.01	—	—	—	—	.29	—	—
09/25/68	1400	2,120	—	—	—	—	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 97—USGS NO. 13-1545 SNAKE RIVER AT KING HILL, IDAHO														
11/02/66	0940	4,220	—	—	—	—	—	—	—	—	—	—	—	—
12/12/66	1245	10,900	—	—	—	—	—	—	—	—	—	—	—	—
01/03/67	1620	10,500	—	—	—	—	—	—	—	—	—	—	—	—
02/06/67	1030	5,440	.01	—	—	—	—	—	.02	—	—	—	—	—
03/16/67	1930	8,350	—	—	—	—	—	—	.01	—	—	—	—	—
04/17/67	1250	11,300	—	—	—	—	—	—	.04	—	—	—	—	—
05/28/67	1300	11,300	—	—	—	—	—	—	—	—	—	—	—	—
06/21/67	1726	22,500	.02	—	—	—	.01	—	—	—	—	—	—	—
08/22/67	0920	4,270	—	—	—	—	—	—	—	—	—	.14	—	—
09/25/67	1430	12,000	—	—	—	—	—	—	—	—	—	—	—	—
10/31/67	1540	13,300	—	—	—	.02	—	—	—	—	—	.06	—	—
12/01/67	1300	13,100	—	—	—	.01	—	—	—	—	—	—	—	—
01/08/68	1300	14,600	—	—	—	.01	—	—	—	—	—			
02/13/68	1625	11,900	—	—	—	—	—	—	—	—	—	—	—	—
03/18/68	1105	5,570	—	—	—	—	—	—	—	—	—	—	—	—
04/24/68	1245	8,370	—	—	—	—	—	—	—	—	—	—	—	—
05/26/68	1230	7,620	—	—	—	—	—	—	—	—	—	—	—	—
06/25/68	1110	5,870	—	—	—	—	—	—	—	—	—	.05	—	—
07/23/68	1145	6,360	—	—	—	—	—	—	—	—	—	.10	—	—
08/26/68	1030	7,840	—	—	—	—	—	—	—	—	—	—	—	—
10/01/68	1315	10,900	—	—	—	.02	—	—	—	—	—	—	—	—
IRRIG. NETWORK NO. 102—USGS NO. 14-1057 COLUMBIA RIVER AT THE DALLES, OREG.														
10/16/66	0800	94,200	—	.01	—	—	.01	—	—	—	—	—	.03	—
11/21/66	0925	113,200	—	—	—	—	—	—	—	—	—	—	—	—
12/19/66	1400	107,300	—	—	—	—	—	—	—	—	—	—	—	—
01/26/67	0800	151,000	—	—	—	—	—	—	.01	—	—	—	—	—
02/08/67	1100	159,400	.01	—	—	—	—	—	.01	—	—	—	—	—
03/21/67	1045	146,100	—	—	—	—	—	—	.02	—	—	—	—	—
05/03/67	1040	152,700	—	—	—	—	—	—	—	—	—	—	—	—
06/14/67	1400	590,400	—	—	—	.01	—	—	.01	—	—	—	—	—
08/29/67	1615	154,100	—	—	—	—	—	—	—	—	—	—	—	—
09/19/67	1200	125,900	—	—	—	—	—	—	—	—	—	—	—	—
11/02/67	1120	108,300	—	—	—	.01	—	—	—	—	—	.02	—	—
11/30/67	0900	157,500	—	.01	.01		—	—	—	—	—	—	—	—
01/02/68	1235	133,700	—	.01	—	.01	—	—	—	—	—	—	—	—
02/20/68	1530	166,200	—	—	—	—	—	—	—	—	—	—	—	—
04/04/68	0945	182,000	—	—	—	—	—	—	—	—	—	—	—	—
05/13/68	1645	108,100	—		—	.01	—	—	—	—	—	.03	—	—
06/26/68	1020	348,200	—	—	—	—	—	—	—	—	—	—	—	—
08/08/68	1600	202,000	—	—	—	—	—	—	—	—	—	—	—	—
09/30/68	1600	112,600	—	—	—	—	—	—	—	—	—	—	—	—

TABLE 3.—*Occurrence of pesticides, October 1967 to September 1968*

Stream and location	Aldrin	DDD	DDE	DDT	Dieldrin	Endrin	Heptachlor	Heptachlor epoxide	Lindane	2,4-D	Silvex	2,4,5-T	Totals
Missouri River at Nebraska City, Nebr.	1	0	0	2	1	0	0	0	0	3	0	0	7
Yellowstone River near Billings, Mont.	0	0	0	1	0	0	0	0	0	2	0	0	3
James River at Huron, S. Dak.	0	0	0	1	0	0	0	0	0	5	0	0	6
Platte River at Brady, Nebr.	0	0	0	1	1	0	0	0	0	0	0	0	2
Arkansas River below John Martin Reservoir, Colo.	0	0	0	3	4	0	0	0	1	2	0	2	12
Arkansas River at Van Buren, Ark.	0	0	0	3	0	0	0	0	0	5	0	7	15
Canadian River near Whitefield, Okla.	0	1	0	3	0	0	0	0	0	2	0	7	13
Brazos River at Richmond, Tex.	0	4	8	6	1	1	0	0	1	3	0	2	26
Colorado River at Wharton, Tex.	0	6	5	9	1	1	0	0	0	1	1	1	25
Rio Grande below Anzalduas Dam, Tex.	0	1	5	3	0	0	0	0	0	0	0	0	9
Pecos River near Artesia, N. Mex.	0	0	0	0	0	0	0	0	1	0	0	1	2
Yuma Main Canal at Yuma, Ariz.	0	0	0	2	0	0	0	0	0	0	0	0	2
Green River at Green River, Utah	0	0	0	2	0	0	0	0	0	1	0	1	4
Gila River below Gillespie Dam, Ariz.	0	6	9	7	3	1	0	0	7	0	0	0	33
Humboldt River near Rye Patch, Nev.	0	0	0	2	0	0	0	0	0	1	8	0	11
Sacramento River at Verona, Calif.	0	0	1	6	0	0	0	0	0	1	1	3	12
Yakima River at Kiona, Wash.	0	6	8	11	5	0	0	0	0	5	0	0	35
Snake River at King Hill, Idaho	0	0	0	4	0	0	0	0	0	3	0	0	7
Columbia River at The Dalles, Oreg.	0	2	1	3	0	0	0	0	0	2	0	0	8
Feather River at Oroville, Calif.	0	0	0	3	0	0	0	0	0	0	0	0	3
TOTALS	1	26	37	72	16	3	0	0	10	36	10	24	235

APPENDIX

Chemical Names of Compounds Mentioned in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1, 4-*endo-exo*-5,8-dimethanonaphthalene
BHC	1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers
2,4-D	2,4-dichlorophenoxyacetic acid
DDD (TDE)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDD contains some *o,p'*-isomer also.
DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
DDT (including its isomers and dehydrochlorination products)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in a ratio of about 3 or 4 to 1)
DIELDRIN	Not less than 85% of 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-dimethano=naphthalene
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-dimethanonaphthalene
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer
SILVEX	2-(2,4,5-trichlorophenoxy) propionic acid
2,4,5-T	2,4,5-trichlorophenoxyacetic acid

ERRATA

PESTICIDES MONITORING JOURNAL, Volume 2, Number 4, p. 159: Under *Organic Phosphate Pesticide Chemicals,* it was erroneously reported that "The incidence and quantities of organic phosphate pesticide residues were quite low and comprised 5.5% and 15.5% of the total organic pesticide chemical residues in 1967 and 1968, respectively." The percentage figures in this statement are reversed and should read "15.5% and 5.5%."

Under *Herbicide and Carbamate Chemicals,* second paragraph, it was erroneously reported that "The incidence and amounts of carbamate chemicals detected were very low and comprised 3.7% and 11.2% of the total organic pesticide residues in 1967 and 1968, respectively." The percentage figures in this statement also were reversed and should read "11.2% and 3.7%."

Information for Contributors

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and interlaboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

——Preparation of manuscripts should be in conformance to the STYLE MANUAL FOR BIOLOGICAL JOURNALS, American Institute of Biological Sciences, Washington, D. C., and/or the STYLE MANUAL of the United States Government Printing Office.

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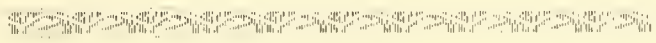
We regret to announce that Dr. James B. DeWitt, Member, Editorial Advisory Board, died suddenly on August 15, 1969. His loss will be felt keenly by his associates on the Editorial Board and the Journal staff.



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The parent committee is composed of representatives of the U. S. Departments of Agriculture, Defense, the Interior, and Health, Education, and Welfare.

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Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Pesticide Monitoring Subcommittee which participate in operation of the national pesticides monitoring network, are expected to be principal sources of data and interpretive articles. However, pertinent data *in summarized form*, together with interpretive discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both within and without the United States. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the *Journal* is not intended as a primary medium for the publication of basic research. Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Subcommittee. Authors are given the benefit of review comments prior to publication.

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Editorial Manager

PESTICIDES MONITORING JOURNAL
Pesticides Program
Food and Drug Administration
4770 Buford Highway, Bldg. 29
Chamblee, Georgia 30341

CONTENTS

Volume 3 December 1969 Number 3

RESIDUES IN FOOD AND FEED

Arsenic in Cottonseed Products and Various Commodities [1]

Reno Bradicich, Norman E. Foster[2], Frank E. Hons, Marshall T. Jeffus, and Charles T. Kenner[3]

ABSTRACT

Arsenic was determined on routine samples of various commodities obtained in 1963 for pesticide residue and radioactivity determinations from areas in which arsenical defoliation was known to be practiced. The study was continued in 1964, 1965, and 1966 on cottonseed products. The results indicated that levels of arsenic in commodities for human consumption from areas in which arsenical defoliation is practiced are well below the established tolerance of 4 ppm (as As_2O_3). Of the 159 cottonseed product samples tested, 143 were positive, but only 3 were above the established tolerance, and the overall average was less than 0.9 ppm.

Introduction

Arsenic is determined on samples collected in the study of pesticide residues in total diet samples being conducted by the Food and Drug Administration *(1-5)*. These studies have shown that for any 1 year up to 18% of the composite samples tested contained measurable arsenic residues and that during the period from June 1967 through April 1968, 3 of 30 composite samples of oils, fats, and shortenings contained from 0.1 to 0.4 ppm arsenic (as As_2O_3). However, no studies have been reported concerning cottonseed products from areas where defoliants are in general use.

In order to furnish background material on the arsenic content of various crops in areas where arsenical defoliants are used on cotton, the Dallas District Laboratory of the Food and Drug Administration determined the arsenic content of 107 routine samples collected by regular FDA procedures in 1963 for the determination of pesticide residues or radioactivity. Seventy-two percent of these samples showed measurable amounts of arsenic, but all were well below the tolerance of 4 ppm (as As_2O_3). Since arsenic was found in over 95% of the cottonseed oil and cottonseed meal samples at values which were in general signifieantly higher than the other commodities, the study was continued in 1964, 1965, and 1966, utilizing the random cottonseed product samples collected by FDA Inspectors for the determination of pesticide content during routine cottonseed oil mill inspections. In each case, a portion of the composited sample prepared for the pesticide or radioactivity determination was retained for the arsenic determination.

The samples were colleeted from mills in all the major cotton-growing areas in Texas in which defoliation with arsenicals was known to be practiced. A few were obtained from similar areas in Oklahoma. The samples are probably representative of the areas in which the mills were located but cannot be connected directly to defoliation since it was not possible to trace the individual samples to specific cottonfields. Similarly, it was not possible to relate the various products picked up at any one mill with each other since the cottonseed utilized in the preparation of one product was not neeessarily from the same lot as that used in the preparation of the other products.

Analytical Procedures

The silver diethyldithiocarbamate procedure of Morrison *(6)* was used for the determinations with minor modifications. Bulky samples such as cottonseed hulls required more than the stated amounts of the MgO-$Mg(NO_3)_2$ slurry to offset the loss of arsenic

[1] Dallas District, Food and Drug Administration, U. S. Department of Health, Education, and Welfare, 3032 Bryan Street, Dallas, Tex. 75204.
[2] Present address: School of Pharmacy, Southwestern State College, Weatherford, Okla. 73096.
[3] Present address: Department of Chemistry, Southern Methodist University, Dallas, Tex. 75222.

during the ashing step. Many of the determinations in the 1963 pilot study were made on the ash used for the determination of the radioactivity of the samples. These samples were dried to incipient charring in a microwave oven and then ashed at 550-600 C without the addition of the MgO-$Mg(NO_3)_2$ slurry.

Recovery studies were performed in both 1963 and 1964 to determine the efficiency of the determinations.

Results and Discussion

The arsenic content of various commodities from the pilot study in 1963 is shown in Table 1. Since the sensitivity of the Morrison method *(6)* is 0.2 μg of As(0.26 μg of As_2O_3), selection of proper sample weights allows estimation of values to the closest 0.01 ppm. The values below 0.1 ppm in the table, however, should be considered as estimates rather than absolute values. All the samples were well below the established tolerance of 4 ppm (as As_2O_3). A majority (77 out of 107) of the samples showed a positive test for arsenic, and over 95% of the cottonseed oil and cottonseed meal samples were positive at levels significantly higher than the other commodities. The recovery study conducted at the same time showed an average recovery of 71%. The low value is due to the fact that the MgO-$Mg(NO_3)_2$ slurry was not added to a large number of these samples before ashing. The values in Table 1 have not been corrected for this average recovery.

The results for cottonseed products for the years 1963 through 1966 are shown in Table 2. Of the 159 samples tested, 143 were positive, but only 3 were above the established tolerance of 4 ppm As_2O_3, and the overall average was less than 0.9 ppm. Two of those above 4 ppm were hull samples, one was a meal sample, and all three came from different areas of the State. One of the hull samples occurred in 1965; the other two samples were found in 1966. The average for all hull samples was 1.2 ppm and for all meal samples was 1.4 ppm, while the average for oil samples (the main product for human consumption) was 0.4 ppm. Recovery studies in 1964 showed an average recovery of 88%. The values in Table 2, however, have not been corrected for this average recovery.

These results indicate that levels of arsenic in cottonseed products for human consumption from areas in which arsenical defoliation is practiced are well below established tolerances.

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TABLE 1.—*Arsenic (as As_2O_3) in various commodities, Texas, 1963*

Product	No. of Counties Sampled	No. of Samples	No. of Positives [1]	Avg. ppm [2]	Max. ppm [2]
Potatoes	1	2	2	0.02	0.02
Mustard greens	3	5	4	0.04	0.08
Turnip greens	2	4	3	0.03	0.04
Cabbage	3	7	2	0.01	0.01
Sweet potatoes	1	1	0	0.00	
Radishes and tops	1	1	1	0.01	0.01
Lettuce	3	27	12	0.01	0.08
Carrot tops	1	1	1	0.16	0.16
Carrots	3	10	9	0.03	0.05
Corn	1	1	0	0.00	
Bell peppers	2	2	0	0.00	
Nonfat dry milk	1	1	1	0.01	0.01
Tomatoes	1	1	1	0.01	0.01
Peaches	2	6	6	0.07	0.08
Rough rice	1	4	4	0.16	0.22
Raw unshelled peanuts	1	2	2	0.01	0.01
Wheat	1	3	2	0.03	0.03
Cucumbers	1	2	2	0.03	0.03
Soybean oil	1	2	2	0.09	0.10
Cottonseed oil	6	13	12	0.13	0.52
Cottonseed meal	5	9	9	0.90	3.72
Spinach	1	1	1	0.04	0.04
Collards	2	2	1	0.01	0.01

[1] Sensitivity of method is 0.01 ppm.
[2] Not corrected for average recovery of 71%.

TABLE 2.—*Arsenic (as As_2O_3) in cottonseed products, Texas, 1963-1966*

Product	Year	No. of Counties Sampled	No. of Samples	No. of Positives [1]	Avg. ppm [2]	Max. ppm [2]
Meal	1963	5	9	9	0.90	3.72
	1964	11	12	12	1.72	3.39
	1965	13	13	12	1.15	2.77
	1966	13	13	13	[3] 1.67(1.18)	[4] 7.52(3.25)
Hulls	1964	11	12	12	0.64	1.57
	1965	7	7	5	[3] 2.08(0.89)	[4] 6.86(2.24)
	1966	7	8	6	[3] 1.29(0.17)	[4] 6.86(0.26)
Oil	1963	6	13	12	0.13	0.51
	1964	22	29	29	0.84	1.33
	1965	22	22	16	0.04	0.13
	1966	8	9	7	0.08	0.13
Cake	1964	3	3	3	1.05	1.90
	1966	3	3	1	0.13	0.13
Pellets	1966	2	2	2	0.12	0.13
Pepper dust	1964	1	1	1	1.40	1.40
Flour	1964	1	3	3	[5] 0.13	[5] 0.15

[1] Sensitivity of method is 0.01 ppm.
[2] Not corrected for average recovery of 88%.
[3] The values in parentheses are averages excluding the over-tolerance value.
[4] The values in parentheses are maximums excluding the over-tolerance value.
[5] Expressed as ppm As instead of As_2O_3.

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Pesticide Residues in Eagles [1]

William L. Reichel, Eugene Cromartie, Thair G. Lamont, Bernard M. Mulhern, and Richard M. Prouty

ABSTRACT

Bald and golden eagles found sick or dead in 18 States and Canada during 1964-1965 were analyzed for pesticide residues. Residues in bald eagles were considerably higher than in golden eagles. Residues of DDE, DDD, and dieldrin were detected in all samples of bald eagle carcasses; other compounds found less frequently were heptachlor epoxide, endrin, and DCBP, a metabolite of DDT. DDE was detected in all samples of golden eagle carcasses; DDD, DDT, dieldrin, and heptachlor epoxide were detected less frequently.

Introduction

In 1960 the Patuxent Wildlife Research Center initiated analyses of pesticide residues in samples of the declining bald eagle (*Haliaeetus leucocephalus*) population. Subsequently, eagles were included in the pesticide monitoring program, because they are carnivorous and at the top of food chains and their residues would therefore reflect contamination in lower organisms. Golden eagles (*Aquila chrysaëtos*) were analyzed for comparison, because they are not a declining species and are at the top of a different food chain.

The purpose of this paper is to report the residues found in bald and golden eagles collected in 1964 and 1965.

Sampling

A systematic sampling scheme for bald eagles could not be considered because of their relatively low population and their protected status. Bald and golden eagles found dead or moribund are collected by Federal, State, and private cooperators, packed in dry ice, and shipped air express to this laboratory for analyses. The collection areas for the 66 samples included in this report are shown in Table 1. Specimens that were decomposed or held in captivity were not analyzed.

TABLE 1.—*Distribution of eagles collected, by State and year of death*

Area	Bald Eagles		Golden Eagles	
	1964	1965	1964	1965
Alabama	1			
Alaska		2		
Arizona		1		
California		1		2
Florida		1		
Indiana	3	1		
Iowa	1	2		
Massachusetts	1			
Michigan	1			
Minnesota	3	2	1	
Misouri	1			
Nebraska		3	1	2
North Dakota		1		
Ohio	1			
Oregon		1		
South Dakota	1	3	3	12
Vermont	1			
Wisconsin	2	9		
Quebec		1		
Nova Scotia		1		
Total	16	29	5	16

Analytical Procedures

The bald eagles collected in 1965 were prepared and samples cleaned up and analyzed by electron capture gas chromatography by the method described by Reichel *et al. (3).* Briefly, this method consists of Soxhlet extraction and cleanup by acetonitrile partition and Florisil column procedures. The pesticides are then separated and removed in four fractions from a silica gel thin layer plate. Each fraction is analyzed separately on a 3% OV-17 column, and the residues are confirmed on a 3% XE-60 or a 10% QF-1 column. The determination of hepatchlor epoxide and 4, 4′-dichlorobenzophenone (DCBP), a metabolite of DDT, was initially carried out

[1] Bureau of Sport Fisheries and Wildlife, Patuxent Wildlife Research Center, Laurel, Md. 20810.

on the QF-1 column. However, this column was replaced by a DEGS column (12% DEGS on 100/110 mesh Anakrom SD operated at 190 C) which produced better resolution of these two compounds.

Sample extracts of all golden eagles and of the bald eagles collected in 1964 were prepared and cleaned up as described. However, the extracts were not separated into four fractions before analysis by thin layer chromatography. These samples were initially analyzed on a 3% SE-30 on 80/90 mesh Anakrom ABS column operated at 150 C. The samples were reanalyzed on a 3% OV-17 60/80 mesh Gas Chrom Q column operated at 170 C as described by Menzie *et al. (2)*. The residues were confirmed by thin layer chromatography using aluminum oxide G plates, developed with hexane, and visualized with silver nitrate spray and UV light. Residues of endrin and DCBP were not determined in the 1964 samples.

The average recovery for the common pesticides ranged from 85 to 96% from eagle carcass tissue fortified at the 2.5 ppm level. The lower limit of sensitivity was approximately 0.05 ppm.

Results and Discussion

The chlorinated pesticides found in bald eagles are shown in Table 2. Median values are presented instead of means because of the skewness of the data. All bald eagle carcass samples contained residues of *p,p'*-DDE, *p,p'*-DDD, and dieldrin and in general contained high residues of DDE. However, due to the wide range of residue levels and the small sample size, no trend could be determined between 1964 and 1965. Results of 12 of the 1964 bald eagles have been briefly mentioned by Stickel *et al. (4)*. One specimen contained 8 ppm of dieldrin in the brain, and dieldrin probably caused the death of this bird.

The residues in golden eagles (Table 3) are considerably lower than those in bald eagles. This may reflect the differences in food habits. Both species feed on a wide range of vertebrate animals, but the diet of the bald

TABLE 2.—*Pesticide residues in bald eagles, 1964-1965*

[T = <0.05 ppm]

Compound	Year	Residues in ppm [1]								
		Carcass			Liver			Brain		
		Median	Range	N [2]	Median	Range	N [2]	Median	Range	N [2]
p,p'-DDE	1965	8.90	0.30-93.1	28	4.91	0.09-132.8	28	1.37	T-72.8	28
	1964	7.80	0.50-91.2	16	5.15	0.12- 40.5	16	1.00	0.25-12.0	16
p,p'-DDD	1965	0.44	T-12.0	28	0.54	T- 24.0	27	0.40	T- 6.3	17
	1964	1.60	0.20-10.4	16	0.60	T- 6.8	16	0.16	T- 7.2	16
p,p'-DDT	1965	0.20	T- 1.6	17	T	T- 0.4	12	T	T- 1.0	6
	1964	0.42	T- 3.9	12	0.10	T- 0.2	12	T	T- 0.8	13
Dieldrin	1965	0.33	T- 1.4	28	0.21	T- 11.9	28	0.08	T- 3.9	21
	1964	0.65	T- 3.4	16	0.35	T- 5.1	16	0.10	T- 8.0	14
Heptachlor epoxide	1965	0.06	T- 0.8	21	T	T- 2.0	20	T	T- 0.6	12
	1964	0.09	T- 0.7	6	0.15	0.10- 0.3	4	0.10	T- 0.3	4
Endrin	1965	0.09	0.08- 0.5	4	0.09	T- 0.1	6	T	T- 0.1	5
DCBP	1965	0.31	0.20- 0.7	8	0.19	T- 1.0	8	0.30	T- 1.1	5

[1] Calculated on a wet-weight basis.
[2] Number of specimens that contained reisdues; the median is based on this number.
NOTE: A total of 29 birds were analyzed during 1965; however, one sample of carcass, liver, or brain was missing from three different birds. During 1964, 16 birds were analyzed.

TABLE 3.—*Pesticide residues in golden eagles, 1964-1965*

[T = <0.05 ppm]

Compound	Residues in ppm [1]								
	Carcass (21 Samples)			Liver (19 Samples)			Brain (20 Samples)		
	Median	Range	N [2]	Median	Range	N [2]	Median	Range	N [2]
p,p'-DDE	0.49	T-2.9	21	0.33	T-10.6	19	0.10	T-5.2	19
p,p'-DDD	T	T-0.7	7	T	T	6	T	T	7
p,p'-DDT	T	T-0.3	12	T	T- 0.1	10	T	T-0.3	8
Dieldrin	0.09	T-0.4	19	T	T- 0.4	19	T	T-0.4	16
Heptachlor epoxide	T	T-0.1	16	T	T- 0.3	14	T	T-0.3	7

[1] Calculated on wet-weight basis.
[2] Number of specimens that contained residues; the median is based on this number.
NOTE: A total of 21 birds were analyzed during 1964-1965.

eagle consists mainly of fish and birds whereas the diet of the golden eagle is composed primarily of mammals. The analyses of bald eagles revealed many unidentified compounds that can interfere with the gas chromatographic analysis of endrin, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT. However, these unknowns do not interfere when the analytical procedure described for the bald eagles collected in 1965 is employed.

The unknowns in the eagle samples have recently been identified as polychlorinated biphenyls (PCB) by mass spectrographic analysis. The mass spectra of the unknowns were obtained using a combined gas chromatograph-mass spectrometer and were compared with the mass spectra obtained from a commercial preparation of PCB. The presence of PCB in wildlife samples has also been demonstrated by mass spectrographic analysis in Sweden (*5*) and the Netherlands (*1*).

The quantification of PCB was not attempted, but it was evident from the gas chromatograms that these compounds were present in the same order of magnitude as DDE. It would appear from our analyses that PCB compounds should be detected in other types of environmental samples such as water, aquatic invertebrates, and fish.

Acknowledgments

Acknowledgments are due many individuals who participated in one or more portions of this study. Calvin M. Menzie, on the staff of the Patuxent Wildlife Research Center until 1967, performed gas chromatographic determinations of many of the eagles collected in 1964. Louis Locke, Dan Frye, and Nancy C. Coon performed the autopsies and dissections of eagles. Cooperators from many States and organizations submitted eagles for analysis. Particular thanks are due to the U. S. Game Management Agents throughout the country who submitted specimens and provided the field data.

See Appendix for chemical names of compounds mentioned in this paper.

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Organochlorine Insecticide Residues in Fish (National Pesticide Monitoring Program)

Croswell Henderson[1], Wendell L. Johnson[2], and Anthony Inglis[2]

ABSTRACT

As a part of the National Pesticide Monitoring Program, fish were collected from 50 sampling stations located in the Great Lakes and in major river basins throughout the United States. Three composite samples, consisting of five adult fish of each of three species, were collected at all stations during the spring and fall of 1967 and 1968. The composite whole fish samples were analyzed by commercial laboratories for residues of 11 organochlorine insecticides. DDT and/or metabolites were found in 584 of the 590 composite samples, with values ranging to 45 ppm (mg/kg wet weight, whole fish). Dieldrin was found in 75% of the samples, with values ranging upward to nearly 2 ppm. Other organochlorine insecticide residues were found in fewer samples, but some had fairly high residue levels. Relatively high residues of DDT and metabolites, dieldrin, heptachlor, heptachlor epoxide, and chlordane were found consistently during all sampling periods at some stations.

Introduction

In the President's Science Advisory Committee report, "Use of Pesticides," (*19*) one of the recommendations was that various concerned agencies ". . . develop a continuing network to monitor pesticide residues in air, water, soil, man, wildlife and fish." To implement this recommendation, the Federal Committee on Pest Control established a subcommittee to develop monitoring programs and objectives.

* "The objectives of the National Pesticide Monitoring Program are: (1) a continuing nationwide assessment of the general levels of pesticide residues in the environment, and (2) the location of possible problem areas within specific segments of the environment.

"These objectives are to be attained by sampling all elements of the environment on a nationwide basis. Sampling systems will be designed to represent the national picture as well as the major categories of environment within the United States. Data will be collected so that for each category, both the mean levels and the range of variation can be determined. Sampling will be repeated at appropriate intervals so that real trends in levels of pesticide residues can be detected.

"Possible problem areas will be located where the survey data indicate the concentration of a pesticide has developed above the general level or where there is an increasing concentration over a period of time."

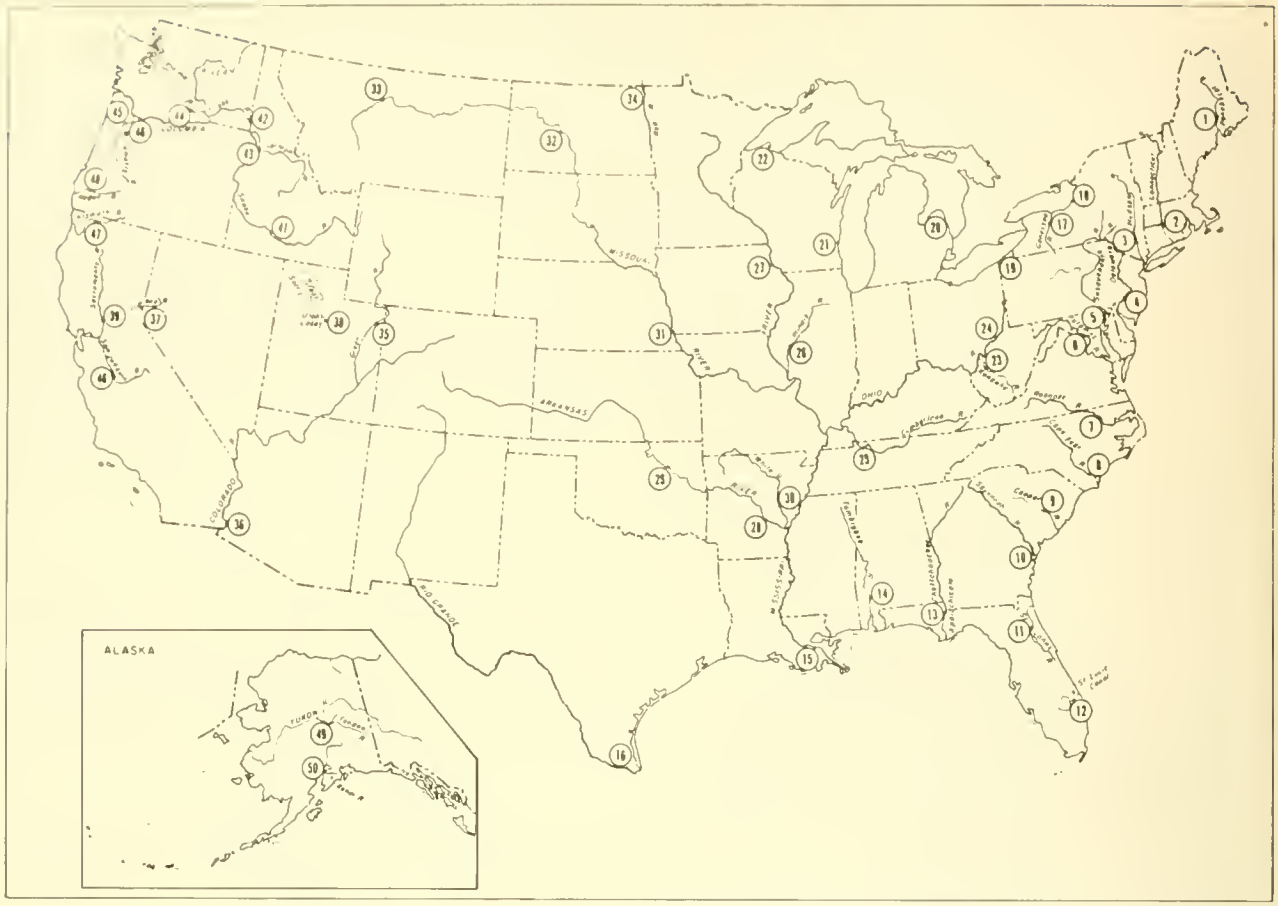
A nationwide fish monitoring program was initiated by the Bureau of Sport Fisheries and Wildlife in the spring of 1967. The procedures, described in some detail by Johnson *et al.* (*12*), were followed as closely as possible.

This report contains data on organochlorine insecticide residues in fish at 50 nationwide sampling stations during the spring (April, May) and fall (October, November) of 1967 and 1968.

[1] Division of Fishery Services, Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, Fort Collins, Colo. 80521.
[2] Division of Fishery Services, Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, Washington, D.C. 20240.

* Adopted by the FCPC Subcommittee on Pesticide Monitoring and accepted by the Federal Committee on Pest Control.

FIGURE 1.—*Fish sampling stations—National Pesticide Monitoring Program*



Methods

LOCATION OF SAMPLING STATIONS

Fish sampling stations were located as nearly as possible to coincide with those described by Johnson *et al.* (*12*). These stations, numbered 1 to 50, correspond in consecutive order to numbers 100045 to 100094 listed in the FCPC Catalog of Federal Pesticide Monitoring Activities (*7*). Stations were located in the Great Lakes and in major river systems throughout the United States (Fig. 1); all were near locations where water is monitored by other participants in the National Monitoring Program (*4, 9, 22*). Specific locations are listed in Table 4. Many stations were located near Bureau of Sport Fisheries and Wildlife facilities where assistance could be obtained in collecting fish.

FISH COLLECTIONS

It was realized initially that the same fish species could not be sampled at all stations. Instructions were issued to field personnel to collect composite samples of each of three species at each station, preferably from a list of indicator species near the top of the food chain—carp, buffalo, black bass, channel catfish, green sunfish, yellow perch, rainbow trout, and squawfish. Because of some difficulty in obtaining preferred species, the list was expanded to include suckers, other catfish, other trout, etc. Species were to be selected that would probably be easily obtainable during each successive sampling period. Each composite was to consist of five uniform size adult fish of the same species. Three composites, preferably the same three species, were to be collected each spring (April, May) and fall (October, November) at each of the 50 stations.

Fish were collected by various means, including seines, gill nets, traps, hook and line, electrofishing, etc., and some were purchased from commercial fishermen. The only method not permitted was the use of fish toxicants or other chemicals to avoid possible interference with the residue analyses.

Each composite sample (five whole fish) was wrapped separately in aluminum foil, frozen, packed in dry ice; then the three composites from each station were shipped immediately by air express to commercial laboratories for organochlorine insecticide analysis.*

* During the spring and fall 1967 and the spring 1968 collections, the brain was dissected from each fish, packaged in a separate vial, frozen, and shipped in dry ice to laboratories for brain cholinesterase determination. The cholinesterase data are not included in this report but may be reported separately at a later date.

Accompanying the shipment was a legend showing location, date collected, name of collector, method of collecting, species of fish, and the length, weight, and estimated age of each fish in each composite sample. Laboratories were notified by telephone or telegraph approximately when the shipment would arrive.

LABORATORY ANALYSIS

Five commercial laboratories in various sections of the United States participated in the residue analyses during one or more of the four sampling periods. These laboratories are designated by letter code A, B, C, D, and E throughout this report. Initially, it was believed that the use of sectionally located laboratories would expedite delivery and analysis of samples. Laboratories selected had been used previously for pesticide residue analyses by other Bureau of Sport Fisheries and Wildlife divisions with apparently satisfactory results. It was believed that cross-checks of samples between laboratories would show up any major differences or discrepancies and serve as an adequate quality control measure.

When arrangements were made with laboratories for residue analyses, they were notified as to the approximate number of samples to be shipped and approximate dates they would be received. They were requested to analyze each composite sample (usually five whole fish) for eleven organochlorine insecticides—DDE, TDE, DDT, dieldrin, aldrin, endrin, lindane, heptachlor, heptachlor epoxide, chlordane, and toxaphene. These pesticides were believed to be the most significant with regard to residues in fish. Results were to be reported as ppm (mg/kg) wet weight, whole fish. No particular method of analysis was specified, but each laboratory was requested to furnish a description of the method used. Details of methods as reported by each of the laboratories are as follows:

Laboratory A

The procedure with some minor modifications was taken from the *Guide to the Analysis of Pesticide Residues* published by the U.S. Department of Health, Education and Welfare (*21*).

Sample preparation: Each frozen composite sample was ground with a meat grinder and mixed thoroughly. Extraction: A 25-g representative sample was blended with 250 ml of petroleum ether and 50 g Na_2SO_4 for 5 minutes. The mixture was filtered through Na_2SO_4 into a 250-ml flask. Using the flash evaporator with the water bath at 40 C, the solvent was evaporated from the sample and the residue transferred to a 250-ml separatory funnel with five 5-ml rinsings of hexane. Partitioning: Twenty-five ml of hexane-saturated acetonitrile was added, and the separatory funnel was shaken for 1½ minutes. The two layers were allowed to separate, and the lower layer was drained into a 1-liter separatory funnel. The acetonitrile extraction was repeated three times, transferring each acetonitrile rinse to the separatory funnel. The acetonitrile fraction was mixed with 500 ml of water and 100 ml of petroleum ether. The mixture was shaken gently, and the layers allowed to separate. The water layer was discarded, and the petroleum ether layer was filtered through Na_2SO_4 into a 250-ml flask. The filtrate was evaporated to dryness.

Column chromatography: A chromatographic column, 25 mm O.D. x 30 cm with Teflon stopcocks, was prepared with 4 inches of settled Florisil topped with a ½-inch layer of Na_2SO_4. The Florisil had been activated at 650 C and stored at 130 C in glass bottles. The tissue extract, in approximately 5 ml of petroleum ether, was added to the top of the column and allowed to percolate through it at a rate of about 5 ml/minute. The flask which contained the extract was rinsed with two successive 5-ml portions of petroleum ether, and the rinsings poured onto the column. The walls of the chromatographic column were rinsed with an additional small quantity of petroleum ether. When the solvent reached the top of the Na_2SO_4 layer, elution with 200 ml of 6% diethyl ether in petroleum ether was commenced at a rate of 5 ml/minute, and the eluate was collected. When the last of the eluting solvent reached the upper surface of the Na_2SO_4 layer, the receiver was changed, and elution cotninued with 200 ml of 15% diethyl ether and the eluate from the column collected. Fraction I contained lindane, aldrin, heptachlor, heptachlor epoxide, DDE, TDE, DDT. Fraction II contained dieldrin and endrin. Each fraction was evaporated to dryness and the residue dissolved in 10 ml of hexane. Gas chromatography: The final analysis was done on an Aerograph Hy-FI Model 600 C with an electron capture detector. The 5′ x ⅛″ column was packed with 5% DC-200 on acid-washed, DMCS treated, 60/80 mesh Gas Chrom Q. Column temperature was 200 C and N_2 flow was 40 ml/minute. Results were calculated by comparison of the sample chromatograms with those obtained from standards injected under the same conditions.

No recovery rates were determined, and the results are not corrected for recovery. The sensitivity was reported as 0.001 ppm for all organochlorine insecticides.

Laboratory B

The method used is given in the *Guide to the Analysis of Pesticide Residues* (*21*).

Sample preparation and analysis: The fish were first thawed and ground in a Staub Model 4E Laboratory

Mill with grinding plates for wet materials. A sample was taken from the ground composite by standard quartering techniques. The analysis consisted of a hexane extract, acetonitrile partitioning, Florisil cleanup and gas chromatography using a Micro Tek MT220 equipped with a Ni^{63} detector. The column used was a prepared DC200 Gas Chrom Q column (Applied Science Laboratories, State College, Pa.). Good separations were obtained on this column for all of the pesticides analyzed with the exception of dieldrin and DDE. Both dieldrin and DDE were separated from each other during the Florisil cleanup. However, recent literature published by the Analytical Reference Service of the U.S. Public Health Service indicates that an incomplete separation of these two substances occurs which results in a somewhat lower than actual value for DDE.

No recovery rates were determined, and the results were not corrected for recovery. The sensitivity was reported as 0.001 ppm for all organchlorine insecticides.

Laboratory C

The spring and fall 1967 and spring 1968 samples were analyzed according to the 1964 revision of the FDA *Pesticide Analytical Manual* (*3*). Fall 1968 samples were analyzed according to the 1968 revision of the same manual (sections 211 and 311 for fatty foods and sections 212 and 311 for non-fatty foods) with modifications.

Sample preparation: The samples were received (frozen and packed in dry ice) from individual collectors. The samples were given an identification number and kept frozen until grinding. Each sample was chopped into about 1-lb pieces and then ground in a model 84181D Hobart food chopper until it looked homogeneous. A 200-g portion was placed in an 8-ounce bottle and frozen until analysis was performed. Extraction and cleanup: The 200-g samples were removed from the freezer, thawed and mixed, and 20 g of each sample was weighed into a 150-ml beaker. Each sample was then transferred to a 1-quart Waring Blendor jar and blended for 2 minutes with acetonitrile. The acetonitrile was filtered through a plug of glass wool into a 1-liter separatory funnel containing about 500 ml of tap water. The sample was then blended for about ½ minute with an additional 50 ml of acetonitrile and filtered into the separatory funnel. Two hundred ml of petroleum ether was added to the separatory funnel and shaken for 2 minutes. The layers were allowed to separate, and the bottom layer was drawn off. The petroleum ether extract was washed two more times with about 600 ml of tap water, discarding the water layer both times. Ten grams of Na_2SO_4 was added to the petroleum ether extract, and the sample was filtered into a 300-ml Erlenmeyer flask (rinsing the separatory funnel with about 70 ml of petroleum ether). The sample was then taken down to about 5 ml on a steam bath and made to 25 ml with petroleum ether. A 15-ml aliquot was taken and an acetonitrile partition run (*3*). The sample was then run through a Florisil column. The column elutions were made up to 25 ml.

Ten micrograms or less of the extract were injected into a gas chromatograph and the peaks measured for residue concentrations.

Gas chromatography: A Barber-Coleman Pesticide Analyzer Model 5360 equipped with a Sr^{90} detector was used. The ¼" x 4' glass column was packed with 5% DC-200 on Chromport XXX, 80/90 mesh. Temperatures were as follows: column—195 C, injector—250 C, and detector—240 C. The flow rate of N_2 carrier gas was adjusted to 100 ml/minute or to the rate at which *p,p'*-DDT had a retention time of 8-10 minutes.

Laboratory D

The procedures were adapted from the FDA *Pesticide Analytical Manual*, Volume 1 (*3*).

Samples as received were ground to the consistency of hamburger. An aliquot was weighed and then ground with twice to three times its weight of anhydrous Na_2SO_4 until free-flowing powder resulted. This sometimes required two or three separate grinding-mixing operations in an Osterizer blender-mixer. The mixed sample was placed in a Whatman thimble and inserted into a Soxhlet extraction apparatus where it was subjected to 4 hours of continuous extraction, using a solvent mixture of 10% (v/v) ethyl ether in 30-60C petroleum ether. The solvent extract was then exaporated just to dryness in an air stream, taken up in 30 ml of hexane, and transferred to a 125-ml separatory funnel, to which was added 30 ml of redistilled acetonitrile. The contents were shaken for several minutes, the layers allowed to separate, and the lower or acetonitrile layer drawn off into a 250-ml beaker. An additional 30 ml of fresh acetonitrile was added to the hexane solution in the separatory funnel; the mixture was shaken again for several minutes, then allowed to separate, and the acetonitrile was drawn off into the same 250-ml beaker. The acetonitrile solution, containing the pesticide residue, was evaporated in an air stream until just dry. The dry residue was then dissolved with several small portions of 10% ethyl ether in petroleum ether, in order to rinse the residue onto a 50%-50% (v/v)

Celite-MgO adsorption column (½ I.D.), in which the adsorbent was packed to a depth of approximately 4 inches. The column was prewetted with solvent, and a total of about 30 ml of solvent was used to transfer the contents of the beaker to the column. The solvent was then forced through the column with air pressure, into a 50-ml beaker. The eluate was evaporated to dryness and then transferred, by multiple washings with a solvent mixture of petroleum ether and ethyl ether, into 4-dram vials, and again allowed to evaporate to a dry residue. Just prior to injecting samples into a chromatograph, the dry residue in the 4-dram vials was dissolved and mixed with *n*-hexane (reagent) in an amount equivalent to 10 mg of original sample to 1 μl of solvent. Thus, if the original sample weighed 20 g, 2 ml of hexane would be added to the vial. This dilution was used for samples containing only tenths of parts per million of pesticide. For samples, which proved on chromatography to contain 1 or more parts per million, additional dilution was performed to provide proper conditions for the dynamic range of response of the gas chromatograph used. A 1-μl sample, contained in a Hamilton microliter syringe was injected into the Dow 11-packed column of an Aerograph Model 204B instrument, equipped with a tritium electron capture detector and operated at 8X attenuation with a standing current of at least 150 mv. Column temperature was 170 C, and injector and detector temperatures were about 200 C. After completing the sample chromatogram, a standard solution, containing known concentrations of several pesticide residues in hexane solution was injected, and its chromatogram obtained. The sample was next injected on the QF-1 packed column of the instrument, the chromatogram obtained, and a comparison made to a standard run on this column also. Measurement of retention times identified the pesticide present in the sample for each column, and its identification was dependent upon its being present in chromatograms from both columns. Next, peak areas for the identified materials were computed, using peak height x half-band width, and calculated as parts per million, upon comparison with standard peak areas. The results obtained were corrected by multiplication by 1.2, a factor obtained assuming 90% recovery on partition, and 90% recovery on the column cleanup, for a 1.1 x 1.1 correction.

The sensitivity was reported as 0.01 ppm for all organochlorine residues.

Laboratory E

These samples were analyzed following the procedures outlined in the FDA *Pesticide Analytical Manual* (*3*).

Extraction: A 20-g representative sample was ground with sufficient powdered anhydrous Na_2SO_4 to combine with the water present and to disintegrate the sample. The sample was transferred to a centrifuge bottle and shaken vigorously with 100 ml of petroleum ether. The residue was re-extracted twice with 50-ml portions of petroleum ether after centrifuging and drawing off the organic layer. The combined extracts were then evaporated to obtain the fat. No more than 3.0 g of fat was taken for acetonitrile partitioning.

Partitioning: The fat was dissolved in 15 ml of petroleum ether and placed in a 125-ml separatory funnel. This was shaken vigorously for 1 minute with 30 ml of acetonitrile which had been saturated with petroleum ether. The lower acetonitrile layer was drained off and the petroleum ether solution extracted three more times with 30-ml portions of acetonitrile. The acetonitrile layers were combined in a 1-liter separatory funnel and shaken with 700 ml of petroleum ether. The petroleum ether was removed and washed with two 100-ml portions of water. The aqueous washings were discarded and the petroleum ether layer dried by passing it through a 2-inch layer of granular anhydrous Na_2SO_4. The separatory funnel and drying column were rinsed three times with 10 ml of petroleum ether and the combined petroleum ether layers evaporated to about 10 ml.

Florisil column cleanup: A 25-mm (O.D.) by 300-mm column containing 4 inches of activated Florisil was prepared and topped with one-half inch of granular sodium sulfate. The column was prewetted with 40 ml of petroleum ether and the partitioned petroleum ether extract added to the top of the column. The sample was rinsed onto the column with two 5-ml portions of petroleum ether. The column was eluted at a rate not faster than 5 ml per minute with 200 ml of 6% ethyl ether (v/v) in petroleum ether. The receiver was changed and the elution continued at the same rate using 200 ml of 15% ethyl ether in petroleum ether. These two fractions were concentrated to 5 ml in calibrated 15-ml centrifuge tubes using Kuderna-Danish evaporative concentrators. Lindane, heptachlor, aldrin, heptachlor epoxide, γ-chlordane, *p,p'*-DDE, DDD, *p,p'*-DDT, and toxaphene are eluted by 6% ethyl ether from the Florisil column. Dieldrin and endrin are eluted in the 15% ethyl ether fraction.

Gas chromatography: The purified sample extract was analyzed on a Microtek 220 electron capture gas chromatograph using a 6′ x ½″ I.D. glass column packed with 10% DC 200 on 90/100 mesh Anakrom ABS. The nitrogen flow rate was about 110 ml per minute. The column temp was 205 C, the injector 250 C, and the detector temperature 270 C. Standard curves were prepared daily for each pesticide.

Recovery ratios were not determined, and the results were not corrected for recovery.

Laboratory F

Method adapted from FDA *Pesticide Analytical Manual* (*3*). Details of this method are to be published in *Handbook of Procedures for Pesticide Residue Analysis, Bureau of Sport Fisheries and Wildlife, Fish-Pesticide Research Laboratory* (in press).

Sorvall blender method: This is the primary technique for extraction of fish tissue. Fish must be small (2 g) or they must be pre-ground. Fish eggs, vegetation, mud, etc., may also be extracted by this procedure.

(1) Tare a standard pint Mason jar.
(2) Add the sample (15-35 g) and record sample weight.
(3) Add anhydrous Na_2SO_4 equal to the sample weight.
(4) Add 100 ml of redistilled petroleum ether solvent.
(5) Assemble Sorvall blender assembly and sample jar.
(6) Lower the sample into an ice bath.
(7) After 30 seconds, turn on the blender to a low speed at about 20% of full power.
(8) When the sample is blending smoothly, increase the power to 80% and blend for 2 minutes.
(9) Decant the solvent. Using a large spatula, press the solid mass to remove any adhering solvent and add this to the decanted solvent.
(10) Add 100 ml of fresh solvent and reassemble the blender.
(11) Repeat steps 7-9.
(12) Pass the combined extracts through a column of anhydrous Na_2SO_4.

The extract is then ready for cleanup. If the extract exhibits considerable turbidity at this point, it may be necessary to repeat the drying step. If difficulty is encountered in obtaining a clean break between solvent and water layers, it may be necessary to add a third extraction step.

Acetonitrile-hexane partition: This method may be used with most types of sample extracts. Large amounts of lipids in the sample, however, seriously interfere with this method. See the FDA *Pesticide Analytical Manual*, section 621, for explanation and use of p-values. Those pesticides which have low p-values will be recovered in good yield by this method.

(1) Evaporate the sample extract to near dryness. Do not allow the residue to become completely dry as pesticide losses may ensue.
(2) Transfer the residue to a 250-ml separatory funnel with 30 ml of hexane.
(3) Add 30 ml of hexane-saturated acetonitrile.
(4) Shake the funnel for 2 minutes.
(5) Allow the layers to separate. If the layers do not separate within 10 minutes, add 30 ml each of acetonitrile and hexane and rock the funnel for 30 seconds. This rocking allows the droplets to coalesce.
(6) After the layers have separated, draw off the lower acetonitrile layer. Save this solution.
(7) Repeat steps 3-6. Combine the extracts. Discard the hexane layer. Note: When calculating efficiency using the p-value tables the fact of double extraction must be taken into account.
(8) Evaporate the acetonitrile solution to about 5 ml.
(9) Add 10 ml benzene and evaporate to 5 ml.

The extract may be made to volume and analyzed at this point if interferences are absent. However, this method is usually used as the first step in a two-step cleanup procedure (e.g., Florisil as the second step).

Adsorption chromatography—Florisil: This is a general procedure for most types of samples with most pesticides. Large amounts of fat in the sample, however, interfere with recovery of the pesticides. When samples containing appreciable amounts of fat are processed, smaller samples should be used, so that the amount of fat added to the column does not exceed 0.5 g. If smaller samples are impractical, a prior cleanup step will be required.

(1) Prepare the Florisil column as follows:
Column—20-mm x 40-cm glass column with a glass frit. To the clean, dry column add, in order, 10 g anhydrous Na_2SO_4, 10 g Florisil (5% deactivated), and 10 g anhydrous Na_2SO_4.
(2) Evaporate the extract of 30 g (or less) of sample to about 5 ml.
(3) Add 30 ml of petroleum ether to the prepared Florisil column. Have the evaporated extract ready for immediate transfer to the column and have 100 ml of 5% diethyl ether in petroleum ether measured and ready.
(4) When the top of the wash solvent just reaches the top of the upper Na_2SO_4 layer, immediately add the sample using a small portion (5 ml) of the elution solvent to effect transfer.
(5) When the sample has been added, immediately place the collection container below the column to receive the eluate.
(6) When the sample solution has reached the level of the Na_2SO_4, add the elution solvent.

The eluate from this procedure may be used directly

for gas chromatography after it has been made to a known volume.

Gas chromatography: A Beckman GC-4 gas chromatograph was used with an electron capture detector. For quantitation, a 4′ x 2-mm I.D. glass column was packed with 0.3% Dow 200 on Corning GLC 110 glass beads. The column was operated using a 30 ml/minute helium flow with a temperature of 155 C for both injector port and column and a temperature of 235 C for the detector. For confirmation, a column with a 3% QF-1, Anakrom ABS, 80/90 mesh packing was used. This column was operated using a 50-60 ml/minute flow of N_2 with injector temperature at 200 C, column temperature at 180 C and the Ni^{63} detector at 235 C.

Recoveries reported were: Dieldrin—85 ±5%, DDE—64 ± 5%, TDE—90 ± 5%, DDT—81 ± 5%. Analytical values were corrected for recovery. Sensitivity was reported as ranging from 0.002 to 0.01 ppm.

Laboratory G

Method adapted from FDA *Pesticide Analytical Manual* (*3*). Each sample was cleaned up by two methods. Both methods gave similar results. Sweep co-distillation gave somewhat higher recoveries in more cases than did the partitioning method. The method of analysis was as follows:

Extraction: The issue was mixed with five times its own weight of purified anhydrous Na_2SO_4 and extracted for 6 hours in a Soxhlet extractor using a solvent mixture of 10% ethyl ether and 90% petroleum ether (50 g of tissue was used to prepare each sample).

Cleanup I: The extract was partitioned with normal hexane and acetonitrile.

Cleanup II: The sample extract was sweep co-distilled using a Kontes Model No. K50075 sweep co-distillation apparatus according to recommended procedure.

Gas chromatography: The cleaned-up residues were analyzed on an Aerograph Hy-Fl Model 600C with a tritium electron capture detector, using two separate columns for each sample. The 5′ x ⅛″ O.D. Pyrex columns were packed with: (1) 5% DC-200 acid washed, DMCS treated 100/120 mesh, Hi Performance Chromosorb W; (2) 5% QF-1 on the same solid support. The operating parameters were as follows: The QF-1 column (used for quantitation) was operated with a N_2 flow of 40 ml/minute, injection temp of 185 C, column temp of 174 C and detector temp of 178 C; the Dow-Corning 200 column with the same carrier gas flow was operated with an injection temp of 200 C, column temp of 190 C and detector temp of 194 C.

If corrections are desired, they may be made by multiplying the results for partitioned samples by 1.1. Correction factors for sweep co-distillation are as follows: DDE—no corrections needed; DDT—1.2; dieldrin—1.1; TDE—not derived but estimated to be 1.1. The sensitivity for analysis of DDT, TDE, DDE, and dieldrin was reported as 0.1 ppm.

Only one laboratory reported confirmation of results by other methods. Laboratory G confirmed the presence of DDT, TDE, and DDE in two of the laboratory cross-check samples (S-3-21-LC and S-1-44-C, see Table 3) by thin-layer chromatography. Other laboratories stated that they did not confirm by other methods, but some of them confirmed by using two or more columns.

One laboratory (G) reported the presence of polychlorobiphenyls (PCB's) but attributed them to bottle-cap liners in which the cross-check samples were stored. Other laboratories made no analyses to identify possible interferences from PCB's.

Laboratories A, B, and C conducted the analyses on the spring and fall 1967 samples; Laboratories C, D, and E on the spring 1968 samples; and Laboratory C analyzed all of the fall 1968 samples.

Laboratory cross-checks were conducted on the fall 1967 and spring 1968 samples. One laboratory prepared 10 regular composite samples and sent subsamples of the fish homogenate to each of the other participating laboratories for residue analyses. Laboratories A, B, C, D, and E participated in the fall 1967 cross-checks and Laboratories C, D, E, F, and G in the spring 1968 cross-checks. Laboratories F and G were Bureau of Sport Fisheries and Wildlife laboratories which did not participate in the regular monitoring program but only in the laboratory cross-checks.

Results

FISH COLLECTIONS

More difficulty was encountered than had been anticipated in collecting the same species of fish at a particular station during all sampling periods. Only at 9 stations were the same 3 species collected during all 4 sampling periods. Two of the same species were collected at an additional 11 stations and 1 at an additional 21 stations. Thus 41 of the 50 stations had at least 1 species collected during all periods.

Also, more species were collected than had been anticipated. There were 62 species in the 590 composite samples. However, of these, 21 species were collected at only 1 station, 12 at 2 stations and an additional 6 at only 3 of the 50 stations. On the other hand, some species or genera were represented at many stations. A total of 97 samples of carp were collected at 34 stations, 105 samples of catfish at 31 stations, 111 samples of suckers at 35 stations, and 61 samples of black bass at 22 stations. A list of species collected is shown in Table 1. Common and scientific names are those specified by the American Fisheries Society (*1*). Code letters are included in this table in order to identify the species in Table 4.

Much of the variation in species collected and the number of fish in a composite sample was in the first (spring 1967) collection and was due, apparently, to inadequate initial instructions to the field collectors. Much more uniformity was obtained in later collections. It is believed that in the future at least two and possibly three species can be collected consistently at a station. Results indicate also that collection of the same species would be expedited if samples were taken only in the fall.

LABORATORY CROSS-CHECKS

The results of the fall 1967 laboratory cross-checks are shown in Table 2. It is apparent that there are inconsistencies in the results reported by different laboratories on subsamples of the same homogenate. One laboratory (A) found relatively low levels of DDT and its metabolites, and little or no residues of other pesticides. Laboratory B reported somewhat higher values, but the abnormal DDT/(DDE + DDT + TDE) ratios in many samples make some of their results open to question. DDT results for Laboratories C, D, and E were in fair agreement in most samples; however, Laboratory D did not differentiate among members of the DDT complex. Some high aldrin values reported by Laboratories D and E, and the high toxaphene values by Laboratory D might also be questioned.

Actually only Laboratories A, B, and C participated in the regular sampling program during the spring and fall of 1967. The data on the cross-check samples were not adequate to attempt any corrections in the regular sampling data. However, as the data for Laboratories C, D, and E appeared more comparable, these laboratories were selected to conduct analyses on the regular spring 1968 collections.

The spring 1968 cross-checks (Table 3) appear more consistent than was found in the previous cross-checks; however, some inconsistencies remained. Laboratory E reported lower and Laboratory F higher results for the DDT complex than the other laboratories. Laboratory D reported higher dieldrin results and Laboratories D and E higher aldrin results on some samples. Laboratory F did not find residues other than DDT in any samples. Only Laboratories C, D, and E participated in the regular spring 1968 sampling program. The data from the cross-check samples still did not justify a correction factor for the regular samples; however, it did point out possible places to look for inconsistencies. As there were still uncertainties regarding the data, only one laboratory was used for analysis of the fall 1968 samples.

RESIDUE LEVELS IN FISH

Results of residue analyses for 11 organochlorine insecticides at the 50 sampling stations are shown in Table 4. Results are reported as ppm (milligrams per kilogram) wet weight, whole fish. Also shown are station locations, collection dates, species of fish (see code—Table 1), number of fish, and the average length and weight of all fish in the composite. When interpreting these data, consideration must be given to laboratory differences as shown in cross-check samples and to possible variations in species and size of fish, seasonal variation, etc.

It is interesting to note that some stations were consistently high or low in residues compared with other stations during all sampling periods regardless of the laboratory conducting the analyses or the species collected.

DDT and metabolites were found in all but 6 of the 590 composite samples examined. Five of those without DDT were at Station 50 in Alaska. Total DDT residue levels ranged up to 45 ppm and were consistently above 1.0 ppm (mean levels 1.0-16.0 ppm) at Stations 3, 4, 18, 20, 21, and 39 during all sampling periods and also above this level at Stations 2, 24, 28, 44, and 48 during three of the four sampling periods. The latest data (October 1968) show DDT residues at three other stations at comparatively high levels. Values reported from Stations 14, 16, and 30 exceeded 5 ppm.

Dieldrin residues were reported in approximately 75% of all samples analyzed. Values of individual composite samples ranged upward to a maximum of 1.94 ppm. Mean values above 0.1 ppm were reported from four sampling stations (Sta. 2, 4, 26, 31) during three of the four sampling periods. Values exceeding 0.1 ppm were also reported in the spring and fall 1968 from Stations 10, 14, 34, and 40.

Aldrin residues were not reported consistently from any station during all sampling periods. A few scattered values greater than 0.1 ppm were reported in the spring 1968 samples. However, practically all of these were reported from one laboratory which had also reported relatively high values in the laboratory cross-checks.

Endrin was reported consistently in samples from only three stations (Sta. 15, 28, and 30) and then at relatively low levels (<0.1 ppm). A few scattered higher values were reported from several other stations but usually represented only one or two composite samples.

Some lindane residues were found in 16% of the total samples; however, levels were usually less than 0.1 ppm. While reported from a fairly large number of samples, lindane was not found consistently at any stations during all sampling periods.

Next to DDT and dieldrin, heptachlor and/or heptachlor epoxide were found in the largest number of samples, 32% of the 590 samples examined. Residues were found consistently during different sampling periods at a number of stations and at levels greater than 0.1 at Stations 2, 3, 18, and 24.

Chlordane residues were also reported from a fairly large number of samples, 22% of the total, with some samples containing relatively high levels. While lower levels were reported consistently during all sampling periods from several stations, levels greater than 0.1 ppm were reported from Station 26 during three of the four sampling periods.

Discussion

While there are variations in results from different laboratories and possible differences in residue levels in various species of fish and in individuals within a species, these data (Table 4) show some waters with fish consistently high in DDT, dieldrin, and some other organochlorine insecticides. Recently, the Food and Drug Administration announced an interim guideline of 5 ppm total DDT (including derivatives) residues in fish shipped in interstate commerce, pending review by an appointed commission (*20*). The latest data reported by this monitoring study in fall 1968 (Table 4) show that mean DDT levels in whole fish exceed this level at 8 of the 50 monitoring stations. Also, some of the DDT, dieldrin, and other organochlorine insecticide residues are considerably higher than those established by the FDA for milk, meat, fruits, vegetables, and other food and feed crops (*18*). FDA tolerances for meat are on a fat basis, while the results reported here are on a whole-fish basis. If these results were reported as residues in fat, the levels shown would be roughly tenfold higher. Much accumulation of these residues may be in portions of the fish not normally consumed by humans, but which are consumed by and might be hazardous to fish-eating birds and other animals.

The data (Table 4) are presented in a manner that can be interpreted while taking into consideration the above variations. A major value of the data may be to point out possible problem areas where special studies are needed and to serve as a base for such studies. Some of its utility might be lost if summaries only were presented.

VARIATION AMONG LABORATORIES

It is obvious from the cross-checks (Tables 2 and 3) that there are differences in residue results reported by different laboratories. However, an examination of the overall data (Table 4) does not reveal differences as extensive as those shown in the laboratory cross-checks. The reasons for this are not definitely known. Some differences might be due to incomplete homogenization of samples of whole fish, so that fat, stomach contents, etc., were not equally divided in subsamples distributed to different laboratories. However, consistently high or low results from the same laboratory would indicate other reasons. These could include incomplete extraction, partitioning, cleanup, instrument performance, and interpretation.

Most laboratories use a referenced procedure but with their own modifications. Each usually considers its method the best and its results accurate. Who is to say which of the laboratory results presented here most nearly represent the actual picture? It is certainly necessary to use different laboratories for various Federal and State monitoring programs. Standardization of procedures for a particular substrate is mandatory if results are to be comparable (*23*). In a study such as this, it may be necessary to use only one laboratory, especially to determine yearly trends, until such standardization is effected.

VARIATION IN RESIDUE LEVELS IN FISH

Following the large-scale use of DDT and other organochlorine insecticides and the development of suitable analytical methods and tools in the late 1950's and early 1960's, many studies were initiated by various groups to determine residue levels in fish. Most early studies were concerned with the use of DDT or DDD in specific watersheds. Such studies may be illustrated by those in Clear Lake, Calif. by Hunt and Bishoff (*10*); in the Yellowstone River by Cope (*6*); in New York lakes by Burdick *et al.* (*5*); and in Sebago Lake, Maine, by Anderson and Everhart (*2*). These studies usually consisted of the analysis of a relatively small number of fish and in some cases different species. Among conclusions reached were that DDT residues were present in practically all samples, that levels were far above those found in the water, and that individual fish varied greatly in residue levels. Differences in residue levels in individuals were attributed to fish movement, size, food habits, and fat content. Some indication was given that there may be differences in levels concentrated by different species. In the above studies, the large variation in residues in individual fish somewhat overshadowed the differences in species. A summary of these

and many other field and laboratory studies showing vast differences in residue levels in fish is reported by Johnson (*11*). More recent studies in Tule Lake by Godsil and Johnson (*8*), and in a Wisconsin stream by Moubry *et al.* (*16*), tend to support the above conclusions.

Extensive monitoring studies involving numerous bodies of water and larger numbers of different species of fish have been reported from New York by Mack *et al.* (*15*), from Massachusetts by Lyman *et al.* (*14*) and from Wisconsin by Kleinert *et al.* (*13*). These studies, the latter including dieldrin as well as DDT, show even wider variations in residue levels in diffrent samples than had previous studies. In the Wisconsin study (*13*), no differences in residue levels were observed in different species but, in the other two studies (*14, 15*), species differences were indicated. Differences in residue levels in different sizes of fish of two species were not apparent in the Massachusetts study (*14*).

A more detailed fish monitoring study is that conducted by the Bureau of Commercial Fisheries in Lake Michigan (*17*). In that study, where large numbers of fish from the same body of water were analyzed for DDT and dieldrin residues, there were obvious differences in residue levels in different species of fish. Also, larger fish of the same species were shown to have the highest residue levels. A relationship was shown between residues in fat and the whole fish and also between edible and nonedible portions of fish.

In the present study (Table 4), it is somewhat difficult to make a comparison between residue levels in species because of the small number of samples collected from the same location. An examination of the data reveals obvious differences at some stations (Sta. 4, 21, 22, and 24) but little, if any, at others. On the basis of total samples, regardless of the magnitude of DDT levels at particular stations, some species such as carp, channel catfish, white perch, and lake trout appear in the high category more often than other species such as bullheads and bluegills, which are most often low. Other species appear in the high, medium, or low categories about equally. No differences in residue levels are obvious from these data with regard to fish size. However, all these samples were adult fish with most in the 2- to 5-year age groups.

Overall, the residue levels of DDT and dieldrin reported in this study are of a magnitude and variation similar to those reported from other studies (*13, 14*) at comparable locations. No comparable information was available on residues of other organochlorine insecticides.

SEASONAL LEVELS AND TRENDS

On the basis of present data (Table 4), no definite conclusions can be reached regarding differences in residue levels between samples collected in different seasons or in different years. A direct examination of the data indicates that levels of total DDT and heptachlor were higher in the fall than in the spring and that levels in 1968 were higher than in 1967. On the other hand, dieldrin values appear higher in the spring than in the fall, but an increase is also shown for 1968. However, when variation in laboratory cross-check samples is considered, the picture is not clear. If only the data in which one laboratory analyzed all of the samples from a station during all sampling periods are considered, there are no major differences in seasonal or annual levels, with the possible exception of heptachlor epoxide. Other studies reported somewhat different observations regarding trends. The Masachusetts study (*14*) states that generally DDT levels showed an increase during the 3-year study (1965, 1966, and 1967). The Wisconsin study (*13*) concludes that their 3-year survey (1965, 1966, and 1967) did not indicate the rate at which DDT and dieldren levels were building up or diminishing and that resurveys will be necessary to establish trends.

Conclusions

The major conclusions that can be drawn from this study to date are: first, there are a number of widely scattered waters in which fish show consistently high residues of DDT, dieldrin, and other organochlorine insecticides (some of these waters are in agricultural drainages and others in highly industrialized areas); and second, there is considerable variation in residue levels in different samples, which could be caused by variation in laboratory analyses, or variation in fish from movement, food habits, species, size, age, fat content, etc. Because of these variations, caution should be applied in using and interpreting these data.

A nationwide fish monitoring program of the present modest magnitude could not be expected to resolve all of the differences. The major functions should be to provide a continuing assay which would indicate the magnitude of pesticide residues in this substrate of the environment, to determine trends in residue levels, and to locate possible problem areas where significantly high levels may indicate the need for special studies.

Special studies could be made by Federal or State agencies, universities, industrial concerns, conservation organizations, or other groups to trace down sources of insecticide contamination and to resolve other differences such as variation in laboratories, fish samples, etc., as mentioned previously.

Until these differences are resolved, the present monimonitoring program should continue with the use of the same indicator species at each station during each sampling period and the use of a single laboratory for residue determinations. The data might be more useful if lipid content were determined for each sample. The addition of a few more sampling stations would provide more uniform nationwide coverage.

In the future it may be possible to correlate the fish data with residue data in other substrates, such as water, soils or wildlife (especially waterfowl), which are being obtained by other participants in the National Pesticide Monitoring Program.

Acknowledgments

Fish collections were made by a large number of individuals, without whose help this program would have been impossible. While the program was spearheaded in the various Bureau of Sport Fisheries and Wildlife regions by the Division of Fishery Services, other divisions also participated in the field collecting. State fish and game personnel also assisted greatly in making many collections.

See Appendix for chemical names of compounds mentioned in this paper.

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TABLE 1.—*Code for fish species*

Family	Common Name	Scientific Name	Code
Amiidae—bowfins	Bowfin	*Amia Calva* Linnaeus	BF
Clupeidae—herrings	American shad	*Alosa sapidissima* (Wilson)	ASh
	Gizzard shad	*Dorosoma cepedianum* (LeSueur)	GSh
Salmonidae—trouts, whitefishes, and graylings	Lake whitefish	*Coregonus clupeaformis* (Mitchill)	LWh
	Bloater	*Coregonus hoyi* (Gill)	Blo
	Round whitefish	*Prosopium cylindraceum* (Pallas)	RWh
	Mountain whitefish	*Prosopium williamsoni* (Girard)	MWh
	Coho salmon	*Oncorhynchus kisutch* (Walbaum)	CSa
	Sockeye salmon	*Oncorhynchus nerka* (Walbaum)	SSa
	Cutthroat trout	*Salmo clarki* Richardson	CTT
	Rainbow trout	*Salmo gairdneri* Richardson	RBT
	Lake trout	*Salvelinus namaycush* (Walbaum)	LkT
	Arctic grayling	*Thymallus arcticus* (Pallas)	AGr
Hiodontidae—mooneyes	Goldeye	*Hiodon alosoides* (Rafinesque)	GE
	Mooneye	*Hiodon tergisus* LeSueur	ME
Esocidae—pikes	Chain pickerel	*Esox niger* LeSueur	ChPi
	Northern pike	*Esox Lucius* Linnaeus	Npi
Cyprinidae—minnows and carps	Chiselmouth	*Acrocheilus alutaceus* Agassiz	CM
	Goldfish	*Carassius auratus* (Linnaeus)	GF
	Carp	*Cyprinus carpio* Linnaeus	C
	Golden shiner	*Notemigonus crysoleucas* (Mitchill)	GSn
	Northern squawfish	*Ptychocheilus oregonensis* (Richardson)	NSq
	Tui chub	*Siphateles bicolor* (Girard)	TCh
Catostomidae—suckers	Carpsucker	*Carpiodes sp.*	CpSu
	Longnose sucker	*Catostomus catostomus* (Forster)	LNSu
	Bridgelip sucker	*Catostomus columbianus* (Eigenmann)	BLSu
	White sucker	*Catostomus commersoni* (Lacépède)	WhSu
	Flannelmouth sucker	*Catostomus latipinnis* Baird	FMSu
	Largescale sucker	*Catostomus macrocheilus* Girard	LSSa
	Klamath sucker	*Catostomus rimiculus* Gilbert	KSSu
	Tahoe sucker	*Catostomus tahoensis* Gill	TaSu
	Lake chubsucker	*Erimyzon sucetta* (Lacépède)	LCSu
	Smallmouth buffalo	*Ictiobus bubalus* (Rafinesque)	SMBu
	Bigmouth buffalo	*Ictiobus cyprinellus* (Valenciennes)	BMBu
	Spotted sucker	*Minytrema melanops* (Rafinesque)	SpSu
	Redhorse (sucker)	*Moxostoma sp.*	RSu
	Humpback sucker	*Xyrauchen texanus* (Abbott)	HBSu
Ictaluridae—freshwater catfishes	White catfish	*Ictalurus catus* (Linnaeus)	WhC
	Blue catfish	*Ictalurus furcatus* (LeSueur)	BlC
	Black bullhead	*Ictalurus melas* (Rafinesque)	BkBH
	Brown bullhead	*Ictalurus nebulosus* (LeSueur)	BrBH
	Channel catfish	*Ictalurus punctatus* (Rahnesque)	ChC
	Flathead catfish	*Pylodictis olivaris* (Rafinesque)	FHC
Gadidae—codfishes and hakes	Burbot	*Lota lota* (Linnaeus)	Bot
Serranidae—sea basses	White perch	*Roccus americanus* (Gmelin)	WhP
	White bass	*Roccus chrysops* (Rafinesque)	WhB
	Striped bass	*Roccus saxatilis* (Walbaum)	StB
Centrarchidae—sunfishes	Rock bass	*Ambloplites rupestris* (Rafinesque)	RkB
	Sacramento perch	*Archoplites interruptus* (Girard)	SaP
	Redbreast sunfish	*Lepomis auritus* (Linnaeus)	RBS
	Green sunfish	*Lepomis cyanellus* Rafinesque	GrS
	Pumpkinseed	*Lepomis gibbosus* (Linnaeus)	PkS
	Bluegill	*Lepomis macrochirus* Rafinesque	BGS
	Smallmouth bass	*Micropterus dolomieui* Lacépède	SMB
	Largemouth bass	*Micropterus salmoides* (Lacépède)	LMB
	White crappie	*Pomoxis annularis* Rafinesque	WhCp
	Black crappie	*Pomoxis nigromaculatus* (LeSueur)	BkCp
Percidae—perches	Yellow Perch	*Perca flavescens* (Mitchill)	YeP
	Sauger	*Stizostedion canadense* (Smith)	Sag
	Walleye	*Stizostedion vitreum* (Mitchill)	WE
Sciaenidae—drums	Freshwater drum	*Aplodinotus grunniens* Rafinesque	FWD
Mugilidae—mullets	Striped mullet	*Mugil cephalus* Linnaeus	StMu

TABLE 2.—*Laboratory cross-check samples, organochlorine insecticides, fall 1967*

Sample Number & Location	Species: No. Fish	Species: Total Wt. (Lb)	Date Coll.	Analysis Report: Lab.	Analysis Report: Date	Organochlorine Insecticides (ppm)[1]: DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor epoxide	Chlordane	Toxaphene
F-5-1-OF	Chain		11/6	A	2/17	.01	.01	.01	.03	—	—	—	—	.01	—	—	—
Stillwater R.	Pickerel			B	3/18	.21	.01	.44	.66	.02	.02	.08	—	.01	—	.02	—
Old Town,	5	5.3		C	1/26	.06	.04	.03	.13	.01	—	—	.10	—	—	—	—
Maine				D	12/22	.20	—	—	.20	.06	—	—	—	—	.04	—	.36
				E	1/29	.08	.02	.04	.14	—	—	—	—	—	—	—	—
F-5-3-LMB	Largemouth		10/4	A	2/17	.01	.02	.03	.06	—	—	—	—	—	—	—	—
Hudson R.	Bass			B	12/1	.03	.07	.05	.15	.01	.04	—	.03	.01	.29	.07	—
Poughkeepsie,	5	5.4		C	1/29	.95	1.31	.92	3.18	.18	—	—	—	—	1.18	—	—
N. Y.				D	12/22	2.31	—	—	2.31	—	—	—	—	—	3.00	—	—
				E	1/29	1.40	.52	.89	2.81	.19	2.30	—	—	—	1.70	—	—
F-5-4-Su	White		10/5	A	2/17	.01	.02	.03	.06	—	—	—	—	—	—	—	—
Delaware R.	Sucker			B	3/18	.08	.07	.27	.42	.01	—	.01	—	.01	.01	.01	—
Burlington,	4	4.4		C	1/25	2.08	1.92	.58	4.58	.35	—	—	.04	—	—	—	—
N. J.				D	12/22	.37	—	—	.37	.19	.09	—	—	—	.10	—	1.06
				E	1/29	2.60	2.30	.60	5.50	.35	.03	—	—	—	.09	—	—
F-5-18-OF	White		10/24	A	2/17	.02	.02	.03	.07	—	—	—	—	.01	—	—	—
L. Ontario	Perch			B	3/18	.07	.02	.54	.63	.02	—	.09	.01	.02	.07	.01	—
Port Ontario,	5	4.4		C	1/26	.55	.31	.47	1.33	.04	—	—	.06	—	—	—	—
N. Y.				D	12/22	.36	—	—	.36	.25	.19	—	—	—	.17	—	1.25
				E	1/29	1.40	.49	.56	2.45	—	.21	—	—	—	.33	—	—
F-5-19-OF	Freshwater		10/11	A	2/17	.01	.02	.03	.06	—	—	—	—	—	—	—	—
L. Erie	Drum			B	3/18	.11	.03	.28	.42	.02	—	.06	.01	.02	.01	—	.01
Erie,	5	3.0		C	1/25	.09	.10	.13	.32	.03	—	—	—	—	—	—	—
Pa.				D	12/22	.22	—	—	.22	.11	.08	—	—	—	.12	—	.24
				E	1/29	.18	.06	.21	.45	.04	.01	—	—	—	.03	—	—
F-3-20-C	Carp		10/4	A	2/17	.01	.01	.01	.03	—	—	—	—	—	—	—	—
L. Huron	5	7.9		B	12/1	.03	.09	.04	.16	—	.04	—	.04	.01	.09	.10	—
Bayport,				C	1/29	.21	.28	.09	.58	.01	—	—	.01	—	.17	—	—
Mich.				D	12/22	.74	—	—	.74	.13	.03	—	—	—	1.10	—	—
				E	1/29	.33	.23	.11	.67	—	.15	—	—	—	.33	—	—
F-3-26-B	Bigmouth		10/11	A	2/17	.02	.02	.01	.05	—	—	—	—	—	—	—	—
Illinois R.	Buffalo			B	3/18	.06	.02	.45	.54	.02	—	.04	—	.02	—	—	—
Beardstown,	5	9.1		C	1/24	.04	.08	.04	.16	.52	—	—	.02	—	.01	.24	—
Ill.				D	12/22	.16	—	—	.16	—	—	—	—	—	—	—	—
				E	1/29	.08	.07	.04	.19	.32	.04	—	—	—	.04	.11	—
F-3-27-B	Bigmouth		10/14	A	2/17	.01	.02	.02	.05	—	—	—	—	—	—	—	—
Mississippi R.	Buffalo			B	12/1	.01	.07	.05	.13	—	—	—	.04	.02	.03	.05	—
Gutenberg,	4	15.0		C	1/25	.05	.09	.07	.22	.04	—	—	.02	—	—	—	—
Iowa				D	12/22	.23	—	—	.23	.12	—	—	—	—	—	—	—
				E	1/29	.09	.05	.11	.25	.04	.03	—	—	.01	.05	.06	—
F-3-32-C	Carp		9/26	A	2/17	.01	—	—	.01	—	—	—	—	—	—	—	—
Missouri R.	5	8.7		B	3/18	.03	.06	.04	.13	—	—	.07	.02	.01	.03	.03	—
Garrison Res.,				C	1/25	.03	.02	.01	.06	.01	—	—	—	—	—	—	—
N. Dak.				D	12/22	.15	—	—	.15	—	—	—	—	—	.10	—	—
				E	1/29	.06	.02	.03	.11	—	—	—	—	—	.02	—	—
F-3-34-Su	White		10/3	A	2/17	.06	.08	.13	.27	—	—	—	—	—	—	—	—
Red R.	Sucker			B	3/18	.02	.10	.08	.20	.01	—	—	.06	.01	.04	.03	—
Noyes, Minn.	4	8.0		C	1/25	.61	.95	1.79	3.35	.08	—	—	.03	—	—	—	—
				D	12/22	3.45	—	—	3.45	—	—	—	—	—	—	—	—
				E	1/29	.75	1.80	.33	2.88	.08	—	—	—	—	.02	—	—

[1] Milligrams per kilogram wet weight—whole fish.

TABLE 3.—*Laboratory cross-check samples, organochlorine insecticides, spring 1968*

Sample Number & Location	Species		Date Coll.	Analysis Report		Organochlorine Insecticides (ppm)[1]											
	No. Fish	Total Wt. (Lb)		Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor epoxide	Chlordane	Toxaphene
S-3-20-C	Carp		4/16	C	8/16	.44	.39	.10	.93	.02	—	—	—	—	—	—	—
L. Huron				D	5/18	.35	.30	.10	.75	0.26	—	—	—	—	—	—	—
Bayport,				E	7/22	.18	.04	.14	.36	—	.17	—	—	.10	.07	—	—
Mich.	5	17.9		F	7/17	.29	.09	.06	.44	—	—	—	—	—	—	—	—
				G	7/26	.5	.5	.2	1.2	—	—	—	—	—	—	—	—
S-3-20-CC	Channel		4/16	C	8/16	1.09	.81	.62	2.52	.04	—	—	—	—	—	—	—
L. Huron	Catfish			D	5/18	3.50	.83	.25	4.58	2.58	.10	—	—	—	—	—	—
Bayport,				E	7/22	.52	—	.35	.87	—	.31	—	—	.11	.17	—	—
Mich.	5	8.4		F	7/17	7.56	.03	3.90	11.49	—	—	—	—	—	—	—	—
				G	7/26	1.4	1.0	.8	3.2	—	—	—	—	—	—	—	—
S-3-21-LC	Bloater		5/10	C	8/16	4.79	—	2.10	6.89	.02	—	—	.04	—	.18	.07	—
L. Michigan				D	5/18	6.25	2.70	2.40	11.35	2.04	.82	—	—	—	—	—	—
Sheboygan,				E	7/22	2.87	.10	1.30	4.27	—	.02	—	—	—	.12	—	—
Wis.	5	6.7		F	7/17	11.40	—	5.86	17.26	—	—	—	—	—	—	—	—
				G	7/26	2.9	.6	4.0	7.5	.2	—	—	—	—	—	—	—
S-3-22-W	Lake		5/8	C	8/16	.33	.08	.27	.68	.02	—	—	—	.08	—	—	—
L. Superior	Whitefish			D	5/18	.49	.25	.34	1.08	.20	.02	—	—	—	.02	—	—
Bayfield,				E	7/22	.23	.04	.28	.55	—	.01	—	—	—	.01	—	—
Wis.	5	11.9		F	7/17	1.44	.36	1.30	3.10	—	—	—	—	—	—	—	—
				G	7/26	.5	.5	.6	1.6	.1	—	—	—	—	—	—	—
S-3-22-LT	Lake		5/8	C	8/16	.81	.08	.34	1.23	.02	—	—	.04	—	—	—	—
L. Superior	Trout			D	5/18	.40	.25	.27	.92	.19	.02	—	—	—	.01	—	—
Bayfield,				E	7/22	.46	.01	.20	.67	—	—	—	—	.01	.01	—	—
Wis.	5	14.8		F	7/17	.24	—	.14	.48	—	—	—	—	—	—	—	—
				G	7/26	.4	.1	.4	.8	—	—	—	—	—	—	—	—
S-3-26-OC	Brown		4/24	C	8/16	.19	.04	.06	.29	.10	—	—	—	—	—	—	—
Illinois R.	Bullhead			D	5/18	.40	.10	.10	.60	.26	—	—	—	—	—	—	—
Beardstown,				E	7/22	.05	.06	.08	.19	.09	.02	—	—	—	.01	—	—
Ill.	5	2.0		F	7/17	.26	.12	.21	.59	—	—	—	—	—	—	—	—
				G	7/26	.3	.3	.1	.7	.2	—	—	—	—	—	—	—
S-3-26-OS	White		4/24	C	8/16	.31	.10	.27	.68	.24	—	—	—	—	—	—	—
Illinois R.	Crappie			D	5/18	.36	.10	.12	.58	.28	—	—	—	—	—	—	—
Beardstown,				E	7/22	.11	.15	.14	.40	.11	.04	—	—	.03	.03	—	—
Ill.	5	3.2		F	7/17	.29	.10	.07	.46	—	—	—	—	—	—	—	—
				G	7/26	.5	.4	.2	1.1	.3	—	—	—	—	—	—	—
S-3-32-OF	Goldeye		5/14	C	8/16	.15	.37	.24	.76	.01	.13	—	—	—	.23	—	—
Missouri R.				D	5/18	.36	.10	.20	.76	.12	.05	—	—	—	—	—	—
Garrison Dam,				E	7/22	.07	.03	.12	.22	.01	.01	—	—	.01	.01	—	—
N. Dak.	5	2.2		F	7/17	.26	.15	.21	.62	—	—	—	—	—	—	—	—
				G	7/26	.2	.2	.2	.6	—	—	—	—	—	—	—	—
S-1-44-C	Carp		4/10	C	8/16	2.43	.45	.16	3.04	.06	—	—	.02	—	—	—	—
Yakima R.				D	5/18	3.35	.96	.05	4.36	.26	—	—	—	—	—	—	—
Granger,	4	4.5		E	7/22	1.53	.28	.20	2.01	.02	—	—	—	—	.07	—	—
Wash.				F	7/17	1.70	.34	.19	2.23	—	—	—	—	—	—	—	—
				G	7/26	1.4	.8	.2	2.4	—	—	—	—	—	—	—	—
S-1-46-Su	Largescale		4/12	C	8/16	.45	.58	.27	1.30	.02	—	—	—	—	—	—	—
Columbia R.	Sucker			D	5/18	.35	.30	.05	.70	.11	—	—	—	—	—	—	—
Bonneville Dam,				E	7/22	.14	.14	.09	.37	.01	.01	—	—	.01	.01	—	—
Oreg.	5	8.1		F	7/17	.12	.02	.04	.18	—	—	—	—	—	—	—	—
				G	7/26	1.1	.3	.1	1.5	—	—	—	—	—	—	—	—

[1] Milligrams per kilogram wet weight—whole fish.

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*

Collection Data							Organochlorine Insecticides (ppm)[1]											
Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and Met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor epoxide	Chlordane	Toxaphene
ATLANTIC COAST STREAMS																		
Stillwater R.	WhSu	7	16.0	1.6	C	S-67	.06	.05	.08	.19	.01	—	—	—	—	—	—	—
Old Town,		5	16.7	1.8	C	F-67	.09	.07	.06	.22	.03	—	—	.36	—	—	—	—
Maine		5	16.3	1.6	E	S-68	.16	.14	.19	.49	.22	—	—	—	.01	.01	—	—
# 1		5	14.4	1.2	C	F-68	.04	.05	.06	.14	—	—	—	—	—	—	—	—
	YeP	5	9.0	0.3	C	F-67	.09	.06	.07	.22	.02	—	—	.27	—	—	—	—
		5	10.7	0.5	E	S-68	.08	.03	.08	.19	—	—	—	—	—	—	—	—
		5	7.3	0.2	C	F-68	.05	.04	.05	.14	—	—	—	—	—	—	—	—
	WhP	9	9.7	0.5	C	S-67	.19	.15	.09	.43	.01	—	—	—	—	—	—	—
	ChPi	7	13.3	0.7	C	S-67	.12	.06	.05	.23	—	—	—	—	—	—	—	—
		5	16.9	1.1	C	F-67	.06	.04	.03	.12	.01	—	—	.10	—	—	—	—
		5	16.4	0.8	E	S-68	.10	.04	.08	.22	—	.01	—	—	—	.01	—	—
		5	15.8	0.8	C	F-68	.06	.03	.05	.14	—	—	—	—	—	—	—	—
Connecticut R.	WhC	6	11.5	0.8	C	S-67	.91	1.06	.91	2.88	.28	—	—	—	—	—	—	—
Windsor Locks,		4	10.0	0.5	C	F-67	.53	.68	.50	1.71	1.58	—	—	—	—	—	—	—
Conn.		5	11.3	0.7	C	F-68	1.29	1.37	1.16	3.82	.37	—	—	—	—	.52	—	—
# 2	BrBH	5	10.9	0.7	E	S-68	.04	.09	.12	.25	.16	.03	—	—	.04	.04	—	—
	YeP	5	8.9	0.4	C	S-67	1.41	1.09	.91	3.41	.31	—	—	—	—	—	—	—
		5	8.9	0.4	C	F-67	.34	.47	.41	1.22	1.94	—	—	—	—	—	—	—
		4	8.3	0.3	E	S-68	.33	.25	.53	1.11	.24	.14	—	—	.19	.19	—	—
	WhP	12	9.2	0.4	C	S-67	.72	1.25	1.84	3.81	.53	—	—	—	—	—	—	—
		5	8.5	0.4	C	F-67	.24	.42	.46	1.12	1.21	—	—	—	—	—	—	—
		5	8.8	0.4	E	S-68	.35	.28	.54	1.17	.19	.13	—	—	.13	.17	—	—
		1	8.4	0.3	C	F-68	1.17	.76	.78	2.71	.30	—	—	—	—	.65	.38	—
Hudson R.	C	3	20.0	4.0	C	S-67	.59	1.31	.56	2.46	.02	—	—	—	—	—	—	—
Poughkeepsie,																		
N. Y.	WhSu	5	15.8	1.6	C	S-67	.47	.37	.37	1.21	.06	—	—	—	—	—	—	—
# 3	GF	5	9.1	0.7	C	F-67	.82	1.21	.52	2.55	.35	—	—	—	—	—	—	—
		5	10.4	0.9	E	S-68	.94	.63	.82	2.39	.17	1.25	—	—	.83	.83	—	—
		5	11.0	1.1	C	F-68	5.02	5.89	3.49	14.40	.22	—	—	—	—	8.46	7.29	—
	GSn	20	8.2	0.2	C	S-67	.56	.47	.28	1.31	.04	—	—	—	—	—	—	—
	PkS	5	6.0	0.2	C	F-67	.15	.29	.18	.62	.10	—	—	—	—	—	—	—
		5	6.2	0.2	C	F-68	1.54	1.72	1.15	4.41	.09	—	—	—	—	2.40	2.24	—
	WhP	5	6.9	0.2	E	S-68	1.00	.39	.85	2.24	.24	.14	—	.01	.10	.23	—	—
	LMB	5	12.1	1.1	C	F-67	.95	1.31	.92	3.18	.18	—	—	—	—	1.18	—	—
		5	8.8	0.4	E	S-68	.86	.63	.88	2.37	.19	2.43	—	—	2.58	1.79	—	—
		5	12.6	1.3	C	F-68	3.70	4.61	3.18	11.49	.14	—	—	—	—	6.93	4.22	—
Delaware R.	WhSu	9	13.2	0.9	C	S-67	4.22	5.15	.50	9.87	.22	—	—	—	—	—	—	—
Camden,		4	13.9	1.1	C	F-67	2.08	1.92	.58	4.58	.35	—	—	.04	—	—	—	—
N. J.		5	14.2	1.0	E	S-68	.94	.46	.18	1.58	.04	.02	—	—	.01	.04	—	—
# 4		5	13.0	0.9	C	F-68	2.76	2.03	.66	5.45	.10	—	—	—	—	.20	—	—
	BrBH	6	11.1	0.8	C	S-67	2.46	3.85	.28	6.59	.16	—	—	—	—	—	.14	—
		4	11.2	0.8	C	F-67	2.89	3.15	.31	6.35	.39	—	—	.08	—	—	—	—
		3	11.1	0.5	E	S-68	1.71	1.67	.31	3.69	.03	.02	—	—	.02	.02	—	—
		5	10.6	0.5	C	F-68	2.68	2.89	.52	6.09	.17	—	—	—	—	.18	.41	—
	WhP	8	10.3	0.6	C	S-67	14.40	15.60	1.72	31.72	.81	—	—	—	—	—	—	—
		5	10.7	0.8	C	F-67	18.40	16.60	1.73	36.73	1.24	—	—	.05	—	—	—	—
		5	11.4	0.7	E	S-68	17.80	20.80	6.67	45.27	.22	.29	—	—	.07	.09	—	—
		5	9.9	0.5	C	F-68	18.20	13.00	2.92	34.12	.25	—	—	—	—	.68	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor epoxide	Chlordane	Toxaphene
ATLANTIC COAST STREAMS—(Continued)																		
Susquehanna R.	C	5	12.0	1.9	C	S-67	2.11	.73	.08	2.92	.02	—	—	—	—	—	—	—
Conowingo,		3	20.9	5.7	B	F-67	.03	.02	1.51	1.56	.05	—	1.50	—	.01	.02	.11	—
Md.		3	21.0	4.6	E	S-68	.44	.23	.11	.78	.02	.01	—	—	.01	.01	—	—
# 5		2	23.2	6.3	C	F-68	.41	.40	.30	1.11	.08	—	—	—	—	.07	—	—
	ChC	10	12.7	0.7	C	S-67	1.11	.68	.65	2.43	.04	—	—	—	—	—	—	—
		5	15.1	1.2	B	F-67	.01	.09	.01	.10	—	—	—	—	—	—	.01	—
		5	14.7	0.8	E	S-68	.60	.56	.53	1.69	.03	.01	—	—	.01	.02	—	—
		5	14.2	0.8	C	F-68	.31	.24	.20	.75	.12	—	—	—	—	.04	—	—
	YeP	10	8.0	0.2	C	S-67	.46	.39	.22	1.07	.13	—	—	—	—	—	—	—
		5	8.9	0.4	B	F-67	—	.05	.01	.06	.01	—	.01	—	—	.01	.01	—
		5	8.4	0.3	E	S-68	.13	.04	.11	.28	.03	.01	—	—	.01	.02	—	—
		5	8.2	0.2	C	F-68	.48	.30	.30	1.08	.10	—	—	—	—	.09	—	—
Potomac R.	C	5	11.9	1.1	C	S-67	.12	.24	.02	.38	.19	—	—	—	—	—	—	—
Little Falls,		3	14.9	2.0	B	F-67	.05	.15	—	.20	.02	.01	—	.01	—	—	.01	—
Md.		3	19.5	3.4	E	S-68	.12	.29	.10	.51	.15	.01	—	—	.01	.02	—	—
# 6		5	17.5	2.2	C	F-68	.78	.78	.27	1.83	.07	—	—	—	—	.13	—	—
	WhSu	3	14.2	1.3	B	F-67	.03	.07	.10	.20	.01	.01	—	—	—	—	—	—
		5	14.5	1.2	E	S-68	.07	.09	.13	.29	.03	.01	—	—	.02	.02	—	—
		5	14.1	1.2	C	F-68	.18	.17	.19	.54	.07	—	—	—	—	.06	—	—
	BGS	12	5.2	0.1	C	S-67	.11	.06	.10	.27	.02	—	—	—	—	—	—	—
	SMB	13	8.1	0.3	C	S-67	.21	.12	.08	.41	.05	—	—	—	—	—	—	—
		4	10.0	0.4	B	F-67	.02	.06	.03	.11	.01	—	.01	—	—	—	.01	—
	LMB	5	10.6	0.6	E	S-68	.05	.04	.07	.16	.03	.01	—	—	.01	.01	—	—
		5	10.0	0.5	C	F-68	.66	.55	.57	1.78	.06	—	—	—	—	.11	—	—
Roanoke R.	C	2	23.0	6.3	B	S-67	.07	.10	.11	.29	.04	—	—	—	—	.03	.13	—
Roanoke Rapids,		3	18.3	2.7	B	F-67	.01	.10	—	.11	—	—	.01	.01	—	—	—	—
N. C.																		
# 7	SpSu	3	16.3	1.8	B	S-67	.04	.09	.12	.25	.09	—	—	—	—	.01	.08	—
	Rsu	5	10.4	0.7	D	S-68	.49	.17	—	.66	.13	—	—	—	—	—	—	—
		5	13.4	1.4	C	F-68	.29	.31	.26	.86	.07	—	—	—	—	.03	—	—
	LCSu	5	10.6	0.7	B	F-67	.02	—	.08	.10	—	—	—	.01	.01	—	.01	—
	ChC	5	9.4	0.4	D	S-68	.19	—	—	.19	.05	—	—	—	—	—	—	—
	BrBH	12	9.0	0.3	B	S-67	.08	.12	.23	.43	.04	—	—	—	.01	—	.04	—
		4	9.4	0.4	B	F-67	.01	.06	—	.07	—	—	.03	—	.01	—	.03	—
		5	8.4	0.4	C	F-68	.23	.14	.07	.44	.02	—	—	—	—	—	—	—
	LMB	2	13.1	1.2	B	F-67	.07	.16	.09	.32	.01	—	—	.01	.01	—	.02	—
		4	7.7	0.2	C	F-68	.56	.45	.39	1.40	.06	—	—	—	—	.03	—	—
	BF	6	14.1	1.2	D	S-68	.34	.08	—	.42	.14	—	—	—	—	—	—	—
Cape Fear R.	GSh	5	13.8	1.0	B	S-67	.14	.18	.21	.54	.09	.01	—	.02	—	.03	.20	—
Elizabethtown,		5	12.2	1.0	B	F-67	.02	.69	.35	1.06	—	—	—	.01	—	—	.03	—
N. C.		5	13.9	0.8	D	S-68	.31	.10	—	.41	.14	—	—	—	—	—	—	—
# 8	RSu	5	17.3	1.3	D	S-68	.44	.18	—	.62	.12	—	—	—	—	—	—	—
	ChC	5	14.6	1.6	C	F-68	.49	.71	.58	1.78	.07	—	—	—	—	.07	—	—
	BrBH	9	10.8	0.6	B	S-67	.02	.03	.06	11	.02	.01	—	—	.02	—	—	—
		5	9.4	0.5	B	F-67	.02	.08	.03	.13	—	—	.01	—	—	—	.01	—
		5	10.4	0.6	C	F-68	.05	.07	.07	.19	.02	—	—	—	—	—	—	—
	LMB	5	9.5	0.6	B	F-67	.02	.19	.21	.43	.05	—	—	—	.01	—	.01	—
		5	12.0	0.7	C	F-68	.52	.73	.48	1.73	.07	—	—	—	—	.05	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Organochlorine Insecticides (ppm)[1]											
ATLANTIC COAST STREAMS—(Continued)																		
Cooper R. Summerton,	C	3	18.3	2.4	B	S-67	.05	.15	.19	.39	.02	.01	—	—	—	.01	.04	—
S. C.	SpSu	2	16.9	2.0	B	S-67	.07	.32	.21	.60	.02	.02	.01	.02	.02	.01	.12	.03
# 9		3	17.2	2.3	B	F-67	.04	.06	.07	.16	.01	—	.04	.01	.01	—	.01	—
		5	11.4	0.8	D	S-68	.77	.08	—	.85	.10	—	—	—	—	—	—	—
		5	15.4	1.8	C	F-68	.73	.76	.62	2.11	.02	—	—	—	—	.07	—	—
	BGS	5	6.5	0.2	B	F-67	.02	.02	.06	.10	—	—	.01	.01	.01	—	.02	—
		5	7.8	0.4	D	S-68	1.31	.21	—	1.52	.07	—	—	—	—	—	—	—
		5	5.8	0.2	C	F-68	.61	.34	.62	1.57	—	—	—	—	—	.04	—	—
	LMB	2	16.8	2.1	B	S-67	.02	.12	.12	.25	.09	—	—	—	—	—	.01	—
		4	11.4	0.9	B	F-67	.09	.17	.16	.42	—	—	—	.01	.01	.03	.05	—
		5	13.8	1.1	D	S-68	5.87	.50	—	6.37	.27	—	—	—	—	—	—	—
		5	12.4	1.0	C	F-68	1.65	1.02	1.39	4.06	—	—	.01	—	—	—	—	—
Savannah R.	C	3	22.2	5.0	B	S-67	.08	.03	.13	.24	.06	—	—	—	—	.01	.04	—
Savannah,		3	21.3	5.2	B	F-67	—	.06	.01	.07	—	—	—	—	—	—	.02	—
Ga.		4	18.9	3.3	D	S-68	.78	.05	—	.83	.62	—	—	—	—	—	—	—
# 10		3	18.6	4.7	C	F-68	.27	.30	.24	.81	.52	—	.02	—	—	.08	—	—
	StMu	3	13.7	1.3	C	F-68	.20	.30	.25	.75	1.37	—	.03	—	—	.08	—	—
	ChC	4	16.3	1.4	B	S-67	.10	.04	.18	.32	.07	—	—	.01	—	.01	.02	—
	WhC	5	13.1	1.3	B	S-67	.01	.09	.06	.16	.11	—	—	.09	—	.01	.05	—
	BGS	5	6.9	0.4	B	F-67	—	.07	—	.07	—	—	—	—	—	—	.03	—
		5	6.8	0.3	D	S-68	.17	.01	—	.18	.25	—	—	—	—	—	—	—
	LMB	5	13.9	1.2	B	F-67	.02	—	.08	.10	—	—	—	.03	.02	—	.05	—
		5	14.0	1.2	D	S-68	.15	.02	—	.17	.26	—	—	—	—	—	—	—
		2	13.0	1.1	C	F-68	.08	.07	.07	.22	.15	—	—	—	—	.02	—	—
St. Johns R.	StMu	5	15.0	1.1	B	S-67	.04	.05	.13	.22	.04	.01	.01	—	.01	.01	.14	—
Welaka,		3	17.3	2.0	B	F-67	.02	—	.09	.11	—	—	.02	—	—	—	.01	—
Fla.		5	13.4	0.9	D	S-68	.22	.12	—	.34	—	—	—	—	—	—	—	—
# 11		4	13.5	1.1	C	F-68	.14	.16	.15	.45	—	—	—	—	—	.02	—	—
	ChC	12	10.5	0.5	B	S-67	.02	.02	.06	.10	.03	.01	—	—	—	.01	.02	—
		5	13.1	0.7	B	F-67	.01	.04	.06	.11	—	—	—	.01	—	—	—	—
		5	9.7	0.3	D	S-68	.11	.02	—	.13	—	—	—	—	—	—	—	—
		5	10.4	0.4	C	F-68	.05	.08	.04	.17	—	—	—	—	—	.02	—	—
	RBS	17	7.2	0.5	B	S-67	.17	.14	.14	.45	.05	—	—	.01	—	—	.09	—
		5	8.4	0.4	B	F-67	.01	.14	.04	.19	.01	—	—	.01	.01	—	.03	—
		5	7.4	0.3	C	F-68	.05	.06	.04	.15	—	—	—	—	—	.02	—	—
	LMB	2	17.0	2.4	B	F-67	.02	.09	.04	.15	—	—	—	—	.01	—	.07	—
		2	16.7	2.4	D	S-68	.14	.02	—	.16	.03	—	—	—	—	—	—	—
St. Lucie Canal	WhC	6	11.5	0.8	B	S-67	.15	.16	.20	.51	.09	—	.01	—	—	—	.09	—
Indiantown,		5	12.2	0.9	B	F-67	.03	.06	.03	.12	—	—	—	—	—	—	.01	—
Fla.		1	12.0	0.9	D	S-68	1.87	1.90	.05	3.82	—	—	—	—	—	—	—	—
# 12	ChC	5	11.4	1.3	C	F-68	3.07	2.50	1.69	7.26	—	—	—	—	—	—	.15	—
	BGS	10	8.1	0.5	B	S-67	.13	.17	.15	.44	.09	—	—	—	—	—	.09	—
		5	6.7	0.3	B	F-67	—	.16	.02	.18	—	—	.01	—	—	—	.01	—
		5	6.8	0.3	D	S-68	1.46	.20	.10	1.76	—	.02	—	—	—	—	—	—
		5	7.0	0.2	C	F-68	.76	.60	.68	2.04	.04	—	—	—	—	.05	—	—
	LMB	3	17.3	2.7	B	S-67	.09	.16	.21	.45	.04	—	—	—	—	—	.07	—
		4	11.5	0.8	B	F-67	.01	.18	.06	.25	—	—	—	—	—	—	.04	—
		5	10.2	0.4	D	S-68	1.72	.28	—	2.00	—	—	—	—	—	—	—	—
		5	11.0	0.6	C	F-68	.57	.52	.67	1.76	—	—	—	—	—	.03	.04	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and Met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Organochlorine Insecticides (ppm)[1]											
GULF COAST STREAMS																		
Apalachicola R.	SpSu	3	17.7	2.4	B	S-67	.08	.11	.12	.31	.04	—	—	—	—	.01	.04	—
Jim Woodruff Dam,		3	18.2	2.8	B	F-67	.24	.06	3.24	3.54	.02	.02	.27	—	.01	—	.02	—
Fla.		5	14.5	1.3	D	S-68	.18	.05	—	.23	.06	—	—	—	—	—	—	—
# 13		5	18.4	2.5	C	F-68	1.83	.67	.44	2.94	.15	—	—	—	—	.04	.08	—
	ChC	5	17.0	1.7	B	S-67	.22	.18	.30	.70	.04	—	—	.01	—	.01	.27	—
		3	15.5	1.4	B	F-67	.02	.33	.04	.39	.02	—	—	—	—	—	—	—
		5	8.8	0.2	D	S-68	.31	.08	—	.39	.19	—	—	—	—	—	—	—
		5	8.2	0.2	C	F-68	2.68	1.64	1.72	6.04	—	—	—	—	—	—	.17	—
	LMB	3	15.3	2.4	B	S-67	.18	.46	.46	1.10	.38	—	.02	.02	.01	.01	.66	—
		5	15.8	2.1	B	F-67	.07	.01	1.03	1.11	.01	—	.06	—	—	—	—	—
		5	10.9	0.8	D	S-68	.38	.02	.08	.48	.24	—	—	—	—	—	—	—
		5	11.2	0.8	C	F-68	1.68	1.32	.80	3.80	.45	—	—	—	—	.09	.14	—
Tombigbee R.	C	5	15.0	1.6	B	F-67	.04	.09	.03	.16	—	—	—	—	—	—	—	—
McIntosh,		5	17.0	2.7	C	F-68	9.48	4.82	1.33	15.63	.01	—	—	.37	—	—	—	—
Ala.																		
# 14	CpSu	8	11.8	0.8	B	S-67	.10	.24	.10	.44	.05	—	.03	.01	—	—	1.12	—
		5	14.8	2.2	D	S-68	5.15	1.20	—	6.35	.48	—	—	—	—	—	—	—
	StMu	5	14.4	1.3	B	S-67	.49	.40	.72	1.61	.34	—	.02	.02	.01	—	1.65	—
		5	13.6	0.8	B	F-67	.01	.10	.03	.14	—	—	—	—	—	—	.01	—
		5	16.0	1.7	D	S-68	12.00	3.60	—	15.60	1.26	—	—	—	—	—	—	—
		5	15.8	1.7	C	F-68	3.28	2.21	1.26	6.75	.04	—	—	—	—	—	—	—
	LMB	4	12.3	1.0	B	F-67	—	.10	.03	.13	—	—	—	—	—	—	.01	—
		5	11.2	0.8	D	S-68	5.15	—	—	5.15	—	—	—	—	—	—	—	—
		5	13.2	1.2	C	F-68	7.94	3.70	1.69	13.33	.06	—	—	—	—	—	—	—
	BF	3	22.7	4.4	B	S-67	.04	.10	.10	.24	.12	—	.01	.02	—	.01	.13	—
Mississippi R.	C	3	17.3	2.3	B	S-67	.02	.07	.06	.15	.04	.02	.09	.03	—	.01	.19	.03
Luling,		5	9.8	0.7	B	F-67	.01	.05	.02	.08	.01	.01	.01	—	—	.01	—	—
La.		3	22.0	5.6	D	S-68	.42	.10	—	.52	.08	.58	—	—	—	—	—	—
# 15		5	12.6	1.4	C	F-68	.07	.19	.06	.32	.09	—	.10	—	—	.08	.09	—
	StMu	4	13.5	0.9	B	F-67	—	.03	.01	.04	—	—	.01	—	.01	—	—	—
		5	12.2	0.7	C	F-68	.29	.44	.78	1.51	.18	—	.14	—	.89	.73	—	—
	FWD	5	9.8	0.4	D	S-68	.62	.24	—	.86	.05	—	—	—	—	—	—	—
	ChC	3	13.0	0.9	B	S-67	.04	.08	.07	.19	.05	.01	.01	.03	—	.02	.30	—
		5	11.2	0.6	B	F-67	—	.06	—	.06	—	—	—	—	—	—	—	—
		5	11.9	0.6	D	S-68	.16	—	—	.16	—	—	—	—	—	—	—	—
		5	12.0	0.6	C	F-68	.24	.45	.53	1.22	.17	—	.14	—	—	—	.23	—
	LMB	2	14.4	1.9	B	S-67	.02	.05	.09	.16	.03	—	—	.01	—	.01	.08	—
Rio Grande R.	C	4	16.6	2.3	B	S-67	.02	.04	.27	.33	.10	—	—	—	.02	.01	.06	—
Brownsville,																		
Tex.	BMBu	2	17.0	3.1	B	S-67	.08	.08	.11	.27	.11	—	—	—	—	—	.10	—
# 16																		
	GSh	2	11.5	0.9	B	F-67	.05	.03	.03	.11	—	—	—	—	—	—	.01	—
		5	11.7	0.7	D	S-68	2.40	.10	—	2.50	.12	—	—	—	—	—	—	—
		5	12.2	0.6	C	F-68	2.34	.16	.13	2.63	—	—	—	.02	—	—	—	—
	ChC	5	15.5	1.1	B	S-67	.11	.31	.22	.64	.03	—	.01	—	—	.01	.46	—
		5	12.6	0.6	B	F-67	.03	.01	.02	.06	—	—	—	—	—	—	.01	—
		3	12.5	0.6	D	S-68	2.69	.30	—	2.99	.48	.02	—	—	—	—	—	—
		4	16.6	1.5	C	F-68	.61	.01	.02	.64	—	—	—	—	—	—	—	—
	FHC	1	21.1	4.1	B	F-67	.08	.07	.05	.20	.01	—	—	—	—	—	—	—
	BIC	4	10.5	0.3	D	S-68	2.84	.05	—	2.89	.11	.07	—	—	—	—	—	—
		2	10.4	0.3	C	F-68	10.70	1.30	1.17	13.17	.01	—	.02	.02	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	Organochlorine Insecticides (ppm)[1] DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
GREAT LAKES DRAINAGE																		
Gennesse R.	WhSu	5	13.1	0.8	C	F-67	.06	.06	.08	.20	.02	—	—	.01	—	.01	—	—
Scottsville, N. Y.		5	13.6	0.7	E	S-68	.01	—	.07	.08	—	—	—	—	—	.01	—	—
# 17		5	12.7	0.7	C	F-68	.10	.08	.10	.28	.02	—	—	—	—	.02	—	—
	RSu	7	14.0	1.0	C	S-67	.35	.23	.12	.70	.04	—	—	—	—	—	—	—
	RkB	9	7.2	0.9	C	S-67	.08	.06	.06	.20	.01	—	—	—	—	—	—	—
		5	7.9	0.3	E	S-68	.16	1.42	.24	1.82	.03	.04	—	—	.03	.04	—	—
		5	8.4	0.4	C	F-68	.15	.15	.13	.43	.03	—	—	—	—	.08	—	—
	WE	4	14.8	1.0	C	S-67	.11	.15	—	.26	.01	—	—	—	—	—	—	—
		1	25.2	4.0	C	F-67	1.27	1.57	1.39	4.23	.11	—	—	.01	—	.71	—	—
		2	16.6	1.5	E	S-68	.06	.03	.10	.19	.01	.03	—	—	.02	.03	—	—
		3	16.0	1.3	C	F-68	.76	.81	.44	2.01	.10	—	—	—	—	.65	.39	—
Lake Ontario	YeP	8	11.4	0.7	C	S-67	1.15	.58	.73	2.46	.02	—	—	—	.42	—	—	—
Port Ontario,		5	11.8	1.0	C	F-67	1.60	.90	1.23	3.73	.01	—	—	.36	—	.47	—	—
N. Y.		5	9.8	0.6	E	S-68	.25	.05	.20	.49	.02	.01	—	.01	.02	.02	—	—
# 18		5	11.0	0.7	C	F-68	2.81	2.55	2.53	7.89	.05	—	.02	—	—	1.64	—	—
	WhP	10	10.1	0.7	C	S-67	1.43	.75	.93	3.11	.01	—	—	—	—	—	—	—
		5	10.7	0.9	C	F-67	.55	.31	.47	1.33	.04	—	—	.06	—	—	—	—
		5	9.9	0.6	E	S-68	1.67	2.54	3.25	7.46	.50	7.50	—	—	8.33	3.54	—	—
		5	11.0	0.8	C	F-68	4.84	3.36	3.59	11.79	.09	—	.02	—	—	1.74	—	—
	RkB	10	8.6	0.5	C	S-67	.69	.34	.41	1.44	.04	—	—	—	—	—	—	—
		5	8.8	0.6	C	F-67	.43	.27	.28	.98	.03	—	—	.09	—	.12	—	—
		5	6.9	0.3	E	S-68	.07	.11	.31	.49	.01	.01	—	—	.01	.02	—	—
		5	8.3	0.5	C	F-68	2.97	2.14	2.14	7.25	.03	—	—	—	—	.86	—	—
Lake Erie	WhSu	8	13.2	1.0	C	S-67	.12	.18	.20	.50	.02	—	—	—	—	—	—	—
Erie, Pa.		5	14.1	1.2	C	F-67	.09	.11	.13	.33	.03	—	—	.01	—	—	—	—
# 19		5	12.7	0.9	E	S-68	.02	.04	.10	.16	.01	.01	—	—	—	.01	—	—
		5	13.8	1.0	C	F-68	.23	.27	.43	.93	.02	—	—	—	—	.03	—	—
	FWD	10	10.2	0.5	C	S-67	.28	.40	.30	.98	.03	—	—	—	—	—	—	—
		5	11.0	0.6	C	F-67	.09	.10	.13	.32	.03	—	—	—	—	—	—	—
		5	13.8	1.2	E	S-68	.18	.09	.32	.59	.01	.03	—	—	—	.04	—	—
		5	11.0	0.6	C	F-68	.25	.41	.56	1.22	.07	—	—	—	—	.08	—	—
	YeP	10	9.4	0.4	C	S-67	.29	.24	.55	1.08	.03	—	—	—	—	—	—	—
		5	9.1	0.4	C	F-67	.23	.17	.26	.66	.04	—	—	.01	—	—	—	—
		5	9.7	0.5	E	S-68	.05	.04	.13	.22	.01	.01	—	—	—	.01	—	—
		5	9.0	0.2	C	F-68	.11	.30	.58	.99	.05	—	—	—	—	.05	—	—
Lake Huron	C	6	15.9	1.9	C	S-67	1.30	2.30	.49	4.09	.02	—	—	—	—	—	—	—
Bayport,		5	14.8	1.6	C	F-67	.21	.28	.09	.58	.01	—	—	.01	—	.17	—	—
Mich.		5	18.7	3.6	C	S-68	.44	.39	.10	.93	.02	—	—	—	—	—	—	—
# 20		5	18.0	3.1	C	F-68	.15	.19	.08	.42	—	—	—	—	—	—	—	—
	WhSu	6	16.4	1.5	C	S-67	.60	1.10	—	1.70	.01	—	—	—	—	—	—	—
	ChC	6	16.2	1.5	C	S-67	1.90	1.70	—	3.60	.50	—	—	—	—	—	—	—
		5	14.7	1.0	C	F-67	1.08	1.13	.30	2.51	.04	—	—	.03	—	—	—	—
		5	16.8	1.7	C	S-68	1.09	.81	.62	2.52	.04	—	—	—	—	—	—	—
		3	19.8	3.2	C	F-68	1.63	1.80	1.29	4.72	.04	—	—	.29	—	—	—	—
	YeP	11	11.2	0.8	C	S-67	1.10	.60	—	1.70	.03	—	—	—	—	—	—	—
		5	11.6	0.7	C	F-67	.59	.57	.43	1.59	.04	—	—	.01	—	—	—	—
		5	11.4	0.9	C	S-68	.40	.46	.26	1.12	.01	—	—	.02	—	.28	—	—
		5	9.3	0.4	C	F-68	.25	.32	.16	.73	—	—	—	—	—	—	—	—
Lake Michigan	Blo	18	12.1	0.8	C	*S-67	4.40	.84	1.50	6.74	.14	—	—	—	—	—	—	—
Sheboygan,		11	11.5	0.6	C	S-67	4.40	.94	1.30	6.64	.14	—	—	—	—	—	—	—
Wis.		5	11.4	0.6	C	F-67	3.55	.35	1.97	5.87	.22	—	—	.01	—	—	—	—
# 21		5	14.0	1.3	C	S-68	4.79	—	2.10	6.89	.02	—	—	.04	—	.18	.07	—
		5	11.7	0.8	C	F-68	3.26	.59	2.58	6.43	.16	—	—	—	—	—	—	—
		5	11.3	0.7	C	**F-68	3.91	.55	2.99	7.45	.15	—	—	—	—	—	—	—
	YeP	5	10.0	0.4	C	S-68	1.18	.36	1.23	2.77	.08	—	—	—	—	—	—	—
		5	8.3	0.3	C	***F-68	.45	.24	.48	1.17	.07	—	—	—	—	—	—	—

*Two separate samples analyzed; **Sample collected at St. Joseph, Mich.; ***Sample collected at Michigan City, Ind.

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Collection Data				Organochlorine Insecticides (ppm)[1]							
GREAT LAKES DRAINAGE—(Continued)																		
Lake Superior	LWh	9	17.3	1.8	C	S-67	.45	.06	.36	.87	.06	—	—	—	—	—	—	—
Bayfield, Wis.		5	18.8	2.4	C	S-68	.33	.08	27	.68	.04	—	—	—	.08	—	.05	—
# 22	RWh	5	13.8	0.7	C	F-67	.44	.04	.15	63	.01	—	—	.01	—	—	—	—
		6	10.2	0.4	C	F-68	.29	.04	.12	.45	—	—	—	—	—	—	—	—
	LkT	11	17.4	1.5	C	S-67	.61	.15	.12	.88	.02	—	—	—	—	—	—	—
		4	13.7	0.8	C	F-67	.51	.04	.25	.80	.03	—	—	.01	—	—	—	—
		5	20.7	3.0	C	S-68	.81	.08	.34	1.23	.02	—	—	.04	—	—	—	—
		5	22.5	3.3	C	F-68	.78	.14	.46	1.38	.03	—	—	—	—	—	—	—
MISSISSIPPI RIVER SYSTEM																		
Kanawha R.	C	4	15.0	1.7	C	S-67	.11	.30	.06	.47	.02	—	—	—	—	—	—	—
Winfield,		5	12.9	1.1	C	F-67	.03	.06	.02	.11	.02	—	—	—	—	.01	—	—
Va.		5	8.3	0.4	E	S-68	.02	.07	.05	.14	.01	.08	—	—	—	.02	—	—
# 23		5	12.5	1.1	C	F-68	.34	.57	.46	1.37	.03	—	—	.48	.72	.42	—	—
	ChC	5	14.1	0.9	C	F-67	.07	.13	.11	.31	.05	—	—	—	—	.02	—	—
	BrBH	6	11.5	1.0	C	S-67	.06	.23	.07	.36	.04	—	—	—	—	—	—	—
		5	12.0	0.9	C	F-67	.05	.10	.05	.20	.04	—	—	—	—	.01	—	—
		5	10.0	0.5	E	S-68	.02	.11	.08	.21	.01	.08	—	—	—	.04	—	—
		5	12.0	1.0	C	F-68	.47	.66	.31	1.44	.03	—	—	.36	.64	.35	—	—
	LMB	10	8.9	0.5	C	S-67	.15	.25	.13	.53	.04	—	—	—	—	—	—	—
	WhCp	5	9.2	0.4	E	S-68	.17	.10	.19	.46	.01	.28	—	—	—	.04	—	—
		5	6.0	0.1	C	F-68	.36	.46	.34	1.16	.03	—	—	.32	.65	.38	—	—
Ohio R.	C	5	12.8	1.1	C	S-67	.50	.56	.34	1.40	.04	—	—	—	—	—	—	—
Marietta,		5	15.0	2.3	C	F-67	.06	.12	.08	.26	.02	—	—	.10	—	.05	—	—
Ohio		5	16.7	2.5	C	S-68	.19	.35	.20	.74	.02	—	—	—	—	—	—	—
# 24		5	15.5	2.0	C	F-68	.77	.38	.37	1.52	.03	—	—	—	—	.89	.56	—
	RSu	4	14.1	1.1	C	S-67	.23	.44	.20	.87	.01	—	—	—	—	—	—	—
		5	13.0	1.0	C	F-67	.12	.25	.07	.44	.02	—	—	.16	—	.09	—	—
		5	13.8	1.1	C	S-68	.21	.31	.20	.72	.02	—	—	.02	—	—	—	—
		5	14.5	1.4	C	F-68	.20	.35	.22	.77	.03	—	—	—	—	.46	.31	—
	ChC	6	14.5	1.0	C	S-67	.86	1.10	.47	2.43	.05	—	—	—	—	—	—	—
		5	14.3	0.9	C	F-67	.64	.89	.73	2.26	.05	—	—	.27	—	.23	—	—
		5	14.9	1.0	C	S-68	.65	1.05	.36	2.06	.04	—	—	—	—	—	—	—
		5	14.5	0.8	C	F-68	1.29	1.24	.78	3.31	.03	—	—	—	—	.93	.66	—
Cumberland R.	C	7	12.0	0.8	B	S-67	.01	.03	.01	.05	.03	—	—	—	—	.01	.02	—
Clarksville,		5	9.8	0.4	B	F-67	.02	.04	.05	.11	—	—	.01	.01	—	—	.01	—
Tenn.		5	13.4	1.2	D	S-68	.83	.07	—	.90	.17	.11	—	—	—	—	—	—
# 25		5	11.2	0.7	C	F-68	.30	.38	.18	.86	.02	—	—	—	—	.12	—	—
	BGS	13	7.3	0.3	B	S-67	.05	.03	.42	.50	.03	—	—	—	—	.02	.05	—
		4	6.6	0.2	B	F-67	.04	—	.13	.17	—	—	.01	.02	—	—	.02	—
		5	6.7	0.2	D	S-68	.16	.05	—	.21	.04	—	—	—	—	—	—	—
		5	6.6	0.2	C	F-68	.31	.26	.16	.73	.03	—	—	—	—	.09	—	—
	LMB	8	10.8	0.6	B	S-67	.08	.07	.18	.33	.06	.01	—	—	.01	.02	.03	—
		5	10.3	0.4	B	F-67	.01	.03	.01	.05	—	—	.02	.01	—	—	.03	—
		5	14.5	1.7	D	S-68	.16	.05	—	.21	.05	—	—	—	—	—	—	—
		5	10.6	0.8	C	F-68	.67	.85	.56	2.08	.04	—	.01	—	—	.29	—	—
Illinois R.	C	4	16.3	2.5	C	S-67	.28	.30	.09	.67	.30	—	—	—	—	—	.50	—
Beardstown, Ill.																		
# 26	BMBu	5	14.7	1.8	C	F-67	.04	.08	.04	.16	.52	—	—	.02	—	.01	.24	—
		3	14.8	2.1	C	F-68	.17	.22	.21	.60	.35	—	—	.07	—	.11	.17	—
	CpSu	5	12.7	0.9	C	S-68	.16	.11	.16	.43	.20	—	—	—	—	—	—	—
	ChC	8	12.6	0.8	C	S-67	.35	.45	.15	.95	.38	—	—	—	—	—	.65	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and Met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Organochlorine Insecticides (ppm)[1]											
MISSISSIPPI RIVER SYSTEM—(Continued)																		
# 26 (Continued)	BkBH	5	10.3	0.6	C	F-67	.06	.13	.06	.25	.18	—	—	—	—	—	.18	—
		5	9.2	0.4	C	S-68	.19	.04	.06	.29	.10	—	—	—	—	—	—	—
		5	10.6	0.5	C	F-68	.30	.45	.40	1.15	.30	—	—	.05	—	.11	.24	—
	WhCp	5	9.3	0.4	C	F-67	.06	.09	.04	.19	.23	—	—	—	—	—	.13	—
		5	10.4	0.6	C	S-68	.31	.10	.27	.68	.24	—	—	—	—	—	—	—
		5	8.7	0.4	C	F-68	.19	.25	.28	.72	.27	—	—	.04	—	.08	.15	—
Mississippi R. Gutenberg, Iowa # 27	C	4	17.8	2.5	C	S-67	.13	.16	.06	.35	.02	—	—	—	—	—	—	—
		4	13.7	1.9	C	S-68	.27	.29	.15	.71	.02	—	—	—	—	—	—	—
		4	19.5	3.3	C	F-68	.30	.38	.27	.95	.04	—	—	—	—	.12	—	—
	BMBu	4	16.1	2.7	C	S-67	.17	.24	.13	.54	.05	—	—	—	—	—	—	—
		4	18.0	4.0	C	F-67	.05	.09	.07	.21	.04	—	—	.02	—	—	—	—
	SpSu	5	15.9	2.0	C	S-67	.20	.27	.21	.68	.04	—	—	—	—	—	—	—
	RSu	5	16.2	1.4	C	F-68	.26	.36	.35	.97	.05	—	—	—	—	.10	—	—
	BGS	5	7.6	0.4	C	F-67	.08	.12	.10	.30	.03	—	—	—	—	—	—	—
		5	4.2	0.2	C	S-68	.06	.03	.04	.13	.01	—	—	—	—	—	—	—
		5	8.6	0.3	C	F-68	.10	.14	.17	.41	.02	—	—	—	.01	.03	—	—
	LMB	5	12.5	1.7	C	S-67	.08	.10	.07	.25	.01	—	—	—	—	—	—	—
		5	12.6	1.0	C	F-67	.04	.03	.03	.10	.02	—	—	—	—	—	—	—
		4	10.5	0.8	C	S-68	.15	.18	.14	.47	01	—	—	—	—	.04	—	—
		5	12.6	1.0	C	F-68	.14	.21	.22	.57	.02	—	—	—	—	.03	—	—
Arkansas R. Pine Bluff, Ark. # 28	C	3	22.0	4.6	B	S-67	.01	.13	.04	.18	.08	.01	.01	—	—	.05	.05	—
		5	17.7	2.9	B	F-67	.01	.01	1.57	1.59	.03	—	.04	—	.01	—	—	—
		4	18.1	3.2	D	S-68	.65	.16	—	.81	.06	—	—	—	—	—	—	—
		3	19.3	3.9	C	F-68	5.63	2.79	.67	9.09	.02	—	—	—	—	—	—	—
	SMBu	3	17.0	3.1	B	S-67	.11	.15	.24	.50	.10	.01	.02	.02	—	.01	.11	.01
		5	16.2	2.4	B	F-67	.08	.64	.39	1.11	.02	.01	.11	.02	.04	.01	.02	.02
		3	18.1	3.2	D	S-68	1.39	.47	—	1.86	.17	—	—	—	—	—	—	—
		3	17.0	2.6	C	F-68	1.83	2.03	1.95	5.81	.05	—	—	—	—	.20	—	—
	ChC	2	15.0	1.0	C	F-68	.89	.78	1.02	2.69	.02	—	—	—	—	.12	—	—
	FHC	3	23.0	5.4	B	S-67	.16	.34	.77	1.27	.08	.01	.03	.07	.01	.05	.54	—
		4	21.3	3.8	B	F-67	.05	.03	1.16	1.24	.02	—	.11	.01	.01	.01	.01	—
		3	19.6	3.5	D	S-68	2.28	1.03	—	3.31	.40	—	—	—	—	—	—	—
Arkansas R. Keystone Res., Okla. # 29	C	4	13.8	1.4	B	S-67	.05	.03	.14	.22	.01	.01	—	—	—	.01	.03	—
		5	12.7	1.0	B	F-67	.01	.06	.02	.08	—	—	—	—	—	—	—	—
		5	11.8	0.8	D	S-68	.13	.03	—	.16	.01	.01	—	—	—	—	—	—
		5	12.2	0.8	C	F-68	.15	.13	.10	.38	.01	—	—	—	.02	.04	.09	—
	SMBu	9	10.7	0.7	B	S-67	.07	.02	.15	.23	.02	—	—	—	.03	.01	.03	—
	BGS	5	5.9	0.1	B	F-67	—	.01	.02	.02	—	—	—	—	—	—	.02	—
		5	5.8	0.1	D	S-68	.13	.02	—	.15	.02	.05	—	—	—	—	—	—
		5	5.8	0.1	C	F-68	.17	.10	.10	.37	—	—	—	—	.02	.12	.06	—
	LMB	4	14.0	1.7	B	S-67	.05	.05	.06	.15	.04	—	—	—	—	.01	.04	.01
		5	13.6	1.7	B	F-67	—	.17	.02	.19	.01	—	.01	—	.01	—	.01	—
		5	14.5	2.3	D	S-68	.19	.02	—	.21	.10	.07	—	—	—	—	—	—
		5	13.8	1.6	C	F-68	.15	.14	.11	.40	.03	—	—	—	—	.08	.72	—
White R. DeValls Bluff, Ark. # 30	C	3	20.0	4.1	B	S-67	.01	.09	.04	.14	.07	—	—	—	—	.01	.10	—
		4	20.8	4.5	B	F-67	.01	.01	1.73	1.75	.01	—	.01	—	—	—	—	—
		3	20.0	3.5	D	S-68	2.76	1.35	—	4.11	.34	—	—	—	—	—	—	—
		2	21.0	4.9	C	F-68	1.56	1.30	.32	3.18	.04	—	.06	—	—	—	—	—
	BMBu	3	17.3	2.7	B	S-67	.07	.13	.13	.33	.10	—	.01	—	—	—	.07	—
		5	15.8	2.3	B	F-67	.05	.02	.42	.49	—	—	.01	—	.01	.01	—	—
		4	16.6	2.5	D	S-68	1.30	—	—	1.30	.17	—	—	—	—	—	—	—
		3	18.0	3.5	C	F-68	2.19	2.21	2.32	6.72	.04	—	.06	—	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	Organochlorine Insecticides (ppm)[1] DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
MISSISSIPPI RIVER SYSTEM—(Continued)																		
# 30 (Continued)	ChC	3	19.0	1.7	B	S-67	.10	.08	.19	.37	.09	—	—	—	—	.01	.04	—
		4	13.4	0.7	B	F-67	—	.09	.02	.10	—	—	—	—	—	—	.01	—
		4	15.2	1.3	D	S-68	.91	.59	—	1.50	—	—	—	—	—	—	—	—
		1	18.0	3.0	C	F-68	2.81	2.21	2.73	7.75	.06	—	.02	—	—	.19	—	—
Missouri R. Nebraska City, Nebr. #31	C	9	14.2	1.6	C	S-67	.22	.26	.15	.63	.09	—	—	—	—	—	.28	—
		5	16.3	2.5	C	F-67	.14	.16	.11	.41	.11	—	—	.01	—	.03	.22	—
		5	15.7	2.1	C	S-68	.03	.05	.03	.11	.05	—	—	—	—	.01	—	—
		5	16.8	2.9	C	F-68	.27	.28	.24	.81	.09	—	—	—	—	—	—	—
	BMBu	2	16.5	3.1	C	S-67	.11	.21	.28	.60	.22	—	—	—	—	—	.30	—
	ME	5	12.8	0.7	C	S-68	.72	.14	.15	1.01	.22	.04	—	—	—	—	—	—
	ChC	5	14.5	1.1	C	F-67	.43	.73	.87	2.03	.12	—	—	.02	—	.01	.24	—
		5	17.2	1.9	C	S-68	.04	.09	.08	.21	.18	.01	—	—	—	—	—	—
		5	15.3	1.1	C	F-68	.15	.22	.26	.63	.04	—	—	—	—	.05	—	—
	BkBH	1	8.7	0.4	C	S-67	.01	.02	.03	.07	.02	—	—	—	—	—	—	—
	WhCp	5	9.0	0.3	C	F-67	.09	.06	.06	.21	.06	—	—	.01	—	—	—	—
	WE	3	11.0	0.3	C	F-68	.02	.20	.22	.44	.24	—	—	—	—	.06	—	—
Missouri R. Garrison Dam, N. Dak. #32	C	5	16.2	2.3	C	S-67	.05	.03	.01	.08	.01	—	—	—	—	.01	—	—
		5	15.6	1.7	C	F-67	.03	.02	.01	.06	.01	—	—	—	—	—	—	—
		2	18.3	3.6	C	F-68	.08	.06	.07	.21	.04	—	.03	—	—	.01	—	—
	WhSu	15	12.1	0.8	C	S-67	.02	.02	.02	.06	.01	—	—	—	—	.01	—	—
		5	12.7	1.0	C	F-67	.02	.02	.01	.05	.01	—	—	—	—	—	—	—
		5	13.3	0.9	C	S-68	—	—	—	—	—	—	—	—	—	—	—	—
	GE	20	11.5	0.5	C	S-67	.08	.07	.05	.20	.02	—	—	—	—	—	—	—
		5	11.4	0.6	C	F-67	.03	.02	.03	.08	.02	—	—	—	—	—	—	—
		5	10.8	0.4	C	S-68	.15	.37	.24	.76	.01	—	—	—	—	.23	—	—
		5	12.2	0.5	C	F-68	.05	.04	.05	.14	.01	—	—	—	—	.01	—	—
	NPi	3	27.1	4.0	C	S-67	.06	.05	.08	.18	.01	—	—	—	—	.01	—	—
	WE	5	19.4	2.7	C	S-67	.12	.06	.20	.38	.03	—	—	—	—	.01	—	—
		4	17.1	1.9	C	F-68	.06	.09	.08	.23	.02	—	—	—	—	—	—	—
	Sag	4	16.0	1.2	C	S-67	.06	.04	.13	.23	.01	—	—	—	—	—	—	—
		3	16.8	1.0	C	S-68	.06	.03	.10	.19	.02	—	—	—	—	—	—	—
Missouri R. Great Falls, Mont. #33	C	1	15.5	1.7	A	S-67	.04	.02	.03	.09	.02	—	—	—	—	—	—	—
	LSSu	5	10.4	0.5	A	F-67	—	—	—	.01	—	—	—	—	—	—	—	—
	LNSu	5	15.7	1.4	C	S-68	.14	.24	.13	.51	.01	—	—	—	—	.02	—	—
	RSu	1	18.0	1.9	A	S-67	.05	.05	.07	.17	.01	—	—	—	—	—	—	—
		5	16.6	1.6	C	F-68	.75	.67	.96	2.38	.04	—	—	—	—	.11	—	—
	BLSu	2	16.9	1.6	A	S-67	.07	.04	.09	.20	.02	—	—	—	—	—	—	—
	GE	6	13.0	0.7	A	S-67	.01	—	.01	.03	.01	—	—	—	—	—	—	—
		5	12.9	0.8	C	S-68	.07	.03	.06	.16	.01	—	—	—	—	.01	—	—
		5	12.7	0.5	C	F-68	.09	.08	.16	.33	—	—	—	—	—	—	—	—
	FWD	1	15.5	1.7	A	S-67	.01	—	.01	.02	.01	—	—	—	—	—	—	—
	ChC	1	18.0	2.0	C	F-68	.74	.50	.57	1.81	.04	—	—	—	—	.05	—	—
	BkBH	1	11.0	0.5	A	S-67	.01	—	.01	.02	—	—	—	—	—	—	—	—
	YeP	5	6.1	0.1	A	F-67	.03	.03	.02	.08	—	—	—	—	—	—	—	—
	Sag	5	14.8	0.8	C	S-68	.04	.03	.04	.11	—	—	—	—	—	—	—	—
	RBT	4	8.5	0.3	A	F-67	.01	.01	—	.01	—	—	—	—	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and Met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
HUDSON BAY DRAINAGE																		
Red R.	C	7	10.9	0.9	C	S-67	.29	.16	—	.45	.07	—	—	—	—	.01	—	—
Noyce,		2	12.5	1.0	C	S-68	.12	.04	.01	.17	.05	—	—	—	—	—	—	—
Minn.																		
# 34	WhSu	4	10.4	0.8	C	S-67	.10	.12	—	.22	.09	—	—	—	—	.01	—	—
		4	16.0	2.0	C	F-67	.61	.95	1.79	3.35	.08	—	—	.03	—	—	—	—
		1	11.5	0.8	C	F-68	.17	.09	.37	.63	.03	—	—	—	—	—	—	—
	GE	5	10.5	0.7	C	F-67	1.04	.52	.69	2.25	.25	—	—	.03	—	—	—	—
		1	10.1	0.5	C	F-68	1.90	.25	.21	2.36	.03	—	—	—	—	—	—	—
	ChC	11	9.1	0.5	C	S-67	.55	.57	.53	1.65	.12	—	—	—	—	.02	—	—
		2	10.2	0.4	C	S-68	.75	.09	.24	1.08	.37	—	—	—	—	—	—	—
	Sag	5	12.5	0.8	C	F-67	1.16	.75	1.87	3.78	.23	—	—	.06	—	—	—	—
		1	12.0	0.5	C	S-68	.10	.18	.07	.35	.19	—	—	—	—	—	—	—
		3	11.5	0.5	C	F-68	.39	.30	.37	1.06	.06	—	—	.06	.04	.07	.06	—
	Bot	5	13.8	0.9	C	S-67	.14	.14	—	.28	.04	—	—	—	—	.01	—	—
COLORADO RIVER SYSTEM																		
Green R.	C	10	15.6	1.8	B	S-67	.01	—	.03	.03	—	—	—	—	—	—	—	—
Vernal,		5	14.4	1.4	B	F-67	.01	.02	.02	.05	—	—	—	—	—	—	.01	—
Utah		5	15.7	1.9	D	S-68	.16	.01	—	.17	.01	.01	—	—	—	—	—	—
# 35		5	9.0	0.3	C	F-68	.04	.03	.03	.10	—	—	—	—	—	—	.02	—
	HBSu	4	19.6	2.8	B	S-67	.01	.01	.08	.10	.01	—	—	—	—	—	.01	—
	FMSu	5	17.8	2.4	D	S-68	.53	.03	—	.56	.05	.05	—	—	—	—	—	—
	ChC	1	15.5	1.1	B	F-67	—	.05	.01	.06	—	—	.01	—	—	—	.02	—
	BkBH	7	6.7	0.2	B	S-67	.02	.06	.16	.24	.10	—	—	—	—	—	.06	—
		5	8.1	0.3	B	F-67	.01	.39	.10	.50	.01	—	—	—	—	—	.01	—
		2	7.1	0.3	D	S-68	.10	—	—	.10	—	.05	—	—	—	—	—	—
		5	5.2	0.1	C	F-68	.02	.02	.02	.06	—	—	—	—	—	—	—	—
	GrS	5	4.0	0.1	C	F-68	.03	.02	.02	.07	—	—	—	—	—	—	—	—
Colorado R.	C	6	15.2	1.6	B	S-67	.04	.01	.13	.17	.02	—	—	—	.02	—	.01	.01
Imperial Res.,		4	17.2	2.1	B	F-67	.04	.01	2.71	2.76	.01	—	.02	.01	.01	—	—	—
Ariz.		5	16.8	1.9	D	S-68	.25	.06	—	.31	.01	.08	—	—	—	—	—	—
# 36		3	19.4	3.1	D	F-68	.18	—	—	.18	—	—	—	—	—	—	—	—
	ChC	6	15.0	1.3	B	S-67	.07	.03	.22	.31	.05	—	.01	—	.02	.01	.02	—
		3	18.5	1.9	B	F-67	.03	—	4.75	4.79	.04	.01	.71	.01	—	—	—	—
		3	12.3	0.8	D	S-68	.21	.01	—	.22	.03	.09	—	—	—	—	—	—
	BGS	3	6.6	0.2	D	F-68	.06	—	—	.06	—	.01	—	—	—	—	—	—
	LMB	8	11.6	0.9	B	S-67	.02	.03	.08	.12	.06	—	—	—	.02	—	—	—
		4	13.3	1.2	B	F-67	.02	.01	.01	.04	—	—	—	—	—	—	.01	—
		5	12.0	1.0	D	S-68	.19	.01	—	.20	.02	.11	—	—	—	—	—	—
		3	10.3	0.4	D	F-68	.09	—	—	.09	—	—	—	—	—	—	—	—
INTERIOR BASINS																		
Truckee R.	C	1	27.5	11.5	A	S-67	.01	.01	—	.02	—	—	—	—	—	—	—	—
Fernley,		3	12.1	1.1	A	F-67	.02	.01	.01	.03	—	—	—	—	—	—	—	—
Nev.		5	18.8	3.2	C	F-68	.25	.17	.06	.48	.01	—	—	—	—	—	—	—
# 37	LSSu	5	10.5	0.6	A	F-67	.02	.01	—	.02	—	—	—	—	—	—	—	—
	TaSu	5	10.6	0.5	C	S-68	.16	.10	.07	.33	.01	—	—	—	—	—	—	—
	TCh	3	12.1	0.9	A	S-67	.05	.01	.01	.06	—	—	—	—	—	—	—	—
	ChC	5	10.1	0.3	A	S-67	.02	.02	.02	.06	.01	—	—	—	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
INTERIOR BASINS—(Continued)																		
# 37 (Continued)	BrBH	5	11.2	1.0	A	S-67	.03	.01	.01	.06	—	—	—	—	—	—	—	—
		5	10.4	0.7	C	S-68	.22	.16	.06	.44	.02	—	—	—	—	—	—	—
		5	9.5	0.4	C	F-68	.09	.08	.05	.22	.02	—	—	—	—	—	—	—
	SaP	4	7.8	0.3	A	S-67	.04	.01	.01	.06	—	—	—	—	—	—	—	—
	LMB	5	12.0	1.0	C	S-68	.74	.43	.20	1.37	.03	—	—	—	—	—	—	—
		5	13.1	1.4	C	F-68	.42	.35	.35	1.12	.06	—	—	—	—	—	—	—
Utah Lake, Provo, Utah # 38	C	7	18.6	2.8	B	S-67	—	.03	.19	.22	.02	—	—	—	—	—	.02	—
		5	16.3	2.2	B	F-67	—	.07	.01	.08	—	—	.01	—	—	—	.01	—
		5	15.0	1.6	D	S-68	.26	.03	—	.29	.04	.01	—	—	—	—	—	—
		5	13.0	1.1	C	F-68	.06	.06	.02	.14	.02	—	—	—	—	—	—	—
	ChC	9	17.7	2.0	B	S-67	.02	.04	.08	.14	.04	—	—	—	—	—	.03	.01
	BrBH	5	9.9	0.5	B	F-67	—	.05	.01	.06	—	—	—	—	—	—	.02	—
		5	8.6	0.4	D	S-68	.16	.04	—	.20	.04	.01	—	—	—	—	—	—
		5	9.2	0.5	C	F-68	.02	.03	.02	.07	—	—	—	—	—	—	—	—
	WhB	6	12.3	0.8	B	S-67	.01	—	.03	.04	—	—	—	—	—	—	—	—
		5	11.9	0.8	B	F-67	.01	.13	.06	.20	—	—	—	.01	—	—	.03	—
		5	10.1	0.4	D	S-68	.19	.01	—	.20	.02	.05	—	—	—	—	—	—
		2	10.6	0.5	C	F-68	.08	.09	.06	.23	—	—	—	—	—	—	—	—
CALIFORNIA STREAMS																		
Sacramento R. Sacramento, Calif. # 39	C	5	15.8	1.9	A	S-67	.06	.43	.32	.81	.10	—	.01	.02	—	.01	—	—
		5	14.1	1.4	A	F-67	.86	.57	.07	1.50	—	—	—	—	—	—	—	—
		5	15.9	1.5	C	S-68	4.84	1.56	.83	7.23	.15	—	—	—	—	—	—	—
		5	11.7	0.7	C	F-68	.81	.28	.28	1.37	—	—	—	—	—	—	—	—
	ChC	2	13.0	0.8	C	S-68	1.87	1.04	.47	3.38	.06	—	—	.01	—	.04	—	—
		3	13.3	1.1	C	F-68	1.19	.81	.53	2.53	.02	—	—	.13	—	—	.04	—
	BrBH	5	9.4	0.6	A	F-67	1.36	1.01	.31	2.68	—	—	—	—	—	—	—	—
	LMB	4	13.0	1.5	A	S-67	2.53	3.44	3.14	9.11	.14	—	—	—	—	—	—	—
		1	16.0	2.3	C	S-68	4.48	1.95	.87	7.30	.06	—	—	.01	—	—	—	—
		3	17.2	3.2	C	F-68	1.17	1.03	1.26	3.46	.05	—	.02	—	—	.04	—	—
	NSq	4	16.7	1.9	A	F-67	.24	.12	.05	.40	—	—	—	—	—	—	—	—
Son Joaquin R. Los Banos, Calif. # 40	C	5	11.5	0.9	A	S-67	.07	.03	.02	.11	.01	—	—	—	—	—	—	—
		3	15.3	1.4	A	F-67	.09	.04	—	.13	—	—	—	—	—	—	—	—
		5	14.7	1.5	C	S-68	.49	.21	.04	.74	—	—	—	—	—	—	—	—
		4	15.2	1.6	C	F-68	.19	.18	.07	.44	.04	—	—	—	—	.02	—	—
	ChC	4	16.3	1.3	A	F-67	1.29	.51	.01	1.80	.01	—	—	—	—	—	—	—
		4	15.7	1.6	C	S-68	.72	.82	.29	1.83	.14	—	—	—	—	—	—	—
		5	15.6	1.4	C	F-68	1.15	1.33	.30	2.78	.31	—	—	—	—	.10	—	—
	WhC	4	10.7	0.7	A	S-67	.22	.08	.09	.39	.03	—	.01	—	—	—	—	—
	GrS	1	8.0	0.7	A	S-67	.05	.02	.02	.09	—	—	—	—	—	—	—	—
	BkCp	5	8.4	0.4	A	F-67	.02	.02	.01	.05	—	—	—	—	—	—	—	—
		2	11.3	0.9	C	S-68	.56	.62	.20	1.38	.15	—	—	—	—	—	—	—
		5	12.0	1.2	C	F-68	.48	.65	.37	1.50	.29	—	—	—	—	.04	—	—
	StB	1	25.0	5.1	A	S-67	.76	.28	.54	1.58	.03	—	.01	—	—	—	—	—
COLUMBIA RIVER SYSTEM																		
Snake R. Hagerman, Idaho # 41	C	3	22.5	5.8	A	S-67	.17	.07	.03	.27	.01	—	—	—	—	—	—	—
	LSSu	5	18.2	2.5	A	S-67	.09	.02	.03	.14	.01	—	—	—	—	—	—	—
		5	16.1	1.5	A	F-67	.08	.02	.02	.12	—	—	—	—	—	—	—	—
		5	18.7	2.2	C	S-68	1.46	.20	.05	1.71	.02	—	—	—	—	—	—	—
		5	17.1	1.9	C	F-68	.60	.23	.18	1.01	.04	—	—	—	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Collection Data				Organochlorine Insecticides (ppm)[1]							
COLUMBIA RIVER SYSTEM—(Continued)																		
# 41 (Continued)	MWh	5	11.5	0.6	A	F-67	.01	—	—	.02	—	—	—	—	—	—	—	—
	BkBH	1	12.5	0.9	C	S-68	.05	.02	.01	.08	—	—	—	—	—	—	—	—
	RBT	3	13.7	1.3	A	S-67	.04	.01	.01	.06	.01	—	—	—	—	—	—	—
		1	10.8	0.6	A	F-67	.07	—	.01	.08	—	—	—	—	—	—	—	—
	NSq	3	12.0	0.5	A	F-67	.60	.05	—	.66	—	—	—	—	—	—	—	—
		5	15.4	1.4	C	S-68	.86	.12	.04	1.02	.01	—	—	—	—	—	—	—
		5	16.6	1.5	C	F-68	1.43	.16	.08	1.67	.02	—	—	—	—	—	—	—
Snake R. Lewiston, Idaho # 42	C	1	16.3	2.0	A	F-67	.09	.02	.01	.11	—	—	—	—	—	—	—	—
	LSSu	4	17.4	2.1	A	S-67	.05	.03	.04	.11	.01	—	—	—	—	—	—	—
		5	19.0	2.1	A	F-67	.05	.03	.05	.13	—	—	—	—	—	—	—	—
		5	18.0	2.0	C	S-68	.22	.07	.13	.42	.02	—	—	—	—	—	—	—
		5	17.4	2.0	C	F-68	.31	.17	.26	.74	.05	—	—	—	—	—	—	—
	CM	2	12.6	1.1	A	S-67	.05	.02	.01	.08	.01	—	—	—	—	—	—	—
	ChC	1	23.5	5.2	A	F-67	.39	.07	.10	.56	—	—	—	—	—	—	—	—
	SMB	5	13.3	1.2	C	S-68	.55	.15	.07	.77	.03	—	—	—	—	—	—	—
		4	8.3	0.3	C	F-68	.30	.11	.14	.55	.07	—	—	—	—	—	—	—
	NSq	5	13.7	1.0	A	F-67	.22	.04	.02	.28	—	—	—	—	—	—	—	—
		5	14.9	1.2	C	S-68	.83	.17	.05	1.05	.02	—	—	—	—	—	—	—
		5	11.2	0.5	C	F-68	.44	.12	.14	.70	.06	—	—	—	—	—	—	—
Salmon R. Riggins, Idaho # 43	LSSu	5	18.5	2.3	A	S-67	.05	.01	.02	.08	—	—	—	—	—	—	—	—
		5	17.2	1.8	A	F-67	.03	—	.01	.04	—	—	—	—	—	—	—	—
		5	18.0	2.1	C	S-68	.15	.04	.04	.23	—	—	—	—	—	—	—	—
		3	16.9	1.8	C	F-68	.19	.08	.11	.38	—	—	—	—	—	—	—	—
	MWh	5	13.8	0.9	C	S-68	.13	.02	.03	.18	—	—	—	—	—	—	—	—
	SMB	1	17.0	2.8	A	S-67	.12	.01	.05	.18	—	—	—	—	—	—	—	—
		2	10.2	0.7	A	F-67	.08	—	.04	.12	—	—	—	—	—	—	—	—
	NSq	3	12.3	0.7	A	S-67	.05	.01	.01	.07	—	—	—	—	—	—	—	—
		2	12.8	0.8	A	F-67	.10	.02	—	.12	—	—	—	—	—	—	—	—
		4	11.1	0.5	C	S-68	.31	.04	.01	.36	—	—	—	—	—	—	—	—
Yakima R. Grainger, Wash. # 44	C	3	12.5	1.3	A	S-67	.18	.10	.03	.31	.05	—	—	—	—	—	—	—
		5	9.7	0.7	A	F-67	1.36	.50	.22	2.08	—	.02	—	—	—	—	—	—
		4	13.5	1.1	C	S-68	2.43	.45	.16	3.04	.06	—	—	.02	—	—	—	—
		5	13.4	1.2	C	F-68	2.73	.89	.33	3.95	.08	—	—	—	—	—	—	—
	LSSu	5	17.3	2.2	A	S-67	.23	.25	.31	.78	.06	—	—	—	.01	—	—	—
		3	18.0	1.8	A	F-67	.23	.03	.08	.33	—	—	—	—	—	—	—	—
		5	15.5	1.1	C	S-68	.91	.31	.48	1.70	.05	—	—	—	—	—	—	—
	CM	5	12.8	0.8	C	F-68	1.09	.25	.32	1.66	.03	—	—	—	—	—	—	—
	SMB	3	10.2	0.9	C	S-68	.73	.20	.09	1.02	.01	—	—	—	—	—	—	—
	BkCp	5	6.8	0.2	C	F-68	.99	.50	.09	1.58	.10	—	—	—	—	—	—	—
	NSq	1	15.0	1.0	A	F-67	1.01	.33	.04	1.38	—	—	—	—	—	—	—	—
Willamette R. Oregon City, Oreg. # 45	C	1	19.5	4.1	A	F-67	.12	.12	.03	.27	—	—	—	.02	—	—	—	—
	LSSu	5	18.0	2.2	A	S-67	.12	.15	.14	.42	.03	—	.01	.01	—	.01	—	—
		5	14.7	1.3	A	F-67	1.85	.28	.52	2.65	—	—	—	.02	—	—	—	—
		5	15.1	1.5	C	S-68	.28	.21	.17	.66	.01	—	—	.11	—	.03	—	—
		5	18.0	2.5	C	F-68	.31	.39	.40	1.10	.03	—	—	—	—	.05	—	—
	WhCp	5	8.0	0.3	A	S-67	.13	.11	.05	.29	.01	—	—	—	—	—	—	—
	CSa	3	12.9	0.9	A	F-67	.34	.01	—	.35	—	—	—	—	—	—	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Organochlorine Insecticides (ppm)[1]											
COLUMBIA RIVER SYSTEM—(Continued)																		
# 45 (Continued)	NSq	3	11.8	0.7	A	F-67	.14	.10	—	.25	—	—	—	—	—	—	—	—
		5	16.2	1.7	C	S-68	.78	.28	.10	1.16	.03	—	—	.09	—	—	—	—
		5	16.5	2.2	C	F-68	.62	.29	.41	1.32	.03	—	—	—	—	.05	—	—
Columbia R. Bonneville Dam Oreg. # 46	C	2	19.5	3.6	C	F-68	3.41	.39	.23	4.03	.04	—	—	—	—	—	.17	—
	LSSu	5	14.2	1.1	A	S-67	.13	.20	.17	.50	.07	.01	—	.01	.02	.01	—	—
		2	17.4	2.0	A	F-67	—	.02	.02	.04	—	—	—	—	—	—	—	—
		5	15.6	1.6	C	S-68	.45	.58	.27	1.30	.02	—	—	—	—	—	—	—
	BrBH	5	10.3	0.6	A	S-67	.12	.13	.05	.30	.01	—	.01	—	—	—	—	—
	RBT	1	15.3	1.4	A	F-67	.09	.01	—	.10	—	—	—	—	—	—	—	—
	NSq	4	16.0	1.4	A	S-67	.14	.30	.07	.51	.05	—	.01	.01	.01	.01	—	—
		3	8.7	2.2	A	F-67	.01	.45	.04	.50	—	.01	—	—	—	—	—	—
		5	15.0	1.2	C	F-68	1.93	.99	.32	3.24	—	—	—	—	—	—	—	—
PACIFIC COAST STREAMS																		
Klamath R. Hornbrook, Calif. # 47	KSSu	5	13.5	1.0	C	F-68	.03	.02	.01	.06	—	—	—	—	—	—	—	—
	BrBH	4	8.7	0.4	A	S-67	.18	.09	.10	.37	.09	—	—	—	—	—	—	—
	PkS	3	5.1	0.1	C	F-68	.02	.02	.01	.04	—	—	—	—	—	—	—	—
	YeP	5	8.5	0.3	A	S-67	.27	.33	.20	.80	.09	—	—	—	—	.01	—	—
		5	9.5	0.4	A	F-67	.18	.10	.05	.33	—	—	—	—	—	—	—	—
		5	9.4	0.4	C	S-68	.03	.02	.02	.07	—	—	—	—	—	—	—	—
		5	10.1	0.5	C	F-68	.02	.02	.02	.06	—	—	—	—	—	—	—	—
	RBT	2	19.1	2.9	A	F-67	.03	—	.02	.04	—	—	—	—	—	—	—	—
		5	14.6	1.1	C	S-68	.34	.27	.09	.70	—	—	—	—	.02	.02	.02	—
Rogue R. Gold Ray Dam, Oreg. # 48	C	2	21.1	4.7	A	S-67	1.20	.70	.20	2.10	.52	—	—	.01	—	—	—	—
	LSSu	4	16.4	1.8	A	S-67	.47	.48	.60	1.55	.44	.01	—	.01	.04	.01	—	—
	BLSu	5	11.1	0.6	A	F-67	.07	.04	.07	.18	—	—	—	—	—	—	—	—
		5	14.9	1.4	C	S-68	.51	.41	.54	1.46	—	—	—	—	—	—	—	—
		5	12.6	0.8	C	F-68	.39	.50	.62	1.51	.02	—	—	—	—	.04	—	—
	BrBH	5	9.8	0.5	A	F-67	.02	—	—	.02	—	—	—	—	—	—	—	—
		5	10.5	0.6	C	S-68	.33	.24	.10	.67	.01	—	—	—	—	—	—	—
	LMB	2	12.7	1.4	A	F-67	.15	.10	.22	.46	—	—	—	—	—	.01	—	—
	SMB	4	6.9	0.2	C	F-68	.34	.47	.44	1.25	—	—	—	—	—	.04	—	—
	RBT	5	11.2	0.5	C	F-68	1.33	.75	.77	2.85	.01	—	—	—	—	.08	—	—
	CTT	2	14.8	1.1	C	S-68	.68	.61	.48	1.77	.02	—	—	—	—	—	—	—
ALASKAN STREAMS																		
Chena R. Fairbanks, Alaska # 49	LNSu	5	13.4	0.9	A	S-67	.14	.01	.02	.16	—	—	—	—	—	—	—	—
		4	10.1	0.7	A	F-67	.04	.02	.06	.12	—	—	—	—	—	—	—	—
		5	13.8	0.9	C	S-68	.14	.07	.08	.29	—	—	—	—	—	—	—	—
		5	12.3	0.7	C	F-68	.24	.21	.45	.90	—	—	—	—	—	.04	—	—
	LWh	4	12.4	0.9	A	S-67	.04	.02	.05	.10	.01	—	—	—	.02	—	—	—
		2	8.3	0.5	A	F-67	.09	.06	.10	.24	—	—	—	—	—	—	—	—
	RWh	4	13.5	0.8	C	S-68	.09	.05	.08	.22	—	—	—	—	—	—	—	—
		5	8.6	0.2	C	F-68	.19	.22	.53	.94	—	—	—	—	—	.03	—	—
	AGr	3	12.5	0.8	A	S-67	.04	.01	.06	.11	.01	—	—	—	.03	—	—	—
		5	9.9	0.4	C	F-68	.33	.34	.94	1.61	—	—	—	—	—	.08	—	—

TABLE 4.—*Organochlorine insecticide residues in fish, 1967-1968*—Continued

Location & Sta. No.	Species	No. Fish	Average Length (Inches)	Average Wt. (Lb)	Lab.	Date	DDE	TDE	DDT	DDT and met.	Dieldrin	Aldrin	Endrin	Lindane	Heptachlor	Heptachlor Epoxide	Chlordane	Toxaphene
							Collection Data											
							Organochlorine Insecticides (ppm)[1]											
ALASKAN STREAMS—(Continued)																		
# 49 (Continued)	NPi	4	12.9	0.6	C	S-68	.10	.07	.04	.21	—	—	—	—	—	—	—	—
	CSa	5	7.5	0.3	A	F-67	.02	—	.01	.03	—	—	—	—	—	—	—	—
Kenai R.	LNSu	5	15.9	1.4	A	S-67	.03	—	.01	.05	—	.01	—	—	—	—	—	—
Soldatna,		5	14.4	1.4	A	F-67	—	—	—	—	—	—	—	—	—	—	—	—
Alaska		5	17.2	1.5	C	S-68	—	—	.01	.01	—	—	—	—	—	—	—	—
# 50		5	16.0	1.7	C	F-68	—	—	—	—	—	—	—	—	—	—	—	—
	LWh	4	12.8	0.5	C	S-68	—	—	—	—	—	—	—	—	—	—	—	—
	RWh	5	11.7	0.5	C	F-68	—	.01	.03	.04	—	—	—	—	—	—	—	—
	RBT	3	16.4	1.6	A	S-67	.01	—	.01	.02	—	.01	—	—	—	—	—	—
		5	12.9	1.0	A	F-67	—	—	—	—	—	—	—	—	—	—	—	—
	LkT	3	19.6	3.4	A	S-67	.03	—	.11	.14	—	.01	—	—	—	—	—	—
		4	15.8	1.0	C	S-68	.05	.03	.02	.10	—	—	—	—	—	—	—	—
		5	13.8	1.0	C	F-68	.05	.03	.07	.15	—	—	—	—	—	—	—	—
	SSa	5	9.4	0.4	A	F-67	—	—	—	—	—	—	—	—	—	—	—	—

[1] Milligrams per kilograms wet weight—whole fish.

PESTICIDES IN AIR

A System for Monitoring Atmospheric Concentrations of Field-Applied Pesticides [1]

G. H. Willis[2], J. F. Parr[2], R. I. Papendick[3], and S. Smith[2]

ABSTRACT

A system comprised of a stainless steel boom with regularly spaced ports, stainless steel regulating valve, vapor trap, pressure-vacuum pump, and flow-meter, was designed to monitor atmospheric concentrations of field-applied pesticides and other chemicals. The system is easily installed and can be readily modified to meet special conditions and experimental requirements.

A field study revealed that volatilization could be a significant factor contributing to the net loss of endrin when applied to sugar cane. The mean atmospheric concentration of endrin reached a maximum of 540 ng/m³ during the 3-day period after application and decreased asymptotically to 30 ng/m³ 77 days later.

Introduction

The ultimate fate of applied pesticides in the environment has been the subject of considerable research effort in recent years. Various mechanisms of adsorption, desorption, and reaction of different pesticides with soil organic and inorganic components have been reported, as well as the rate and extent of degradation, losses through runoff and deep percolation, and absorption by roots and leaves of plants. Nevertheless, most attempts to apply a balance-sheet approach to the problem of pesticide persistence in the environment have been unsuccessful since relatively large amounts of many pesticides remained unaccounted for even in carefully controlled experiments. Volatilization losses of field-applied pesticides to the atmosphere may be a partial explanation for these discrepancies.

Laboratory and field systems designed for monitoring atmospheric concentration and volatilization* of a number of pesticides and agricultural chemicals have been reported. In a laboratory study, Harris and Lichtenstein (*4*) aerated chambers of insecticide-treated soil with moisturized air at a standard flow rate, the air stream removing any volatilized insecticide, which was then trapped in a suitable solvent.

In a laboratory study to determine the rate of insecticide volatilization from plants, Starr and Johnsen (*8*) described an all-glass vapor-collection system. They used a direct-measurement method whereby the insecticide could be quantitatively collected and recovered from solvent traps. For a field study, Gray (*2*) used a small plastic chamber placed over herbicide-treated soil, with air being drawn through the chamber, at a standard flow rate, into cold traps which retained the volatilized herbicide.

Bramesberger and Adams (*1*) and Hinden *et al.* (*5*) measured atmospheric concentrations of certain pesticides in the field by pulling air into solvent traps through specially designed impingers.

Some investigations of volatilization and atmospheric content of agricultural chemicals other than pesticides have been reported. Malo (*6*) and Malo and Purvis (*7*) measured the ammonia content of air using pH-adjusted filter-paper discs and a system that drew air, at a standard flow rate, through an acid trap. Volk (*9*)

[1] Contribution from the Southern Branch, Soil and Water Conservation Research Division, Agricultural Research Service, U.S. Department of Agriculture, cooperating with the Louisiana State University Agricultural Experiment Station.

[2] USDA, ARS, SWC, Baton Rouge, La. 70803.

[3] USDA, ARS, SWC, Pullman, Wash. 99163.

* The expression "measurement of volatilization" is often incorrectly applied, especially in field studies. It implies that the rate of loss of a compound or component per unit of surface area has been measured, when in fact few researchers actually evaluate the parameters necessary to determine the volatilization rate.

studied the volatilization of ammonia from urea applied to turf and bare soil by placing an acid-treated glass wool pad in an inverted glass vessel directly on the turf or soil. This method has been criticized, because the proximity of the glass wool to the ammonia source may have created a "sink" which promoted a higher volatilization rate than would have occurred naturally. Hansen *et al.* (*3*) investigated ammonia volatilization losses during and after application of anhydrous ammonia to soil by drawing air through acid traps at a standard flow rate.

In a previous unreported study on the fate and persistence of granular endrin applied to sugar cane, the authors noted that a large portion of the insecticide was unaccounted for, i.e., not present in the sugar cane, soil, or runoff from the plots. Because loss of endrin through volatilization was suspected in this study, it was necessary to design a system for determining the atmospheric concentration of endrin under field conditions. The system could be used in future studies to determine the magnitude of volatilization losses in the field.

This paper describes a system suitable for monitoring the atmospheric concentration of endrin in the field. The utility of the methodology and apparatus for monitoring the atmospheric concentration of other pesticides, as well as volatile fertilizer components, is also considered.

Materials and Methods

Preliminary considerations indicated that the system should not contain materials, except for the solvent trap, which would selectively adsorb or absorb volatile pesticide components. It was also decided that air should be sampled at relatively low flow rates to reduce the possibility of creating a "sink," which might lead to erroneous conclusions concerning the rate and extent of volatilization.

INSECTICIDE

The endrin used in the field study was from a commercial source formulated on granules at 2% active material. A 99% pure analytical standard of endrin furnished by Shell Chemical Company was used in the laboratory study and for gas chromatographic analysis.

REAGENTS

Technical grade ethylene glycol, washed with *n*-hexane to remove impurities that might interfere with gas chromatographic analysis of endrin, was used as the vapor-trapping solvent.

Hexane for extraction procedures was of high purity and had been redistilled over sodium.

VAPOR-COLLECTION APPARATUS

The apparatus developed for continuous collection of volatilized endrin is shown in Fig. 1 and 2. Air was drawn through the portholes of the stainless steel boom at a rate of 1 liter/minute by a vacuum pump rated for continuous operation. The air passed through the boom into an ethylene glycol trap which removed pesticide vapors from the air. The air was exhausted from the trap through the vacuum pump and back into the atmosphere.

FIGURE 1.—*Schematic diagram showing arrangement of boom, spacing and positions of portholes in boom, mast, and other structural features of a system for monitoring volatilization of field-applied pesticides*

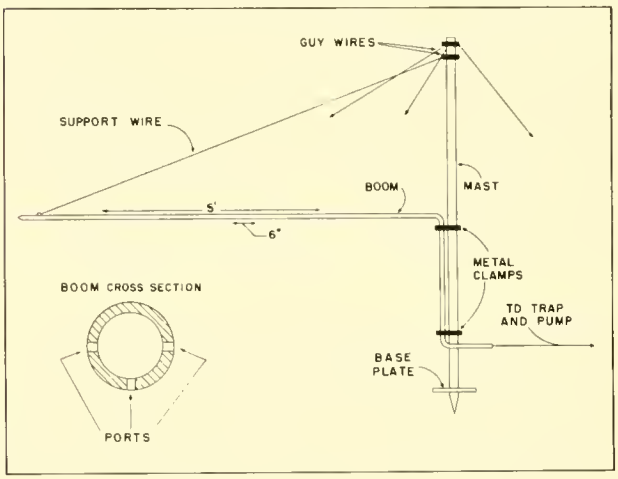
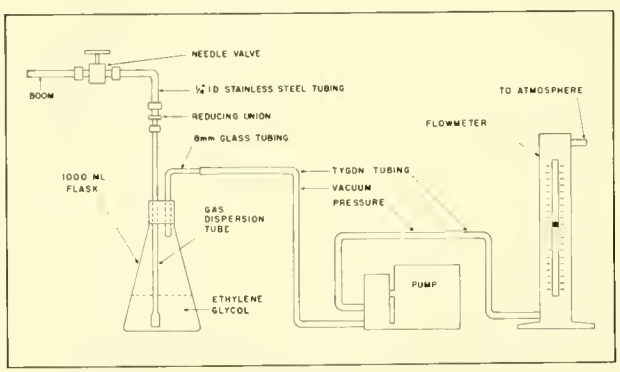


FIGURE 2.—*Schematic diagram of the vapor-trapping assembly of a system for monitoring volatilization of field-applied pesticides*



Boom. The boom was made from stainless steel tubing (¼-inch I.D.; ⅜-inch O.D.). Portholes, 1/16-inch in diameter, were drilled in the tubing at 6-inch intervals along a 5-foot span near the end of the boom. At each 6-inch interval, 3 holes were drilled, 1 in the bottom and 1 on each side of the tube, providing a total of 33 portholes. To prevent water from entering the system during rains, holes were not drilled in the top of the boom. The boom was clamped to a mast for support.

Mast and Supports. The mast was made from 1.5-inch metal pipe fitted with a base plate for stability. Guy wires fitted with turnbuckles were also used to ensure stability. A support wire from the mast to the boom prevented the booms from sagging. The mast could be used to support additional booms at different heights for sampling pesticide concentrations at different levels above the ground surface, depending upon sampling requirements.

Vapor Trap. The vapor trap was a 1-liter Erlenmeyer flask containing 750 ml ethylene glycol and fitted with a No. 9 neoprene stopper. Air entered the trap through a gas dispersion tube of medium porosity to ensure efficient absorption of volatile components.

Valve and Tubing Connector. A Whitey stainless-steel regulating-type valve (6RS-316) was attached to the boom between the sampling ports and the solvent trap to accurately regulate the rate of air flow through the system. The ⅜-inch O.D. boom was connected to the 7-mm O.D. gas dispersion tube with a Swagelok stainless steel reducing union (600-6-5-316).

Vacuum Pump. A Neptune Dyna-Vac pressure-vacuum pump (Model 3) rated for continuous operation was used to pull air through the system. The pump has a capacity of 7.1 liters/minute and a maximum vacuum of 14 inches of mercury. Tygon tubing was used to connect the exhaust port of the ethylene glycol trap to the vacuum side of the pump. By connecting a rotometer-type flow-meter to the pressure side of the pump, flow through the system was accurately measured. The use of a flowmeter and regulating valve in conjunction with the pressure-vacuum type pump permitted accurate measurement and control of air flow over a wide range of flow rates. Throughout the study, the pump was housed in a small "A"-frame shelter for protection from the weather.

EXTRACTION AND ANALYSIS

The 750 ml of ethylene glycol was transferred into a 2-liter flask with appropriate rinsing and was mixed with 375 ml of hexane on a magnetic stirrer for 1 hour. The contents of the flask were then transferred, with rinsings, to a 2-liter separatory funnel. The ethylene glycol was discarded and the hexane washed three times with H_2O. The hexane was then dried with anhydrous Na_2SO_4, and the sample was concentrated to an appropriate volume for gas chromatographic analysis by passing dry air at a low flow rate over the surface of the hexane. Previous laboratory trials with standard endrin solutions have indicated that the extraction and concentration procedure results in greater than 98% recovery of the added endrin. Endrin determinations were made with a Micro Tek MT220 gas chromatograph equipped with a ^{63}Ni electron capture detector. The detector was operated at 290 C, the inlet at 215 C, and the oven at 195 C. The carrier gas was prepurified nitrogen, and the flow rate was 135 cc/minute. The column, a glass U-tube 6 feet by ¼ inch, was packed with 80/90 mesh Chromport XXX coated with 3% SE-30.

LABORATORY STUDY

A laboratory study was designed to determine the suitability (i.e., absorption efficiency) of ethylene glycol as a trapping solvent for volatilized endrin (*8*). A cylindrical glass chamber, 2 inches (I.D.) x 48 inches, was fitted on the ends with neoprene stoppers, each masked with aluminum foil. A ¼-inch (I.D.) stainless steel tube with 16 regularly spaced portholes was inserted through one stopper and across the chamber to the opposite stopper which was provided with three ¼ inch diameter holes for admitting air to the chamber.

Six ml of H_2O and 1 ml of hexane containing 0.1 mg of endrin were placed in a small aluminum foil boat and inserted into the chamber beneath the stainless steel tube. The tube, projecting from one end of the chamber, was connected to a vapor-trapping system similar to Fig. 2, where two traps were placed in a series to measure any possible carry-over of pesticide from the first trap. Air was pulled continuously through the chamber at a rate of 1 liter/minute for 15 days, after which the chamber and all components were rinsed with hexane to remove any residual endrin. Ethylene glycol from the traps was extracted with hexane to recover any endrin which had volatilized.

FIELD STUDY

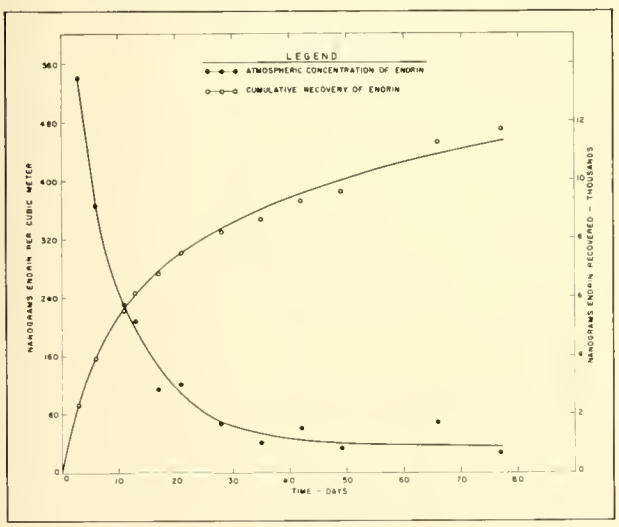
Granular endrin was applied by hand to a sugar cane plot at a rate of 2 lb/acre. Half of the endrin was applied to the cane and half to the soil surface. The sugar cane was approximately 10 feet high. The plot, 24 x 30 feet, was located within a larger field of sugar cane which provided a desirable buffer zone for maintenance of natural field conditions with respect to air movement, temperature, and humidity within the plant canopy. Immediately after endrin application on July 26, 1968, the vacuum pump was activated and allowed to run continuously for 11 weeks. Care was taken to avoid contaminating the boom and trapping system during pesticide application. Ethylene glycol was replaced in the trap at 3-day intervals during the initial phases of the study and later at weekly intervals. Flow rate of air was maintained at 1 liter/minute throughout the study.

Results and Discussion

The results from the laboratory study showed that 28.4% of the applied endrin remained within the glass volatilization chamber, probably from surface adsorption by the chamber and component parts. Analysis of the two ethylene glycol traps revealed that 62.8% of the endrin was in the first trap with none detected in the second. Thus, more than 90% of the endrin could be accounted for. It is possible that the rinsing procedure was not completely effective in desorbing endrin from the system, resulting in 8.8% unaccounted for. It is unlikely that this amount of endrin could pass through both solvent traps without leaving at least a trace in the second trap. Therefore, it was concluded that ethylene glycol would be an effective trapping solvent for volatilized endrin in the field.

Results of a field study on the change in atmospheric concentration of endrin that occurred after application to sugar cane on July 26 until October 11, 1968, is shown in Fig. 3. Cumulative recovery of endrin during this period is also presented. Each data point is a mean value and appears at the end of the time segment it represents. The mean value for the initial 3-day absorption period is plotted at 3 days, even though this value probably does not indicate the highest concentration that occurred during the initial time period. Sampling intervals would need to be shortened considerably during the initial phases to determine the peak concentration.

FIGURE 3.—*Atmospheric concentration of endrin 4 feet above ground level in a sugar cane field and cumulative recovery from July 26 to October 11, 1968.*



The mean atmospheric concentration at the point of measurement (4 feet above soil surface) reached a maximum of 540 ng/m^3 during the 3-day period after application, and then decreased rapidly to a concentration of 123 ng/m^3 at 21 days. Thereafter, the decrease in concentration of endrin appeared to follow an asymptotic relationship, possibly indicating a dependence of volatilization upon concentration. In this regard, definite conclusions cannot be drawn from these data, because such variables as temperature, relative humidity, and wind movement, which would undoubtedly influence the rate of volatilization, were not measured during this study.

The cumulative recovery curve for endrin (Fig. 3) approached 12,000 ng and reflects the decrease in rate of volatilization with time. Based on the data presented, no definite statements can be made on how much of the applied endrin was lost through volatilization. The rate of air turnover above the plot is unknown and would be very difficult to measure, especially when one considers the convective vertical air movements that occur in conjunction with horizontal air movement through the plot. Estimates based on a mean lateral air movement of 0.1 mph through the plot voume, 24 feet x 30 feet x 10 feet (w x l x h), indicate a volatilization loss of 5% of the total endrin applied However, this estimate is speculative and should not be considered a "real value."

The results of this study indicate that volatilization may be a significant process whereby certain chlorinated hydrocarbon pesticides, including chemicals having very low vapor pressures, are lost from their locus of application. Of particular significance is the fact that the process occurs over extended periods of time Future studies of pesticide volatilization, using the methodolgy and apparatus described herein, should be accompanied by measurement of several climatic variables including wind, temperature, and relative humidity profiles. Such measurements made in conjunction with pesticide concentration gradients should enable use of an aerodynamic approach to obtain some quantitative estimates of pesticide volatilization.

The air sampling system should be useful in monitoring the atmospheric concentration of any chemical for which a suitable trapping solvent is available. The system is easily installed, and its simplicity allows for various modifications. For example, additional booms and traps could be connected to a single pump, through a manifold arrangement, to obtain an atmospheric profile characterization, or a rotating boom could be added to obtain an integrated sample from a larger area.

See Appendix for chemical name of endrin.

Mention of trade names or commercial materials is for the convenience of the reader and does not constitute any preferential endorsement by the U. S. Department of Agriculture over similar products available.

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PESTICIDES IN SOIL

The Persistence and Movement of Picloram in Texas and Puerto Rican Soils [1]

R. W. Bovey[2], C. C. Dowler[3], and M. G. Merkle[4]

ABSTRACT

The persistence and movement of the herbicide picloram was studied in two Texas, and three Puerto Rican soils. Picloram applied at 1 lb/acre moved downward and disappeared in 12 to 18 months from the upper soil profile, especially under high rainfall in clay and sandy soils. Picloram applied at higher rates (3 and 9 lb/acre) was usually detectable in the soil pofile after 12 to 18 months. Loss of picloram will occur also through photodecomposition if it is not leached into the soil following treatment. Bioassay and gas chromatographic methods of picloram detection produced comparable results. Other possible reasons for dissipation and movement of picloram in soils are discussed.

Introduction

Effective control of many tropical and subtropical woody species can be accomplished with picloram (*3,4,6,20*). Picloram is persistent in soils (*8,10,12,14,23*) and may injure crops seeded following treatment (*2,11,16*). Higher rates of picloram are usually required for brush control on grazing lands than are required for control of perennial weeds in noncrop lands (*1,4,20*). This is especially true for effective brush control in tropical areas (*20,21,22*). Data from studies in Texas (*15*) and Puerto Rico (*6*) indicated that less than 0.05 ppm of picloram was found 1 year after treatment at 8 and 9 lb/acre, respectively. However, the study in Puerto Rico was conducted on Janica and Nipe clay and Guineos clay loam soils which were sampled to a depth of 48 inches; whereas, the study in Texas was conducted on sandy loam soils which were sampled to only 24 inches. Applications of picloram were made to plots containing dense vegetation at both locations.

Several environmental factors have been reported as responsible for the dissipation of picloram from soils (*7,8,14,16,19,23*). Leaching is one of the more important factors contributing to picloram loss from soils in areas of high rainfall (*2,6,15,20*). Degradation of picloram by sunlight may be an important means of loss in dry areas (*9,15*). Chemical (*14*) and microbial (*7*) decomposition of picloram is relatively slow.

Materials and Methods

The loss of picloram was studied on two soils in Texas and three soils in Puerto Rico under different rainfall conditions. Vegetation on the experimental areas was destroyed by cultivation. Soil types studied were Nipe and Fraternidad clay and Catano sand near Mayaguez, Puerto Rico and Erving clay loam and Lakeland sand near College Station, Tex. The Nipe clay is derived from serpentine rock, high in iron content, and low in fertility. This lateritic soil contains more than 70% clay of colloidal size but exhibits the physical properties of a loam. Water penetrates rapidly and is poorly retained. The Fraternidad clay is a brown calcareous heavy clay showing lime accumulation at lower depths. Rock fragments occur to a depth of about 4 feet. The subsoil contains some salt and drains slowly after rainfall or irrigation. The Catano sand occurs close to the ocean, uually at such a low elevation that the water table is within 18 inches of the surface. It is mapped as a poorly drained phase. The soil has a grayish-brown, friable, single-grained, sandy surface and a lighter textured, friable calcareous subsoil. Coconut palms often grow on these areas (*18*).

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[1] Cooperative investigations of the Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture and Texas A & M University

[2] Crops Research Div., ARS, USDA, College Station, Tex. 77843.

[3] Crops Research Div., ARS, USDA, Coastal Plain Experiment Station, Tifton, Ga. 31794.

[4] Soil and Crop Sciences Dep., Texas A & M University, College Station, Tex. 77843.

The Lakeland sand soil near College Station had a fine-sand surface (8 to 15 inches). The subsurface sand graded into yellowish-brown to reddish-brown acid sandy clay loam at 36 to 72 inches or more. The Erving clay loam had a dark gray clay loam surface 7 to 12 inches thick over a dark gray blocky subsurface clay. The acid soil forms a crusty, tight surface when dry.

The potassium salt of picloram was applied to bare soil in each plot at rates of 1, 3, and 9 lb/acre. The Puerto Rican plots were 6 by 15 feet and the Texas plots, 10 by 30 feet; all plots were replicated three times in a randomized block. A buffer space was left between all plots, and a small ditch was dug around each to prevent cross-contamination after heavy rainfall. Plots were treated in mid-June 1966 at all locations.

Picloram content (ppm) was bioassayed in the Puerto Rican soils using cucumber (*Cucumis sativus* L., var. Puerto Rico 39) as the indicator plant. Eight cucumber seeds were placed in 1-quart cups containing treated soil. Plants were thinned to two plants 7 days after planting and grown for 28 days. Abnormal growth was recorded on a 10-point scale where 0 equals "no effect" and 10 equals "dead plants." A standard injury curve was established for cucumber plants exposed to known amounts of picloram in the soil (*5*). These data were used to determine ppm of picloram in soils treated in the field.

Picloram content in clay soils treated at the 3 lb/acre rate was also determined by gas chromatography (*15*). All samples were analyzed with a Barber-Coleman Model 5360 pesticide analyzer equipped with a radium-226 electron capture detector. The column, carrier gas flow rate, and temperature suitable for picloram detection have been given (*15*). Picloram was extracted from the sand with 50 ml of 0.1N NaOH and from the clay and sandy loam with a 1:1 mixture of 0.1N NaOH and methyl alcohol. The addition of alcohol is essential for rapid filtration of the soil-water suspension. However, picloram recovery from the mixture is only 80% as compared to 90% when water is used alone. After filtering, the mixture was heated until the alcohol evaporated. The aqueous portion was acidified with HCl, and the picloram extracted with three 30-ml portions of ethyl ether. The ether portions were combined in a 150-ml beaker and evaporated on a steam bath. Four milliliters of reagent containing 125 g of boron trifluoride per liter of methanol was added. The samples were again heated until only a trace of methanol remained. Care was taken to avoid complete evaporation since some of the methylated picloram may also be vaporized. After esterification, the beaker was washed with 10 ml of water and 10 ml of redistilled hexane. These washings were mixed thoroughly in a 50-ml separatory funnel and the aqueous portion discarded. One μl of the hexane portion was injected into the chromatograph. The methylated picloram content was determined by comparing sample peak heights with those obtained from known quantities of herbicide. All samples of Texas soils were analyzed for picloram content by gas chromatography; samples collected on the last date of sampling were also bioassayed with beans (*Phaseolus vulgaris L.*, var. Black Valentine). Beans were grown for 3 to 4 weeks in the treated soil.

Soils were sampled at 1-foot intervals to a depth of 4 feet intermittently for a period of 1 or 1 ½ years after treatment. A 3-inch bucket auger was used to collect at least 1 quart of soil for bioassay and analysis by gas chromatography. Duplicate soil samples were taken from each plot in Puerto Rico and a single sample from the Texas plots. The soil was sealed in airtight plastic bags and frozen when immediate analysis was not possible. Untreated soils were sampled first, followed by the soils treated with 1, 3, and 9 lb/acre of picloram.

Results

Table 1 shows rainfall accumulated at each date of soil sampling for the Texas and Puerto Rican locations. Lowest accumulated rainfall 1 year after treatment was at College Station, Tex., with 28 inches, and highest was at Tres Hermanos, P. R., with 77 inches.

TEXAS STUDIES

Picloram was applied to dry soil which received small amounts of rainfall during the first 6 weeks after treatment (Table 2). Loss of picloram was rapid during this period. This was presumably due to photodecomposition (*14*) since the picloram was directly exposed to sunlight on bare soil. After 3 months, the picloram applied at 1 lb/acre disappeared from the sandy soil. Picloram concentration in the sand and clay soils treated at all rates was considerably reduced; these soils received 9 and 12 inches of rainfall, respectively.

Six months after treatment at rates of 1, 3, and 9 lb/acre, picloram applied to clay soils was present in the upper 6, 12, and 36 inches, respectively. Picloram was detected at nearly all levels down to 4 feet in sand, except where the 1 lb/acre rate was used. However, 18 months after treatment a small amount of picloram was found in only the top 6 inches of clay soil treated at 3 lb/acre. No picloram was found in the sand at any depth.

Plots treated with 9 lb/acre contained detectable picloram in the top 3 feet of clay at the 3- and 6-month samplings but only in the top 2 feet of soil at 18 months. Most of the picloram in the sandy soil was found 3 to 4 feet deep at the 6- and 18-month sampling dates. Bioassay with beans, 18 months after treatment, detected

no picloram in plots receiving 1 lb/acre on clay and sandy soils, and none in the sandy soil at 3 lb/acre. However, beans grown in the top foot of the clay soil treated with picloram at 3 lb/acre were injured. Greatest injury to beans occurred to plants grown in the top 24 inches of clay soil receiving 9 lb/acre of picloram. Some injury was also recorded at depths of 24 to 36 and 36 to 48 inches. The greatest injury in the sand was in samples taken from the 4-foot level, indicating the greater tendency of picloram to leach in sandy soils receiving abundant rainfall. The lower limit of sensitivity with gas chromatography was 0.01 ppm, whereas beans show visual symptoms at 0.001 ppm (*13*). Consequently, beans may show injury in soils that show no detectable picloram by gas chromatography.

PUERTO RICAN STUDIES

Three months after treatment, picloram was distributed throughout the soil profile in the clay soils at all rates of treatment (Table 3). Picloram residue concentration increased as the rate was increased. Some picloram persisted in the clay soils for a year, although the amount of picloram at 3 lb/acre in Nipe clay was only 1 ppb. Disappearance of picloram was related to soil type and rainfall. Picloram was most persistent in the Fraternidad clay where rainfall was lowest (Table 1). Disappearance of picloram from the Catano sand was rapid; no herbicide was detected a year after treatment in the upper 3 feet of soil. Abundant rainfall apparently leached the picloram from the soil (Table 1).

Bioassay and gas chromatographic techniques are compared in Fig. 1 for Nipe and Fraternidad clay soils receiving 3 lb/acre of picloram. Both methods show similar trends in picloram concentrations at most depths of sampling, but for undetermined reasons the bioassay consistently gave higher readings for the Fraternidad clay than did gas chromatography. Bioassay procedures with cucumbers are accurate and sensitive to minute quantities of picloram (5 ppb); however, growth may be altered by pathogens and other soil toxins which may alter sensitivity of the method.

Discussion

The persistence of picloram in the soil is not unique. Dowler *et al.* (*6*) found that the herbicides fenac and prometone were more persistent than picloram in a Jacana clay at Guanica, P. R., 1 and 2 years after treatment. Both compounds were leached to at least 4 feet

TABLE 1.—*Total rainfall received in Texas and Puerto Rico from the time of picloram treatment until the soils were sampled*

Time of Sampling—Months after Treatment	Total Rainfall in Inches				
	Texas		Puerto Rico		
	Bryan	College Sta.	Las Mesas	Tres Hermanos	Lajas
	Erving clay loam	Lakeland sand	Nipe clay	Catano sand	Fraternidad clay
1½	<0.1	<0.4	—	—	—
3	12	9	18	31	5
6	14	13	49	48	21
12	29	28	69	77	32
18	40	46	—	—	—

TABLE 2.—*Picloram concentration in Erving clay loam and Lakeland sand near Bryan and College Station, Tex., respectively*

Picloram (lb acre)	Depth sampled (inches)	Gas chromatographic analysis—Residues in PPM								Bioassay [1]	
		Immediately [2]		3 months [2]		6 months [2]		18 months [2]		18 months [2]	
		clay	sand	clay	sand	clay	sand	clay	sand	clay	sand
1	0-6	0.76	0.48	0.15	0	0.02	0	0	0	0	0
	6-12			0	0	0	0	0	0	0	0
	12-24			0	0	0	0	0	0	0	0
	24-36			0	0	0	0	0	0	0	0
	36-48			0	0	0	0	0	0	0	0
3	0-6	2.11	1.75	0.67	0	0.15	0.02	0.03	0	6	0
	6-12			0	0.04	0.14	0	0	0	3	0
	12-24			0	0.07	0	0.05	0	0	1	0
	24-36			0	0.06	0	0.08	0	0	0	0
	36-48			0	0	0	1.01	0	0	1	0
9	0-6	6.92	6.99	0.33	0.07	0.22	0.03	0.61	0	10	2
	6-12			1.13	0.12	0.21	0.01	0.17	0.01	10	2
	12-24			0.05	0.23	0.08	0.05	0.04	0.01	9	2
	24-36			0.03	0	0.01	0.06	0	0	5	7
	36-48			0	0	0	0.06	0	0.11	4	10

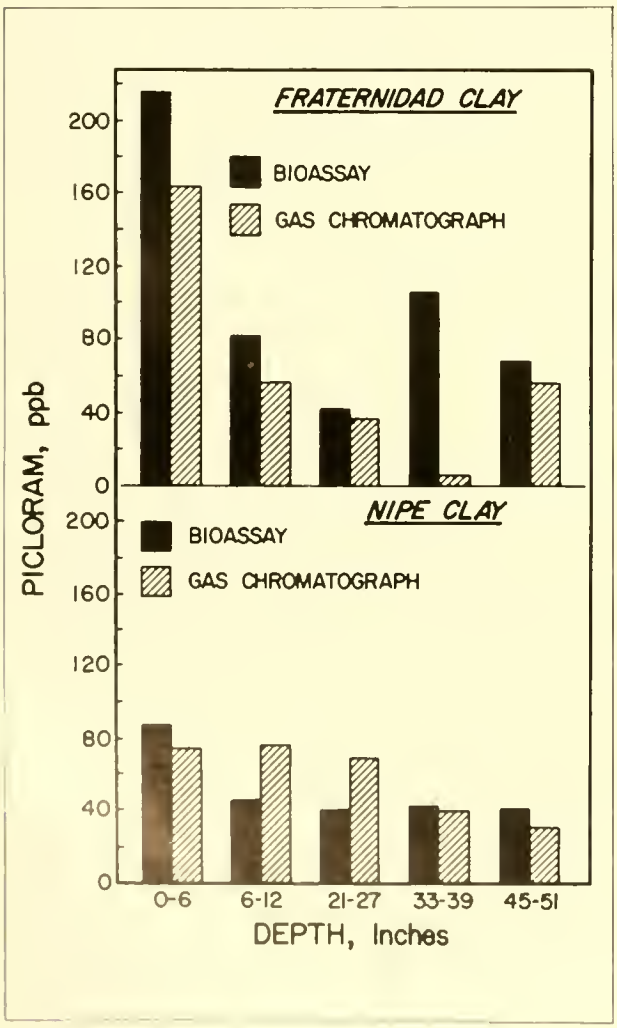
[1] Bioassay evaluation is an arbitrary scale in the range of 0 to 10 in which 10 equals "complete kill" and 0 equals "no effect" on bean growth.
[2] Time of sampling after treatment.

TABLE 3.—*Picloram concentration from various depths of three soil types after treatment with 1, 3, and 9 lb/acre near Mayaguez, P. R.*

Soil Type	Depth sampled (Inches)	Picloram Residues in PPB								
		3 months [1]			6 months [1]			12 months [1]		
		Treatment rate (lb acre)			Treatment rate (lb acre)			Treatment rate (lb/acre)		
		1	3	9	1	3	9	1	3	9
Nipe clay	0-6	2	88	372	0	1	883	0	0	1
	6-12	9	46	413	0	5	612	0	0	9
	21-27	3	41	243	3	9	215	0	0	2
	33-39	5	43	343	3	10	62	0	0	6
	45-51	11	42	190	8	16	109	0	1	8
Fraternidad clay	0-6	32	215	883	2	520	846	0	178	525
	6-12	7	82	692	3	5	187	0	4	222
	21-27	24	42	377	8	218	729	0	1	48
	33-39	180	106	98	15	224	575	0	1	49
	45-51	55	69	225	23	218	729	1	2	198
Catano sand	0-6	0	0	0	0	0	0	0	0	0
	6-12	0	0	11	0	0	0	0	0	0
	21-27	1	1	2	0	0	0	0	0	0
	33-39	0	3	3	0	0	0	0	0	0

[1] Time of sampling after treatment.

FIGURE 1.—*Comparison of cucumber bioassay and gas chromatography in determining picloram content in Nipe and Fraternidad clay in Puerto Rico 3 months after application of picloram at 3 lb/acre*



and were distributed throughout the upper soil profile. Phillips (*17*) reported persistence of 2, 3, 6-TBA in soil in Kansas at depths up to 8 feet for several years.

The presence of vegetation on the treated areas would probably reduce picloram residues in soils because of the interception of sprays by vegetation. Data indicate that the amount of picloram reaching the soil may only be 10% of that applied to dense stands of live oak (*15*).

These and other studies indicate that leaching by rainfall is one of the most important means of picloram disappearance from the soil (*2, 6, 15*). Loss by leaching is most rapid from sandy soils and slowest from heavy clay soils for obvious reasons. Photodecomposition may also be an important means of loss if picloram is exposed to intense sunlight (Table 2) (*9, 14*). Further study is needed to determine loss of picloram by chemical or biological degradation in the soil.

Lateral movement of picloram was indicated, because small amounts of picloram were sometimes found in untreated areas adjacent to plots receiving high rates of picloram (9 lb/acre). However, this contamination could be due to surface movement of picloram by runoff water after heavy rainfall (*19*). Contamination could also result from spray drift, wind movement, and soil sampling techniques. Further studies are needed to determine the extent and conditions responsible for lateral movement of herbicides in and on soil.

These studies indicate that we cannot account for all the herbicide applied to soils. Further investigations are needed to elucidate the fate of this and other compounds in the environment.

See Appendix for chemical names of compounds mentioned in this paper.

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Absorption of Organochlorine Insecticide Residues from Agricultural Soils by Crops Used for Animal Feed [1]

C. R. Harris and W. W. Sans[2]

ABSTRACT

Several crops used for animal feed were planted in sandy loam, clay, and muck soils containing residues of five to six organochlorine insecticides or their metabolites. DDT and its metabolites were present in the soil, but the crops contained little or no residue of DDT, DDE, or DDD. Aldrin, dieldrin, and endrin were also present in the soils, but only dieldrin and endrin were detected in the crops, dieldrin being detected more frequently and in greater quantities. Sugar beets absorbed the most dieldrin, followed by carrots, potatoes, and sugar beet tops. Corn, oats, and alfalfa absorbed equal amounts of dieldrin but in lesser quantities than the other crops. The influence of soil type on absorption of dieldrin by crops was apparent in that the higher the organic content of the soil, the lower the amount of residue absorbed by the plant.

Introduction

A previous study (4) established the presence of residues of organochlorine insecticides, particularly DDT, its metabolites, and aldrin, dieldrin, and endrin, in agricultural soils in southwestern Ontario. In order to establish the significance of these residues, additional studies were conducted. It was found that levels of the cyclodiene insecticides were sufficiently high, particularly in tobacco and vegetable soils, to cause constant selection pressure on soil insect populations with the resultant development of a high level of cyclodiene insecticide resistance in several species of soil insects (*1, 3*). A study (*2*) investigating the extent to which residues of the organochlorine insecticides are absorbed from soil by crops has shown that, although root crops absorb residues of dieldrin and endrin from soil, the residues usually do not exceed the acceptable levels established for human consumption. Since other crops generally absorb less insecticide residues than root crops, it seems safe to assume that residues of the cyclodiene insecticides in Ontario soils are not sufficiently high to result in residues in crops in excess of the tolerances. However, residue levels of the organochlorine insecticides which can be tolerated in crops for human consumption cannot be tolerated in crops used for animal consumption, since even minute quantities of some organochlorine insecticides in animal feeds may result in significant residue levels in milk and other animal products. The object of this study was to determine if residues of the organochlorine insecticides in soils in southwestern Ontario are sufficiently high to result in unacceptable residue levels in crops used for animal feed.

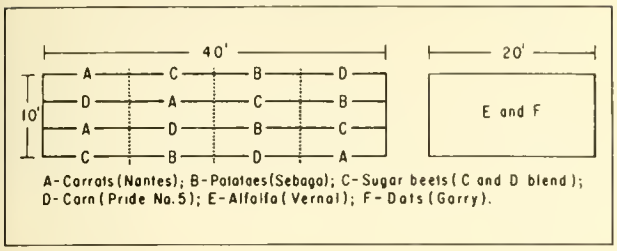
Procedures

The procedures used have been published elsewhere (*2, 6*) and will be summarized only briefly here. The experimental plots were set up in 1967 at four locations in southwestern Ontario. Plot A, located on a Beverly fine sandy loam soil (2.4% organic matter), was utilized as a control since insecticides had never been applied directly to the soil in this area, and repeated tests had indicated that only trace amounts of the organochlorine insecticides were present. The three remaining plots were located on farms which previous studies had indicated contained excessively high residues of the organochlorine insecticides for that particular soil type. Plot B was situated on a Fox fine sandy loam soil (1.4% organic matter); Plot C on a clay (3.6% organic matter); and Plot D on a muck (66.5% organic matter). The plot layout and varieties of crops grown are illustrated in Fig. 1. Soil samples were taken throughout the plot area before planting to determine the initial

[1] Contribution No. 402, Research Institute, Canada Department of Agriculture, London, Ontario.

[2] Research Institute, Canada Department of Agriculture, London 72, Ontario.

FIGURE 1.—*Plot layout and varieties of crops used in experiment*



residue levels in the soil. One hundred 6- x 1-inch cores were taken at random in each plot and pooled to form a uniform sample for analysis. The crops were seeded between May 19-31 and kept free of weeds throughout the summer. Harvest dates which varied with the crop and location were as follows: oats, August 8-10; corn, August 17-30; carrots, September 7-29; potatoes, September 29-October 6; sugar beets, October 25-31. Lack of rainfall during much of the growing season resulted in poor germination and growth making it impossible in some instances to obtain sufficient crop samples for analysis. The first adequate sample of alfalfa was not obtained until May of the following year. On completion of the final harvest of the row crops, soil samples were again taken to determine the postharvest residue levels in the soil. With oats and corn the entire aerial portion of the plant was analyzed; with potatoes and carrots the tubers only were analyzed; and with sugar beets the roots and tops were analyzed separately. The samples were extracted immediately after harvesting. The procedures for extraction, cleanup, liquid-solid fractionation, and analysis by gas-liquid chromatography have been described elsewhere (*6*).

Results and Discussion

Results of the study are summarized in Table 1. Analysis of the pre-planting soil samples indicated that all four plots contained residues of the organochlorine insecticides. Plot A, the control plot, which had never received a direct treatment of any insecticide, contained 0.02 ppm of DDT and traces (less than 0.01 ppm) of DDE and dieldrin. Plot B, the Fox fine sandy loam, contained 0.22 ppm DDT and its metabolites and 0.76 ppm of the cyclodiene insecticides, with the predominant material being dieldrin. Plot C, the clay, contained 0.54 ppm DDT and its metabolites, and 1.39 ppm of aldrin/dieldrin. Plot D, the muck, contained residues of DDT and its metabolites totaling 16.81 ppm, and 10.44 ppm of the cyclodiene insecticides. Analysis of the postharvest soil samples did not indicate any significant decrease in the total residue levels in the soil, but in plots C and D a decrease in the aldrin content was accompanied by a slight increase in the concentration of dieldrin in the soil.

It is generally accepted that residues of DDT in the soil are not absorbed by crops to any significant extent, and in this experiment the root crops grown contained little or no residue of DDT or its metabolites. Residues of DDT were usually present in the aerial portions of the plants, but this contamination was probably a result of drift from treatment to adjacent fields.

Although residues of aldrin were present in the soil in Plots B, C, and D, no residues were detected in any of the crops. Somewhat similar results were obtained in a previous study (*2*). This would indicate either that aldrin is not absorbed from soil by plants, or that it may be converted to dieldrin prior to or immediately after being absorbed. There is recent evidence (*5*) that plants contain an enzyme system capable of oxidizing aldrin to dieldrin.

In Plots B and D, where residues of endrin were present in the soil, small amounts were detected in the majority of the crops.

Dieldrin was present at fairly high levels in the soils in Plots B, C, and D and was also present in the majority of the crops (Table 1). The importance of soil type in relation to the uptake of dieldrin from soil by plants has been discussed in a previous paper (*2*). However, it is again apparent in this study that soil type plays a major role in moderating the uptake of insecticides from soils by plants. The two mineral soils in Plots B and C contained approximately 1/5 and 1/2, respectively, the amount of dieldrin present in Plot D. Yet the residues of dieldrin in the crops in the former were considerably higher than those grown in the muck soil in Plot D.

Numerous authors have shown that the absorption of residues of cyclodiene insecticides from soil varies with the crop. It is therefore of interest to compare the results obtained in this study where different crops were grown in the same plots under identical growing conditions. The best results were obtained in Plot C, where good germination and development of all crops occurred. As can be seen in Fig. 2, the crops varied considerably in their ability to absorb dieldrin from the soil. Alfalfa, oats, and corn absorbed the least amount of dieldrin, while sugar beet tops and potatoes were intermediate. The highest dieldrin levels were found in carrots and sugar beets. The data obtained on sugar beets compare closely to that obtained by Walker *et al.* (*7*) in studies conducted in Washington. Since beet pulp is used extensively as an animal feed supplement, this crop should not be grown on soils containing excessive residues of the cyclodiene insecticides. On heavy mineral soils, a concentration of 1 ppm could be considered to be excessive.

The results of this study indicate that crops used for animal feed are capable of absorbing residues of dieldrin from contaminated soil, particularly mineral soils. There is little agreement concerning the concentrations of dieldrin in crops which will result in unacceptable residue levels in milk and other animal products. It is obvious that the significance of residue levels in crops used for animal consumption will be dependent on a variety of factors, including the dieldrin concentration in the crop, the proportion of the crop included in the animal diet, and the length of time that the crop in question is fed to the animals. However, it is often assumed that levels as low as 0.02 ppm dieldrin in a crop could result in unacceptable residue levels in milk. On this basis, it is apparent that in a number of instances in these experiments, the residues of dieldrin in the soils were sufficiently high to result in significant residue levels in the crops grown for animal feed.

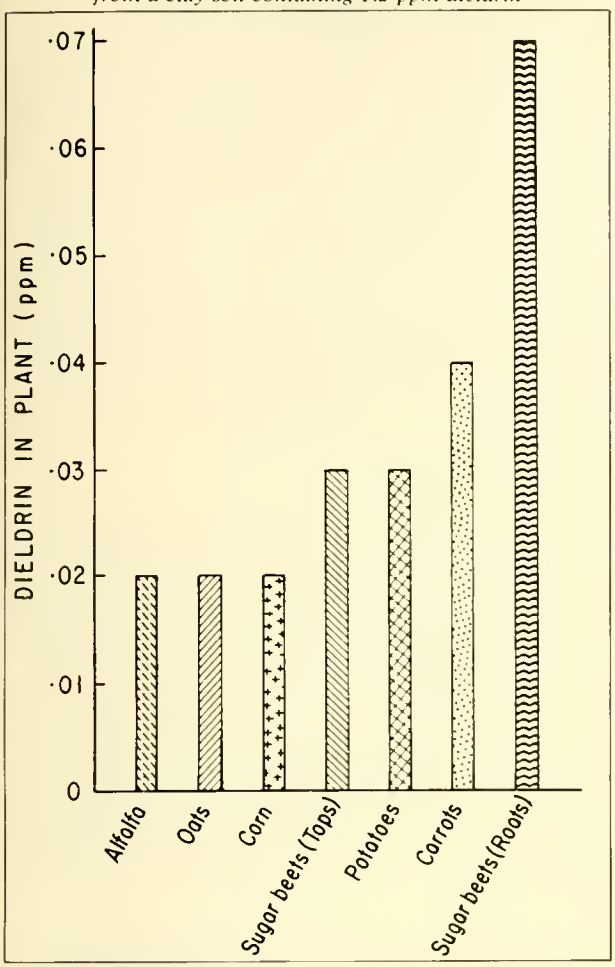
TABLE 1.—*Residues of organochlorine insecticides in soil and residues absorbed by crops used for animal feed*

[T = trace = <0.01 ppm]

Soil and Crop Samples	Residues in PPM [1]							
	DDT	DDE	DDD	Total DDT	Aldrin	Dieldrin	Endrin	Total Cyclodiene Residues
PLOT A (CONTROL)—SANDY LOAM								
Soil								
Before planting	.02	T	0	.02	0	T	0	T
After harvest	.02	T	0	.02	0	0	0	0
Crops								
Alfalfa	.02	0	0	.02	0	T	0	T
Oats	.06	T	0	.06	0	T	0	T
Corn	.02	0	0	.02	0	0	0	0
Sugar beets (tops)	.01	0	0	.01	0	.01	0	.01
Potatoes	0	0	0	0	0	0	0	0
Carrots	0	0	0	0	0	T	0	T
Sugar beets (roots)	0	0	0	0	0	0	0	0
PLOT B—SANDY LOAM								
Soil								
Before planting	.16	.06	T	.22	.06	.56	.14	.76
After harvest	.16	.07	T	.23	.06	.57	.11	.74
Crops								
Alfalfa	.02	0	0	.02	0	T	0	T
Oats	no germination							
Corn	.12	T	T	.12	0	.01	.01	.02
Sugar beets (tops)	no germination							
Potatoes	0	0	0	0	0	.03	T	.03
Carrots	0	0	0	0	0	.05	.01	.06
Sugar beets (roots)	no germination							
PLOT C—CLAY								
Soil								
Before planting	.39	.13	.02	.54	.37	1.02	0	1.39
After harvest	.43	.15	.02	.60	.14	1.19	0	1.33
Crops								
Alfalfa	.01	0	0	.01	0	.02	0	.02
Oats	.03	0	0	.03	0	.02	0	.02
Corn	.04	0	0	.04	0	.02	0	.02
Sugar beets (tops)	.03	0	.01	.04	0	.03	0	.03
Potatoes	0	0	0	0	0	.03	0	.03
Carrots	0	0	0	0	0	.04	0	.04
Sugar beets (roots)	.01	0	.02	.03	0	.07	0	.07
PLOT D—MUCK								
Soil								
Before planting	14.73	1.73	.35	16.81	2.24	2.26	5.94	10.44
After harvest	15.09	1.99	.50	17.58	1.15	2.35	5.80	9.30
Crops								
Alfalfa	no germination							
Oats	.04	0	0	.04	0	.01	.01	.02
Corn	.01	0	0	.01	0	0	0	0
Sugar beets (tops)	.02	0	T	.02	0	0	0	0
Potatoes	T	0	0	T	0	.01	.01	.02
Carrots	.01	0	0	.01	0	.01	.02	.03
Sugar beets (roots)	.01	0	0	.01	0	T	.01	.01

[1] Calculated on the oven-dry weight of soil and fresh weight of crop.

FIGURE 2.—*Dieldrin residues absorbed by various crops from a clay soil containing 1.2 ppm dieldrin*



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See Appendix for chemical names of compounds mentioned in this paper.

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Behavior and Reactions of Copper Sulfate in an Irrigation Canal [1]

J. L. Nelson[2], V. F. Bruns[3], C. C. Coutant[2], and B. L. Carlile[2]

ABSTRACT

Measurements of copper concentrations in water, in suspended sediment, and in bottom sediment of an irrigation canal after a copper sulfate treatment at 1 lb/cfs indicate that, after dissolution, much of the copper is sorbed by suspended sediment which gradually settles to the canal bottom. A large part of the copper in the deposited sediment is then slowly fed back into the canal water over a period of many hours. Buildup of copper in irrigated soils appears to be very minor.

Introduction

Copper sulfate has been used for many decades as an algicide in canals, lakes, and reservoirs (*4, 6*). It is still used extensively for that purpose even though many new organic compounds with algicidal properties have been discovered and developed.

Few studies have been made on the fate of copper after it is added to irrigation canals. The copper ion does not volatilize or break down chemically and is not degraded biologically like many of its organic counterparts. The objective of our study was to determine the chemical and physical behavior of copper sulfate when applied as an algicide in water of an irrigation canal.

Methods and Materials

A total of 411 lb of copper sulfate crystals were applied to the Roza Main Canal immediately below the check (water elevation control structure) at Mile 61.4 north of Sunnyside, Wash., in late June 1966. The flow of water in the canal was 411 cfs. This rate (1 lb/cfs) is the one most commonly used for control of algae in canals. Copper sulfate crystals up to about 2 cm in diameter were poured into a concrete-lined section (.5 mile long) of the canal during a period of 30 seconds. The crystals dissolved rapidly in the swift current. The pH of the water ranged between 7.0 and 7.3, and the alkalinity ranged from 90 to 100 ppm ($CaCO_3$ equivalent).

Sampling stations were established at four sites .5, 5.9, 11.5, and 23.2 miles downstream from the copper sulfate introduction point. Rhodamine-B dye was applied at the same time as the copper sulfate to serve as a visible tracer of the treated water. Samplings were started 5 to 15 minutes prior to arrival of the visible tracer at sampling stations. Samples of water, suspended sediment, and bottom sediment were taken before and during the treatment and daily thereafter for 1 week.

Aquatic weeds may sorb copper from the water (*2*). Although small clumps of filamentous green algae were starting to accumulate in farmers' head-ditches and were clogging screens, siphon tubes, sprinkler heads, etc., the population of such growths as well as rooted pondweeds in the main canal was too sparse to sorb significant quantities of copper from the treated water.

Copper content of water and sediment was determined by a cuproine (spectrophotometric) method (*3, 5*). Four hundred milliliters of filtered canal water was measured into a 16-ounce clear glass bottle, to which 10 ml of a 10% solution of hydroxylamine hydrochloride was added. The pH was then buffered to between

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[2] Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, Wash.

[3] Crops Research Div., ARS, USDA, Irrigated Agriculture Research and Extension Center, Prosser, Wash. 99350.

4.0 and 5.0 with 10 ml of 1M sodium acetate. A 25-ml portion of .05% cuproine in isoamyl alcohol was then added, and the mixture was shaken on a shaker for 10 minutes. After separation of phases, 10 to 15 ml of the surface solvent was drawn off with a transfer pipette and placed in a small centrifuge tube. Centrifugation at high speed for 1 to 2 minutes removed air bubbles. The solution was then transferred to a cuvette and the absorbance read at 546 mμ. Copper values were read from a standard curve which had been developed by analyzing water samples spiked with copper and by using the foregoing procedure. The lower limit of detection of copper in the canal water by this analytical method was 0.001 ppm. Deionized or glass-distilled water was used for all dilutions and rinsing of glassware.

Total copper was not determined in soil samples, but 0.1N HCl-extractable copper was used as the index of available copper. Twenty grams of soil was placed in a 60-ml vial with a polyseal cap, to which 20 ml of 0.1N HCl were added. The slurry was shaken gently for 1 hour and then suction-filtered through a Buchner funnel that contained Whatman #40 filter paper. The soil on the filter was leached with 0.1N HCl until the volume approached 250 ml. The extract was transferred to a 250-ml volumetric flask and brought to volume with more acid. It was then transferred to a 16-ounce bottle and analyzed for copper in the same manner as a water sample.

Two- to four-liter samples of canal water were filtered immediately in the field by means of a 0.3μ pore size pressure-membrane plexiglass filter apparatus and compressed CO_2 gas. The membrane filters themselves were found to contain appreciable amounts of 0.1N HCl-extractable copper. Thus, the filter and sediment could not be leached directly for measurement of copper associated with the sediment on the filter. Therefore, the filters and sediment were air-dried, and the sediment was carefully scraped from the surface of the membrane filter. The dry sediment was weighed and placed in a 60-ml vial, and the copper was extracted and analyzed in the same manner as the soil and water samples with only slight modification. Eight-ounce bottles, 100 ml 0.1N HCl, 5 ml each of hydroxylamine hydrochloride and buffer, and 10 ml of cuproine solution were used.

A few of the cuproine extracts were analyzed on an atomic absorption spectrometer to cross-check the methods. Results from the two procedures were similar. Until the concentration factor with cuproine was established, the concentrations of copper in the canal water were too low to be read directly on the atomic absorption spectrometer.

Before the copper sulfate was applied, caged, young-of-the-year rainbow trout were planted in the canal 50 ft above and .5, 11.5, and 23.2 miles below the point of introduction.

Results and Discussion

Copper measurements or values herein are expressed in terms of copper ion unless stated otherwise. The copper ion constitutes approximately 25% of copper sulfate pentahydrate (the form in which copper is usually applied for control of algae).

The copper content of the water did not return to background levels until 1 to 3 days after the copper sulfate application (Table 1). This much tailing would not result merely from longitudinal dispersion of the water. Thus, the extended, above-normal copper levels apparently resulted from releases from bottom sediments. This conjecture was substantiated in several ways. About 50% of the copper in the canal water prior to the test application was carried by suspended sediment (Table 2). After the application, the total copper carried by suspended sediment increased gradually from a low of 16% at Mile .5 to 39% at Mile 23.2. Apparently the added copper was first dissolved in the water and then a portion of it was sorbed by suspended sediment. In the first 11.5 miles, redistribution of copper between water and suspended sediment and deposition of the sediment occurred. In the last 11.5 miles, the process was primarily deposition, because the copper in water and suspended sediment had neared equilibrium.

Before the test application, copper levels in bottom sediments ranged from 3.9 ppm at Mile .5 to 8.1 ppm at Mile 23.2. At the same locations, peak concentrations of 6.1 and 9.8 ppm, respectively, were reached within 2 to 3 days after the application. The concentrations fluctuated at all locations but returned to pretreatment levels within about 7 or 8 days, which indicates that copper was gradually released again (probably by hydrolysis) into the flowing stream.

The peak concentrations and total amounts of copper that passed the sampling stations diminished progressively as the treated water moved downstream. The recovery of copper from water and suspended sediment was about 50% at Mile .5, and less than 10% at the last sampling site 23.2 miles downstream. The first .45 mile of canal was concrete-lined, and the waterflow in this section was nearly 2 mph. Some small undissolved crystals of copper sulfate were swept past Mile .5 near the bottom of the canal, and accurate sampling was extremely difficult. This undoubtedly accounts for the low rate of recovery of copper at Mile .5.

The test canal had been treated with copper sulfate three or four times each year since 1943 for algae control. A few soil samples (0 to 4-inch depth) from cropland near the canal as well as from virgin non-irrigated land were analyzed. The .1N HCl-extractable copper averaged .8 ppm in the virgin soil and 1.0 ppm in the irrigated soil. The buildup of copper in the irrigated soil apparently is not significant and far below levels toxic to crop plants.

None of the caged fish were killed by the copper sulfate treatment and a re-treatment 1 week later. The fish apparently survived the treatments, because the high or peak concentrations were of short duration (less than 2 minutes at Mile .5) and because dead algae did not accumulate in the running water in sufficient quantity to clog gills and cause suffocation.

For 20 years (1942-62), the permissible concentration of copper in drinking water was 3 ppm (12 ppm copper sulfate) as set forth by the U. S. Public Health Service (*1*). In 1962, the recommended limit was lowered to 1 ppm, because undesirable tastes of copper were detected at 1 to 5 ppm, and not because copper constituted a health hazard. Presently, the permissible dosage of copper sulfate pentahydrate in such waters as 2.3 ppm (approximately .58 ppm copper ion). The measured concentrations of copper in water or sediment in the treated canal did not exceed .58 ppm, except during a 20-minute period at .5 mile between 14 and 34 minutes after the application (Table 1). During that 20-minute period, the measured concentrations exceeded 1 ppm (1.610 ppm maximum) for only a few minutes. Thus, the possibilities of harmful effects from the release of such treated water for irrigation or domestic purposes are extremely remote. As indicated in the introduction, similar treatments have been used commonly for decades to control algae in aquatic situations. To our knowledge, harmful effects from such usage in irrigation canals have never occurred or been reported.

Acknowledgment

The authors are grateful for the technical assistance of Allen Kelley, Charles Veverka, and Gaylon Berg.

TABLE 1.—*Copper in water and suspended sediment (water basis) at .5, 5.9, 11.5, and 23.2 miles below the application point in canal*

.5 MILE			5.9 MILES			11.5 MILES			23.2 MILES		
TIME AFTER APPLICATION	COPPER IN PPM		TIME AFTER APPLICATION	COPPER IN PPM		TIME AFTER APPLICATION	COPPER IN PPM		TIME AFTER APPLICATION	COPPER IN PPM	
	IN WATER	IN SEDIMENT		IN WATER	IN SEDIMENT		IN WATER	IN SEDIMENT		IN WATER	IN SEDIMENT
0	.001	.001	—	—	—	—	—	—	—	—	—
9m	.001	.003	3h,8m	.004	.001	7h,5m	.001	.001	14h,15m	.002	.002
13m	.013	.007	3h,45m	.002	.002	8h,25m	.006	.003	17h,41m	.002	.001
15m	.740	.073	4h	.128	.027	8h,50m	.065	.008	21h,45m	.018	.015
17m	1.610	.179	4h,15m	.359	.255	9h,15m	.231	.208	21h,48m	.038	.014
19m	1.150	.292	4h,30m	.236	.238	10h,15m	.022	.019	22h,45m	.007	.006
27m	.835	.215	4h,45m	.110	.025	11h,21m	.012	.006	23h,45m	.007	.004
35m	.560	.167	5h,30m	.016	.017	12h,50m	.005	.005	26h,45m	.005	.002
44m	.475	.053	6h,20m	.008	.003	14h,51m	.007	.002	29h,45m	.004	.002
53m	.186	.011	7h	.005	.005	23h,20m	.003	.002	75h,30m	.002	.001
1h,30m	.008	.011	9h,30m	.003	.004	31h,15m	.004	.001	97h	.001	.001
6h	.010	.004	22h,45m	.001	.002	76h	.002	.002	126h,30m	.001	.001
22h	.003	.002	30h,53m	.002	.001	97h,50m	.001	.002	168h,10m	.002	.001
30h,25m	.002	—	76h,45m	.001	.002	127h,10m	.002	—	218h,30m	.001	.001
77h,30m	.001	.000	99h,7m	.002	.001	167h,15m	.001	—			
99h,50m	.001	.002	127h,50m	.003	—	215h,30m	.001	.003			
122h,50m	.001	—	169h,20m	.001	.001						
170h	.001	.000	216h	.001	.001						

TABLE 2.—*Peak concentrations and distribution of copper in an irrigation canal after a copper sulfate treatment at the rate of 1 lb/cfs*

	PRIOR TO TREATMENT	MILES BELOW APPLICATION POINT			
		.5	5.9	11.5	23.2
Peak concentration of Cu in water (ppm)	.001	1.610	0.359	0.231	0.038
Peak concentration of Cu in suspended sediment (ppm—water basis)	.001	0.292	0.255	0.208	0.015
Peak concentration of Cu in suspended sediment (ppm—sediment basis)	29	6,246	2,600	2,080	220
Percent of total Cu carried by suspended sediment	50	16	36	37	39
Percent of added Cu carried by suspended sediment	—	8	15	16	4
Percent of added Cu carried by water	—	43	21	17	5
Percent of added Cu carried by water and sediment	—	51	36	33	9
Percent depletion of Cu from water and sediment	—	49	64	67	91

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Surface Slicks as Concentrators of Pesticides in the Marine Environment [1]

Douglas B. Seba[2] and E. F. Corcoran[2]

ABSTRACT

Surface slicks in the marine environment have been found to be effective concentrators of the persistent chlorinated pesticides and as such can indicate the presence of pesticides when they are undeterminable in the surrounding water. Because of the high biological activity associated with slicks and their occurrence throughout the oceans, these findings may be of considerable importance in understanding the distribution of pesticides in the marine ecosphere.

Introduction

The occurrence of pesticide residues in the flora and fauna of estuaries both close to (*5*) and remote from (*11*) sites of pesticide application has been reported. Little is known of the method of movement in estuaries, but this undoubtedly depends on a number of factors including the source and type of pesticides, pH, sediments, and microbiological activities (*13*).

Slicks, or calm streaks on a rippled sea, are often seen on coastal waters and lakes and have been reported as occurring throughout the oceans. They are formed by the ripple-damping action of a surface film of organic matter which occurs naturally on biologically reproductive waters (*9*). This film has been reported to concentrate dissolved organics and inorganics (*19*) and marine leptopel (*10*). The ability of films to dampen ripples varies radically with the degree of compaction of the film molecules. Such compaction may be caused by horizontally convergent flow in the water surface or by horizontal convergence of the wind stress. The characteristics of the resultant slicks vary with the force producing compaction (*9*). Thus it seemed reasonable that slicks might be agents in the transport of pesticides in the marine environment.

It is reported here that pesticide distirbution in estuaries and the open sea is influenced by concentration in surface slicks.

Sampling Methods

Samples of surface slicks were collected from Biscayne Bay and the Florida Current during June-August 1968. Samples were collected in 200-ml glass bottles with teflon-lined caps. A sample was taken by holding the lip of the bottle just under the surface of the water and allowing the slick to pull itself into the bottle. Sea water samples were taken in the same manner. At the same time duplicate samples of surface slicks and sea water were taken in prepared bottles for head gas analysis of organic compounds (*7, 16*).

Analytical Procedures

Sea slicks were directly extracted with hexane (1:10) in the collection bottle. The hexane was then evaporated to 1/10 volume under a stream of high purity N_2 passed through a molecular sieve. The hexane, obtained from Burdick and Jackson Laboratories, Muskegon, Mich., could be concentrated 10^2 without producing interfering substances.

Analysis of the hexane extracts was done on one of two similar instruments. A Beckman GC-5 gas-liquid chromatograph with a helium arc emission electron capture detector or a specially designed Aerograph A-600B gas-liquid chromatograph with a Ni^{63} electron capture detector (*16*). Identification was made by both retention time correlation with FDA certified pesticide standards and by the extractive para-values method of

[1] Contribution No. 1121 from the Institute of Marine Sciences, University of Miami.

[2] Institute of Marine Sciences, University of Miami, Miami, Fla. 33149.

Bowman and Beroza (*4*). Three different columns were used so that different retention times could be obtained for any particular pesticide. The columns used were 5% QF-1 with 80/90 mesh Gas Chrom Q support, 3% SE-30 with 42/60 mesh Chromosorb G support, and 3% AN600 with 80/90 mesh Anakrom Q support.

Careful attention was given to every phase of the analysis to avoid any contamination or alteration of samples. Blanks and controls were run throughout, and no contamination was found. Experience has shown that, when contamination has occurred, results usually show the presence of an enormous amount of a particular compound in relation to others present.

Sea water and surface slick samples were assayed for acetone, butyraldehyde, and 2-butanone by the head gas method (*7, 19*). Analysis of the head vapors was done on a Beckman GC-5 gas-liquid chromatograph with dual hydrogen flame ionization detectors. Matched columns of 10% Carbowax 20M with 60/80 mesh Chromosorb W support were used.

Fig. 1 shows the approximate location of the slicks and their relationship to the South Florida Flood Control Canals and the Florida Current. The six canal systems replace natural drainage basins and are the source of surface water discharge into Biscayne Bay from southwest Dade County. The canals were almost continuously flowing into Biscayne Bay during the sampling period due to extremely heavy rainfall. Drainage of the extensive agricultural area southwest of Miami is accomplished exclusively by these canals, particularly C-1 and C-100. Extensive aerial and boat surveys revealed that many of these slicks were semi-permanent features. One slick near the Institute of Marine Sciences, associated with the discharge of the Miami River, was noted every day from June to December 1968. Its width varied greatly from a few to over 100 meters depending on the tide, wind, and water outfall, but its length and location were quite permanent. Permanence of slicks associated with surface water discharges has been reported for other locations (*9*). Aerial photos revealed that during the period of June-August 1968, about 10% of Biscayne Bay was covered with surface slicks with the coverage rising to 20% in the area around Turkey Point. The increase in slick areas around Turkey Point is probably caused by the instability in the water induced by the large thermal addition from the effluent of a power plant located at Turkey Point.

FIGURE 1.—*Location of slicks and their relationship to South Florida Flood Control Canals and the Florida Current*

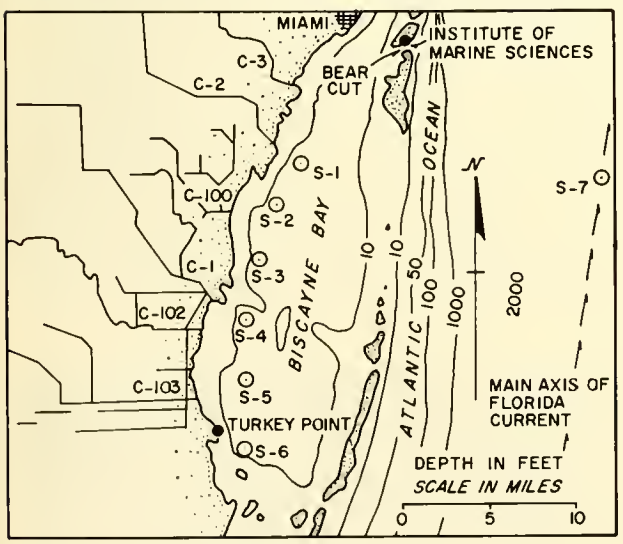

Table 1 gives the concentrations of pesticides in the surface slick samples. In addition to the pesticides mentioned in Table 1, lindane, heptachlor epoxide, and chlordane were identified tentatively on the basis of retention time but were not confirmed due to unknown interfering peaks on the chromatograms. The values given are the average of five to nine slick samples taken at each location over a period of several weeks during June-August 1968. Some locations were sampled more often only because of their accessibility during inclement weather. Variation was about ±25% and sometimes occurred in duplicate samples of the same slick. A total of 53 samples were taken.

TABLE 1.—*Concentration of pesticides in surface slicks*

Slick Number	Residues in parts per billion					
	p,p'-DDT	*p,p'*-DDE	Dieldrin	*o,p*-DDT	Aldrin	Total
S-1	.049	.124	.003	.012	.018	.206
S-2	.090	.266	.004	.013	.015	.388
S-3	3.460	9.250	.022	.005	.017	12.750
S-4	1.460	2.880	.035	.081	.025	4.480
S-5	.114	.266	.010	.002	.034	.426
S-6	.140	.178	.021	.014	.005	.358
S-7	.017	.061	.002	.002	.011	.093

Of particular interest is the large number of pesticides detected and their distribution. Slicks off canals draining heavily farmed areas contained up to 137 times as much pesticide as surface slicks in the Florida Current. The Current can be taken as a background value for Carribbean waters as local shore water does not reach the main axis of the Florida Current as it flows past Miami.

Samples of sea water taken at the same time and in the same manner as the surface slick samples generally had no detectable amounts of pesticides (less than 1 part per trillion). A total of 51 samples were analyzed. Sea water taken from Bear Cut inlet and distributed through a flowing supply system at the Institute of Marine Sciences did not reveal the presence of any chlorinated pesticides during 1966 and 1967 when it was sampled

on a weekly basis. The U. S. Geological Survey reports no detectable amounts of pesticide in C-2 and C-100 (*12*).

Three organic compounds, acetone, butyraldehyde, and 2-butanone, have been recently reported as occurring in the Florida Current and other oceanic waters (*7*). Head gas analysis for these compounds revealed their presence in all slick and sea water samples taken. The averaged values are given in Table 2. While there was some overall concentration of acetone and butyraldehyde in sea slicks, it was sporadic, independent of location, and was never more than threefold, as compared to the at least 10^5 concentration of pesticides in some of the same slicks. The slight concentration of these three organic compounds may be due to their volatility and solubility.

TABLE 2.—*Averaged concentration of organics in sea water and slicks*

Sample type	Concentration of organics (mg/liter)		
	Acetone	Butyraldehyde	2-Butanone
Slick	.0897	.0267	.0297
Sea Water	.0396	.0259	.0297

Discussion

Although no surveys have been made, pesticides apparently exist in very low concentration in the open oceans. Investigators have found or set very low limits on pesticide concentration in estuaries (*12*). In an east coast estuary so polluted with DDT that natural populations were probably being limited, DDT concentration was estimated at less than 50 parts per trillion (*20*).

Croker and Wilson (*8*) deliberately applied DDT to a tidal marsh ditch at a concentration of 70 parts per billion. In less than 24 hours DDT could only be found in the surface water, and these traces disappeared within 5 days. However, a patch of oil found 8 days after the application contained 133 parts per billion DDT.

Similarly, pesticides accumulated in the surface slicks of Biscayne Bay and the Florida Current. A concentration gradient existed because the slicks with the highest pesticide load occurred closest to the major outfalls. The rapid dropoff of pesticide load in the slicks away from the outfalls adds additional support to the argument that the value for slicks in the Florida Current is representative of Caribbean waters.

Up to a fivefold concentration of dissolved organic carbon and up to a 1500-fold concentration of particulate carbon has been reported for sea water surface film (*19*). The findings that acetone, butyraldehyde and 2-butanone, common to all samples, were barely concentrated, if at all, while the pesticides were concentrated by several orders of magnitude, demonstrates that the slick enrichment reported by Williams (*19*) is a highly selective fractionation and so may be of considerable ecological importance.

The distribution of pesticides in the slicks was similar enough to indicate perhaps some degree of causal relationship to the pesticides recovered from trade wind dust at Barbados, West Indies (*15, 17*). The higher amount of *p,p'*-DDT and *p,p'*-DDE in slicks may be a result of the continental dust impinging on the surface of the water. Such dust particles would tend to collect in surface slicks (*10*).

Biological activity was very intense in the water immediately under the slicks in comparison to that in surrounding water. Large, dense schools of small fish (*Clupeidae* and *Engraulidae*) occurred just under the slick. The location of slicks could often be determined before they could be observed by noting the feeding of sea gulls on these fish. Larger game and food fish were often observed feeding on the schools of small fish. Observations and conversations with local fishermen revealed that fishing usually was better when a slick passed under a bridge or a pier. High biological activity from plankton to fish and dolphins in slicks has been carefully documented (*1*). Numerous other authors have noted aspects of this activity (*2, 3, 19*). The concentration of pesticides in surface slicks and the high degree of biological activity associated with them may explain several problems of concern to ecologists.

Suteliffe, *et al.* (*18*) found that when the rate of downwelling of the converging water masses exceeded the spreading speed of the slick, the film is probably compressed, collapsed, and peptized into colloidal micelles which are carried downward in the water column. These nutrient rich particles could be absorbed and utilized by phytoplankton or could coalesce with other particles and become available to filter feeders, thereby increasing biological activity under slicks. Babkov (*1*) has found a large increase in phytoplankton productivity in slicks, yet investigators (*21*) found that just a few parts per billion of DDT inhibited photosynthesis in marine plankton.

Wide variations in the amounts of pesticide residues are often found among individual fish (*14*), even those from the same estuary (*6*). It seems entirely possible that a fish associated with a slick off the C-100 canal would have less than 1/10 the pesticide uptake of a fish associated with a slick just 3 miles to the south.

Acknowledgment

The technical assistance of Miss Tina Slaney is gratefully acknowledged.

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See Appendix for chemical names of compounds mentioned in this paper.

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APPENDIX

Chemical Names of Compounds Mentioned in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
ARSENIC	As_2O_3
CHLORDANE	1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane
COPPER SULFATE	$CuSO_4 \cdot 5\ H_2O$
DCBP	4,4'-dichlorobenzophenone
DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
DDD (TDE)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDD contains some *o,p'*-isomer also.
DDT (including its isomers and dehydrochlorination products)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in a ratio of about 3 or 4 to 1).
DIELDRIN	Not less than 85% of 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-dimethano=naphthalene
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-dimethanonaphthalene
FENAC	2,3,6-trichlorophenylacetic acid
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer
PICLORAM	4-amino-3,5,6-trichloropicolinic acid
PROMETONE	2-methoxy-4,6-bis(isopropylamino)-*s*-triazine
2,3,6-TBA	2,3,6-trichlorobenzoic acid
TOXAPHENE	chlorinated camphene containing 67% to 69% chlorine

ERRATA

PESTICIDES MONITORING JOURNAL, Vol. 3, No. 2 (*Pesticides in Selected Western Streams—A Progress Report* by Manigold and Schulze):

On page 129, TABLE 2, IRRIG. NETWORK NO. 27, the heptachlor content of the sample collected on 04/24/67 should be .10 ppb rather than .01 ppb.

On page 130, TABLE 2, IRRIG. NETWORK NO. 37, the 2,4-D content of the sample collected on 09/22/67 should be .10 ppb rather than. .01 ppb.

Information for Contributors

The PESTICIDE MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and interlaboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

Preparation of manuscripts should be in conformance to the STYLE MANUAL FOR BIOLOGICAL JOURNALS, American Institute of Biological Sciences, Washington, D. C., and/or the STYLE MANUAL of the United States Government Printing Office.

An abstract (not to exceed 200 words) should accompany each manuscript submitted.

All material should be submitted in duplicate (original and one carbon) and sent by first-class mail in flat form—not folded or rolled.

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All copy, including tables and references, should be double spaced, and all pages should be numbered. The first page of the manuscript must contain authors' full names listed under the title, with affiliations, and addresses footnoted below.

Charts, illustrations, and tables, properly titled, should be appended at the end of the article with a notation in text to show where they should be inserted.

Charts should be drawn so the numbers and texts will be legible when considerably reduced for publication. All drawings should be done in black ink on plain white paper.

Photographs should be made on glossy paper. Details should be clear, but size is not important.

The "number system" should be used for literature citations in the text. List references alphabetically, giving name of author/s/, year, full title of article, exact name of periodical, volume, and inclusive pages.

Pesticides ordinarily should be identified by common or generic names approved by national scientific societies. The first reference to a particular pesticide should be followed by the chemical or scientific name in parentheses—assigned in accordance with CHEMICAL ABSTRACTS nomenclature. Structural chemical formulas should be used when appropriate. Published data and information require prior approval by the Editorial Advisory Board; however, endorsement of published information by any specific Federal agency is not intended or to be implied. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will be provided with 100 reprints.

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The *Pesticides Monitoring Journal* is published quarterly under the auspices of the Federal Committee on Pest Control and its Subcommittee on Pesticide Monitoring as a source of information on pesticide levels relative to man and his environment.

The parent committee is comprised of representatives of the U. S. Departments of Agriculture, Defense, the Interior, and Health, Education, and Welfare.

The Pesticide Monitoring Subcommittee consists of representatives of the Agricultural Research Service, Consumer and Marketing Service, Federal Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Federal Water Pollution Control Administration, Food and Drug Administration, Public Health Service, and the Tennessee Valley Authority.

Responsibility for publishing the *Pesticides Monitoring Journal* has been accepted by the Pesticides Program of the Public Health Service.

Pesticide monitoring activities of the Federal Government, particularly in those agencies represented on the Pesticide Monitoring Subcommittee which participate in operation of the national pesticides monitoring network, are expected to be principal sources of data and interpretive articles. However, pertinent data *in summarized form,* together with interpretive discussions, are invited from both Federal and non-Federal sources, including those associated with State and community monitoring programs, universities, hospitals, and nongovernmental research institutions, both within and without the United States. Results of studies in which monitoring data play a major or minor role or serve as support for research investigation also are welcome; however, the *Journal* is not intended as a primary medium for the publication of basic research. Manuscripts received for publication are reviewed by an Editorial Advisory Board established by the Monitoring Subcommittee. Authors are given the benefit of review comments prior to publication.

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PESTICIDES MONITORING JOURNAL
Pesticides Program
Food and Drug Administration
4770 Buford Highway, Bldg. 29
Chamblee, Georgia 30341

CONTENTS

Volume 3 March 1970 Number 4

EDITORIAL

Federal Committee on Pest Control in FY 1969

The Federal Committee on Pest Control met eight times during the 1969 fiscal year—a period when the use of DDT and other persistent pesticides received much public attention.

During the year, the Committee became a Class B member of the Agricultural Research Institute of the National Academy of Sciences/National Research Council.

Most activities of the Committee were concerned with specific pesticide problems. However, on broader issues, the Committee developed pest control objectives designed to help the President's Environmental Quality Council form public policies relating to pesticides; reviewed and endorsed a proposal of the Federal Trade Commission to require that pesticide advertising be consistent with registered uses and recommendations on labels; and began a study to determine how the FCPC can better relate to the States and their pesticide problems.

Working through five subcommittee task forces, the FCPC carried out the following activities during the 1969 fiscal year:

Monitoring. As a culmination of more than 2 years' work, the publication "Catalog of Federal Pesticide Monitoring Activities in Effect July 1967" was released. A task force was established to review and make recommendations for monitoring the environment by the Federal agencies. A revised statement of the Objectives of the National Pesticide Monitoring Program was developed. The Committee helped to have some 500 samples of human tissue, collected by the Armed Forces Institute of Pathology before 1942, established as resource material for scientific reference. These tissue samples are now held at the Food and Drug Administration Primate Research Laboratory, Perrine, Fla.

Review of Federal Pest Control Programs. Over 40 pest control programs from 26 Federal agencies were reviewed during the year requiring at least 1300 hours of staff work and technical review. Typical programs include a wide spectrum of pest control in forests, cropland, parks and urban areas, in and around buildings and facilities. The objective of review is to facilitate safe and efficient practices in the best interests of human health and well being, fish and wildlife, and the various elements of the environment. Special attention was given to weed control in aquatic situations and general use of the herbicide amitrole. One of the more controversial programs reviewed concerned the use of the persistent pesticide dieldrin in relation to Japanese beetle control and pollution in Lake Michigan.

Research. A new publication released by the Committee is entitled "A Study of Federally Financed Research on Pests, Pesticides, and Pest Control." The Committee recommended increased research in evaluating indirect costs and benefits of pest control and established a task force to implement their recommendations. More research on disposal of pesticide wastes was also recommended.

Safety in Pesticide Marketing and Disposal. The Committee established an interagency group to develop a method for coordination of reporting and investigating pesticide accidents. They recommended that the Food and Drug Administration conduct a survey to determine the extent of the re-use of pesticide containers and for what purposes.

Public Information. The Committee started revision of the 1966 brochure "FCPC, What It Is, What It Does." The group recommended that the Departments develop a central office for handling information on pests and pesticides and suggested that the FCPC should find a way to brief the new Secretaries on the role of the Committee in dealing with the pesticide problem.

Recently, the President's Environmental Quality Council announced the establishment of a Committee on Pesticides. This Committee is chaired by the Secretary of Agriculture and includes the Secretaries of Health, Education, and Welfare and the Interior and the Executive Secretary of the Environmental Quality Council, and also representation from the Departments of Defense, Transportation, and State, including the Agency for International Development. The Committee will establish a working group to provide day-to-day coordination and to develop program and policy proposals for its consideration. This group will replace the existing Federal Committee on Pest Control.

R. J. Anderson, D.V.M.
Chairman, Federal Committee on Pest Control

RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Organochlorine Pesticides in Fur Seals

Raymond E. Anas[1] and Alfred J. Wilson, Jr.[2]

ABSTRACT

Samples of liver and brain tissue from 30 northern fur seals (Callorhinus ursinus) *and 7 fur seal fetuses that were collected on the Pribilof Islands, Alaska, in 1968 and off the Washington coast in 1969, were analyzed for organochlorine pesticides. These compounds were found in all of the fur seals and in three of the fetuses. Polychlorinated biphenyls (PCB) were not detected. Of 30 samples of liver tissue from the seals, all contained DDE; 21, DDD; 24, DDT; and 3 contained dieldrin. Of the 30 brain samples, all contained DDE; 5, DDD; 4, DDT; and none contained dieldrin. DDE was present in liver tissue from three of the fetuses and in brain tissue from two.*

Introduction

Pesticides are widespread in the oceans. Organochlorine pesticides have been found in the tissues of marine mammals in Antarctica (*1, 4*), Scotland (*2*), Canada (*2*), and the United States (*A. J. Wilson, Bureau of Commercial Fisheries, unpublished data.*) This report records the amounts of DDE, DDD, DDT, and dieldrin found in the tissues of northern fur seals, *Callorhinus ursinus*, collected on the Pribilof Islands, Alaska, and off the Washington coast.

Thousands of fur seals are taken each year by the United States on the Pribilof Islands, Alaska. The skins are used for fur garments, and the carcasses, minus the blubber, are ground and fed to mink. The liver and meat are eaten by residents of the Pribilof Islands. The U. S. S. R. takes seals on the Commander and Robben Islands, and some seals are taken at sea in research by Canada, Japan, the U. S. S. R., and the United States. Fur seals migrate to the Bering Sea (to return to the Pribilof and Commander Islands) and the Okhotsk Sea (to return to Robben Island) during summer and autumn; they migrate as far south as California and Japan in winter and spring. Fur seals feed principally on small fishes and squids. Killer whales and sharks are probable predators.

Sampling Procedures

Samples of liver and brain tissues were collected from fur seals in July 1968 on the Pribilof Islands, and in February and March 1969 off the Washington coast. Samples of blubber were not collected, but the concentrations of pesticides are usually greater in the blubber than in other tissues (2). Brain and liver tissue samples weighing about 10g each were collected from each of 30 seals and 7 fetuses. Tissues were kept frozen from the time of collection until analysis. Seventeen of the seals were animals of known age that had been tagged previously as pups. The ages of the 13 other seals were determined by counting layers of dentine in upper canine teeth. The fetuses were in their fourth month.

[1] Bureau of Commercial Fisheries, Marine Mammal Biological Laboratory, Seattle, Wash. 98115.
[2] Bureau of Commercial Fisheries, Biological Field Station, Gulf Breeze, Fla. 32561.

Analytical Procedures

Liver and brain tissues were analyzed for BHC, heptachlor, aldrin, heptachlor epoxide, toxaphene, methoxychlor, dieldrin, endrin, and the *o, p'* and *p, p'* isomers of DDE, DDD, and DDT. Tissues were thawed and mixed with anhydrous sodium sulfate in a blender. The mixture was extracted for 4 hours with petroleum ether in a Soxhlet apparatus. Extracts were concentrated and partitioned with acetonitrile. The acetonitrile was evaporated just to dryness and the residue eluted from a Florisil column (*3*). The sample was then identified and quantified by electron capture gas chromatography. Three columns of different polarity (DC 200, QF-1, and mixed DC 200 and QF-1) were used to confrm identification. Operating parameters on Varian Aerograph 204 and 610D gas chromatographs were as follows:

Columns: 5′ x ⅛″ (O.D.), pyrex glass, packed with 3% DC-200, 5% QF-1, and a 1:1 ratio of 3% DC-200 and QF-1, all on Gas Chrom Q

Temperature: Detector 210 C
Injector 210 C
Oven 190 C

Carrier Gas: Prepurified nitrogen at a flow rate of 40 ml/minute.

A few samples were analyzed using thin-layer chromatography. Laboratory tests gave the following recovery rates: *p, p'*-DDE, 80-85%; *p, p'*-DDD (TDE), 82-95%; *p, p'*-DDT, 91-95%; and dieldrin, 85-90%. The lower limit of sensitivity was 0.010 ppm (mg/kg dry weight). Data in this report do not include a correction factor for percentage recovery. Polychlorinated biphenyls (PCB) as reported by Holden and Marsden (*2*) were not detected in these samples.

Results

Some form of pesticide was found in all 30 of the seals examined, and 3 of the 7 fetuses had measurable amounts of pesticide (Table 1). The largest concentration of any pesticide in an individual was in the liver of a male yearling taken on February 20, 1969 (5.1 ppm DDE). Tissue samples from males and females collected in February and March 1969 contained larger concentrations of pesticides, on the average, than those from males collected in July 1968, but some overlap occurred. Of 30 samples of liver tissue from seals other than fetuses, all contained DDE; 21, DDD; 24, DDT; and 3 contained dieldrin. Of the 30 brain samples, all contained DDE; 5, DDD; 4, DDT; and none contained dieldrin. DDE was present in liver tissue from three of the seven fetuses and in brain tissue from two. DDD, DDT, and dieldrin were absent in fetal liver and brain.

TABLE 1.—*Pesticides in liver and brain tissues of northern fur seals*

Field Number	Date Collected	Age (years)	Residues in PPM*							
			DDE		DDD		DDT		Dieldrin	
			Liver	Brain	Liver	Brain	Liver	Brain	Liver	Brain
IMMATURE MALES										
US69-76	2-19-69	1	1.9	0.34	0.17	0.026	0.28	0.044	0.022	nd
US69-78	2-20-69	1	0.20	0.060	0.065	nd	0.090	nd	0.015	nd
US69-82	2-20-69	1	5.1	1.7	0.47	0.077	0.38	0.087	0.091	nd
US69-85	2-20-69	1	0.23	0.069	0.054	nd	0.15	nd	nd	nd
US69-117 [1]	2-25-69	3	0.25	0.084	0.087	nd	0.068	nd	nd	nd
R-6683 [1]	7-2-68	3	0.075	0.019	nd	nd	0.025	nd	nd	nd
R-8317 [1]	7-2-68	3	0.083	0.029	nd	nd	0.038	nd	nd	nd
R-9514 [1]	7-2-68	3	0.042	0.017	nd	nd	0.031	nd	nd	nd
Q-17766 [1]	7-2-68	4	0.044	0.015	nd	nd	nd	nd	nd	nd
Q-19800 [1]	7-2-68	4	0.30	0.079	nd	nd	nd	nd	nd	nd
Q-21025 [1]	7-2-68	4	0.068	0.019	nd	nd	0.025	nd	nd	nd
Q-21777 [1]	7-2-68	4	0.061	0.023	nd	nd	nd	nd	nd	nd
Q-24993 [1]	7-2-68	4	0.054	0.018	nd	nd	0.021	nd	nd	nd
IMMATURE AND NONPREGNANT FEMALES										
US69-74	2-19-69	1	0.16	0.036	0.055	nd	0.12	nd	nd	nd
US69-75	2-19-69	1	0.15	0.042	nd	nd	nd	nd	nd	nd
US69-81	2-20-69	1	0.32	0.082	0.099	nd	0.27	nd	nd	nd
US69-83	2-20-69	1	0.17	0.069	0.056	nd	0.12	nd	nd	nd
US69-87	2-21-69	1	3.9	1.4	0.41	0.16	0.36	0.17	nd	nd
US69-101	2-22-69	1	0.65	0.17	0.066	nd	0.086	nd	nd	nd
US69-103	2-25-69	1	0.31	0.10	0.16	nd	0.23	nd	nd	nd
US69-118 [1]	2-25-69	6	0.55	0.12	0.13	0.029	0.14	0.029	nd	nd
US69-88 [2]	2-21-69	7	0.89	0.18	0.068	nd	0.10	nd	nd	nd
US69-257 [1]	3-26-69	10	0.15	0.043	0.073	nd	nd	nd	nd	nd

TABLE 1.—*Pesticides in liver and brain tissues of northern fur seals*—Continued

Field Number	Date Collected	Age (years)	Residues in PPM*							
			pDE		DDD		DDT		Dieldrin	
			Liver	Brain	Liver	Brain	Liver	Brain	Liver	Brain
PREGNANT FEMALES										
US69-45										
Mother	2-14-69	7	0.21	0.071	0.098	0.017	0.073	nd	nd	nd
Fetus [3]			0.041	nd	nd	nd	nd	nd	nd	nd
US69-77										
Mother	2-19-69	5	0.32	0.060	0.055	nd	0.050	nd	nd	nd
Fetus			0.047	0.030	nd	nd	nd	nd	nd	nd
US69-167 [1]										
Mother	3-9-69	9	0.11	0.050	0.051	nd	nd	nd	nd	nd
Fetus			nd	nd	nd	nd	nd	nd	nd	nd
US69-193 [1]										
Mother	3-11-69	8	0.19	0.045	0.062	nd	0.068	nd	nd	nd
Fetus			nd	nd	nd	nd	nd	nd	nd	nd
US69-200 [1]										
Mother	3-12-69	11	0.23	0.087	0.16	nd	0.11	nd	nd	nd
Fetus			nd	nd	nd	nd	nd	nd	nd	nd
US69-201 [1]										
Mother	3-12-69	6	0.41	0.15	0.11	nd	0.10	nd	nd	nd
Fetus			0.098	0.040	nd	nd	nd	nd	nd	nd
US69-247 [1]										
Mother	3-24-69	10	0.43	0.077	0.20	nd	0.18	nd	nd	nd
Fetus			nd	nd	nd	nd	nd	nd	nd	nd

[1] Known-age seals tagged on Pribilof Islands, Alaska.
[2] Known-age seal tagged on Commander Islands, U.S.S.R.
[3] Fetuses were in their fourth month of development.
* Residues are reported here in parts per million (mg/kg, *wet weight*).
nd = not detectable, <0.010 (mg/kg, *dry weight*).

Acknowledgments

We thank Jerrold Forester and Johnnie Knight for their assistance in the chemical analysis and Clifford H. Fiscus and Hiroshi Kajimura for their assistance in the collection of the samples.

See Appendix for chemical names of compounds mentioned in this paper.

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Absorption of Endrin by the Bluegill Sunfish, Lepomis macrochirus [1]

Harry J. Bennett and John W. Day, Jr.[2]

ABSTRACT

Endrin absorbed by bluegill sunfish in lethal and sublethal concentrations was determined by electron capture gas chromatography. The amount of absorption was measured for the entire body, skeletal muscle, liver, and gastrointestinal tract for varying times up to 24 hours. At the lethal level all the tissues absorbed increasing amounts of endrin throughout the tests. At the sublethal level, the entire body, skeletal muscle, and liver exhibited an N-shaped absorption curve. There was an initial sharp rise in endrin levels, followed by a drop with a subsequent rise. At this level, the gastrointestinal tract absorbed increasing amounts of endrin throughout the tests.

Introduction

The publicity given to the use of pesticides in the last few years has accelerated research on effects of these toxicants on the environment. Much of this research has been concerned with determining the toxicity of these substances to aquatic organisms. Henderson *et al.* (*9*) observed that, among several organic pesticides tested, endrin was the most toxic to fish. Pickering *et al.* (*14*) found bluegills to be generally the most sensitive fish to several organic phosphorus compounds. Tarzwell and Henderson (*16*) measured the toxicity of dieldrin contained in runoff water to three species of fish. A few fish were reported to exhibit the characteristic effects of insecticide poisoning when placed in runoff water from the fourth rain following application of the pesticide. Cope (*3*) reported that trout from a stream sprayed with DDT concentrated the pesticide in fat and in progressively lesser amounts in the kidney, pyloric caeca, and brain. None was found in the liver. Holden (*10*) found that brown trout accumulated ^{14}C-labeled DDT in much the same way as reported by Cope, but he found DDT in the liver. Cutthroat trout have also been reported to concentrate DDT in the liver (*1*).

The bluegill sunfish, *Lepomis macrochirus,* was chosen for use in this research for several reasons. It has been widely used in toxicity studies and is easily maintained in the laboratory. It has a very wide distribution, has great value in recreational fishing, and is important in the food chains of several larger fish.

The purpose of this study was to determine the effects of lethal and sublethal concentrations of endrin on the bluegill sunfish and to study its absorption by the whole fish and several organs.

Materials and Methods

The bluegills in this study were obtained from a small farm in the vicinity of French Settlement, La. The fish were tested at lethal and sublethal concentrations of endrin. A bioassay was run to determine the 24-hour TL_m of endrin to bluegills. This concentration was used as the lethal level, and one tenth of this concentration was chosen as the sublethal level for 24 hours. The dilution water used for the bioassay and for the tests was Reference Dilution Water (RDW) devised by Dowden (*4*). He found (*5*) that RDW supported bluegill for as long as natural waters in laboratory tests and that it did not upset "normal" metabolism as measured by oxygen consumption. The

[1] Industrial Research Laboratory, Department of Zoology, Louisiana State University, Baton Rouge, La.

[2] Present address: Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, N.C. 27514.

fish were tested in a flow-through bioassay system (*6*). Prior to the beginning of a test, the fish to be tested were put into aerated RDW for 48 hours so that they would empty their digestive tracts. One series of tests was run at the lethal concentration, and a second series was run at the sublethal concentration. Six groups of six fish were used for each concentration. The degree of absorption was measured for the whole body, gastrointestinal tract, somatic muscles, and liver at 1.0, 7.7, 12.0 and 24.0 hours. At each of the above times a test was terminated, and whole fish and the selected organs were frozen. Only those fish alive at the end of a test period were used. The samples, consisting of one fish or organ each, were analyzed for endrin content with electron capture gas chromatography. The cleanup and extraction procedure was that described by Barry *et al.* (*2*). Controls gave recovery values ranging from 68 to 100%. A Varian Aerograph 1522-B instrument was used. Thin-layer chromatography was used as a confirmatory test. The following formula was used in computing the amount of endrin in each sample:

$$\frac{C \cdot H_{sa} \cdot D}{H_{st} \cdot W} = \text{concentration of endrin in sample in ng/gram of tissue,}$$

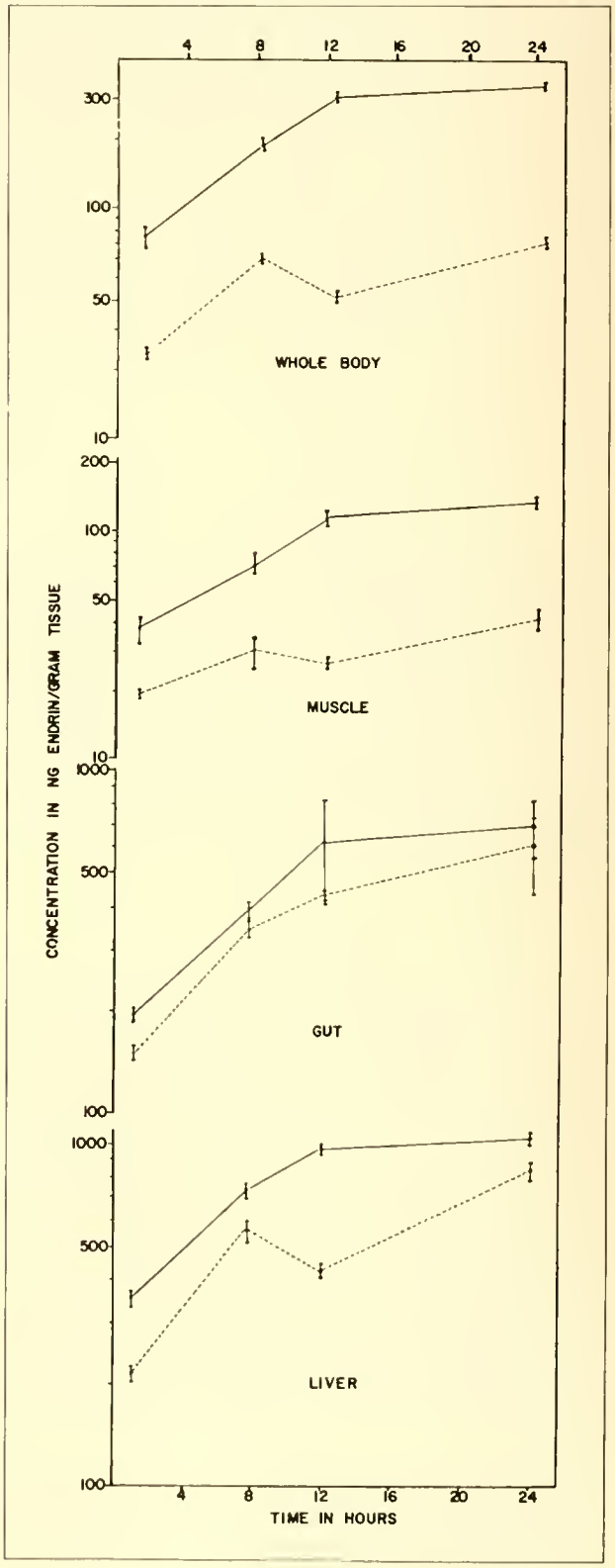
where

H_{st} = peak height of standard in cm
H_{sa} = peak height of sample in cm
W = weight of sample in grams
C = number of nanograms in standard injection
D = dilution factor. This is the reciprocal of the fraction of the sample injected.

Results

The initial bioassay indicated a 24-hour TL_m of 2.0 $\pm$ 0.27 ppb. Thus, 2.0 ppb was used as the lethal exposure concentration, and 0.2 ppb was used as the sublethal exposure concentration. Fig. 1 shows the amount of endrin absorbed by the whole body, muscle, gastrointestinal tract, and liver, respectively. Each graph contrasts the amount of endrin absorbed at 2.0 ppb to that absorbed at 0.2 ppb. In the tests at the lethal concentration, all of the tissues exhibited an absorption curve showing increasing endrin levels with elapsed time. In the tests at the sublethal concentration, the whole body, muscle, and liver exhibited an "N-shaped" absorption curve. For these tissues there was an initial rise in endrin levels followed by a decrease and subsequent increase. The gastrointestinal tract exhibited a sublethal absorption curve showing increasing endrin levels with elapsed time.

FIGURE 1.—*Graphs of time versus concentration in nanograms per gram wet weight for endrin absorption by various tissues. Solid lines show absorption at 2.0 ppb, and dotted lines show absorption at 0.2 ppb. Vertical bars indicate the standard error.*



Discussion

Schatz *et al.* (*15*) describe the type of response noted in this study at the lethal and sublethal concentrations as a paradoxical effect. Dowden (*4*) and Huner *et al.* (*11*) found that the oxygen consumption of bluegills varied in a similar manner when the fish were exposed to pesticides. Fry (*8*) stated that the best overall measurement of metabolism in fish is oxygen consumption. The respiration rates in the above studies are a result of the pesticide to which the organism was exposed; thus, a similar response should be expected in other physiological functions of the fish.

The bluegills used in this study were obtained from an area with no substantial agricultural activity, and probably did not have any prior exposure to endrin. Thus, it can be assumed that the fish had no mechanism for coping with endrin. When the fish were first exposed to the insecticide at sublethal concentrations there was a sharp rise in the endrin levels in their tissues. During this period the fish undoubtedly developed some mechanism to cope with it. By about 7 to 8 hours this mechanism must have been operative because endrin levels started to decrease to a low at about 12 hours. After this time the concentration increased gradually to a high at 24 hours. The fact that endrin levels decreased from 7 to 12 hours suggests that the fish were metabolizing and/or excreting it.

The gastrointestinal tract did not exhibit the paradoxical effect at the sublethal concentration. Holden (*10*) stated that DDT in the liver of brown trout was probably contained mainly in the blood of that organ. If this is correct, then the endrin measured for the liver may be a reflection of the circulating concentration. March *et al.* (*12*) treated two groups of hens with ^{32}P-malathion. The group which was sprayed with an emulsion containing the pesticide had the highest concentration in the blood. A second group which was fed the pesticide in their diet had a much smaller amount in the blood. Mount (*13*) concluded that endrin entered carp mostly with swallowed water. Ferguson and Goodyear (*7*) ligated the esophagus of black bullheads and found that the main pathway for endrin entry was through the gills. From these reports, it may be concluded that bluegills absorb endrin through the gills and gut and probably through the skin. Endrin present in the digestive tract, therefore, could come from both the blood stream and from swallowed water.

Acknowledgments

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See Appendix for chemical name of endrin.

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Distribution Patterns of DDT Residues in the Sierra Nevada Mountains

Lawrence Cory,[1] Per Fjeld,[1] and William Serat[2]

ABSTRACT

Frogs from throughout the Sierra Nevada Mountains in California were examined for pesticide residues. The commonest substance found was p,p'DDE, a metabolite of p,p'-DDT, and its occurrence was regarded as evidence of environmental contamination with DDT residues. Contamination of the range was found to be general throughout, even at altitudes to 12,000 feet above sea level. General patterns of distribution showed that concentrations were highest in the central to southern areas and declined somewhat to the north. Contamination was heavier on the western slope of the mountains than across their crest on the east face. The presence of the residues is ascribed to wind-borne drift of aerosol DDT released in crop-dusting in the central valley of California. Notably high concentrations in a limited area in the Yosemite National Park to Sonora Pass region are considered to be locally persistent residues of forest sprayings with DDT made in this area in 1953 and 1956.

Introduction

Examination of a map of the State of California (Fig. 1) shows the prominence of the central valley, formally designated the Sacramento Valley North of the latitude of San Francisco Bay and the San Joaquin Valley to the south. Located to the east of this valley and extending approximately parallel to it in a north-south direction lies the Sierra Nevada Mountain Range. This range is over 300 miles in length and averages about 40 miles in width. The highest altitude in the continental United States, over 14,500 feet at Mt. Whitney, occurs near its southern end, and the range includes many areas rising to well over 13,000 feet. The several rivers draining various areas of the northern part of the valley converge to a common trunk in the Sacramento River, just as those draining the southern valley regions join to form the San Joaquin River trunk. These two river systems merge in an extensive delta area, through which their common effluent is discharged into San Francisco Bay.

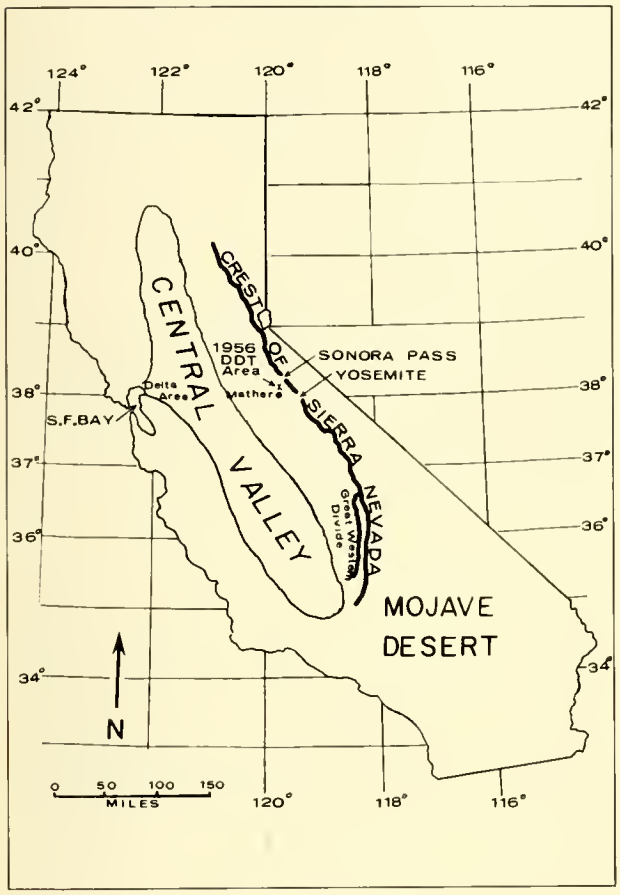
The topographic relationships of these regions to each other and to the Pacific Ocean which lies west of them have important meteorological consequences. For one thing, prevailing winds blowing across the State are from the ocean, so that they sweep from west to east across the central valley and against the Sierra Nevada. In crossing the range, the rising air masses release much of their moisture as precipitation on the western face of the mountains. The amount of preciptation drops sharply to the east of the Sierra Nevada crest, which marks the western boundary of the great desert areas of the Western United States. These topographic and meteorological features have important implications with respect to the distribution patterns of DDT* residues we are finding.

The central valley of California is agriculturally one of the most intensely cultivated areas on the earth. In this agricultural activity enormous amounts of pesticides are employed, including a high percentage of DDT. Exactly how much of this material has been used is impossible to determine, but conservative estimates in the mid-1950's indicated that about 20% of all DDT used in the United States was employed in California agriculture. (*Robert Rawlins, California*

[1] Biology Department, St. Mary's College, Calif. 94575.
[2] California State Department of Public Health, Berkeley, Calif. and Biology Department, St. Mary's College, Calif.

* Term designating *o,p'* and *p,p'* isomers of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane, as well as dehydrochlorination products, as *p,p'*-DDE.

FIGURE 1.—*Map of the State of California showing relationship of the Sierra Nevada Mountain Range to the central valley*



State Department of Agriculture, personal communication). Figures from U. S. Tariff Commission Reports quoted by Frost (*7*) and by Sodergren (*9*) indicate that the annual production and sale of DDT in the United States has increased steadily from 19,000 tons per year in 1946 to a maximum of 79,000 tons per year in 1962, with somewhat of a decline thereafter. Increasing export of the material is indicated by the 79% export fraction of the 69,000-ton U. S. production in 1968. Dobzhansky *et al.* (*6*) quote estimates of 3,243 tons and 3,168 tons of DDT used in California agriculture in the years 1951 and 1955, respectively, values that are consistent with the above figures. At the rate of use indicated by these estimates, the total amount of DDT applied to the central valley of California since its introduction into agricultural use in 1945 becomes an awesome figure.

Most of this material is applied in crop-dusting by airplane. It can be expected that much of this material in aerosol form would be carried eastward from the valley by the prevailing winds, and that much of this transported material would be deposited in the Sierra Nevada, either by direct fallout in local eddies in canyons and glacial cirques or associated with the precipitation of moisture, in the manner indicated by Cohen and Pinkerton (*1*).

Field Methods

A search for DDT residues is being made in body tissues of frogs of the *Rana boylei* group (the "yellow-legged" frogs). Previous work (*2*) had shown the widespread distribution of these animals throughout the Sierra Nevada, especially in the broad band of lakes and ponds in glacial cirques alongside the main crest. Frogs being well along in the series of food chains represent a good indicator species for the assessment of pesticide base levels. In frogs, moreover, the fatty tissues are not widely scattered subdermally throughout the animals, but are concentrated in a discrete pair of fat bodies. It is this tissue that is analyzed.

Collections are made in the course of back-packing expeditions throughout the most remote areas in the mountains, and insofar as possible no use has been made of animals occurring near trans-montane highways or major trails, where random accidental local contamination might occur. Frogs are brought to the laboratory alive. They are killed by being quickly deep-frozen immersed in water, a condition in which they are kept until analyzed.

Analysis

Processing is a modification of the technique of Stanley and LeFavoure (*10*). Fat-body tissue is broken down into an emulsion in a commercial perchloric-acetic acid mixture (BFM Solution, G. F. Smith Chemical Company, Columbus, Ohio). For the small amount of tissue in a pair of fat bodies from the yellow-legged frogs (generally less than 1 gram), 1 ml to 3 ml of the acid mixture is sufficient. Upon standing for 24 hours, the tissue is broken down to an emulsion, and a layer of lipid is visible on the surface. This emulsion is shaken with 10 ml of pure hexane (Mallinckrodt, Nanograde) in a separatory funnel, and the hexane layer containing lipid-soluble materials is separated from the acid residue. The latter is re-extracted a second and a third time with 10-ml portions of hexane, and all three extractions are combined in a separatory funnel. To this combined extract are added 5 ml of analytical grade concentrated sulfuric acid, then 5 ml of analytical grade fuming sulfuric acid (20-23% SO_3). The funnel is quickly stoppered and shaken vigorously by hand for 2 minutes. This treatment destroys fats and many other substances but leaves intact many lipid-soluble components, including the DDT-related compounds. Upon standing, usually for 24 hours, a clear hexane layer separates from the acid phase. This hexane

phase, containing the DDT-related substances, is drawn off and concentrated by evaporation to a small volume, generally about 1 ml. This concentrated extract is retained in a stoppered, calibrated cylinder for examination by gas-liquid chromatography, and together with rinsing from the evaporation vessel, totals a few milliliters in volume.

In the examination of this final hexane extract by gas-liquid chromatography, a Wilkens Aerograph HY-F1 Model 600 instrument was employed, under the following conditions:

Detector:	Electron capture, with 250 μc tritium source
Carrier gas:	Nitrogen
Temperature:	180 C
Columns:	5′ x ⅛″ coiled glass with separate columns: 5% Dow-11 on 60/80 mesh Chromosorb W 2% QF-1 on 60/80 mesh Chromosorb W

The two columns were used separately for mutual confirmation of identifications. The QF-1 column was used for quantification and showed a sensitivity of at least 2.5 mm per picogram of *p,p′*-DDE in peak height on the chromatograms, with injection aliquots as low as 2 μl. The biological material used in this study under the conditions of extraction and cleanup employed produced sufficiently low-noise chromatograms that peak heights of 5 mm could be unambiguously detected. Interlaboratory confirmation of a random sample of identifications was performed by personnel of the California State Department of Public Health, employing a MicroTek chromatograph on an SE-30 + QF-1 column.

Results and Discussion

In the early stages of the work, use of a more elaborate procedure allowing recovery of a more complete spectrum of chlorinated hydrocarbons showed indications of endrin, dieldrin, heptachlor epoxide and other compounds. Since *p,p′*-DDE was by far the most abundant and consistently detected material, our investigation was limited to a search for this compound. Tests of the above simplified procedure on samples "spiked" with known amounts of *p,p′*-DDE showed that recovery is virtually complete. Comparisons made early in the work of DDE content of fat-body tissue as compared with whole-body samples indicated that the former was generally above 1 ppm, while in the latter it was generally much less than .1 ppm. In whole-body analysis, moreover, a much more complicated extraction procedure was required, and chromatograms were not as low in noise, making accurate detection very difficult. Hence, this study is limited to the analysis of fat-body tissue.

Although *p,p′*-DDE is not applied as a pesticide, it is one of the commonest metabolites of *p,p′*-DDT and a frequent storage form in animal tissues (*8*), as found, for example, by Dimond *et al.* (*3, 4, 5*) for salamanders, crayfish, and a variety of small mammals following DDT application in Maine forests. Its occurrence in the frogs in this study, therefore, is considered evidence of environmental DDT.

Geographic distribution of the occurrence of DDE in frog fat bodies is shown in detail in Tables 1-6. Table 7 summarizes comparatively the data of the others, and interpretation of the tables is best done by reference to the map of Fig. 1. Names of lakes, ponds, and streams are as labeled on standard quadrangles of the U. S. Geological Survey (*11*), as are altitudes, distances from the central valley, and geographic coordinates.

Latitudinal zonation is based on our discovery of notably high DDE concentrations in the area from the higher altitudes in Yosemite National Park to the Sonora Pass area. This area lies from about 37°40′ north latitude to about 38°20′. Hence we have designated the zone between these limits as the Yosemite-Sonora zone. North of this we designate as the Northern Sierra Nevada. The area to the south being so much more extensive, we subdivide it at the 37°0′ parallel into the Central and the Southern Sierra Nevada.

The greater amount of data accumulated from the Central Sierra Nevada permits us to compare values from the lower altitudes (below 5,000 feet) with those from higher altitudes on the western slope of the mountains, and both of these with concentrations across the crest, on the eastern face, as shown in Tables 3, 4, and 5.

The first generalization emerging from these data is that contamination of the range is general. In fact, of the several hundred animals we have examined from throughout the mountains, all contained at least some DDE. The 3.46 ppm average of the low-altitude Central Sierra is not significantly different from the 3.19 ppm high-altitude average (Tables 3 and 4), suggesting that concentrations are fairly uniform from low to high altitudes on the western face of the mountains. The abrupt drop to an average of 0.97 ppm (Table 5) just across the crest of the mountains is what would be expected from the hypothesis that the DDT residues are carried eastward from the central valley and that concentrations in the mountains are related to precipitation patterns.

The higher concentrations in the central and southern parts of the mountains (averages of 3.19 ppm, 3.46

ppm, and 2.07 ppm shown in Tables 3, 4, and 6, respectively) as compared to concentrations found in the northern parts of the mountains (average of 1.32, Table 1) are consistent with the greater agricultural area and more intense agricultural activity in the southern half of the central valley. The lower concentration in the Southern Sierra Nevada zone (2.07 ppm) as compared with the Central Sierra Nevada zone is probably attributable to the presence of the Great Western Divide to the west of the former. This Divide extends as a ridge parallel to the main crest and rises to over 13,000 feet. All but one sample (Smith-Failing Meadow) are from the main crest, and their lower DDE concentrations as compared with areas just north of the Great Western Divide probably reflect the protection from DDT of the main crest by fallout on the Divide. It might be predicted that were this Divide to be systematically sampled and tested, it would show DDE values for this part of the Southern Sierra Nevada as high as or higher than those found in the Central Sierra Nevada zone where this type of protection of the main crest is lacking.

Particularly noteworthy is the high concentration of DDE in the Yosemite-Sonora area, averaging 5.38 ppm as compared with the average of 3.19 ppm immediately to the south of this area or the average of 1.32 ppm immediately to the north thereof. It might be suspected that the two extraordinary values of single samples, 16.52 ppm from a pond near Mt. Clark and 30.83 ppm from the Koenig Lake area (Table 2) are mainly responsible for this high average, and that if these are regarded as suspect values, the average DDE concentration in this zone is not significantly higher than in adjacent zones. However, even if these two values were eliminated from Table 2, the mean value would be 4.27 ppm, and the standard error of the mean would be reduced to 0.444. Comparing this mean and standard error with the 3.19 ± 0.27 mean and standard error of the zone just to the south of the Yosemite-Sonora zone by a t-test for the significance of the difference between means shows a real difference at between the 95% and 98% confidence levels. Hence, the indication is that levels in this Yosemite-Sonora zone are significantly higher than elsewhere. There are, in fact, good reasons for expecting greater variability in sample values in this zone than elsewhere (see discussion below), so that these two high values, which are based on the same methodology and as carefully done as any other determinations in the investigation, probably represent elements in this variability and should be left in the table.

The higher average value in this region would not be expected for at least two reasons. For one thing, the average distance of sample sites from the central valley, 82 miles, is greater in this zone than in any of the other zones except the low-concentration zone east of the Sierra Nevada crest (Table 7). For another thing, this zone lies east of the least agricultural part of the central valley due to the large part of this area occupied by the delta of the Sacramento and San Joaquin Rivers, an intermingling of swamps, channels, and small islands that occupy the greater part of the valley width in this region. Also, the urbanization immediately north and south of the delta area is much greater than elsewhere in the central valley, further reducing the intensity of agriculture in this part of the valley. It might be objected that the Yosemite-Sonora zone lies east of an enormous metropolitan area in which much DDT is employed. However, in such regions this material is applied largely within buildings, to gardens and patios, etc. by direct application rather than being applied, as in agricultural areas, in massive aerosol exposures by crop-dusting from airplanes.

Explanation of this unusual concentration seems to be provided by two reports (*12*) of the U. S. Forest Service. The first describes the application in 1953 of 11,024 lb of DDT in diesel oil to 11,140 acres of forest in the Tuolumne Meadows area of Yosemite National Park for control of the lodgepole needle miner. The second report describes the application in 1956 of 10,110 lb of DDT in diesel oil to 9,560 acres of timber in the Stanislaus National Forest for control of the Douglas-fir tussock moth. This acreage was distributed in several closely adjoining areas just to the west of Yosemite National Park and averaging about 10 miles north of the Mather area (Fig. 1). Forest sprayings have been unique in California; these two and one other north of the Sierra Nevada were the only ones found recorded. Hence, the unusual concentrations of DDE in the Yosemite-Sonora zone probably represent locally persistent residues of these 1953 and 1956 sprayings.

This interpretation is consistent with the few previous investigations on the persistence of DDT residues locally in the biota of a forest area. Dimond *et al.* (*3, 4, 5*), for example, found that following the spraying of forest areas in Maine at the rate of 1 lb/acre with DDT, the same rate as used in the 1953 and 1956 Sierra Nevada episodes, there was high concentration, especially of DDE, the first year following the forest application in the biota of the region (salamanders, crayfish, small mammals). A notable drop in concentration occurred the second year after application, but thereafter there was very little further decrease in concentration through a period of 9 years following application of DDT to the forest. These authors estimated that it would be well into the second decade following the forest treatment before there would be further significant drop in residue levels. Our interpretation of high levels in the frogs into the second decade following a forest application of DDT being due to this particular application is perfectly consistent with their findings.

Another feature worthy of note is found in one of the papers (*5*) of Dimond *et al.* This is the much greater

variability in DDT residue concentrations within populations following a single application of DDT than in populations repeatedly exposed or in populations subjected only to general residue drift through the environment. The high variability (2.96 - 16.52 ppm) in the population near Mt. Clark (Table 2) is probably a special consequence of the 1953 spraying episode (note position from geographic coordinates in Table 2 in relation to the Tuolumne Meadows, 1953 spraying). Similarly, the high variability (1.70 - 30.83 ppm) in the population of the Koenig Lake area (Table 2) is probably a consequence of the 1956 episode. This interpretation, at least, is consistent with the findings of the above cited authors and would explain the greater variability in levels found in the Yosemite-Sonora region as well as the greater average concentration present here as compared to that in other regions of the Sierra Nevada range.

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TABLES 1-7.—GEOGRAPHIC DISTRIBUTION OF THE OCCURRENCE OF *p,p'*-DDE IN FROG FAT BODIES (PARTS PER MILLION, WET WEIGHT). EACH *p,p'*-DDE VALUE FROM A SINGLE FROG EXCEPT IN TABLE 7

TABLE 1.—*Northern Sierra Nevada, north of 38°20'*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p'*-DDE
Sutter Creek, between Sutter Creek and Volcano Amador Co.	9/18/66	17	38°26'	120° 4'	1,720	1.44 1.55 1.10 0.89 1.18 0.94 0.39
Pond near Hiram Peak Alpine County	9/16/67	68	38°29'	119°48'	9,000	1.11 0.51
Pond near Kinney Lakes Alpine Co.	9/16/67	70	38°34'	119°49'	8,500	1.52 0.95
Five Lakes area Nevada Co.	9/1/66	55	39°25'	120°33'	7,000	3.04
Snag Lake Sierra Co.	7/15/67	62	39°40'	120°38'	6,680	1.64 0.75 1.02 2.79 1.43 0.53 2.13
Average Values		54			6,580	1.32 ± 0.16 n = 19

TABLE 2.—*Yosemite-Sonora area, 37°40′ - 38°20′*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p′*-DDE
Pond near Mt. Clark Mariposa Co.	7/2/66	72	37°42′	119°25′	9,880	16.52 9.94 2.96
Nydiver Lakes Madera Co.	8/29/68	89	37°42′	119°10′	10,160	2.00 2.50
Pond, Lyell Fork Merced R. Madera Co.	8/28/68	85	37°43′	119°16′	11,100	2.36 2.53
Pond, head Hutchings Cr. Madera Co.	8/27/68	84	37°44′	119°17′	10,960	7.75 6.40
Clark Lakes, Mono Co.	8/16/66	89	37°44′	119° 9′	9,800	5.89
Upper Lyell Base Camp Tuolumne Co.	9/4/66	84	37°46′	119°15′	10,160	5.89 3.57
Lake near Mt. Hoffman Mariposa Co.	8/25/68	73	37°51′	119°30′	9,840	7.56 9.45 5.22
Gaylor Lakes Tuolumne Co.	10/1/66	90	37°55′	119°16′	10,400	1.31 1.85
Pond near Lundy Pass Mono Co.	8/26/68	90	37°59′	119°18′	10,400	3.00 2.00
Greenstone Lake Mono Co.	8/26/68	90	37°59′	119°17′	10,150	4.30
Pond near Gianelli Tuolumne Co.	7/15/67	60	38°12′	119°52′	8,680	1.45 3.56
Upper Relief Valley Tuolumne Co.	8/3/66	63	38°14′	119°47′	8,800	5.45 9.47 4.06
Koenig Lake & vicinity Mono Co.	7/10/66	72	38°17′	119°38′	9,560	30.83 5.91 5.05 2.08 1.70 6.80 3.62 1.58 1.80 1.87
Average Values		82			9,992	5.38 ± 0.93 n = 35

TABLE 3.—*Central Sierra Nevada, 37°0′-37°40′, western slope, 5,000 ft. to crest*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p′*-DDE
Stevenson Creek, Fresno Co.	9/2/66	41	37° 6′	119°15′	5,420	3.79 2.93
Unnamed lake, McGee L area, off Evolution Valley Fresno Co.	8/28/67	76	37° 9′	118°43′	10,900	2.49 2.08 5.36 2.01 2.24
Red Lake Fresno Co.	7/3/67	58	37°11′	119° 5′	9,000	2.41 3.54
Goddard Canyon Fresno Co.	8/16/67	74	37°12′	118°47′	8,500	1.33 0.70
Darwin Canyon Fresno Co.	7/18/68	74	37°12′	118°41′	11,680	1.45 2.65
Dowville, Huntington L. Fresno Co.	8/14/67	55	37°14′	119°14′	6,959	4.42 2.75
Humphries Basin Fresno Co.	7/4/68	87	37°15′	118°42′	11,200	1.08 1.11
Dutch Lake Fresno Co.	7/4/67	71	37°15′	119° 0′	9,200	0.42 0.39
Pond, head of Line Cr. Fresno Co.	8/15/66	62	37°17′	119°11′	9,000	2.11 3.31
Rosebud Lake Fresno Co.	7/16/68	82	37°18′	118°54′	10,800	3.86 1.76

TABLE 3.—*Central Sierra Nevada, 37°0'-37°40', western slope, 5,000 ft. to crest*—Continued

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p'*-DDE
Pond NE of Kaiser Pk. Fresno Co.	8/14/66	63	37°18′	119°10′	9,800	9.07 5.81
Kaiser Pass Meadow Fresno Co.	7/12/67	68	37°18′	119° 6′	9,115	2.28 3.28
Bear Lakes Basin Fresno Co.	7/14/68	90	37°19′	118°48′	11,425	1.94 1.63
Lake near Infant Buttes Fresno Co.	7/20/68	83	37°20′	118°55′	10,400	2.68 3.47
Lake Italy Fresno Co.	7/11/68	92	37°22′	118°48′	11,154	4.22 5.14
Treasure Lakes Inyo Co.	8/22/68	97	37°23′	118°46′	11,160	4.41 5.14
Onion Springs Mdw. Fresno Co.	8/13/67	79	37°24′	119° 4′	7,840	4.35 3.88
Hedrick Meadow Fresno Co.	8/17/68	81	37°26′	119° 4′	9,040	1.30
Snow Lakes Fresno Co.	9/1/67	97	37°26′	118°47′	11,000	5.18 2.95 4.78 3.34
Devil's Bathtub Fresno Co.	8/27/67	85	37°27′	119° 0′	10,160	8.36
Graveyard Meadow Fresno Co.	8/30/66	87	37°27′	118°58′	10,000	3.03
Marilyn Lakes basin Fresno Co.	8/30/66	88	37°28′	118°59′	9,960	6.21 1.43
Duck Lake Fresno Co.	7/27/68	92	37°33′	118°58′	10,427	2.16 1.43
Average Values		77			9,745	3.19 ± 0.27 n = 48

TABLE 4.—*Central Sierra Nevada, 37°0′ - 37°40′, western face below 5,000 feet*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p'*-DDE
Big Creek, tributary So. Fork Kings River near Bretz Mill Fresno Co.	9/11/66	36	37° 2′	119°15′	3,240	2.89 4.35 2.52 4.19 3.17 2.03 3.69 2.41 3.80 3.61
Sycamore Creek Fresno Co.	9/11/66	32	37° 2′	119°19′	4,200	4.59 4.32
Average Values		34			3,720	3.46 ± 0.25 n = 12

TABLE 5.—*Central Sierra Nevada, 37°0′-37°40′, east of main crest.*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p′*-DDE
Bishop Creek canyon, near Long Lake Inyo Co.	10/14/67	83	37° 9′	118°27′	10,700	0.69 1.70 1.00 1.97
Chalfant L., Inyo Co.	7/10/68	94	37°21′	118°46′	11,200	0.06
Little Lakes Valley Mono Co.	8/20/67 8/1/66	100	37°26′	118°45′	10,400	1.12 0.77
Sherwin L., Mono Co.	8/9/68	96	37°37′	118°57′	8,560	0.73
Pond at Pumice Flat Madera Co.	7/3/66	89	37°39′	119° 5′	7,680	0.70
Average Values		92			9,708	0.97 ± 0.19 n = 9

TABLE 6.—*Southern Sierra Nevada, 36°0′ - 37°0′*

Location & County	Date	Miles to Valley	North Latitude	West Longitude	Feet Altitude	ppm *p,p′*-DDE
Smith-Failing Mdw. Tulare Co.	9/9/67	28	36° 9′	118°33′	7,440	1.97 2.32
Lower South Fork Lake Inyo Co.	7/24/68	60	36°28′	118°13′	10,990	1.90
Cottonwood Lakes Inyo Co.	7/23/68	59	36°29′	118°13′	11,120	0.73 2.23
High Lake, Inyo Co.	7/22/68	58	36°29′	118°14′	11,475	3.18
Mdw., Upper Rock Creek Tulare Co.	7/23/68	56	36°30′	118°16′	10,650	2.30 1.50
Pond at Crabtree L. Tulare Co.	9/18/68	55	36°33′	118°19′	11,500	2.10 1.50
Hitchcock Lakes Tulare Co.	9/19/68	54	36°34′	118°19′	11,750	2.77 1.84
Wright Lakes Tulare Co.	9/17/68	54	36°37′	118°22′	11,440	1.72
Pond at Tyndall Creek Tulare Co.	9/17/68	56	36°40′	118°23′	12,000	2.01 4.37
Pond, Vidette Canyon Tulare Co.	9/16/68	54	36°44′	118°24′	10,820	0.48 3.93
Kearsarge Lakes Fresno Co.	9/15/68	61	36°46′	118°24′	10,640	1.00 1.50
Average Values		54			10,893	2.07 ± 0.26 n = 19

TABLE 7.—*Summary of the occurrence of* p,p′-*DDE in fat bodies of frogs from the Sierra Nevada Mountains (parts per million, wet weight)*

Sierra Nevada Mountains	Avg. Feet Altitude	No. of Localities	Avg. Miles to Valley	No. of Samples	Average ppm DDE ± s.e.
Northern (North from 38°20′)	6,580	5	54	19	1.32 ± 0.16
Yosemite-Sonora (37°40′—38°20′)	9,992	13	82	35	5.38 ± 0.93
Central (37°0′-37°40′)					
West face to 5,000 feet	3,720	2	34	12	3.46 ± 0.25
West face over 5,000 feet	9,745	23	77	48	3.19 ± 0.27
East of crest	9,708	5	92	9	0.97 ± 0.19
Southern (36°0′—37°0′)	10,893	11	54	19	2.07 ± 0.26

Possible Selective Mechanisms in the Development of Insecticide-Resistant Fish [1]

Mack T. Finley, Denzel E. Ferguson, and J. Larry Ludke

ABSTRACT

Results of bioassays and gas chromatographic analyses show that populations of insecticide-resistant fish from near heavily treated cotton fields at Belzoni, Miss., are subjected to relatively brief irregular periods of selection after rains. Runoff from cotton fields increased mortality among caged susceptible and native resistant fish. Feeding of endrin-exposed and field-collected resistant mosquitofish (Gambusia affinis) *to resistant and susceptible green sunfish* (Lepomis cyanellus) *showed that selective pressure from residues in the food chain was minimal, compared with direct exposure, provided the consumer was resistant. Live-cage bioassays at top and bottom depths revealed no insecticide stratification in the water.*

Residue analyses revealed DDT and toxaphene as the two insecticides of selective importance. DDT and toxaphene residues increased in whole fish and water samples after runoff. High DDT values, compared with those of DDD and DDE, suggested recent contamination.

Introduction

Fish populations in areas with a history of insecticide contamination may be resistant to insecticides (*3, 6, 8*). The occurrence of small numbers of resistant individuals in susceptible populations, cross-resistance, and retention of resistance in several generations of progeny reared in the absence of insecticides suggest genetic resistance (*3*). Endrin resistance in mosquitofish (*Gambusia affinis*) was attributed to physiological toleration by Ferguson *et al.* (*9*) when no evidence of exclusion, excretion, or detoxication was found.

The selective process that produces resistant populations in nature is poorly known. Laboratory exposure of consecutive generations of mosquitofish to lethal levels of insecticides has yielded strains showing increased tolerances (*5*). In heavily contaminated environments supporting resistant populations, top piscivores such as largemouth bass (*Micropterus salmoides*) are absent, which suggests selection in the food chain through biological magnification. Presumably resistant fish, by accumulating and tolerating high levels of residues, aggravate the problem of pesticide accumulation in terminal trophic levels (*5*).

We investigated possible selective mechanisms, especially food-chain relationships and environmental exposure, in an attempt to determine the forces involved in resistance development. Our data suggest that insecticide contamination resulting from runoff is a major selective factor in the development of resistant fish populations.

Materials and Methods

A ditch draining about 2,800 acres of cotton fields near Belzoni, Humphreys County, Miss., was studied. The ditch averaged 7.6 meters in width and contained a deep accumulation of organic sediment. Water depth averaged about 50 cm but varied with runoff from adjacent fields.

During the growing season, surrounding fields receive weekly applications of DDT, toxaphene, endrin, and methyl parathion, either separately or in some combination. Insecticides enter the ditch as drift from ground applicators, in runoff following rains, and as direct

[1] Department of Zoology, Mississippi State University, State College, Miss. 39762.

contamination from aerial applications. Resistant fish species in the ditch include mosquitofish *(Gambusia affinis)*, golden shiners *(Notemigonus crysoleucas)*, green sunfish *(Lepomis cyanellus)*, and yellow bullheads *(Ictalurus natalis)*.

Susceptible mosquitofish, green sunfish, and black bullheads (*Ictalurus melas*) were obtained from insecticide-free ponds near State College, Oktibbeha County, Miss.

All fish were collected with a fine-meshed seine and held overnight in the laboratory prior to bioassay.

Water and fish samples (2 g) were analyzed for pesticide residues by gas chromatography (Barber-Coleman Pesticide Analyzer Model 5680). The columns used were as follows: (1) Mixed column consisting of 1.5% OV-17 plus 1.95% QF-1 coated on 100/120 Chromosorb WHP, ¼″ × 6′; (2) 10% Dow-200 coated on 80/90 Anachrome ABS, ¼″ × 6′. Operating conditions were: column temperature—198 C, detector temperature—210 C, injection port temperature—225 C, and a gas flow of about 90 ml/minute.

Extraction and cleanup procedures were those of Ferguson *et al.* (*9*), with the following modifications: (1) Hexane was substituted for pentane in extraction and column cleanup; (2) 750-ml water samples were extracted with 100 ml of hexane and shaken for about 12 hours on an Eberbach shaker. At times a technique described by Moats (*13*) was used to separate toxaphene and DDT. Reference standards were injected frequently. Recovery exceeded 75% from tissue samples and 90% from water; values reported are not corrected for recovery and are reported on an "as is" basis. All quantitations are based on peak height; thin-layer chromatography provided qualitative confirmation (*14*). Hexane and acetone were used as a solvent system; plates were coated with Silica Gel G impregnated with 0.2% fluorescein. Residues are reported as parts per million (ppm) wet weight.

Experimental procedures included: (1) feeding endrin-exposed resistant mosquitofish to resistant and susceptible green sunfish; (2) feeding field-collected resistant mosquitofish to susceptible green sunfish; and (3) live-cage assay of susceptible and resistant fish in the drainage ditch.

CONSUMPTION OF ENDRIN-EXPOSED RESISTANT MOSQUITOFISH

Technical grade endrin was prepared in a 1% acetone solution and diluted in tap water (pH 7.8, hardness—28 ppm, temperature 22 ± 2 C) to obtain desired concentrations. Resistant mosquitofish [36-hour TL_m-value (median tolerated limit) about 1.5 ppm endrin] were exposed for 24 hours to a 1.0 ppm solution of endrin in a 57.7-liter aquarium, transferred to tap water for 24 hours, and fed, one each, to resistant and susceptible green sunfish (36-hour TL_m—0.225 ppm and 0.005 ppm endrin, respectively). Each of 40 resistant and 40 susceptible green sunfish was kept in a separate gallon jar in 2 liters of tap water. Five controls from each population were fed unexposed resistant mosquitofish. Mortality was recorded at 3-hour intervals for a 96-hour period begining with ingestion. Death was determined when opercular movements ceased.

CONSUMPTION OF FIELD-COLLECTED RESISTANT MOSQUITOFISH

Susceptible green sunfish (average weight, 30 g) were fed a continuous diet of field-collected resistant mosquitofish. All fish were held in 57.7-liter aquariums at room temperature (22 ± 2 C). A maximum of four green sunfish were placed in each aquarium. Controls were fed susceptible mosquitofish from a pesticide-free environment. Since green sunfish were kept in groups, we were unable to determine the number of mosquitofish devoured by each individual. Tissue samples from dead and dying fish were analyzed for insecticide residues.

LIVE-CAGE ASSAY

Fish were placed in hardware cloth cages (6 and 33 mm mesh) in the drainage ditch at Belzoni. The cage dimensions were 60 × 60 × 10 cm, 60 × 60 × 15 cm, and 30 × 30 × 10 cm. Two cages, one barely submerged and the other resting on the bottom, were suspended from a stake driven into the mud at each of 11 stations. Stations were at 15.25-meter intervals along the center of the ditch.

Between August 1, 1966, and February 2, 1967, 196 susceptible green sunfish (2 to 5 cm in length) and 51 susceptible black bullheads (5 to 10 cm in length) were placed in the larger cages; while 104 resistant green sunfish (2 cm in length) were placed in the smaller cages as controls. Mortality was checked, and fish were added at frequent but irregular intervals to keep the number of live fish at 5 per cage.

Throughout the study, water and fish samples from the caging area were analyzed for insecticide residues. Water samples were taken about 8 cm below the surface in gallon jars.

Between August 9, 1968, and March 6, 1969, susceptible green sunfish (5 to 10 cm in length) were placed in a cage (180 × 60 × 30 cm) to obtain data on survival time and insecticide residue uptake of individual fish. The cage was visited weekly, and live fish were removed and whole body samples analyzed for residues. When mortality approached 70%, the remaining live fish were removed and 20 to 30 new fish added.

Results

CONSUMPTION OF ENDRIN-EXPOSED RESISTANT MOSQUITOFISH

The resistant and susceptible greenfish populations fed endrin-exposed resistant mosquitofish have a 45x difference in endrin tolerances. Susceptible green sunfish ranging from 6.25 to 19.25 g (average weight, 13.11 g) and resistant green sunfish ranging from 5.0 to 58.0 g (average weight 19.04 g) each consumed one mosquitofish (average weight, 0.31 g). All susceptible green sunfish died in 6.25 to 21.50 hours (an average of 11.75 hours). All resistant green sunfish and controls survived the 96-hour test.

Susceptible fish showed symptoms of poisoning (e.g., hyperactivity) soon after consuming the mosquitofish, and 36 of 40 regurgitated the mosquitofish prior to death. No apparent correlation between predator weight and survival time was evident. Resistant green sunfish exhibited no symptoms of poisoning, and all retained the ingested mosquitofish. Three samples (10 whole mosquitofish each) from the group that were consumed contained an average of 180 ppm endrin.

CONSUMPTION OF FIELD-COLLECTED RESISTANT MOSQUITOFISH

Of 20 susceptible green sunfish fed continuous diets of field-collected resistant mosquitofish 7 exhibited symptoms (e.g., hyperactivity, loss of equilibrium) for as long as 2 weeks before dying. Residues of DDT, DDT metabolites (DDD, DDE) and endrin found in four of the green sunfish are shown in Table 1. Although toxaphene was not quantitated, for reasons discussed by Bevenue and Beckman (2), typical multipeaked chromatograms confirmed its presence. The variation in amount of residues found in the dead fish (Table 1) may reflect differences in numbers of mosquitofish consumed.

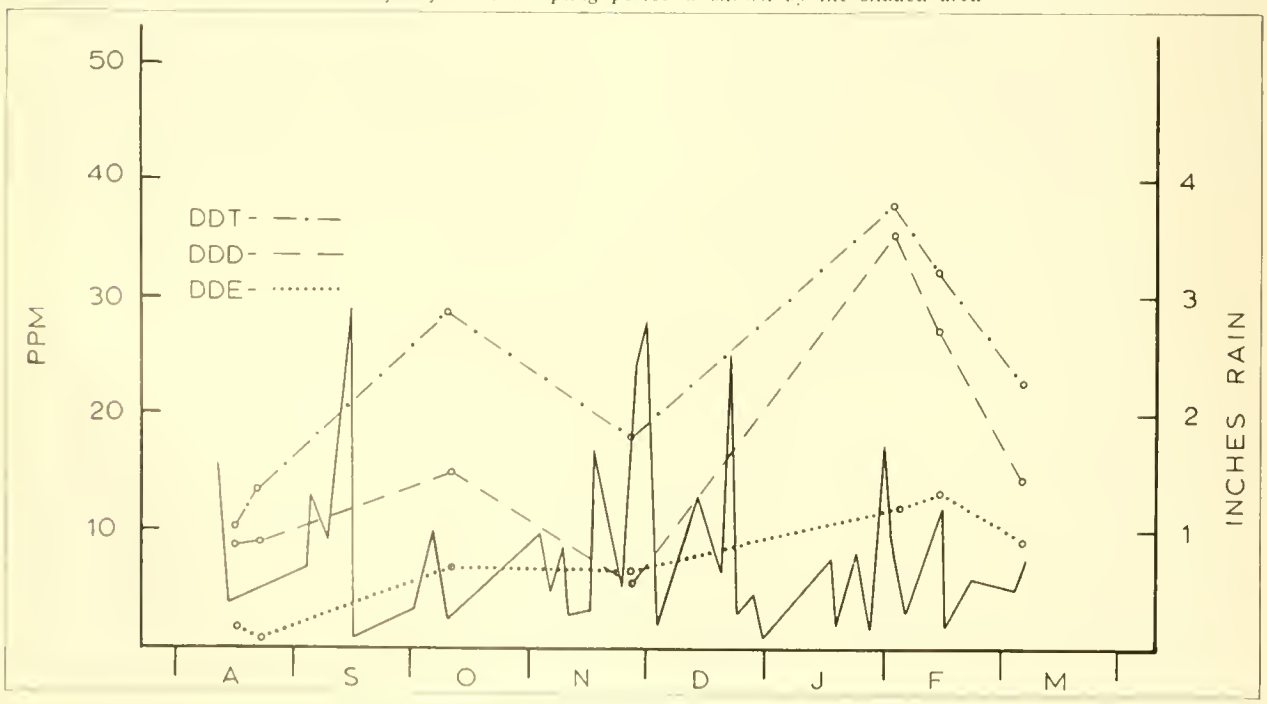
Table 2 shows monthly analyses of pooled samples of resistant mosquitofish. A comparison of Tables 1 and 2 reveals that the time required to kill susceptible green sunfish seemed to decrease as DDT and toxaphene residues increased in the resistant mosquitofish consumed. Water samples (Table 2) exhibit a similar increase.

Residues in resistant mosquitofish (Table 2) reflect the occurrence and amount of runoff after rainfall (Fig. 2). This is also supported by subsequent data shown in Fig. 1, for 1968-1969 mosquitofish samples. Also, relatively accurate toxaphene residue estimates were obtained for these samples. Toxaphene residues approaching 10, 80, 90, and 115 ppm were found in the August, October, November, and February samples, respectively.

LIVE-CAGE ASSAY

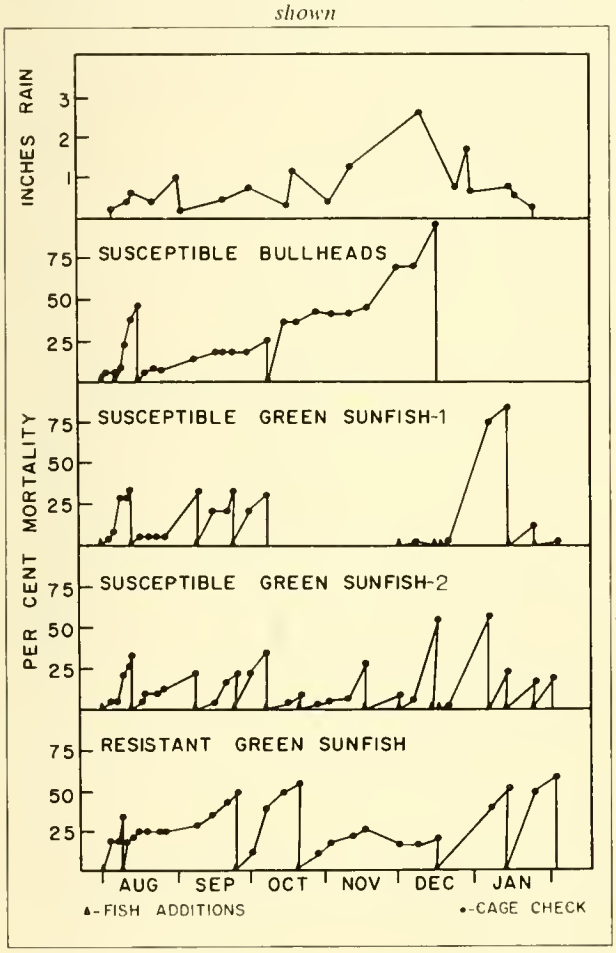
In the study ditch, fish were placed in cages near the bottom to detect possible stratification of insecticides. The number of fish used at the two depths were nearly equal (Table 3). All fish shown in Table 3 died during the caged period.

FIGURE 1.—*DDT and DDT metabolites (ppm) in whole body samples of resistant mosquitofish during 1968-1969—rainfall for the sampling period is shown by the shaded area*



Before December there was little runoff, and no drastic increase in mortality of caged fish (Fig. 2). Increased rainfall in December and January (6.0 and 1.6 inches, respectively) was accompanied by a marked increase in mortality of caged fish. The heavy runoff brought large quantities of mud and silt from adjacent cotton fields.

FIGURE 2.—*Percent mortality in fish during the 1966-1967 live-cage bioassay study—rainfall for the caging period is shown*



Water and fish samples (Table 2) showed a marked increase in DDT and toxaphene that was correlated with increased rainfall and mortality of caged fish (Fig. 2); DDD and DDE residues remained about the same. Extensive die-offs of native resistant fish in the study ditch, primarily yellow bullheads and green sunfish, were noted after the December rains and runoff. Dead fish were collected from the bottom with a 6-meter seine at the rate of 2 to 6 fish per each 10- to 12-meter haul. Numerous live but intoxicated fish were seen floating at the surface exhibiting symptoms similar to those observed in fish exposed to chlorinated hydrocarbons in the laboratory.

In February, after the 1966-1967 live-caging terminated, the ditch was visited when the water level was 1 meter above normal. A thin film of oil covered the water surface, probably the same oil used as a base in insecticide solutions applied on cotton crops. A yellow bullhead was collected that showed symptoms of insecticide poisoning, and a water sample (Table 2) showed the highest level of DDT residues recorded in water during the study.

In March, a pooled sample of resistant mosquitofish showed increased DDT residues (Table 2).

Additional live-caging of susceptible green sunfish in the Belzoni ditch during 1968-1969 (excluding the months of December and January) provided information regarding survival time and insecticide residue uptake by individual fish (Table 4). Live fish were kept longer than 8 days only on three occasions. No fish were living when weekly cage visits were made during September. The increase in DDT and metabolites (Table 4) in a living caged fish analyzed during early October reflects the first significant rainfall in September (Fig. 1). DDT and metabolite residues in native resistant mosquitofish also increased in the October sample (Fig. 1).

These data show that fish mortality, residue accumulation, and runoff after rainfall are closely related factors.

TABLE 1.—*Residues in whole body samples of individual susceptible green sunfish that died on a continuous diet of field-collected resistant mosquitofish (1966-1967)*

[— = no analysis; * = present, not quantitated]

Month Feeding Started	Days Fed	Residues in ppm				
		DDT	DDD	DDE	Endrin	Toxaphene
CONTROL						
Oct.	91	0.043	0.017	0.060	—	—
Oct.	97	0.223	0.147	0.216	—	—
TREATED						
Dec.	44	1.697	1.061	1.886	0.280	*
Dec.	7	1.176	2.353	0.784	—	*
Jan.	28	0.850	0.132	0.486	0.100	*
Jan.	28	0.622	0.462	0.616	0.312	*

TABLE 2.—*Monthly residue analyses of pooled samples (about 2 g) of native resistant mosquitofish and water from the Belzoni caging area (1966-1967)*

[T = <0.001; * = present, not quantitated; nd = not detected]

Sampling Period	Sample	Residues in ppm				
		DDT	DDD	DDE	Endrin	Toxaphene
Aug. 1966	Water	T	T	T	nd	nd
	Water	T	T	T	nd	nd
	Water	nd	nd	nd	nd	nd
	Water	nd	nd	nd	nd	nd
	Mosquitofish	1.531	1.480	1.240	0.540	nd
	Mosquitofish	0.640	0.850	0.800	0.400	nd
Sept. & Oct. 1966	Mosquitofish	1.786	3.701	2.834	T	nd
	Water	0.002	0.002	nd	0.001	nd
	Water	0.001	0.008	0.001	nd	*
	Water	T	nd	T	nd	nd
Nov. 1966	Mosquitofish	1.636	1.660	1.480	nd	nd
	Mosquitofish	2.380	nd	1.639	nd	nd
	Water	T	T	T	nd	*
Dec. 1966	Mosquitofish	4.444	2.080	0.347	0.058	*
	Water	0.006	nd	0.003	0.001	nd
	Water	0.004	nd	0.002	nd	nd
Feb. 1967	Water	0.012	T	T	0.002	*
Mar. 1967	Mosquitofish	15.000	3.175	4.960	nd	nd

TABLE 3.—*Number of resistant and susceptible fish used in top and bottom cages during the 1966-1967 live-cage assays*

Species	Population	Cage Size	Number of Fish Used		
			Top	Bottom	Total
Green Sunfish	Resistant	12" x 4"	49	55	104
Green Sunfish	Susceptible	24" x 4"	48	52	100
Green Sunfish	Susceptible	24" x 6"	45	51	96
Black Bullhead	Susceptible	24" x 6"	25	26	51

TABLE 4.—*Residues in whole body samples of individual susceptible green sunfish caged for a known number of days in the ditch at Belzoni (1968-1969)*

[T = <0.001; * = present, not quantitated; nd = not detected]

Date Removed	Days Caged	Residues in ppm				
		DDT	DDD	DDE	Total DDT	Toxaphene
Aug. 9	3	0.646	1.429	0.531	2.606	nd
Aug. 22	6	0.313	1.907	0.368	2.588	*
Oct. 10	15	1.386	7.395	0.801	9.582	*
Oct. 17	7	0.363	0.447	0.326	1.136	nd
Oct. 22	5	0.070	0.637	0.171	0.878	nd
Nov. 5	14	T	T	0.450	0.450	nd
Feb. 7	4	0.178	nd	0.143	0.321	nd
Feb. 15	8	0.392	0.232	0.222	0.846	*
Feb. 22	7	0.155	0.069	0.084	0.308	nd
Mar. 6	15	0.369	0.226	0.159	0.754	*

Discussion and Conclusions

Our observations suggest that insecticide contamination resulting from relatively brief periods of runoff from adjacent cotton fields constitutes the principal selective mechanism in the development of resistant fish populations in adjacent waters. Both residue analyses and mortality of caged fish reflect the increase in pesticides after rains. Ferguson *et al.* (7) previously reported mortality of resistant fish after runoff from heavily treated agricultural areas.

Throughout this study, residues in resistant mosquitofish increased whenever appreciable runoff occurred. The difficulty of keeping live-caged susceptible green sunfish in the drainage ditch longer than 7 to 8 days during rainy periods emphasizes the importance of runoff as a selective factor. The occurrence of fish kills involving native resistant fish in the drainage ditch substantiates this conclusion.

Selection after runoff may be brief, in part, because of the rapid disappearance of DDT and toxaphene from

water. Bridges *et al.* (*4*) found detectable amounts of DDT in water for only a short time after contamination. During heavy runoff, we recorded a marked increase in DDT and toxaphene. During the fish kill of December 1966, a water sample collected 7 days after the onset of rains contained 0.006 ppm DDT. A water sample taken in February 1967 during heavy runoff contained 0.012 ppm DDT. Presumably, high DDT residues, as contrasted with those of DDD and DDE, indicate recent contamination.

Chlorinated hydrocarbons adsorb on suspended solids (*1*), and presumably the silt contained in runoff from agricultural areas would tend to reduce insecticide availability to fish. Ferguson *et al.* (*10*) found that muds reduce the bioactivity of chlorinated hydrocarbon insecticides to fish by adsorbtion.

Susceptible predacious fish died when fed endrin-exposed and field-collected resistant mosquitofish. When resistant and susceptible green sunfish were each fed one endrin-exposed mosquitofish containing 180.0 ppm, all susceptible fish died in an average of 11.7 hours, while no ill effects were noted in the resistant fish. Regurgitation of the ingested mosquitofish by susceptible fish failed to prevent death.

Susceptible green sunfish died after being fed a continuous diet of field-collected resistant mosquitofish. Although a small number of green sunfish were fed, the time required to produce death in susceptible green sunfish appeared to decrease as DDT and toxaphene residues increased in the resistant mosquitofish. Normal body residues of resistant prey species could be fatal to susceptible predators, but there is no evidence that resistant predators experience selective mortality through the food chain.

The species of fish occurring in the study ditch exhibit levels of resistance ranging from 2 or 3x up to 1,500x to several insecticides and are capable of tolerating massive body burdens in their tissues (*9*). George (*11*) stresses the importance of biological magnification as a potential hazard to animals occupying a position at the top of a food chain. If selection occurred through the food chain, species in higher trophic levels should exhibit the highest levels of resistance. The fact that mosquitofish are the most resistant followed by golden shiners, green sunfish, and yellow bullheads shows that this is not the case. Analyses of stomach contents of larger specimens of green sunfish, which occupy the highest trophic level among fish in the ditch community, indicate that mosquitofish are a major dietary item. Residue accumulation in resistant mosquitofish under normal field conditions does not appear to harm resistant predator species. This suggests that selective pressure resulting from residues in the food chain is of little importance compared with direct uptake during heavy runoff.

Insecticide stratification in the water would appear to be a possible explanation for the interspecific differences in resistance; however, no such stratification was detected when fish were caged near the surface and on the bottom.

DDT and toxaphene were the major selective agents found. These two compounds, along with methyl parathion and endrin, were sprayed weekly during July, August, and September on cotton fields adjacent to the drainage ditch. Although endrin use has declined in the study area, the fish populations are more resistant to endrin, than to any other pesticide, presumably reflecting past use. Methyl parathion, used in extremely large quantities, was not detected in residue analyses. Henderson *et al* (*12*) concluded that organic phosphorus insecticides are not significantly toxic to aquatic organisms due to the rapid hydrolysis to nontoxic products. Since contamination results from runoff, which may not occur until several weeks after insecticide applications, the more stable chlorinated hydrocarbons are of greater importance in the development of resistance.

In highly contaminated environments, such as the one studied here, resistance appears to be essential for survival of fish populations.

See Appendix for chemical names of compounds mentioned in this paper.

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Insecticide Residues in Some Components of the St. Lawrence River Ecosystem Following Applications of DDD [1]

F. J. H. Fredeen[2] and J. Regis Duffy[3]

ABSTRACT

Residues of DDD (TDE) were measured in water, mud, fresh mollusks, and fish from the St. Lawrence River in 1967 during and after applications of DDD to control nuisance insects. The concentrations detected in water (up to 0.0139 ppm) ranged from 1 to 17% of those applied to the river 10 miles upstream. DDD concentrations in mollusks 17 miles upstream from the point of application and 10 and 45 miles downstream averaged 0.002, 0.101, and 0.0 ppm, respectively. In the same samples, concentrations of DDT and DDE combined (from unknown sources) average 0.030, 0.225, and 0.027 ppm. In edible flesh from 216 fish of 5 species, DDD residues averaged 0.156 ppm in samples collected 17 miles upstream and 0.369 in the combined samples from points 10 and 45 miles downstream. Residues of DDT plus DDE in these same samples averaged 0.224 and 0.227 ppm, respectively. The highest concentration of DDD in an individual fish was 1.81 ppm.

Introduction

In 1966 and 1967 an emergency program for the abatement of nuisance insects at the site of Expo 67 required six applications of DDD (TDE) to the St. Lawrence River at Montreal. The concentration of DDD achieved in each of 4 applications in 1967 averaged 0.38 ppm for 16 minutes. Similar dosages were used in 1966 although in one test a concentration of 0.17 ppm for 39 minutes was used. Altogether 36,831 lb of technical grade DDD were applied to the river; 6,188 lb on June 22, 1966; 6,075 on August 19, 1966; 6,813 on May 5, 1967; 5,625 on June 13, 1967; 5,930 on July 10, 1967; and 6,200 on August 7, 1967. Included in the research program for this project was a study of the subsequent distribution of the DDD residues derived in part from these applications, and the residues of DDT and DDE derived entirely from other sources. Information on other aspects of this study has been published elsewhere (*4*, *7*).

There have been many quantitative studies of residues of DDT and DDD in aquatic ecosystems in recent years, but very few of these have begun with applications of known amounts of these chemicals to the system investigated. Two of these studies involved the use of DDD to control nuisance insects in a lake and pond (*6*, *10*). Others involved the use of DDT in large rivers to control black-fly larvae. These proved that DDT was adsorbed onto suspended particles in the water and carried downstream at least 68 miles (*8*). Percentage kills of black-fly larvae were positively related to increased turbidity, presumably because larvae ingested particles with the adsorbed DDT.

Study Area

All six applications of DDD to the St. Lawrence River were from the Canada Department of Transport Ice Control Structure which spanned the river 1,000 feet upstream from the Champlain Bridge near Montreal. The DDD was applied as an emulsifiable concentrate across the entire river excepting 200 to 300 feet at each end of the structure, and in direct proportion to the volume flow through each of some 69 spans on the structure.

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[1] Publication No. 9 resulting from the World Exhibition Shadfly Project; Canada Department of Agriculture, Research Branch; Provincial Department of Agriculture, Quebec; and Canadian Corporation for the 1967 World Exhibition. Contribution No. 359, Research Station, Saskatoon.

[2] Research Station, Canada Department of Agriculture, Saskatoon, Saskatchewan, Can.

[3] Department of Chemistry, St. Dunstan's University, Charlottetown, Prince Edward Island, Can.

Samples for residue analyses were collected only in 1967. These were collected at three sites, one 17 miles upstream from the point of application and two downstream, 10 and 45 miles from the point of application. A site nearer than 10 miles would have been difficult to manage, especially for fish collections. The upstream site was located in Lake St. Louis about 0.5 miles west of the Chateauguay River in water about 15 feet deep. This site was in the mainstream of the St. Lawrence and was not influenced by water from either the Ottawa or Chateauguay Rivers. It was separated from the application site by about 11 miles of basins where the water flow was sluggish and the 6-mile long Lachine Rapids where the drop totaled some 40 feet.

The two downstream sites were located near the south end of Charron Island near Boucherville, and near Sorel.

The St. Lawrence River in the first 4 miles or so immediately downstream from the point of application consisted mainly of rapids, those in the vicinity of the Expo-67 site flowing up to at least 10 miles per hour. Here the riverbed consisted of loose boulders, gravel, and exposed argillite bedrock, clothed much of the time in filamentous algae (especially *Cladophora* sp.). Throughout the main part of the river, however, from Montreal to Sorel, the flow was relatively sluggish in a deep, wide channel navigable by ocean-going vessels. It was assumed that this section of the riverbed consisted of unconsolidated materials including considerable silt. In shallow areas near some shores there were beds of emergent vegetation.

The Boucherville site at the time of the first application was located east of the Ship Channel and near the geographic midpoint of the river. However, for subsequent applications the site was moved westward into the Ship Channel as a result of a study of the flow patterns of the river on June 6. Six drogues were released between piers 22 and 23 of the Ice Control Structure, the midpoint of the total volume discharge at that particular cross section. The point at which these drogues crossed the Louis Lafontaine Tunnel near Charron Island was thereafter used as the sampling point. Since the drogues crossed that site exactly 2.5 hours after leaving the Ice Conrol Structure, it was assumed that the front edge of each band of treated water would pass that site 2.5 hours after the commencement of each application of larvicide.

The residue sampling site at Sorel was located a few hundred yards upriver from the outfall of the Richelieu River and thus was not directly affected by its discharge. This site was about 400 yards from the southeast shore of the St. Lawrence and was in about 50 feet of water.

Materials and Methods

MATERIALS SAMPLED

Four kinds of material were sampled and analyzed: raw river water, riverbed silt, living mollusks, and living fish. Since concentrations of chlorinated hydrocarbon insecticide residues in living organisms are normally related to the position of the organism in the food chain, four trophic levels were sampled: (1) mollusks; (2) bottom feeding fish [suckers: *Cyprinus carpio* L., *Catostomus commersoni* (Lac.) and catfish: *Ameiurus nebulosus* (LeS.)]; (3) mixed feeders [perch: *Perca flavescens* (Mitch.) and bass: *Ambloplites rupestris* (Raf.)]; and (4) fish feeders [pike: *Esox lucius* L.]. All samples were collected by T. W. Beak Consultants Ltd., Montreal, and the residue analyses supervised by one of the authors (J.R.D.) at St. Dunstan's University, Charlottetown, P.E.I.

Samples of water were collected at each of the three sites prior to and after each application except for the first, when post-application samples were omitted. In addition, water samples were collected at the Boucherville site at 15-minute intervals throughout the calculated time of passage of each of the four bands of treated water. Also, following completion of all four applications in the autumn, water samples were collected from all three sites on August 11, September 1, October 1, and October 15. All water samples were collected in 1-gallon metal cans that had been thoroughly washed in acetone. The cans were opened beneath the surface to prevent the entrance of surface water.

One sample of riverbed mud approximately 6 inches deep was obtained with a conventional weighted core sampler from each of the three stations before and after the June 13 and July 10 treatments and before the August 7 application. The top 2 inches plus the silty water were placed in an acetone-washed can, frozen in dry ice on the day of collection, and stored at —20 C until analyzed.

Mollusks were collected on only three occasions: on April 24 to May 3 prior to all 1967 applications; on July 27 to August 1, after the third 1967 application; and in mid-November, about 3 months after the final application. At each of the 3 sites a minimum of 10 g were selected from a minimum of 4 dredge loads taken from each of 10 separate points. Snails (*Campeloma* sp.) were generally abundant but, where required, bivalves (*Pisidium* sp.) were included in the sample to make up the weight to 10 g. Each sample was frozen separately in foil in solid CO_2 on the day of collection and then stored at —20 C until analyzed.

Fish were collected with gill-nets once in May and once between September 5 and 15 at each of the three sites. At the Lake St. Louis site 10 specimens of each of

the three above-named kinds of fish were collected, but at the other two sites full quotas could not be obtained. The fish were frozen whole in foil in solid CO_2 and stored at —20 C until analyzed. The only part of each fish analyzed was a 10-g sample of flesh taken from the abdominal wall after the loose fat had been removed.

ANALYTICAL PROCEDURES

The extraction and cleanup procedures used were those of Onley (*13*); additional details for fish were described by Duffy and O'Connell (*5*). The cans of water were shipped via railway express 2 to 4 days after collection to Charlottetown, P.E.I. Upon arrival 1-liter samples were extracted immediately with 100 ml of hexane and the hexane layer re-extracted with 200 ml of acetonitrile. The acetonitrile extract was then diluted with 600 ml of water and extracted with 100 ml of petroleum ether. The combined petroleum-ether extracts were dried with anhydrous sodium sulfate, concentrated to a volume of 0.5 ml or less, and analyzed by gas-liquid chromatography.

The frozen mud samples were partially dried and then extracted by shaking with acetonitrile for 2 hours. The acetonitrile extract was diluted with 600 ml of water and extracted with 100 ml of petroleum ether. The petroleum ether extract was then washed with water, dried, concentrated to a small volume, chromatographed on a Florisil column, and analyzed by gas-liquid chromatography. An alternate gas chromatographic column was used for confirmatory tests. In addition, thin layer chromatography was used to confirm representative samples as in Duffy and O'Connell (*5*). Reproducibility was ± 8% depending upon how well cleanup was achieved.

Each frozen sample of mollusks was homogenized separately with 150 ml of acetonitrile for 5 minutes and the solid material filtered out and re-extracted with 50 to 75 ml of acetonitrile. The acetonitrile extracts were then partitioned between water and petroleum ether, washed, dried and evaporated, chromatographed on Florisil, and examined by gas-liquid chromatography.

Each 10-g sample of fish flesh was homogenized separately for 2 minutes in a Waring blender with 125 ml of acetonitrile and 30 g of anhydrous sodium sulfate. The homogenate was filtered and the solid material re-extracted by homogenizing with 100 ml of acetonitrile. The filtrates were then combined in a separatory funnel with 600 ml of water and 100 ml of petroleum ether and the procedure followed as described above.

The following percentage recoveries were obtained when the chemicals were added to 10-g samples of fish, extracted, and analyzed as above: DDT—70 to 85%; DDD—80 to 90%; and DDE—80 to 95%. The lower limit of detection was 0.01 ppm. The data presented in Tables 1 to 4 inclusive were not corrected for percent recovery.

Results and Discussion

RESIDUES IN WATER

No DDD was detected in the samples of water collected at Boucherville during the first treatment in 1967, presumably because the samples were not collected at the proper time. The sampling period was corrected following a study of the river flow patterns using drogues on June 6. Thus during the second treatment on June 13, DDD was detected in the Boucherville water samples throughout a 3.75-hour period in concentrations up to 13.9 ppb. This peak value occurred 1.5 hours after the arrival of the leading edge of the treated water. The total dosage reaching this point was calculated to have been about 17% of that applied 10 miles upstream.

During the third 1967 treatment on July 10, concentrations of 0.17 to 2.21 ppb of DDD were detected throughout a 2.25-hour period. The peak occurred about 15 minutes after the arrival of the leading edge of the treated water at that point. The total dosage at Boucherville was calculated to have been only 1% of that applied 10 miles upstream. During the fourth 1967 treatment on August 7, concentrations of 0.1 to 3.3 ppb of DDD were detected throughout a 5.25-hour period with the peak concentration occurring in a sample collected 2.25 hours after the leading edge of the treated water had passed the sampling point. The total dosage at Boucherville was calculated to have been 4% of that applied 10 miles upstream.

Most or all of these losses must have been caused by adsorption of the DDD onto vegetation and the riverbed. The rock rubble on the riverbed was clothed in algae and diatoms at all times. Strands of a filamentous alga, *Cladophora* sp., measured up to 16 inches long.

During the test of June 22, 1966, the larvicidal effect of the treated band of water was also observed to decline rapidly as it passed downriver through the study area. Thus at distances of 2.0, 3.0, and 3.5 miles downstream from the point of application, populations of aquatic insect larvae were reduced by 91, 75, and 30%, respectively.

This relatively rapid loss of DDD from each treated band of water was to be expected in view of reports by several authors of similar rapid losses of DDT from aqueous suspensions (*2, 3, 8, 14*).

With only one exception, DDD was detected in water from the St. Lawrence River at Boucherville only during the bands of treated water past that site. This exception occurred on July 11 at Boucherville when 0.52 ppb was detected. DDD was never detected in any of the water samples collected at Lake St. Louis or Sorel. Additionally, contamination of the river water with DDT and DDE was indicated on October 11, 1967, when water samples from all three sites contained combined DDT and DDE residues of 0.05, 0.09, and 0.03 ppb, respectively. No DDD was detected in these samples, and thus the residues did not originate with the larvicide applications.

RESIDUES IN MUD

Of the 15 samples of mud collected in 1967 from the three sites before and after both of the June 13 and July 10 treatments as well as before the August 7 treatment, DDD was recovered only on one date, June 15. On that date mud from the untreated check site at Lake St. Louis contained 0.02 ppm, the Boucherville mud contained 0.05 ppm, and the Sorel mud 0.07 ppm. No DDT or DDE was recovered from any sample.

RESIDUES IN MOLLUSKS

Clams and/or snails from all three areas in 1967 contained residues of DDT and/or DDD and DDE on April 24 to May 3 (prior to the first application of DDD on May 5) (Table 1). The DDD residues in the samples from Boucherville may have been partly derived from the two DDD applications in 1966. Those from Lake St. Louis could only have originated from some other source. The DDT and DDE in all three samples also originated from some external source.

The second series of samples, taken on July 21 to August 1, about 2 weeks after the third 1967 application of DDD, showed increased average residue levels at Lake St. Louis but decreased residues at the two downriver sites. Thus at this time higher residue concentrations occurred in mollusks from Lake St. Louis than from either of the two sites downriver from the application point.

The third series of samples, collected in November, showed a slight increase in combined residues at Lake St. Louis and Sorel and a large increase at Boucherville. The increase in the Boucherville average was due entirely to an unusually high concentration of DDT in 1 of 12 samples collected at that time. This "hot" sample contained 5 times the total amount of residues as were found in all of the other 11 samples combined and more than 60% of the residue was DDT (from sources other than the shadfly larvicide applications). Some probable sources of these residues are discussed below.

In summary, in samples collected between late April and mid-November, an average of only 0.002 ppm of DDD was detected at Lake St. Louis, 0.101 ppm from Boucherville, and none from Sorel (Table 1). Combined residues of DDT, DDE, and DDD at these same three sites averaged 0.032, 0.326, and 0.027 ppm, respectively, indicating that 69+% to 100% of the combined residues originated from sources outside the larvicide treatments.

RESIDUES IN FISH

On May 1, 1967, prior to any applications of DDD that year, residues of DDT and its breakdown products, DDD and DDE, for the most part were present in all species of fish (three trophic levels) collected from Lake St. Louis and Sorel, and concentrations were higher than in any post-treatment samples of fish (Tables 2 and 3). No fish were obtained from Boucherville at this time. Possibly some of the DDD originated from the two applications made in 1966. However, all of the DDT and DDE, and some of the DDD, must have originated from some other source or sources.

Concentrations of DDD and of the combined residues of DDT, DDD, and DDE in the edible flesh of most species of fish from each of the three sites (with the principal exceptions of pike from Lake St. Louis and perch from Sorel) were considerably smaller in September than at the beginning of the season. Increases in DDD concentrations had been expected rather than the observed decreases because of the four DDD applications during the summer. In a previous study by Bridges *et al.* (*3*) maximum residue concentrations in trout occurred 1 month after an application of DDT to a reservoir. Thus the DDD concentrations in fish in the St. Lawrence River were expected to show further declines after mid-September, until pretreatment levels were attained.

Despite combined residue concentrations that were considerably higher in fish than in mollusks, 11.5% of the fish collected contained no detectable residues, and another 9.3% contained residues of less than 0.05 ppm.

No one fish of the 216 analyzed was considered to be unfit for human consumption by its DDD content alone. The highest concentration discovered was 1.81 ppm in a pike collected at Boucherville on May 30, 1967 (Table 3). Only one fish contained combined residues of DDT, DDD, and DDE at the 7.0 ppm level. This was a perch collected at Sorel on May 1 (prior to any of the 1967 applications). Out of the 7.3 ppm of combined residues in this fish, 6.4 ppm (88%) were DDT, and only 0.9 ppm (12%) were DDD.

It had been expected that pike would have contained the highest concentrations of residues because of their position near the end of the food chain. However, suckers and catfish generally contained the highest concentrations, probably because they fed on the riverbed upon insects disabled by these insecticides.

COMPARISONS OF RESIDUES UPRIVER AND DOWNRIVER FROM MONTREAL

Average residue concentrations in mollusks and fish from the Lake St. Louis site are compared with those from the Boucherville and Sorel sites for the entire 1967 sampling season in Table 4. In summary, in snails and clams, average concentrations of all three chemicals combined were 0.032 ppm (of which 6% was DDD) above Montreal and 0.198 ppm (29% DDD) below Montreal. In all fish combined, average concentrations of total residues were 0.376 ppm (of which 42% was DDD) above Montreal and 0.595 ppm (62% DDD) below Montreal.

SOURCES OF RESIDUES

An analysis of technical grade DDD indicated that it contained 1.6% *p,p'*-DDT. Thus at least 98.4% of the DDT and DDE residues discovered in the water samples, mollusks, and fish must have originated from sources separate from the DDD applied in the shadfly abatement project. Furthermore, a portion of the DDD residues must also have originated as metabolites from this "background" DDT rather than from the DDD applications. Several authors have reported the occurrences of both DDE and DDD in soils that have been treated with DDT. Miskus *et al.* (*12*) reported the conversion of DDT to DDD by lake water and reduced porphyrins.

Large amounts of DDT were used for many years in the Great Lakes drainage basin for the control of insect pests of forests, orchards, cereal, and vegetable crops, and in mosquito and black fly control projects. At Montreal and in other areas DDT was also used for control of the elm bark beetle. On St. Helen's Island alone, between 1965 and 1967, it is estimated that more than 6,000 lb were used annually.

Mack *et al.* (*11*) detected DDT in concentrations ranging up to 40 ppm in selected tissues of several species of fish, collected in part from the Richelieu River drainage basin. Residues of DDT, DDE, DDD, and other organochlorine pesticides were detected in mud, amphipods, and various fish and water birds in Green Bay at Lake Michigan adjacent to a 400-square-mile area of Wisconsin where an estimated 30 tons of DDT and 15 tons of DDD among other insecticides were used annually (*9*). Lakebed mud in Green Bay contained an average of 0.014 ± 0.005 ppm of DDT and metabolites of which 43% was DDT, 36% DDE, and 21% DDD. Fish contained up to 7.87 ppm of residues (35% DDT, 56% DDE, and 9% DDD). DDD and DDE in amounts of up to about 2.0 ppm each and DDT in larger amounts have also been detected in mackerel caught in Canadian Atlantic coast waters (*5*). Related discoveries are also reviewed in this paper.

There are numerous other instances where DDT, DDE, and DDD have been detected in natural waters and their aquatic biota, whether or not DDT was used in nearby terrestrial and aquatic insect pest control projects. Thus despite the low level of solubility of DDT in water (1.2 ppb or less at 25 C) (*1*), it is not surprising that DDT and its metabolites were detected in this current study in biota of the St. Lawrence River. If the average background concentration of DDT and metabolites in the water was only 0.001 ppm during the 15-month period between the first and last applications of DDD (June 1966 to August 1967, inclusive), then the 36,831 lb of DDD added only 6% to this load during this period.

PROBABLE POST-TREATMENT RESIDUE CONCENTRATIONS

DDD concentrations in the riverbed and vegetation following the last application were not determined but presumably declined steadily to pre-treatment levels. Following an application of DDD to a pond to control chironomids, 88% of the DDD in the bottom mud disappeared within 10 months (*6*). This pond had a slow flow of water through it. Similarly, 98% of an accumulation of DDT and metabolites in the bottom mud of a reservoir and in vegetation disappeared in 8 weeks and 12 months, respectively, after a 0.02 ppm treatment with DDT (*3*). This occurred apparently without the benefit of a flow of water out of the reservoir.

The concentrations of DDD in fish were also expected to decline steadily (*3*) from the levels detected in 1967. This process had already begun by the middle of September as indicated by the lower average DDD concentrations in most fish at that time than in May 1967 (Table 2).

In Clear Lake, Calif., concentrations of DDD of up to 221 ppm were detected in the edible flesh of fish following three applications of DDD in 9 years totaling 163,000 lb (*10*). A comparable buildup was not expected to occur in fish in the St. Lawrence River, (a) because much less DDD was used and (b) because of the enormous flushing effect of this river (an average volume discharge throughout the 15 months from June 1966 to August 1967 of 265,000 cfs.

The ultimate fate of the DDD, i.e., its conversion to materials with reduced toxicities, is poorly understood. DDD is itself a product of the reductive dechlorination of DDT in nature.

TABLE 1.—*DDT, DDE, and DDD residues in snails and clams collected from the St. Lawrence River in 1967*

Date	Sample Type [1]	No. of Samples	DDT		DDE		DDD		Combined Residues		
			Avg. ppm	% Positive Samples	Avg. ppm	% Positive Samples	Avg. ppm	% Positive Samples	Avg. ppm	Max. ppm	% Positive Samples
LAKE ST. LOUIS (15 miles upriver from the point of application)											
4/24-5/3	Snails and clams	8	0.000	0	0.013	38	0.000	0	0.013	0.060	38
7/27-8/1	Snails	10	0.006	20	0.028	100	0.005	10	0.039	0.130	100
November	Clams	10	0.006	10	0.036	90	0.001	10	0.043	0.130	90
Total		28	0.004	11	0.026	79	0.002	7	0.032	0.130	79
BOUCHERVILLE (10 miles downriver from the point of application)											
4/24-5/3	Snails	6	0.010	17	0.085	50	0.022	33	0.117	0.400	50
7/27-8/1	Snails	10	0.000	0	0.000	0	0.007	10	0.007	0.070	10
November	Snails	12	0.398	67	0.078	67	0.219	67	0.695	6.960	67
Total		28	0.173	32	0.052	39	0.101	39	0.326	6.960	43
SOREL (45 miles downriver from the point of application)											
4/24-5/3	Snails	4	0.018	25	0.028	50	0.000	0	0.046	0.13	50
	Snails and clams	3	0.000	0	0.000	0	0.000	0	0.000	0.00	0
7/27-8/1	Snails	10	0.000	0	0.026	30	0.000	0	0.026	0.09	30
November	Snails	4	0.008	25	0.025	100	0.000	0	0.033	0.06	100
Total		21	0.005	10	0.022	43	0.000	0	0.027	0.13	43

[1] Clams = *Pisidium* sp.; snails = *Campeloma* sp.

TABLE 2.—*DDT, DDE, and DDD residues in fish collected from the St. Lawrence River in 1967*

[T = Trace, <0.01 ppm]

Date	Species of Fish [1]	No. of Fish	DDT		DDE		DDD		Combined Residues		
			Avg. ppm	% Positive Fish	Avg. ppm	% Positive Fish	Avg. ppm	% Positive Fish	Avg. ppm	Max. ppm	% Positive Fish
LAKE ST. LOUIS (15 miles upriver from the point of application)											
5/1	Sucker	12	0.209	50	0.652	58	0.287	75	1.148	4.73	75
	Perch	12	0.102	33	0.052	25	0.330	50	0.484	1.31	58
	Pike	15	0.027	20	0.000	0	0.044	27	0.071	0.50	47
5/30	No samples collected										
9/5-9/15	Sucker	10	0.009	20	0.114	60	0.132	100	0.255	0.74	100
	Perch	10	0.001	20	0.055	40	0.063	100	0.119	0.33	100
	Pike	11	T	27	0.091	55	0.084	100	0.175	0.48	100
Total		70	0.065	29	0.159	37	0.156	71	0.376	4.73	77
BOUCHERVILLE (10 miles downriver from the point of application)											
5/1	No samples collected										
5/30	Catfish	30	0.117	60	0.168	100	0.537	100	0.822	1.92	100
	Perch	20	0.009	80	0.006	85	0.436	100	0.582	0.99	100
	Pike	4	0.378	100	0.425	100	1.310	100	2.113	2.92	100
9/5-9/15	Catfish	5	0.000	0	0.000	0	0.550	100	0.550	1.22	100
	Bass	26	0.018	12	0.048	62	0.246	100	0.312	0.87	100
	Pike	2	0.000	0	0.020	100	0.070	100	0.090	0.10	100
Total		87	0.083	48	0.108	79	0.451	100	0.642	2.92	100

TABLE 2.—*DDT, DDE, and DDD residues in fish collected from the St. Lawrence River in 1967*—Continued

[T = Trace, <0.01 ppm]

Date	Species of Fish [1]	No. of Fish	DDT		DDE		DDD		Combined Residues		
			Avg. ppm	% Positive Fish	Avg. ppm	% Positive Fish	Avg. ppm	% Positive Fish	Avg. ppm	Max. ppm	% Positive Fish
SOREL (45 miles downriver from the point of application)											
5/1	Sucker	10	0.331	80	0.323	80	0.404	80	1.058	3.14	80
	Perch	12	0.546	17	0.013	8	0.178	42	0.737	7.30	42
	Pike	10	0.097	50	0.231	90	0.267	90	0.595	3.21	100
5/30	No samples collected										
9/5-9/15	Sucker	10	0.000	0	T	10	0.113	100	0.113	0.36	100
	Perch	10	0.000	0	T	10	0.340	100	0.340	0.61	100
	Pike	7	0.014	29	0.017	29	0.123	100	0.154	0.32	100
Total		59	0.186	29	0.099	37	0.241	83	0.525	7.30	85

[1] Suckers = *Cyprinus carpio* L.; and *Catostomus commersoni* (Lac.); catfish = *Ameirus nebulosus* (LeS.); perch = *Perca flavescens* (Mitch); pike = *Esox lucius* L.; Bass = *Ambloplites rupestris* (Raf.).

Note: The portion of the fish analyzed consisted of a 10-g strip of flesh from the abdominal wall, free of loose fat.

TABLE 3.—*Maximum concentrations of DDD detected in individual fish from the St. Lawrence River, 1967*

Collection Date	Sucker		Catfish		Perch		Bass		Pike	
	Max. Conc. (ppm)	No. in Sample	Max. Conc. (ppm)	No. in Sample	Max. Conc. (ppm)	No. in Sample	Max. Conc. (ppm)	No. in Sample	Max. Conc. (ppm)	No. in Sample
LAKE ST. LOUIS										
5/1	1.23	12	—	0	1.40	12	—	0	0.50	15
9/5-9/15	0.40	10	—	0	0.12	10	—	0	0.21	11
BOUCHERVILLE										
5/30	—	0	1.27	30	0.81	20	—	0	1.81	4
9/5-9/15	—	0	1.22	5	—	0	0.71	26	0.08	2
SOREL										
5/1	1.10	10	—	0	0.90	12	—	0	1.30	10
9/5-9/15	0.36	10	—	0	0.61	10	—	0	0.45	7

TABLE 4.—*Average concentrations of DDT, DDE, and DDD in shellfish and fish in the St. Lawrence River, Quebec, May through November 1967*

Material Analyzed [1]	No of Samples	Average Concentration per Sample (ppm)				Proportion of Samples Containing Residues (%)			
		DDT	DDE	DDD	Combined Residues	DDT	DDE	DDD	Combined Residues
LAKE ST. LOUIS									
Snails and clams	28	0.004	0.026	0.002	0.032	11	79	7	79
Suckers and catfish	22	0.118	0.408	0.217	0.740	36	59	86	86
Perch and sunfish	22	0.056	0.053	0.209	0.318	30	35	73	77
Pike	26	0.016	0.039	0.061	0.115	25	25	58	69
Total (fish)	70	0.065	0.159	0.156	0.376	29	37	71	77
BOUCHERVILLE AND SOREL COMBINED									
Snails and clams	49	0.100	0.039	0.058	0.198	22	41	22	43
Suckers and catfish	55	0.124	0.151	0.437	0.710	49	73	96	98
Perch and sunfish	68	0.129	0.038	0.306	0.470	31	51	90	90
Pike	23	0.112	0.182	0.388	0.681	48	74	96	100
Total (fish)	146	0.124	0.103	0.369	0.595	40	63	80	95

[1] Each sample of snails and clams consisted of 10-g of whole shellfish; each sample of fish consisted of a 10-g sample of flesh from the abdominal wall after loose fat had been removed.

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Occurrence of Organochlorine Insecticides in Pheasants of South Dakota [1]

Raymond L. Linder and Robert B. Dahlgren

ABSTRACT

Residues of benzene hexachloride, lindane, dieldrin, DDT, DE, and DDD occurred among 12 of 100 adult pheasants collected in a baseline study during the winters of 1964-67 in the eastern half of South Dakota. DDE was most commonly found, and residue levels of all chemichl ranged from 0-8.0 ppm.

Residues of dieldrin, aldrin, heptachlor epoxide, DDT, DDE, DDD, lindane, and endrin were found in adults, juveniles, or eggs collected in 1967 from study areas in Yankton and Clay Counties where past pesticide usage was highest in the State. Organochlorines occurred in fat or brain of all 48 adult birds collected, with dieldrin and aldrin occurring most frequently. Only two adults contained more than 1 ppm of any one insecticide, and detectable levels ranged from 0.01 ppm to 2.35 ppm for all residues combined. All juveniles contained residues of at least one chemical, and levels were as high as 1.21 ppm for all residues combined. All except 5 of 70 eggs contained residues of at least one insecticide, and dieldrin and heptachlor epoxide occurred more often than other chemicals. The highest concentration of any one chemical was 1.58 ppm of dieldrin in one egg. All residues combined ranged from 0.01 ppm to 2.01 ppm for eggs.

Introduction

To establish a baseline for determining changes in residue levels of chlorinated hydrocarbon insecticides in future years, adult pheasants were collected from 24 counties in eastern South Dakota between 1964-67.

Birds and eggs were also taken from study areas in southeastern South Dakota in 1967 to determine residue levels occurring in areas of highest pesticide use in the State. Chlorinated hydrocarbons had been used in Clay and Yankton Counties during the past 5 years, primarily on corn which was the principal crop and occupied 31% of the farmland acres. Before 1964, aldrin was used routinely at about ½ lb/acre on about 80% of the cropland. Since 1964, an estimated 50% of the cornland received aldrin or heptachlor at about 1 lb/acre every third year (*B. H. Kantack, Extension Entomologist, South Dakota State Univ., Brookings, S. Dak., personal communications, 1968.*)

Procedures

One hundred adult pheasants were shot from 24 counties for the baseline study during the winters from 1964 to 1967. Fat samples were removed from each bird and frozen in glass vials. Analyses were made by State Chemist D. J. Mitchell at Vermillion, S. Dak. according to methods described in the FDA Pesticide Analytical Manual (*3*). Concentrations were determined at the 0.05 ppm level and above.

In February 1967, 26 adult hens and 22 adult cocks were collected from four 9-square-mile study areas in southeastern South Dakota (Yankton and Clay Counties). The center sections of the areas were designated as T95N, R54W, S35-Area 1; T94N, R56W, 56-Area 2; T93N,, R53W, S4-Area 3; and T97N, R52W, S5-Area 4. Seventy eggs and 14 juveniles were also collected from the same areas the following spring and summer.

[1] South Dakota Cooperative Wildlife Research Unit, South Dakota State University, Brookings, S. Dak. 57006. The Cooperative Wildlife Research Unit is supported jointly by the South Dakota Dep. of Game, Fish, and Parks, the U. S. Bureau of Sport Fisheries and Wildlife, South Dakota State Univ., and the Wildlife Management Institute.

Brain and fat samples were removed from each adult bird, frozen and stored in glass vials. Spectran Laboratories, Denver, Colo., analyzed the tissues by methods then currently in use by the Wildlife Research group, U.S. Fish and Wildlife Service, Denver Federal Center (*L. D. Frederickson, Jr., Spectran Laboratories, Inc., Denver, Colo., personal communication, March 28, 1967*). Weighed samples were ground with sodium sulfate followed by extraction using Soxhlet apparatus and 10% ether in petroleum ether; evaporating to dryness; partitioning using hexane-acetonitrile; evaporation of acetonitrile to dryness; column cleanup using a MgO-Celite chromatographic column; dilution of residues to proper volume with hexane; and gas chromatography on both Dow-11 and QF-1 columns. Results were raised by the factor 1.2 to compensate for loss in recovery. One milligram of original sample to 1 microliter was used for chromatographic injection. Standards were used every five or six samples to check drift of temperature and response of the detectors used.

One to three eggs were taken from each of 37 nests during May and June, and juvenile wild pheasants from 5 to 8 weeks of age were collected in July. Brains were analyzed from young birds, and crop material was pooled into one sample of animal material and one of plant material. Analyses of brains and crop material from young birds and whole eggs minus shells were carried out by the Experiment Station, Biochemistry Department, South Dakota State University (*2*). Samples were analyzed by gas-liquid chromatography using Dow-11 and QF-1 silicone columns. Extraction and cleanup were accomplished by Florisil columns. To further verify the identification of insecticides, approximately 20% of the samples were also analyzed by thin-layer chromatography.

The efficiency of extraction of the insecticides was: lindane, 100%; heptachlor, 67%; aldrin, 99%; heptachlor epoxide, 89%; dieldrin, 74%; DDE, 74%; DDD, 81%; DDT, 78%, and endrin, 85%. Values reported have not been corrected for percent recovery, and if insecticide concentration was <0.03 ppm for DDT and endrin and <0.01 ppm for other chlorinated hydrocarbons, values are reported as "not detectable" (nd).

Results and Discussion

Chlorinated hydrocarbons or their metabolites were found in 12 of 100 birds in the baseline sample (*1*). DDE was most commonly found, averaging 1.09 ppm and ranging from 0.24-2.25 ppm among six birds. Benzene hexachloride amounting to 8.0 ppm was found in one bird. DDD and lindane were each found as traces (<0.05 ppm) in two birds. Dieldrin was found as a trace in one bird and 0.1 ppm in another. These levels are quite comparable to those reported in pheasants analyzed from central South Dakota by Greichus *et al.* (*2*).

At least one chlorinated hydrocarbon occurred in each adult bird collected in southeastern South Dakota in 1967 (Tables 1 and 2). Dieldrin and aldrin occurred most frequently. Of 48 birds collected, only two contained more than 1 ppm of any one insecticide. Differences between levels in fat and brain of individual birds varied. In some cases residues were higher in brain than in fat.

Differences in residue levels between collection sites were not great, and birds taken on a State-owned area where pesticides were not used had about the same levels as other areas. This probably resulted from bird movements. Differences in residue levels between sexes also fluctuated between areas.

All young contained residues of at least one chemical (Table 3). Combined residues in one individual totaled more than 1 ppm. Animal material, consisting chiefly of grasshoppers, made up 22% of the contents in the crops and contained only DDT. Plant material, almost entirely farm crops, contained dieldrin, DDD, and DDT.

Dieldrin and heptachlor epoxide occurred in eggs more frequently than any other chemical (Table 4). Levels of combined insecticides between periods of collection and between areas were similar. DDT, DDD, and DDE occurred in a greater percentage of eggs than in the hens the same year. Lindane also occurred frequently in eggs but in only two hens. Differences between levels in adults and eggs may have been due to small samples or additional pesticide ingestion by adults between winter and breeding season.

Acknowledgments

Birds were collected in the eastern half of the State by South Dakota Department of Game, Fish, and Parks personnel. Collections on study areas in the southeast were made under South Dakota Agricultural Experiment Station Project 438, Journal Series Number 917.

See Appendix for chemical names of compounds mentioned in this paper.

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TABLE 1.—*Chlorinated hydrocarbons in hen pheasants collected from southeastern South Dakota in February 1967*

[nd = not detectable, <0.01 ppm]

Compound	No. of Hen Pheasants with Detectable Residues		Residues in PPM			
			Average [1]		Range	
	Fat	Brain	Fat	Brain	Fat	Brain
AREA 1 (7 HENS)						
Dieldrin	7	7	0.01	0.03	0.01-0.02	0.01-0.05
Aldrin	7	7	0.01	0.07	0.01	0.01-0.20
Heptachlor epoxide	0	4	nd	0.03	nd	0.01-0.04
DDD	0	0	nd	nd	nd	nd
DDE	3	0	0.02	nd	0.01-0.03	nd
DDT	0	0	nd	nd	nd	nd
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	7	7	0.03	0.11	0.02-0.05	0.03-0.26
AREA 2 (7 HENS)						
Dieldrin	7	7	0.02	0.03	0.01-0.05	0.01-0.07
Aldrin	5	6	0.07	0.06	0.01-0.24	0.01-0.12
Heptachlor epoxide	6	3	0.06	0.03	0.01-0.18	0.01-0.06
DDD	0	0	nd	nd	nd	nd
DDE	0	0	nd	nd	nd	nd
DDT	0	0	nd	nd	nd	nd
Lindane	1	0	0.04	nd	0.04	nd
Combined residues [2]	7	7	0.13	0.09	0.01-0.26	0.02-0.21
AREA 3 (7 HENS)						
Dieldrin	7	7	0.05	0.04	0.01-0.15	0.02-0.08
Aldrin	7	6	0.04	0.05	0.01-0.12	0.02-0.08
Heptachlor epoxide	3	4	0.66	0.01	0.06-1.81	0.01
DDD	0	0	nd	nd	nd	nd
DDE	0	0	nd	nd	nd	nd
DDT	0	0	nd	nd	nd	nd
Lindane	0	1	nd	0.04	nd	0.04
Combined residues [2]	7	7	0.37	0.10	0.03-1.90	0.05-0.14
AREA 4 (5 HENS)						
Dieldrin	4	5	0.07	0.02	0.02-0.13	0.02-0.04
Aldrin	5	3	0.09	0.02	0.04-0.14	0.01-0.03
Heptachlor epoxide	2	5	0.16	0.01	0.14-0.18	0.01
DDD	0	0	nd	nd	nd	nd
DDE	0	1	nd	0.01	nd	0.01
DDT	0	1	nd	0.01	nd	0.01
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	5	5	0.21	0.04	0.06-0.43	0.03-0.08

[1] Averages represent birds with detectable residues.
[2] Figures in this row are based on combined residues in individual samples.

TABLE 2.—*Chlorinated hydrocarbons in cock pheasants collected from southeastern South Dakota in February 1967*

[nd = not detectable, <0.01 ppm]

Compound	No. of Cock Pheasants with Detectable Residues		Residues in PPM			
			Average [1]		Range	
	Fat	Brain	Fat	Brain	Fat	Brain
AREA 1 (7 COCKS)						
Dieldrin	7	7	0.03	0.02	0.01-0.06	0.01-0.05
Aldrin	7	7	0.02	0.05	0.01-0.04	0.01-0.23
Heptachlor epoxide	1	6	0.17	0.02	0.17	0.01-0.06
DDD	0	0	nd	nd	nd	nd
DDE	0	1	nd	0.02	nd	0.02
DDT	0	0	nd	nd	nd	nd
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	7	7	0.07	0.09	0.03-0.08	0.02-0.32

TABLE 2.—*Chlorinated hydrocarbons in cock pheasants collected from southeastern South Dakota in February 1967*—Continued

[nd = not detectable, <0.01 ppm]

Compound	No. of Cock Pheasants with Detectable Residues		Residues in PPM			
			Average [1]		Range	
	Fat	Brain	Fat	Brain	Fat	Brain
AREA 2 (7 COCKS)						
Dieldrin	7	7	0.02	0.05	0.01-0.04	0.01-0.19
Aldrin	5	5	0.05	0.03	0.01-0.18	0.01-0.14
Heptachlor epoxide	5	2	0.12	0.90	0.01-0.43	0.10-1.70
DDD	0	2	nd	0.31	nd	0.02-0.60
DDE	0	0	nd	nd	nd	nd
DDT	0	0	nd	nd	nd	nd
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	7	7	0.14	0.42	0.02-0.47	0.01-2.35
AREA 3 (7 COCKS)						
Dieldrin	6	7	0.02	0.02	0.01-0.04	0.01-0.05
Aldrin	4	4	0.02	0.02	0.01-0.03	0.01-0.03
Heptachlor epoxide	3	2	0.15	0.02	0.08-0.24	0.01-0.02
DDD	0	0	nd	nd	nd	nd
DDE	0	1	nd	0.02	nd	0.02
DDT	0	0	nd	nd	nd	nd
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	7	7	0.09	0.04	0.02-0.28	0.01-0.09
AREA 4 (1 COCK)						
Dieldrin	1	1	0.03	0.02	0.03	0.02
Aldrin	1	1	0.06	0.02	0.06	0.02
Heptachlor epoxide	0	1	nd	0.01	nd	0.01
DDD	0	0	nd	nd	nd	nd
DDE	0	0	nd	nd	nd	nd
DDT	0	0	nd	nd	nd	nd
Lindane	0	0	nd	nd	nd	nd
Combined residues [2]	1	1	0.09	0.05	0.09	0.05

[1] Averages represent birds with detectable residues.
[2] Figures in this row are based on combined residues in individual samples.

TABLE 3.—*Chlorinated hydrocarbon residues in brain tissue and crop contents of juvenile pheasants collected in southeastern South Dakota, July 1967*

[nd = not detectable, <0.03 ppm DDT and endrin and <0.01 ppm other hydrocarbons]

Sample No.	Age (weeks)	Sex	Residues in PPM									
			Deildrin	Aldrin	Hepta-chlor Epoxide	Hepta-chlor	DDD	DDE	DDT	Lindane	Endrin	Total
BRAIN												
1	5	M	nd	nd	0.03	nd	nd	0.04	nd	nd	nd	0.07
2	7	F	nd	nd	0.04	nd	nd	0.03	nd	nd	nd	0.07
3	5	M	nd	nd	0.05	nd	0.04	0.08	0.20	0.02	nd	0.39
4	6	M	nd	nd	nd	nd	0.04	0.04	nd	nd	nd	0.08
5	7	M	0.37	nd	0.10	nd	nd	nd	nd	nd	nd	0.47
6	6	M	0.49	nd	nd	nd	0.04	0.08	0.60	nd	nd	1.21
7	8	F	0.03	nd	0.03	nd	nd	0.06	0.12	nd	nd	0.24
8	8	M	nd	nd	0.04	nd	nd	0.07	nd	nd	nd	0.11
9 [1]			nd	nd	nd	nd	nd	0.05	0.29	nd	nd	0.34
CROP [2]												
Animal Material			nd	nd	nd	nd	nd	nd	0.04	nd	nd	0.04
Plant Material			0.01	nd	nd	nd	0.01	nd	0.03	nd	nd	0.05

[1] Pooled sample of six birds.
[2] Contents of 17 crops pooled.

TABLE 4.—*Chlorinated hydrocarbons in eggs collected in southeastern South Dakota in May and June 1967*

[nd = not detectable, <0.03 ppm DDT and endrin and <0.01 ppm other hydrocarbons]

Compound	No. of Pheasant Eggs with Detectable Residues [1]	Residues in PPM	
		Average Concentration [2]	Range
AREA 1			
May 2 and 9 (10 eggs)			
Dieldrin	7	0.03	0.01-0.07
Aldrin	1	0.02	0.02
Heptachlor epoxide	8	0.02	0.01-0.04
DDD	1	0.01	0.01
DDE	4	0.01	0.01-0.02
DDT	4	0.04	0.04-0.06
Lindane	3	0.03	0.02-0.04
Endrin	0	nd	nd
Combined residues [3]	9	0.08	0.02-0.13
June 26 and 27 (12 eggs)			
Dieldrin	12	0.04	0.02-0.11
Aldrin	3	0.03	0.02-0.04
Heptachlor epoxide	12	0.10	0.02-0.26
DDD	3	0.04	0.01-0.08
DDE	4	0.03	0.01-0.05
DDT	6	0.07	0.05-0.10
Lindane	9	0.03	0.01-0.06
Endrin	0	nd	nd
Combined residues [3]	12	0.25	0.05-0.50
AREA 2			
May 5 and 9 (10 eggs)			
Dieldrin	9	0.03	0.01-0.12
Aldrin	0	nd	nd
Heptachlor epoxide	10	0.05	0.02-0.09
DDD	1	0.01	0.01
DDE	8	0.01	0.01-0.02
DDT	3	0.07	0.05-0.10
Lindane	2	0.01	0.01
Endrin	0	nd	nd
Combined residues [3]	10	0.11	0.03-0.21
June 26 and 27 (6 eggs)			
Dieldrin	4	0.99	0.46-1.58
Aldrin	0	nd	nd
Heptachlor epoxide	6	0.11	0.01-0.24
DDD	2	0.02	0.02
DDE	6	0.02	0.01-0.06
DDT	2	0.16	0.10-0.22
Lindane	5	0.03	0.01-0.06
Endrin	0	nd	nd
Combined residues [3]	6	0.15	0.05-2.01
AREA 3			
May 2 and 3 (10 eggs)			
Dieldrin	6	0.02	0.01-0.03
Aldrin	0	nd	nd
Heptachlor epoxide	10	0.03	0.01-0.05
DDD	2	0.03	0.01-0.04
DDE	6	0.02	0.01-0.03
DDT	5	0.07	0.03-0.10
Lindane	1	0.02	0.02
Endrin	0	0	0
Combined residues [3]	10	0.09	0.02-0.18
June 26 and 27 (5 eggs)			
Dieldrin	4	0.02	0.01-0.02
Aldrin	0	nd	nd
Heptachlor epoxide	5	0.04	0.01-0.08
DDD	0	nd	nd
DDE	5	0.03	0.01-0.06
DDT	0	nd	nd
Lindane	2	0.01	0.01-0.02
Endrin	0	nd	nd
Combined residues [3]	5	0.09	0.05-0.16

TABLE 4.—*Chlorinated hydrocarbons in eggs collected in southeastern South Dakota in May and June 1967*—Continued

[nd = not detectable, <0.03 ppm DDT and endrin and <0.01 ppm other hydrocarbons]

Compound	No. of Pheasant Eggs with Detectable Residues [1]	Residues in PPM	
		Average Concentration [2]	Range
AREA 4			
May 5 and 9 (7 eggs)			
Dieldrin	7	0.02	0.01-0.04
Aldrin	0	nd	nd
Heptachlor epoxide	5	0.02	0.01-0.03
DDD	1	0.02	0.02
DDE	7	0.02	0.01-0.03
DDT	4	0.17	0.05-0.38
Lindane	1	0.02	0.02
Endrin	0	nd	nd
Combined residues [3]	8	0.13	0.01-0.49
June 26 and 27 (7 eggs)			
Dieldrin	5	0.02	0.02-0.03
Aldrin	0	nd	nd
Heptachlor epoxide	5	0.04	0.03-0.05
DDD	2	0.02	0.01-0.03
DDE	4	0.02	0.02
DDT	4	0.07	0.05-0.08
Lindane	4	0.02	0.01-0.02
Endrin	0	nd	nd
Combined residues [3]	5	0.15	0.10-0.19

[1] Whole eggs minus shells were analyzed.
[2] Averages represent eggs with detectable residues.
[3] Figures in this row are based on combined residues in individual samples.

Pesticide Concentrations in Great Lakes Fish [1]

Robert E. Reinert[2]

ABSTRACT

During the past 4 years the Ann Arbor Great Lakes Fishery Laboratory of the Bureau of Commercial Fisheries has been monitoring insecticide levels in fish from the Great Lakes. The two insecticides found in all Great Lakes fish have been DDT (DDT, DDD, DDE) and dieldrin. Fish from Lake Michigan contain from 2 to 7 times as much of these insecticides as those from the other Great Lakes. Insecticide levels calculated on a whole-fish basis show a marked difference from species to species. Within a species there is also an increase in DDT and dieldrin levels with an increase in size. If these insecticide levels are, however, calculated as ppm of insecticide in the extractable fish oil, the differences in concentration between species and the differences between size groups becomes considerably less. Laboratory experiments indicate that fish can build up concentrations of DDT and dieldrin at the parts-per-million level from parts-per-trillion concentrations in the water.

Introduction

Since 1965 the Great Lakes Fishery Laboratory of the Bureau of Commercial Fisheries has been monitoring insecticide residues in Great Lake fish. The initial objective of the study was to determine the concentrations and types of insecticides present in fish; emphasis was placed on the more important food and game species. As the study progressed, emphasis shifted from a general monitoring program to those species and lakes that contained the highest levels of insecticides. Some of the specific questions we have attempted to answer are the degree to which insecticide concentrations differ among species, lakes, seasons, and different size groups within the same species. Where differences existed, we attempted to determine the factors which cause them.

Methods and Materials

A total of 1,313 analyses have been made on 3,801 fish from the five Great Lakes. The following common and scientific names of the 28 species examined are from the list published by the American Fisheries Society (*1*):

Alewife	*Alosa pseudoharengus*
American smelt	*Osmerus mordax*
Bloater	*Coregonus hoyi*
Brown bullhead	*Ictalurus nebulosus*
Carp	*Cyprinus carpio*
Channel catfish	*Ictalurus punctatus*
Coho salmon	*Oncorhynchus kisutch*
Emerald shiner	*Notropis atherinoides*
Freshwater drum	*Aplodinotus grunniens*
Gizzard shad	*Dorosoma cepedianum*
Goldfish	*Carassius auratus*
Kiyi	*Coregonus kiyi*
Lake herring	*Coregonus artedii*
Lake trout	*Salvelinus namaycush*
Lake whitefish	*Coregonus clupeaformis*
Ninespine stickleback	*Pungitius pungitius*
Rock bass	*Ambloplites rupestris*
Round whitefish	*Prosopium cylindraceum*
Sea lamprey	*Petromyzon marinus*
Slimy sculpin	*Cottus cognatus*
Spottail shiner	*Notropis hudsonius*
Stonecat	*Noturus flavus*
Trout-perch	*Percopsis omiscomaycus*
Walleye	*Stizostedion vitreum vitreum*
White bass	*Roccus chrysops*
White perch	*Roccus americanus*
White sucker	*Catostomus commersoni*
Yellow perch	*Perca flavescens*

[1] Contribution No. 371 of the Great Lakes Fishery Laboratory, Bureau of Commercial Fisheries, Fish and Wildlife Serv., U.S. Dep. of the Interior, Ann Arbor, Mich. 48107.

[2] Great Lakes Fishery Laboratory, Bureau of Commercial Fisheries, Fish and Wildlife Serv., U.S. Dep. of the Interior, Ann Arbor, Mich. 48107.

The pesticides included for analysis were the DDT complex (DDT, DDE, and DDD) and dieldrin. Insecticide levels in fish are expressed in two ways in the present report: (1) parts per million (ppm) in whole fish or a tissue (microgram of insecticide per gram wet weight of fish); and (2) ppm in oil (microgram of insecticide per gram wet weight of fish divided by the fraction of oil in the fish).

Fish for pesticide analyses were collected by the Bureau of Commercial Fisheries, the Michigan Department of Natural Resources, the Wisconsin Department of Natural Resources, and commercial fishermen. The fish were frozen as soon as possible after capture and shipped to the Bureau of Commercial Fisheries Great Lakes Fishery Laboratory, where they were stored at −34 C. The location, date, water depth, species, total length, weight, and sex, if possible, were recorded for each fish.

Insecticide analyses were conducted on two model 204 Aerograph gas chromatographs.* Both are equipped for dual-column operation, and each has two electron capture detectors and two recorders. The glass columns are ⅛-inch I.D. and 6 or 9 feet long. The columns were packed with 5% QF 1 on 100-120 mesh Gas Chrom Q for the first two-thirds of their length. The last one-third was packed with 5% DC 11 on 100-120 mesh Gas Chrom Q. The operating temperatures were 190 C for the oven, 210 C for the detector, and 225 C for the injection port. The nitrogen gas flow rate was 60 ml/minute.

The analytical procedure was as follows: The fish were partially thawed and ground in a meat grinder. A 10-g portion was saponified in alcoholic KOH (10 g of KOH dissolved in 6 ml of water and diluted with 34 ml of absolute ethyl alcohol) for 30 minutes, extracted with 30 ml of hexane, and transferred to a 2-oz teflon-capped bottle containing 1 g of sodium sulfate. Before analysis on the gas chromatograph, 1 ml of the hexane extract was washed through a 9-mm I.D. glass column, 6 inches long, packed with 2 inches of Florisil. The DDT complex was separated from dieldrin by eluting the hexane extract with nine 1-ml portions of a 4:1 hexane:benzene mixture which washed the DDT complex through the column, followed by ten 1-ml portions of benzene which washed the dieldrin through. The portions containing the DDT complex and the dieldrin were then injected separately into the gas chromatograph for identification and quantification.

A second 10-g portion of the ground fish was homogenized for 5 minutes in 20 ml of a 1:1 mixture of isopropanol:benzene and then boiled slowly for 45 minutes in a water bath. To replace solvent lost through evaporation, hexane was periodically added to maintain a volume of about 40 ml. After cooling, the solvent was decanted through a glass wool filter into a graduated 50-ml centrifuge tube. The homogenized fish was washed twice with 5-ml portions of hexane which were then added to the original extract. The total volume of hexane was concentrated to 30 ml and transferred to a 2-oz teflon-capped bottle which contained 1 g of sodium sulfate. For analysis on the gas chromatograph, 1 ml of the hexane was eluted on a Florisil column in the manner described for the saponified samples.

Recovery information from spiked samples suggests an extraction efficiency of better than 90% for each of the constituents of the DDT complex when using the homogenization method. The levels of the DDT complex in fish presented in this paper were obtained using this extraction procedure. The saponification method, which also has an extraction efficiency of better than 90%, is used as a check. If the quantity of DDE as calculated from this method differs more than 20% from the combined DDT and DDE values obtained from the homogenization, the samples are rerun (saponification breaks DDT down into DDE).

Dieldrin concentrations are calculated from the saponified samples. Extraction efficiencies for dieldrin are in the 70% range.

Selected samples of fish were also spotted on thin-layer chromatograph plates, (Aluminum oxide with *n*-heptane as the solvent) and their Rf values compared to those of standards. The spots on the plates identified as insecticides were scraped off, redissolved in hexane, injected into the gas chromatograph, and the retention times of the peaks were compared to those of the standards.

The methods for the separation and analysis of dieldrin from Great Lakes fish have been used only since 1967. In 1968 we began, as an additional standard procedure, percentage oil analyses on all samples examined for insecticides.

The data for each sample is put on punch cards, and the information is stored for use on an IBM 1130 computer. The programs used ensure rapid computation and retrieval of the information.

Insecticide Concentrations in Great Lakes Fish

On the basis of DDT and dieldrin levels in fish, the rank of the Great Lakes, in order of highest to lowest concentrations of insecticides is: Michigan, Ontario, Huron, Erie, and Superior (Table 1). Insecticide values calculated on a whole-fish basis show marked differences

* Trade names referred to in this publication do not imply endorsement of commercial products.

from species to species. DDT and dieldrin concentrations in lake trout and walleye increased with size of fish.

LAKE MICHIGAN

Because Lake Michigan fish generally have higher insecticide concentrations than those in the other Great Lakes, most of the monitoring has been directed to that lake. Twelve Lake Michigan species have been examined; most of the analyses were on alewives, bloaters, American smelt, yellow perch, and lake trout (Table 2). Of these five species, bloaters had the highest whole-fish averages for DDT (8.61 ppm) and dieldrin (0.23 ppm). Two samples of kiyis contained 12.54 and 14.03 ppm DDT and 0.25 and 0.31 ppm dieldrin. Kiyis, which were extremely abundant in Lake Michigan until the mid-1950's, apparently spend much of their life in water deeper than 50 fathoms. The kiyis analyzed were taken 30 miles from shore, off Saugatuck, Mich., at 80 fathoms.

DDT and dieldrin concentrations in lake trout increased with total length of the fish (Table 2). DDT ranged from 0.89 ppm (2.0- to 5.9-inch fish) to 6.96 ppm (16.0- to 21.9-inch fish). Lake trout of equal lengths in Lake Superior averaged only about one-third to one-fourth as much insecticide as those from Lake Michigan. Very large lake trout were unavailable from Lake Michigan, but if the ratio of insecticide in the two lakes prevails for large fish, a 30-inch lake trout in Lake Michigan would contain between 20 and 30 ppm DDT.

Some evidence suggests that pesticide concentrations in Lake Michigan fish differ according to region of the lake. Values for bloaters, alewives, and American smelt in the southern end of the lake averaged slightly higher than those in the same species from the northern end. Small lake trout from the southern end of the lake also had higher DDT and dieldrin concentrations than fish of the same size from the northern portion. The

TABLE 1.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in five species of fish from individual Great Lakes*

	Alewife		American Smelt		Bloater		Lake Herring		Yellow Perch	
	DDT	Dieldrin	DDT	Dieldrin	DDT	Dieldrin	DDT	Dieldrin	DDT	Dieldrin
Lake Michigan										
Concentration (ppm)	3.89	0.11	2.31	0.06	8.61	0.23	6.71	0.20	3.22	0.08
Number of fish	638	239	224	150	439	149	8	4	199	43
Number of analyses	96	56	45	35	72	41	7	4	41	29
Lake Ontario										
Concentration (ppm)	1.99	0.06	1.58	0.10	—	—	3.51	0.07	2.10	0.05
Number of fish	99	6	107	1	—	—	1	1	2	2
Number of analyses	8	1	10	1	—	—	1	1	1	1
Lake Huron										
Concentration (ppm)	2.44	0.05	0.75	0.04	3.60	0.11	—	—	1.59	0.03
Number of fish	11	10	28	14	4	4	—	—	30	13
Number of analyses	3	2	3	2	1	4	—	—	6	3
Lake Erie [1]										
Concentration (ppm)	1.59	0.14	1.06	0.04	—	—	—	—	0.87	0.05
Number of fish	27	27	9	6	—	—	—	—	212	15
Number of analyses	6	6	2	1	—	—	—	—	26	4
Lake Superior										
Concentration (ppm)	0.72	0.05	0.32	0.02	1.09	0.03	1.44	0.02	—	—
Number of fish	2	2	206	99	65	17	10	10	—	—
Number of analyses	2	2	14	8	12	7	6	6	—	—

[1] Analyses for DDT are for 1966-68.

TABLE 2.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in Lake Michigan fish*

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of Fish	No. of Analyses	Concentration (ppm)	No. of Fish	No. of Analyses	Concentration (ppm)
Alewife	638	96	3.89	239	56	0.11
American smelt	224	45	2.31	150	35	0.06
Bloater	439	72	8.61	149	41	0.23
Carp	3	3	1.92	—	—	—
Kiyi	3	2	13.28	3	2	0.28
Lake herring	8	7	6.71	4	4	0.20
Lake trout						
2.0- 5.9 inches	26	11	0.89	18	7	0.03
6.0- 9.9 inches	79	34	2.38	66	27	0.12
10.0-15.9 inches	48	41	3.79	35	28	0.15
16.0-21.9 inches	20	18	6.96	20	18	0.20
Lake whitefish	2	1	0.78	2	1	0.03
Slimy sculpin	36	4	2.29	12	1	0.19
Trout-perch	21	2	0.94	—	—	—
White sucker	13	4	0.29	—	—	—
Yellow perch	199	29	3.22	43	11	0.08

larger lake trout (15.0 to 21.9 inches) collected to date have all been from northern Lake Michigan, mainly from the Grand Traverse Bay area. When large lake trout appear in southern Lake Michigan, they may have concentrations higher than 20 to 30 ppm. Because lake trout move freely throughout the lake, large samples are required to detect significant differences between areas.

Whole fish and selected tissues of coho salmon have been analyzed from samples collected in the lake from early spring to fall and in the Platte River during the fall spawning run. Values for whole fish collected from the southern end of the lake in April-May 1968 averaged 3.51 ppm DDT and 0.11 ppm dieldrin. Ten adult coho salmon caught in Lake Michigan just before the spawning run in August 1968 averaged 12.21 ppm DDT and 0.14 ppm dieldrin. Concentrations in steaks from these fish averaged 14.89 ppm DDT and 0.15 ppm dieldrin. Values for DDT and dieldrin in the whole fish and steaks showed little change during the spawning runs.

Five cans of Lake Michigan coho salmon, consisting of fish captured from the Platte River in the fall of 1968, had average DDT and dieldrin concentrations of 7.10 and 0.09 ppm. Eggs from three fish in Lake Michigan in October 1968 averaged 6.66 ppm DDT and 0.06 ppm dieldrin.

LAKE ONTARIO

Ten species of fish were collected from eastern Lake Ontario in November 1966 and in January and November 1967 (Table 3). Although only one analysis was made for most species, the records suggest that DDT concentrations in Lake Ontario are only about one-half those in Lake Michigan.

Dieldrin values in Lake Ontario fish were also lower than those in Lake Michigan fish, with the exception of the slightly higher level in smelt and an extremely high one (0.47 ppm) in a 22-inch whitefish.

LAKE HURON

DDT and dieldrin concentrations were measured for nine species collected from Lake Huron in August and December 1966 and in January, August, and November 1967 (Table 4). Of the three species which received three or more analyses, alewives contained the highest concentrations of DDT (2.44 ppm) and dieldrin (0.05 ppm). Higher pesticide values were found, however, in fish for which only one analysis was made. A walleye and a channel catfish each contained over 6 ppm DDT, and a lake whitefish had 0.12 ppm dieldrin.

Although the data is scanty for Lake Huron, it suggests that insecticide levels are about one-half those in the same species from Lake Michigan.

LAKE ERIE

Thirteen species of fish were collected from Lake Erie in 1966-1967 (Table 5). Lake Erie fish contained only one-third to one-half as much insecticide as did the same species from Lake Michigan, except alewives, which contained a slightly higher average concentration of dieldrin in Lake Erie (0.15 compared to 0.10 ppm). With the exception of yellow perch and walleyes, all species were collected in the fall. The perch and walleyes, which composed the majority of the fish analyzed, were collected in the western, central, or eastern basins in the spring, summer, and fall of 1966-1967. Insecticide concentrations in Lake Erie fish did not differ by season, but the DDT concentrations in perch were slightly lower in the central basin than in the western and eastern basins (0.67 ppm for 10 analyses from the central basin compared with 1.20 and 1.06 ppm for 9 and 4 analyses from the western and eastern basin).

DDT and dieldrin in walleyes increased with size of fish (Table 5).

LAKE SUPERIOR

Ten species of fish from Lake Superior have been examined for insecticides since 1965 (Table 6). Samples were collected in the summer, fall, and early winter, from the Michigan and Wisconsin waters of the lake.

Insecticide concentrations in Lake Superior fish appear to be lower than any of the Great Lakes; identical species had one-seventh to one-fourth the DDT and one-seventh to one-half the dieldrin of those from Lake Michigan. DDT in lake trout increased steadily with increased size of fish. The average levels ranged from 0.21 ppm for fish 2.0 to 5.9 inches long to 7.44 ppm from 27.0- to 32.9-inch fish (Table 6).

Two Lake Superior coho salmon taken during their spawning run in the Huron River averaged 1.02 ppm DDT and 0.01 ppm dieldrin. Flesh samples from these fish averaged 0.72 ppm DDT and 0.01 ppm dieldrin. Eggs from three coho salmon averaged 2.12 ppm DDT and 0.04 ppm dieldrin.

Factors that Influence DDT and Dieldrin Levels in Great Lakes Fish

The presence of insecticides in Great Lakes fish brings up several questions: (1) How do fish build up concentrations of DDT and dieldrin in the parts per million when only a few parts per trillion (ppt) exist in their environment? (2) Why do concentrations differ from species to species and concentrations increase with increased size of fish? (3) Why do insecticide concentrations differ from lake to lake? Only partial answers to these questions can be offered now.

TABLE 3.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in Lake Ontario fish*

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of Fish	No. of Analyses	Concentration (ppm)	No. of Fish	No. of Analyses	Concentration (ppm)
Alewife	99	8	1.99	6	1	0.06
American smelt	107	10	1.58	1	1	0.10
Gizzard shad	1	1	0.63	1	1	0.04
Lake herring	1	1	3.51	1	1	0.07
Lake whitefish	1	1	5.02	1	1	0.47
Rock bass	1	1	0.40	1	1	0.02
Slimy sculpin	5	1	2.33	—	—	—
White bass	1	1	2.76	1	1	0.10
White perch	1	1	4.32	1	1	0.10
Yellow perch	2	1	2.10	2	1	0.05

TABLE 4.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in Lake Huron fish*

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of Fish	No. of Analyses	Concentration (ppm)	No. of Fish	No. of Analyses	Concentration (ppm)
Alewife	11	3	2.44	10	2	0.05
American smelt	28	3	0.75	14	2	0.04
Bloater	4	1	3.60	4	1	0.11
Channel catfish	1	1	6.90	1	1	0.07
Lake whitefish	1	1	2.43	1	1	0.12
Sea lamprey	1	1	1.27	1	1	0.02
Walleye	1	1	6.02	1	1	0.08
White sucker	1	1	1.14	1	1	0.02
Yellow perch	30	6	1.59	13	3	0.03

TABLE 5.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in Lake Erie fish*

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of Fish	No. of Analyses	Concentration (ppm)	No. of Fish	No. of Analyses	Concentration (ppm)
Alewife	27	6	1.59	27	6	0.15
American smelt	9	2	1.06	6	1	0.04
Brown bullhead	7	2	0.28	4	1	0.00
Emerald shiner	6	2	0.94	5	1	0.00
Freshwater drum	12	5	0.62	5	2	0.04
Gizzard shad	9	2	0.53	9	2	0.09
Goldfish	2	1	0.70	—	—	—
Spottail shiner	9	3	0.25	—	—	—
Stonecat	2	1	0.28	—	—	—
Walleye						
12.0-15.9 inches	31	20	1.08	3	3	0.06
16.0-18.9 inches	16	12	1.12	2	2	0.13
White bass	3	1	1.89	3	1	0.04
White sucker	3	1	0.37	3	1	0.02
Yellow perch	212	26	0.87	15	4	0.05

TABLE 6.—*Average concentrations (whole fish) of DDT (1965-68) and dieldrin (1967-68) in Lake Superior fish*

Species	DDT (DDT, DDE, DDD)			Dieldrin		
	No. of Fish	No. of Analyses	Concentration (ppm)	No. of Fish	No. of Analyses	Concentration (ppm)
Alewife	2	2	0.72	2	2	0.05
American smelt	206	14	0.32	99	8	0.02
Bloater	65	12	1.09	17	7	0.03
Coho salmon	2	2	1.02	2	2	0.01
Flesh	2	2	0.72	2	2	0.01
Eggs	3	3	2.12	3	3	0.04
Lake herring	10	6	1.44	10	6	0.02
Eggs	1	1	0.64	1	1	0.02
Lake trout						
2.0- 5.9 inches	17	3	0.21	2	1	0.03
6.0- 9.9 inches	9	2	0.63	—	—	—
10.0-15.9 inches	16	8	0.97	7	5	0.02
16.0-21.9 inches	1	1	2.84	1	1	0.05
22.0-26.9 inches	5	5	3.99	5	5	0.05
27.0-32.9 inches	3	3	7.44	3	3	0.05
Lake whitefish	6	2	0.45	2	2	0.02
Round whitefish	6	2	0.57	6	2	0.03
Slimy sculpin	18	2	0.22	18	2	0.03
Stickleback	114	4	0.43	114	4	0.02

TABLE 7.—*DDT and dieldrin concentrations in whole fish and in fish oil (Lake Michigan)*

Species	Whole Fish		Percent Oil	Oil	
	DDT (ppm)	Dieldrin (ppm)		DDT (ppm)	Dieldrin (ppm)
Alewife	3.88	0.10	10.29	37.6	0.97
Bloater	9.83	0.22	20.40	48.4	1.07
Lake trout					
3.0- 5.9 inches	1.07	0.02	4.06	26.35	0.49
6.0- 9.9 inches	2.99	0.11	8.55	34.95	1.28
10.0-15.9 inches	4.31	0.13	10.88	39.95	1.19
16.0-20.9 inches	6.61	0.21	18.55	35.62	1.13
Yellow perch	2.93	0.07	7.94	36.9	0.88

UPTAKE OF INSECTICIDES FROM WATER

Concentrations of DDT and dieldrin in water samples from Lake Michigan have been in the low range of 1 to 3 ppt. Despite this low concentration, the fish build up relatively high contents of DDT and dieldrin. Unlike terrestrial animals, which are exposed to insecticides mostly through their food, fish are in constant contact with these materials in the water.

Chlorinated hydrocarbon insecticides have very high partition coeffcients, i.e., they are extremely more soluble in oil than in water. (DDT is about 80 million times more soluble in olive oil than in water.) The entry of molecules into cells increases with increase in partition coefficient of a material.

The gills of a fish, which strain large quantities of water, are extremely efficient for the removal of insecticides from water. For example, Premdas and Anderson (*2*) found that after a 5-minute exposure to 1 ppm of C^{14}-labeled DDT, Atlantic salmon concentrated 1.56 ppm in the liver and spleen; after 1 hour of exposure this value reached 31 ppm.

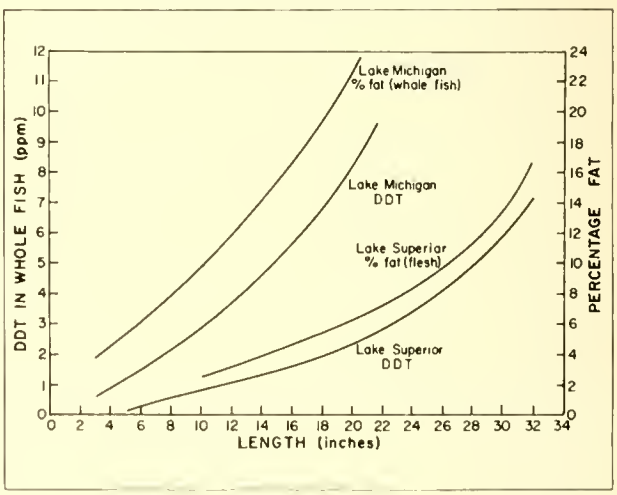
Experiments underway in the Great Lakes Fishery Laboratory have shown that goldfish build up high concentrations of dieldrin (up to several ppm) through constant exposure to low levels (a few ppt) in water.

RELATIONSHIP BETWEEN FAT AND INSECTICIDE LEVELS

Differences in insecticide levels among different species and size groups within a species can be lessened considerably if the insecticide concentrations are calculated on an oil basis (Table 7). For example, on a whole-fish basis, the average DDT and dieldrin values in bloaters are 3.4 and 3.1 times greater than those in yellow perch. On an oil basis, however, residues in bloaters are only 1.3 and 1.2 times greater than those in yellow perch. Since chlorinated hydrocarbon insecticides are extremely soluble in oil, the higher the fat content in a fish the more insecticide it can store. On a whole-fish basis, concentrations of insecticides increase in lake trout with increase in size, but on an oil basis the concentrations reach an equilibrium when the fish are between 10 and 12 inches long. As these fish grow, their percentage of fat increases and consequently they are able to store more insecticide. For example, the percentage of oil calculated for Lake Michigan lake trout was directly proportional to the whole-fish DDT values in the fish (Fig. 1).

Although oil values were not available for all lake trout analyzed for insecticides from Lake Superior, a similar relationship is evident between the percentage oils for "lean" Lake Superior lake trout determined by Eschmeyer and Phillips (*3*) and the whole-fish DDT values for these fish in later years (Fig. 1).

FIGURE 1.—*DDT and fat in lake trout of various lengths from Lake Michigan and Lake Superior. The percentages of fat for Lake Superior were given by Eschmeyer and Phillips (1965) for "lean" lake trout*



A comparison between the percentage of total oil and percentage of total DDT in fillets and scraps of bloaters and yellow perch shows that the greatest amounts of

DDT are in the portions having the highest percentages of oil (Table 8). Considerable oil and insecticides are lost when fish of high oil content are cooked (baked, broiled, or fried). For example, chub fillets that lose 60 to 70% of their oil during cooking lose about the same percentages of DDT.

TABLE 8.—*Percent distribution of weight, oil, and DDT in yellow perch and bloaters in Lake Michigan*

Species	Portion of Fish	Percent		
		Weight	Oil	DDT
Yellow perch	Fillets	38	4	3
	Scraps	62	96	97
Bloater	Fillets	55	39	46
	Scraps	45	61	54

Fish with little oil in their fillets, such as yellow perch, lose very little insecticide during cooking. The majority of the insecticides in these fish is in the scraps and consequently is removed when the fish are filleted.

USE OF INSECTICIDES IN THE GREAT LAKES WATERSHED

Insecticide concentrations in a lake depend upon those in tributary streams, use in the watershed, and the volume, productivity, and water retention time of the lake. Lake Michigan has an average water retention time of approximately 30.8 years (*4*); at least theoretically, the lake presently contains some water that was there before chlorinated hydrocarbon insecticides were first used in the late 1940's. Only 10 to 11 tons of DDT would be required to give a uniform concentration of 2 ppt in Lake Michigan. Although no comprehensive records exist of the amounts of pesticides used in the Lake Michigan watershed, some estimates of use are available for certain areas. For agricultural purposes, 18 counties in the Great Bay watershed were estimated to have used 1,767 lb of dieldrin and 87,289 lb of DDT in 1963 (*5*). A total of 13,702 lb of aldrin (which degrades to dieldrin), 3,913 lb of dieldrin, and 127,516 lb of DDT were estimated to have been used in the Wisconsin Lake Michigan watershed in 1962.

The use of insecticides in Michigan was also very heavy because of large field-crop and orchard areas. Over the years municipalities have applied large quantities of DDT for the control of Dutch elm disease and mosquitoes. State and Federal agencies have used large amounts of DDT for control of forest insects. DDT and dieldrin have been used by dry cleaners and woolen mills for mothproofing, and waste products from these users are sometimes released in the rivers. Both DDT and dieldrin have been recommended for use against a number of household pests.

Although DDT and dieldrin have been supplanted to a considerable degree by other, less stable compounds in the past few years, they are still recommended for a number of uses. As recently as 1968, 3,000 acres of Berrien County, Mich., were treated aerially with 6,000 lb of dieldrin for control of the Japanese beetle.

Considering the length of time water is retained in Lake Michigan, the tremendous amounts of insecticides that have been applied to its watershed in the past 20 years, and the extremely long half-life these materials have in the environment, present concentrations in Lake Michigan water should not seem unreasonable.

The biomass of Lake Erie is much greater than that of Lake Michigan. The productivity of a body of water appears to speed up the rate of degradation of chlorinated hydrocarbon insecticides. In comparison with Lake Michigan, the use of insecticides in the Lake Superior watershed is small. Also, the volume of Lake Superior is 2½ times that of Lake Michigan. Consequently, the amounts of insecticides needed to produce a concentration of 2 ppt in Lake Michigan would yield a concentration of only 0.8 ppt in Lake Superior. A large portion of the water flowing into Lake Huron comes from the relatively insecticide-free waters of Lake Superior.

Conclusion

The works of Burdick *et al.* (*6*) on lake trout, the research of Johnson (*7*) on the effects of endrin on medaka (a small Japanese freshwater poeciliid), and the work of Macek (*8*) on brook trout all show that relatively low concentrations of chlorinated hydrocarbon insecticides have a deleterious effect on fish reproduction. Concentrations of DDT in Lake Michigan coho salmon eggs are similar to those found by Burdick *et al.* (*6*) and Macek (*8*). The amounts of DDT and dieldrin in Lake Michigan fish and eggs, therefore, are close to a level that could adversely affect reproduction.

The Food and Drug Administration has established temporary tolerance levels for residues permitted in fish shipped across State borders—0.3 ppm for dieldrin (set in 1968) and 5 ppm for DDT (set in April 1969). A number of species in Lake Michigan are approaching the level set for dieldrin, and a number have already exceeded the level set for DDT.

The blame for the contamination of the Great Lakes cannot be placed on any single organization, agency, or municipality. All are to some degree responsible—in fact, all users of insecticides over the past 20 years have contributed to the present concentration in the Great Lakes.

Because we are dealing with concentrations in the environment that must be given in ppt, very rigid controls are needed to ensure that contamination of the

aquatic environment is reduced to a minimum. The only sure control is the replacement of these troublesome insecticides with less persistent materials.

See Appendix for chemical names of compounds mentioned in this paper.

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PESTICIDES IN SOIL

Organochlorine Insecticide Residues in Soils and Soil Invertebrates from Agricultural Lands

Charles D. Gish[1]

ABSTRACT

Soils and earthworms and other soil invertebrates were collected from 67 agricultural fields in eight States. Samples were analyzed by gas chromatography for DDE, DDD, DDT, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, and gamma-chlordane insecticides. Organochlorine insecticides in soils averaged 1.5 ppm, dry weight, and in earthworms, 13.8 ppm. Residues in earthworms averaged nine times that in soils. Residues ranged from a trace to 19.1 ppm in soils and from a trace to 159.4 ppm in earthworms. Residues in beetle larvae from two fields averaged 0.6 ppm; in snails from two fields, 3.5 ppm; and in slugs from four fields, 89.0 ppm. Amounts of insecticides in earthworms varied directly with amounts in soils. Coefficients of correlation between residues in soils and residues in earthworms usually were significant for DDE, DDD, and DDT regardless of crop or soil type.

Introduction

Persistence of pesticides in the environment was a remote problem when DDT was introduced in 1946 for the control of agricultural pests. Since then, many organochlorine insecticides have come into use. The literature contains many examples of the ubiquitous distribution of organochlorine insecticides in the environment (*1, 11, 21, 22, 26, 28*).

The accumulation of insecticide residues from the environment by earthworms was demonstrated in 1958 by Barker (*3*). Investigators of terrestrial ecosystems have since shown that various invertebrates—beetles, earthworms, and slugs—can accumulate such residues (*4, 9, 14, 17, 18, 19, 20, 23, 24, 29*).

A few investigators have determined the amount of organochlorine insecticides in agricultural environments treated with many insecticides. The reports on such studies have contained data either on residues in soils (*10, 15, 30*) or in invertebrates (*6, 7, 8*). In only two studies of arable fields in England were residues reported both for soils and for invertebrates (*9, 29*). No such reports were available when the present survey was begun in 1965, and no such studies have yet been reported for North America. The objectives of the survey were: (1) to establish quantitatively the extent to which the organochlorine insecticides were accumulating in soils and soil invertebrates of agricultural lands; and (2) to provide clues to the factors which contribute to the buildup of pesticides in terrestrial food chain organisms.

Materials and Methods

Soil and invertebrate samples were collected in March, April, May, and October 1965 from 67 fields planted to 1 of 14 crops. The fields were located in 22 counties of 8 States of the Southern and Midwestern United States. A history of the cropping practices and insecticide treatments of most fields was obtained from the cooperating farmers.

COLLECTION AND PRESERVATION OF SAMPLES

Invertebrates were selected by the following criteria: (1) they were sufficiently large and abundant to attract feeding vertebrates; (2) their degree of mobility restricted them to a small area; and (3) their requirements for feeding and development confined them to the soil. Four faunal types were collected for analysis: earthworms, insect larvae, slugs, and snails. The earthworms were represented by four genera: *Allolobophora*,

[1] Patuxent Wildlife Research Center, Bureau of Sport Fisheries and Wildlife, U.S. Department of the Interior, Laurel, Md. 20810.

Diplocardia, Helodrilus, and *Lumbricus.* The beetle larvae were white grubs belonging to the family Scarabaeidae. Slugs belonged to either *Deroceras* or *Limax;* the large land snails were not identified.

The collection site was limited to the area from which a sufficient number of earthworms could be obtained for chemical analysis. In the sampling procedure earthworms were obtained first, other invertebrates next, and soil cores last, so that the collection site of the soil cores corresponded exactly to the area required to obtain an adequate worm sample.

Soil samples consisting of 10 cylindrical cores, 1 inch deep by 2¼ inches in diameter were collected where possible. When the soil was too crumbly to obtain cores, a shovel was used to collect the samples. All visible roots, stems, rocks, and soil animals were removed in the field. Soil texture determinations were made in the field; confirmatory identifications were made in the laboratory. Soils were placed in acetone-rinsed wide-mouth quart jars fitted with enamel lids with rubber seals. Soils were frozen at the end of each field trip and the holding period before freezing ranged from 3 days to 6 weeks. Approximately 1,000 g of soil were collected from each site.

Invertebrates were placed in acetone-rinsed 2-ounce screw-type jars fitted with plastic lids and were preserved in a 10% formalin solution or were frozen. Approximately 50 g of each invertebrate were collected from each site; unfortunately, a few areas were so dry that less than 10 g were obtained. Before preservation, all invertebrates were rinsed lightly with water to remove excess soil. Invertebrates of different types and from different sites were preserved separately.

EXTRACTION PROCEDURES—INVERTEBRATES

Extraction procedures for earthworms were similar to those for tissues as recommended by the Food and Drug Administration (*27*). Each invertebrate sample with its preservative was homogenized in a Waring blender. Either a 10-g aliquot of a large sample or the entire amount of a small one was weighed into a beaker and dried for 48-72 hours at 40 C. The dried samples were ground with sodium sulfate, and extracted for 8 hours on Soxhlet apparatus using 70 ml of ethyl ether and 170 ml of petroleum ether. A 25-ml aliquot of the invertebrate sample was placed on a standardized Florisil column (60-100 mesh), and the pesticide was eluted with either 150 ml of 5% ethyl ether in petroleum ether or 250 ml of 15% ethyl ether in petroleum ether.

Total micrograms of lipids were determined by evaporating to dryness a 25-ml aliquot of the extract.

EXTRACTION PROCEDURES—SOILS

Extraction procedures for soils were similar to those being recommended by the Food and Drug Administration (*27*). Soil samples were sifted through a ⅛-inch screen. Twenty grams of each sample was weighed into a beaker with 50 ml of water. After 1 hour the sample was transferred to a 1-quart Waring blender jar, extracted for 3 minutes with 200 ml of acetonitrile, and filtered through a glass wool plug into a 1-liter separator. To the solution 200 ml of petroleum ether and 250 ml of tap water were added and the separator was shaken for 2 minutes. The petroleum ether layer was decanted from the remainder, washed two times with 600-ml portions of tap water, and dried with 10-15 g of sodium sulfate. The remaining portion was transferred to a flask through a glass wool plug. The remainder of the cleanup steps were identical to those for invertebrates except that the entire soil sample was placed on a Florisil column.

Soil moisture was determined by transferring from 2-10 g of soil to a porcelain crucible and placing the crucible into a 100 C vacuum oven for 5 hours. The cooled sample was weighed for moisture determination and then placed into a 550 C muffle furnace for 4 hours. The cooled sample was weighed then to calculate the organic fraction. Soil pH was determined by adding 50 g of water to 5 g of soil in a beaker. The beaker was placed on a magnetic stirrer and read to the nearest 0.1 unit on a Beckman Zeromatic II pH meter.

DETERMINATION OF RESIDUES

Determinations in the clean extracts were accomplished with a Barber Coleman 5360 gas chromatograph equipped with an electron capture (Sr 90) detector. The column was glass (4 mm by 1.2 m) and was packed with 5% DC-200 on Chromport XXX (70/90 mesh). Nitrogen flow rate was 70-90 ml per minute; temperatures were: column, 200 C; injector, 230 C; detector, 240 C. Confirmatory analyses were made by thin-layer chromatography on approximately 10% of the samples, or on those samples that presented problems. No thin-layer chromatography results are presented in this paper. Gas and thin-layer chromatographic techniques were similar to those recommended by the Food and Drug Administration (*27*).

RECOVERY VALUES

Soil and earthworm samples obtained from an untreated field were homogenized separately and divided into subsamples. Two subsamples of each were analyzed for organochlorine insecticides. The remaining subsamples were fortified with analytical grade compounds to determine recovery percentages.

Recoveries from two soil subsamples fortified with 0.05 ppm each of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE averaged 112, 111, 129, and 111%, respectively.

When two soil subsamples were fortified at the 5.0 ppm level, recoveries averaged 101, 112, 123, and 109%, respectively. Recoveries from earthworm subsamples with 0.5 ppm added averaged 109, 100, 106, and 103%, respectively, and those treated at the 50.0 ppm level averaged 110, 103, 104, and 106%, respectively.

The addition of dieldrin at 0.05 and 5.0 ppm to each of two soil subsamples and at 0.5 and 50.0 ppm to each of two earthworm subsamples resulted in recoveries averaging 52, 67, 88, and 96%, respectively. When 0.05 ppm of heptachlor and of heptachlor epoxide were added to each of two soil subsamples, recoveries averaged 64 and 84%, respectively. At the 5.0 ppm level in soil, recoveries averaged 98 and 94%, respectively. When two earthworm subsamples were fortified at the 0.5 ppm level, recoveries averaged 93 and 102%, respectively; recoveries averaged 94 and 93%, respectively, at the 50.0 ppm level.

The untreated subsamples of soil contained a trace of *p,p'*-DDT and *p,p'*-DDE; those of earthworms averaged 0.022 ppm *p,p'*-DDT, 0.020 ppm *p,p'*-DDE, and 0.012 ppm dieldrin. Percentage recoveries were not corrected for amounts in the controls nor were data in the tables corrected for the percentage recoveries.

RESIDUE VALUES

Residues in soils and invertebrates are expressed as parts per million (ppm), dry weight. Owing to the different circumstances under which the samples were collected, dry weight seemed less variable than wet weight or fresh weight and, thereby, less subject to measuring errors. Expressions of residue values as ppm, dry weight, were 1.3 times the wet weight values for soils, and 5.8 times for earthworms.

Limits of detection for residues were 0.005 ppm wet weight, in soils and 0.015 ppm, wet weight, in invertebrates. Values detected below the limits are expressed as trace amounts.

STATISTICAL EVALUATION

Correlation and regression analysis were used to compare certain aspects of the relationship between soil and earthworm residues. This technique required that the trace values be quantified. Quantified trace values were calculated by dividing the values for the limits of detection by 2 and expressing the quotient on a dry-weight basis for each sample.

The data were transformed to logarithms to meet the normality requirements of correlation and regression analysis. The untransformed data, containing many zero, trace, or near-trace values, and a few large values, were positively skewed. The skewness was consistent for each residue component as well as for the total residue load, and it occurred in both soil and earthworm residues. The transformed data presented a more nearly normal frequency distribution, but with a definite tailing of the large residue values. Heath (*16*) reported that a tailing effect may persist even after residue data are transformed to logarithms.

Results and Discussion

RESIDUES IN SOILS

One of 67 soil samples had residues of two insecticides, 22 had three, 16 had four, 24 had five, 3 had six, and 1 had seven (Table 1). DDT, DDE, and DDD occurred in approximately 98, 98, and 93%, respectively, of the samples (Table 2). All samples with DDT also contained DDE; only four orchard soils with DDT did not contain DDD. DDT in 20 samples, DDD in 20, and DDE in 26 amounted to 0.1 ppm or greater. DDT, DDD, and DDE accounted for 38, 26, and 23%, respectively, of the average total amount of all organochlorine insecticides.

Aldrin occurred in about 19% of the samples and dieldrin in about 55%. Dieldrin was present in each sample containing aldrin, but only one sample with aldrin and nine with dieldrin exceeded 0.1 ppm. Nearly 24% of the samples contained endrin, but only in six samples did the amount exceed 0.1 ppm.

Gamma-chlordane occurred in about 10% and heptachlor epoxide in about 13% of the samples. They were found in heptachlor-treated pastures in Louisiana and in cornfields and a peafield in Illinois; the peafield sample was the only one containing heptachlor. Gamma-chlordane was found only in soils with residues of heptachlor epoxide. Heptachlor epoxide in one sample was the only one of the three that exceeded 0.1 ppm.

The largest amounts and varieties of organochlorine pesticides were applied to cottonfields and orchards; pastures received the least. Soil residues reflected in part the amounts and kinds of insecticides that were applied (See Table 1). Discrepancies in Table 1 between amounts applied and residues in soil and invertebrates could be due to the length of time between application and sampling, to different degradation rates, to inaccurate records of amounts applied, and to sampling error.

Total organochlorine insecticide residues amounted to 12.3 ppm in an Alabama cottonfield, 13.6 and 18.8 ppm in two Maryland apple orchards, and 19.1 ppm in a Maryland peach orchard. Pasture soils contained the least; the largest total amount of all organochlorine insecticide residues in pastures was 0.25 ppm in a Louisiana pasture. The total organochlorine insecticide content of the soil samples from 39 of the 67 fields exceeded 0.1 ppm, whereas only 4 samples contained no more than a trace of any insecticide. Many fields with a history of no organochlorine insecticide application, or with an unknown history, contained only trace

amounts. Samples from these fields were convenient checks on the chemical and sampling methods.

RESIDUES IN EARTHWORMS

One of 67 earthworm samples had residues of two insecticides, 5 had three, 29 had four, 28 had five, 3 had six, and 1 had seven (Table 1). DDT and DDE occurred in every earthworm sample; DDD was found in all but four (Table 3). Forty samples with DDT, 37 with DDE, and 31 with DDD contained at least 0.1 ppm of those residues. Six samples with DDT, five with DDE, and seven with DDD exceeded 10.0 ppm of those compounds. DDT, DDD, and DDE accounted for approximately 46, 24, and 19%, respectively, of the average total amount of all organochlorine insecticides.

Aldrin was found in 10% of the samples and dieldrin in 76%. Dieldrin was found in each earthworm sample containing aldrin. Two samples with aldrin and 28 with dieldrin exceeded 0.1 ppm. Endrin occurred in 39% of the samples; 20 samples exceeded 0.1 ppm endrin. Heptachlor, heptachlor epoxide, and gamma-chlordane were found in earthworms collected in Louisiana and Illinois. Heptachlor was detected in one sample. Gamma-chlordane was found in 10% of the samples and heptachlor epoxide in 13%; only four samples exceeded 0.1 ppm of either.

Earthworms from cottonfields, cornfields, and orchards contained the highest residues; those from pastures contained the lowest. The total organochlorine insecticide content of earthworms was 114.67 ppm in a Louisiana cottonfield, 159.43 ppm in an Alabama cottonfield, 89.37 ppm in a Missouri cornfield, 20.91 and 48.52 ppm in two Maryland apple orchards, and 112.06 ppm in a Maryland peach orchard.

Residues in worms from a Louisiana pasture (No. 18) totaled 108.9 ppm. The large amount of residues in worms from this pasture sample could not be accounted for by the history of the insecticide application or the residues in the soil. Since the residue readings of both soils and worms were double checked and found accurate, the lack of agreement between soils and worms in Louisiana No. 18 was considered an unreasonable question.

SOIL-EARTHWORM RELATIONSHIP

Soil samples were classified by crops grown and by soil textures in an attempt to reveal the factors which influence the amount of residues that earthworms may obtain from the soil. These data were then analyzed by correlation and regression techniques. Less than three fields were sampled from those planted to alfalfa, clover, oats, peaches, peas, sorghum, and soybeans; therefore, correlation and regression techniques could not be used to compare residues in samples planted to those crops (Table 4).

The relationship of the amount of residues in earthworms to the amount of residues in soil, when soils were classified by crops, is shown in Table 4. Coefficients of correlation were significant ($p<0.05$) for DDE in apple, corn, and cotton crops; for DDD in apple and cotton crops; for DDT and metabolites in apple, corn, cotton, and rice crops; and for the total organochlorine insecticide content in apple, corn, and cotton crops.

The variability of the correlation coefficients from one residue component to another and from one crop to another may be due to unevenly distributed residues in the fields. Apple orchards and cottonfields usually were sprayed with DDT. Stringer and Pickard (*24, 25*) found that the use of DDT in apple orchards resulted in more residues under trees than between trees. All but one of the orchard samples in this survey were collected under trees. Insecticides were uniformly distributed in the ricefields, because the fields were flooded during and after pesticide application. In cornfields, insecticides were applied in bands extending several inches to each side of the rows or were sprayed. Pastures generally were not treated, but when they were, spraying usually was directed toward specific targets such as fire ant mounds. Thus, the insecticide distribution was more uniform in apple orchards under the trees, in cottonfields, and in ricefields than in cornfields and pastures. Earthworms from apple orchards and cottonfields contained amounts of residues which were proportionately greater than in their corresponding soil samples and less variable than residues in worms from other crops.

Soil textures were not determined for 16 Louisiana pastures. The remaining 51 were grouped into 4 primary types—sand loam, silt loam, clay loam, and clay. Coefficients of correlation between residues in the worms and residues in the soils (Table 5) were significant ($p<0.05$) in all soil textures for DDE and for total organochlorine insecticide content, in all but clay soils for DDD, in clay loam and clay soils for DDT, and in silt loam soils for dieldrin.

When soils were classified by crops or soil textures, the relationship between residues in earthworms and soils varied greatly from one insecticide compound to the next. In this study the number of significant coefficients of correlation between residues in soil and worms appeared to be in close agreement with the published results on the persistence of organochlorine insecticides in the soil (*12*) since correlations were higher for the more persistent insecticides. The coefficients of correlation between DDE in soils and worms were highly significant ($p<0.01$) for all soil textures and most crops. Fewer significant relationships were found for DDD, DDT, and dieldrin (Table 5), and no significant relationships were found for the less persistent aldrin,

endrin, gamma-chlordane, heptachlor, and heptachlor epoxide compounds.

Although DDT was reported to be the most persistent of the organochlorine insecticides (*12*), no literature was cited on the relative persistence in soils of DDT, DDD, and DDE. Not as many significant coefficients of correlation between soils and worms were found for DDT as for DDE or DDD. This may indicate that DDE and DDD are more persistent in soils than DDT and that earthworms metabolize DDT to the more stable DDE and DDD.

Organic content of the soil was determined for each sample. The average organic content in sandy loam soils was 2.98% of the total soil weight; in silt loam soils, 3.81%; in clay loam soils, 4.03%; and in clay soils, 6.70%. Percentage organic matter was tested by analysis of variance and found significantly greater ($p<0.05$) in the clay soils and significantly less ($p<0.05$) in the sandy loam soils; there was no significant difference between silt loam and clay loam soils. Although organic content of soils has been shown to increase retention of residues in soil (*2, 13*), the ability of earthworms to accumulate insecticide residues from the soil appeared unaffected by soil organic content.

The soil and earthworm samples were collected from the same site within a field (paired samples), but they did not always contain the same insecticides (Table 1). There were 20 soil or earthworm samples with dieldrin, 10 with endrin, 9 with DDD, 8 with aldrin, 6 with gamma-chlordane, 6 with heptachlor epoxide, and 1 with DDE and DDT whose corresponding paired samples contained no detectable levels. Earthworms may not contain the same kinds of residues as the soils from which they were collected simply because they were recent arrivals to the sample site. This may be especially relevant for worms collected from the fields in which the residues were unevenly distributed. Earthworms also appear capable of metabolizing some compounds into other forms, especially unstable compounds such as aldrin and heptachlor.

RATIO: STORAGE/EXPOSURE

A ratio of storage to exposure was calculated by dividing the average amount of residue in the worms by the average amount in the soils (Table 3). The ratios varied with the chemical, but the largest ratios belonged to the most persistent compounds. Each insecticide on the average appeared to be present in greater amounts in earthworms than in soils. These ratios are a guide for relating residues in worms to those in soils. They are not the true "concentration factors" found in many food chain studies.

OTHER SOIL INVERTEBRATES

When soil invertebrates other than earthworms could be found in sufficient quantities, a sample was collected at the same site as the soil and worm samples. Adequate numbers of beetle larvae were collected from two sites, slugs from four sites, and snails from two sites. The beetle larvae averaged 0.62 ppm organochlorine insecticides; soils from the same sites averaged a trace, and worms averaged 0.19 ppm. The slugs, collected at four sites, averaged 89.0 ppm, the soils 6.7 ppm, and the worms 24.0 ppm. The snails, analyzed with their shells, averaged 3.5 ppm; soils and worms from the same sites averaged 10.9 and 40.1 ppm. Residues in snails were lower than those in earthworms; residues in earthworms were lower than those in slugs. The differences may be due to dissimilar feeding habits. Some differences were due to the inclusion of the snails' shells in the analysis.

The amounts of organochlorine insecticide residues in the beetle larvae were 3.3 times those in earthworms from the same sites. Residues in slugs were 3.7 times those in worms from the same sites. At sites with snails, earthworm insecticide levels were 11.5 times those of snails with their shells.

Summary and Conclusions

Earthworms from 38 fields contained organochlorine insecticide residues exceeding 1.0 ppm, dry weight; the amounts ranged from 1.08 to 159.43 ppm. Earthworms from 15 of those fields contained amounts ranging from 12.14 to 159.43 ppm. The worms contained more parts per million of insecticides than did their corresponding soil samples as can be seen by the storage-exposure ratios. Amounts of insecticides in the soils from the above-mentioned 38 fields generally were higher than amounts in the soils of the remaining fields.

The correlation between residues in earthworms and residues in soils was less variable for samples collected from cotton- and ricefields and under apple trees than for samples from fields planted to other crops. The correlation of residues in earthworms to residues in soils was more consistent for samples collected from clay loam and silt loam soils than for samples collected from sandy loam and clay soils. Although there were differences in the organic content of the soil types, organic content did not appear to influence the ability of earthworms to acquire insecticides from the soil.

The correlation between residues in soils and in earthworms was consistent for certain compounds in spite of the classification of soils by crops and soil textures. The greatest number of significant coefficients of correlation between residues in soils and in worms occurred for DDE. Fewer significant correlations occurred for

DDD, DDT, and dieldrin; none occurred for the remaining insecticides. The insecticides known to persist longest in soils were the ones with the greatest number of significant correlation coefficients.

Earthworms are a major food item for various species of birds, moles, salamanders, shrews, and snakes, and during the spring and fall they are occasional food items for other species. Since the kinds of invertebrates analyzed in this survey are typical of those readily consumed by vertebrate species, the amount of residues in these invertebrates becomes important. Evidence is available that the amount of residues found in worms from 15 of the fields is within the range of levels found to kill birds in short-term feeding studies (*5*). Residues in invertebrates from 38 fields—57% of those sampled—could kill some vertebrate species directly in short-term feeding or lead to indirect effects on the ecosystem through impairing reproduction, altering behavior, or disrupting species composition (*11*).

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TABLE 1.—*Residues in soil and invertebrate samples from agricultural lands*

Sample No.	Type Soil	Cropping and Organochlorine Insecticide History				Sample Type	Residues in Soil and Invertebrate Samples (ppm, dry weight)								
		Crops	Insecticides Applied	Years from Treatment to Sampling	Total Amount Applied (lb a.i./acre)		DDE	DDD	DDT	Aldrin	Dieldrin	Endrin	Heptachlor Epoxide	γ-Chlordane	Total Residues [1]
ALABAMA															
1	Silty clay loam	Cotton	DDT, BHC, Endrin	1	10-15	Soil	0.072	0.13	0.13	—	—	—	—	—	0.332
						Earthworm	0.42	—	1.57	—	[2] *0.042*	—	—	—	1.99
2	Silty clay loam	Soybean	DDT	6	1+	Soil	0.17	0.019	0.02	—	—	—	—	—	0.209
						Earthworm	0.77	*0.045*	0.36	—	—	—	—	—	1.13
3	Clay loam	Cotton	DDT, Endrin	1	12+	Soil	0.31	0.65	0.28	—	—	0.11	—	—	1.35
						Earthworm	4.20	1.76	8.86	—	—	5.40	—	—	20.22
4	Loam	Cotton	DDT, Endrin	1	1	Soil	2.06	2.80	7.10	—	0.34	—	—	—	12.3
						Earthworm	3.14	2.52	1.45	—	—	5.60	—	—	12.71
5	Loam	Corn	None	—	—	Soil	0.29	0.42	0.19	—	—	—	—	—	0.90
						Earthworm	0.083	*0.042*	0.22	—	—	*0.042*	—	—	0.303
6	Sandy loam	Cotton	?	—	—	Soil	0.015	0.010	0.0091	—	—	—	—	—	0.0341
						Earthworm	1.10	—	5.38	—	—	—	—	—	6.48
7	Sandy loam	Corn	?	—	—	Soil	*0.0028*	0.007	0.011	—	—	—	—	—	0.018
						Earthworm	*0.037*	*0.037*	0.095	—	*0.037*	—	—	—	0.095
						Beetle larvae	0.44	*0.060*	0.19	—	—	—	—	—	0.63
8	Fine sandy loam	Cotton	?	—	—	Soil	0.43	2.63	3.43	—	*0.0029*	—	—	—	6.49
						Earthworm	6.19	12.33	140.74	—	0.17	—	—	—	159.43
ARKANSAS															
1	Silty clay loam	Rice	?	—	—	Soil	0.0081	0.011	0.0067	*0.0034*	*0.0034*	—	—	—	0.0258
						Earthworm	*0.073*	0.17	0.40	*0.073*	0.40	—	—	—	0.97
2	Silt loam	Rice	Aldrin	1	1	Soil	0.014	0.024	0.0080	*0.0029*	0.083	—	—	—	0.129
						Earthworm	0.21	0.24	0.60	*0.074*	0.78	—	—	—	1.83
3	Silt loam	Rice	Aldrin, DDT	1	1.5	Soil	0.021	0.032	0.026	—	0.013	—	—	—	0.092
						Earthworm	0.25	0.18	1.14	—	0.63	—	—	—	2.20
4	Clay loam	Cotton	DDT	1	5	Soil	0.13	0.34	0.14	—	*0.0030*	—	—	—	0.610
						Earthworm	1.81	1.18	21.33	—	*0.059*	0.31	—	—	24.63
5	Silty loam	Cotton	DDT	1	8.5	Soil	0.28	0.22	0.24	—	0.01	0.021	—	—	0.771
						Earthworm	1.10	1.47	2.93	—	0.18	0.31	—	—	5.99
ILLINOIS															
1	Silty clay loam	Corn	?	—	—	Soil	*0.0032*	*0.0032*	*0.0032*	—	*0.0032*	—	—	—	0.000
						Earthworm	*0.06*	*0.06*	0.17	—	0.12	—	—	—	0.29
						Beetle larvae	*0.12*	*0.12*	*0.12*	—	0.60	—	—	—	0.60
2	Silty clay loam	Corn	Aldrin	1	1	Soil	0.007	*0.0033*	*0.0033*	0.026	0.28	—	—	—	0.313
						Earthworm	*0.054*	*0.054*	*0.054*	*0.054*	1.93	—	—	—	0.93

TABLE 1.—*Residues in soil and invertebrate samples from agricultural lands*—Continued

Sample No.	Soil Type	Cropping and Organochlorine Insecticide History: Crops	Insecticides Applied	Years from Treatment to Sampling	Total Amount Applied (lb a.i./acre)	Sample Type	Residues in Soil and Invertebrate Samples (ppm, dry weight): DDE	DDD	DDT	Aldrin	Dieldrin	Endrin	Heptachlor Epoxide	γ-Chlordane	Total Residues [1]
ILLINOIS—Continued															
3	Silty clay loam	Peas	DDT, Dieldrin, Heptachlor	3	7.5	Soil	0.21	0.11	0.069	0.006	0.25	—	0.011	—	0.656
						Earthworm	2.03	—	1.21	—	1.64	—	*0.059*	—	4.88
4	Loam	Corn	None	—	—	Soil	0.019	0.034	0.012	—	*0.0030*	—	0.018	0.023	0.106
						Earthworm	*0.049*	*0.049*	0.11	—	*0.049*	0.13	0.20	—	0.44
5	Silty clay loam	Corn	None	—	—	Soil	0.0062	0.0075	0.011	—	0.016	—	—	—	0.0407
						Earthworm	*0.048*	*0.048*	*0.048*	—	0.13	—	—	—	0.13
6	Silty clay loam	Alfalfa	Dieldrin	3	0.25	Soil	0.02	0.028	0.02	—	0.0076	—	—	—	0.0756
						Earthworm	*0.047*	*0.047*	*0.047*	—	0.26	—	—	—	0.26
7	Silty clay loam	Corn	Aldrin, Heptachlor	1	1+	Soil	0.11	0.037	0.02	*0.0031*	0.23	—	—	—	0.397
						Earthworm	0.86	0.25	0.41	0.15	0.92	—	—	—	2.59
8	Silty clay loam	Corn	Aldrin, Heptachlor	1	1.75	Soil	0.007	0.016	0.013	0.02	0.15	—	0.027	—	0.233
						Earthworm	0.33	*0.058*	*0.058*	—	3.10	0.58	—	—	4.01
9	Silty clay	Oats	Aldrin, Heptachlor	1	1.75	Soil	*0.0034*	*0.0034*	*0.0034*	0.15	0.52	—	—	—	0.67
						Earthworm	*0.047*	*0.047*	*0.047*	0.094	3.50	—	—	—	3.594
KANSAS															
1	Silty clay loam	Corn	Aldrin	1	4	Soil	*0.0031*	*0.0031*	*0.0031*	0.096	0.35	—	—	—	0.446
						Earthworm	*0.062*	*0.062*	*0.062*	*0.062*	0.78	—	—	—	0.78
2	Clay loam	Corn/oats	Aldrin, Dieldrin	10	0.1	Soil	*0.0031*	0.0075	0.0099	—	—	—	—	—	0.0174
						Earthworm	*0.051*	*0.051*	0.10	—	*0.051*	—	—	—	0.10
3	Loam	Corn	Aldrin	2	2	Soil	0.013	0.021	0.021	—	0.072	—	—	—	0.127
						Earthworm	*0.063*	*0.063*	*0.063*	—	0.36	—	—	—	0.36
LOUISIANA															
1	Silt loam	Sugar cane	Endrin	1	—	Soil	*0.0032*	*0.0032*	*0.0032*	—	*0.0032*	0.0065	—	—	0.0065
						Earthworm	0.078	0.078	0.078	—	—	0.57	—	—	0.57
2	Silt loam	Sugar cane	Endrin	1	—	Soil	0.0074	0.016	0.018	—	—	0.012	—	—	0.0534
						Earthworm	*0.074*	*0.074*	*0.074*	—	—	0.57	—	—	0.57
3	Sandy loam	Cotton	?	—	—	Soil	0.86	1.52	0.19	—	0.026	0.05	—	—	2.646
						Earthworm	11.85	23.80	75.54	—	0.76	2.72	—	—	114.67
4	Silty clay loam	Cotton	?	—	—	Soil	0.077	0.070	0.036	—	*0.0033*	0.009	—	—	0.192
						Earthworm	0.30	0.16	0.63	—	0.11	0.23	—	—	1.43
5	—	Pasture	Heptachlor	2.5	—	Soil	*0.0056*	0.018	0.033	—	—	—	0.12	0.076	0.247
						Earthworm	0.063	0.063	*0.028*	—	*0.028*	—	0.063	*0.028*	0.189
6	— [2]	Pasture	Heptachlor	3.5	—	Soil	*0.0043*	*0.0043*	0.014	—	—	—	*0.0043*	0.0087	0.0027
						Earthworm	*0.035*	*0.035*	*0.035*	—	*0.035*	—	0.074	0.092	0.166

7	—	Pasture	None	—	—	Soil	*0.0047*	0.011	0.013	—	—	—	—	—	0.024
						Earthworm	*0.048*	*0.048*	*0.048*	—	*0.048*	—	—	—	0.000
8	—	Pasture	None	—	—	Soil	*0.0043*	*0.0043*	*0.0043*	—	—	—	—	—	0.000
						Earthworm	0.074	0.085	*0.028*	—	*0.028*	—	—	—	0.159
9	—	Pasture	Heptachlor	1.5	—	Soil	*0.0032*	*0.0032*	0.010	—	—	—	—	—	0.01
						Earthworm	0.18	0.20	*0.027*	—	—	—	*0.027*	*0.027*	0.38
10	—	Pasture	None	—	—	Soil	*0.0039*	*0.0039*	*0.0039*	—	—	—	—	—	0.000
						Earthworm	*0.027*	0.054	0.061	—	*0.027*	—	—	—	0.115
11	—	Pasture	None	—	—	Soil	*0.0039*	*0.0039*	0.0078	—	—	—	—	—	0.0078
						Earthworm	*0.023*	*0.023*	*0.023*	—	*0.023*	—	—	—	0.000
12	—	Pasture	None	—	—	Soil	*0.0043*	0.0086	*0.0043*	—	—	—	0.029	*0.0043*	0.0376
						Earthworm	*0.036*	*0.036*	*0.036*	—	—	—	0.14	—	0.14
13	—	Pasture	None	—	—	Soil	*0.0041*	0.0081	0.011	—	—	—	—	—	0.0191
						Earthworm	*0.023*	*0.023*	*0.023*	—	—	—	—	—	0.000
14	—	Pasture	None	—	—	Soil	*0.0034*	*0.0034*	0.0068	—	—	—	—	—	0.0068
						Earthworm	*0.028*	0.055	*0.028*	—	0.028	—	—	—	0.055
15	—	Pasture	None	—	—	Soil	*0.0034*	0.0069	0.014	—	—	—	0.0097	0.011	0.0416
						Earthworm	*0.041*	0.092	*0.041*	—	*0.041*	—	—	—	0.092
16	—	Pasture	Heptachlor	0.5	—	Soil	*0.0035*	*0.0035*	0.013	—	—	—	—	—	0.013
						Earthworm	0.31	0.080	*0.026*	—	—	—	0.084	*0.026*	0.474
17	—	Pasture	None	—	—	Soil	*0.0031*	*0.0031*	0.0086	—	—	—	—	—	0.0086
						Earthworm	*0.027*	*0.027*	*0.027*	—	*0.027*	—	—	—	0.000
18	—	Pasture	Heptachlor	2	—	Soil	*0.0033*	0.0065	0.016	—	—	—	*0.0033*	*0.0033*	0.0225
						Earthworm	18.49	82.77	7.14	—	*0.032*	—	—	0.50	108.90
19	—	Pasture	None	—	—	Soil	*0.0031*	*0.0031*	*0.0031*	—	*0.0031*	—	*0.0031*	*0.0031*	0.000
						Earthworm	0.065	0.18	*0.022*	—	*0.022*	—	*0.022*	*0.022*	0.245
20	—	Pasture	None	—	—	Soil	0.029	0.014	0.0090	—	—	—	—	—	0.052
						Earthworm	0.41	0.46	0.083	—	—	—	0.13	*0.031*	1.083

MARYLAND

1	Sandy loam	Apples	DDD, DDT, Endrin	1	5-10	Soil	4.36	5.56	5.38	—	—	3.47	—	—	18.77
						Earthworm	17.63	18.76	1.09	—	—	11.04	—	—	48.52
						Slugs	14.96	12.18	7.33	—	3.90	95.81	—	—	134.18
						Slugs	15.93	15.93	13.26	0.48	18.30	134.06	—	—	197.96
						Snails	1.06	0.83	0.32	—	0.069	2.72	—	—	4.999
2	Loam	Apples	DDD, DDT, Endrin	1	5-10	Soil	4.28	5.56	1.64	—	0.030	2.10	—	—	13.61
						Earthworm	9.58	5.23	0.73	—	0.24	5.13	—	—	20.91
3	Loam	Apples	DDD, DDT, Endrin	1	5-10	Soil	0.89	—	2.50	0.022	0.024	1.29	—	—	4.726
						Earthworm	2.74	1.29	1.13	—	0.82	0.23	—	—	6.21
						Slugs	4.24	2.56	11.93	—	2.84	11.65	—	—	33.22
4	Loam	Apples	DDD, DDT, Endrin	1	5-10	Soil	0.20	—	0.52	0.015	0.019	0.25	—	—	1.004
						Earthworm	1.13	1.68	0.59	—	0.42	0.92	—	—	4.74
5	Loam	Apples	DDD, DDT, Endrin	1	5-10	Soil	0.22	—	0.55	0.036	0.021	0.31	—	—	1.137
						Earthworm	1.31	0.50	2.03	—	0.16	0.45	—	—	4.45
6	Loam	Peaches	DDD, Diel-drin	1	4-10	Soil	5.33	—	12.73	0.022	1.02	—	—	—	19.102
						Earthworm	56.01	30.87	2.12	—	22.54	0.52	—	—	112.06

TABLE 1.—*Residues in soil and invertebrate samples from agricultural lands*—Continued

Sample No.	Soil Type	Cropping and Organochlorine Insecticide History				Sample Type	Residues in Soil and Invertebrate Samples (ppm, dry weight)								
		Crops	Insecticides Applied	Years from Treatment to Sampling	Total Amount Applied (lb a.i./acre)		DDE	DDD	DDT	Aldrin	Dieldrin	Endrin	Heptachlor Epoxide	γ-Chlordane	Total Residues [1]
MISSISSIPPI															
1	Silty clay loam	Cotton	?	—	—	Soil	0.063	0.055	0.019	—	—	—	—	—	0.137
						Earthworm	0.32	—	1.23	—	—	*0.042*	—	—	1.55
2	Silty clay	Cotton	DDT	1	4+	Soil	0.72	0.95	1.14	—	—	—	—	—	2.81
						Earthworm	1.19	1.66	5.56	—	*0.05*	*0.05*	—	—	8.41
3	Silty clay	Grain sorghum	?	—	—	Soil	0.0069	*0.0034*	*0.0034*	—	—	—	—	—	0.0069
						Earthworm	*0.056*	*0.056*	*0.056*	—	*0.056*	—	—	—	0.000
4	Clay	Cotton	?	—	—	Soil	0.035	0.051	0.026	—	0.0067	—	—	—	0.1187
						Earthworm	0.27	0.20	1.45	—	*0.077*	—	—	—	1.92
5	Clay	Cotton	?	—	—	Soil	0.13	0.24	0.34	—	0.025	0.052	—	—	0.787
						Earthworm	0.51	*0.064*	4.70	—	1.71	0.77	—	—	7.69
6	Clay	Cotton	Endrin	1	1+	Soil	0.15	0.34	0.17	—	—	—	—	—	0.66
						Earthworm	1.94	1.63	21.39	—	—	—	—	—	24.96
7	Silt	Cotton	DDT	1	3	Soil	0.63	1.68	0.63	—	0.01	0.013	—	—	2.963
						Earthworm	5.99	4.86	20.85	—	*0.042*	*0.042*	—	—	31.70
						Slugs	10.00	6.03	36.67	—	0.43	1.14	—	—	54.27
						Snails	0.74	1.85	0.49	—	*0.046*	—	—	—	3.08
						Snails	0.66	1.51	0.28	—	—	—	—	—	2.45
8	Silty clay loam	Cotton	DDT	1	14	Soil	0.12	0.31	0.075	—	*0.0034*	0.024	—	—	0.529
						Earthworm	1.35	0.75	7.37	—	*0.056*	*0.056*	—	—	9.47
						Slugs	4.37	4.75	15.00	—	0.21	1.06	—	—	25.39
9	Silt loam	Cotton	Endrin	1	7+	Soil	0.24	0.34	0.097	—	0.015	0.091	—	—	0.783
						Earthworm	1.43	0.53	4.02	—	—	9.40	—	—	15.38
10	Silty clay loam	Cotton	DDT, Endrin	1	6+	Soil	0.28	1.52	0.64	—	—	—	—	—	2.44
						Earthworm	1.59	1.19	9.36	—	*0.06*	*0.06*	—	—	12.14
11	Silt loam	Cotton	DDT	1	4-8	Soil	0.11	0.28	0.066	—	0.01	—	—	—	0.466
						Earthworm	3.64	10.71	5.25	—	0.23	0.25	—	—	20.08
12	Fine sandy loam	Cotton	DDT	1	4-8	Soil	0.23	0.45	0.073	—	0.017	0.024	—	—	0.794
						Earthworm	1.53	0.87	5.07	—	0.23	0.20	—	—	7.90
MISSOURI															
1	Silty clay loam	Clover	None	—	—	Soil	0.0068	0.0068	0.0068	—	*0.0034*	—	—	—	0.0204
						Earthworm	*0.071*	*0.071*	0.14	—	*0.071*	—	—	—	0.14
2	Loam	Corn	Aldrin	2	1	Soil	—	—	—	*0.0031*	0.024	—	—	—	0.024
						Earthworm	*0.057*	*0.057*	0.11	—	1.91	—	—	—	2.02
3	Silty clay loam	Clover	Aldrin	2	1	Soil	0.02	0.018	0.015	—	0.22	—	—	—	0.273
						Earthworm	*0.044*	*0.044*	0.087	—	1.10	—	—	—	1.187
4	Silty clay	Sweet corn	Aldrin, DDT	1	18	Soil	0.76	0.036	0.14	—	—	—	—	—	0.936
						Earthworm	14.84	14.84	54.92	0.16	4.61	—	—	—	89.37

[1] Totals do not include trace amounts. [2] Italicized values represent trace amounts (see Section on STATISTICAL EVALUATION).

TABLE 2.—*Soils: organochlorine insecticides (ppm dry weight) in 67 fields*

Pesticide	No. of Fields	A.M.[a]	S.D.[b]	Range	Median	G.M.[c]	S.D.[d]
DDE	66	0.36	1.001	T- 5.33	0.020	0.036	9.25
DDD	62	0.43	1.108	T- 5.56	0.0185	0.037	9.46
DDT	66	0.59	1.930	T-12.73	0.0195	0.041	8.65
DDD+DDT	66	0.99	2.573	T-12.73	0.044	0.090	9.05
DDE+DDD+DDT	66	1.36	3 517	T-18.06	0.060	0.13	8.96
Aldrin	13	0.03	0.044	T- 0.15	0.020	0.014	3.74
Dieldrin	37	0.10	0.200	T- 1.02	0.017	0.023	5.85
Aldrin+Dieldrin	37	0.11	0.216	T- 1.042	0.017	0.026	6.00
Endrin	16	0.49	0.982	T- 3.47	0.051	0.079	7.25
Heptachlor	1	0.003	—	T	T	—	—
Heptachlor epoxide	9	0.03	0.037	T- 0.12	0.011	0.013	3.31
γ-Chlordane	7	0.02	0.026	T- 0.076	0.0087	0.0096	3.20
Hept.+Hept. epox.+γ-Chlordane	9	0.04	0.060	T- 0.196	0.0207	0.021	2.95
Total Fields	67	1.52	3.900	T-19.102	0.192	0.20	7.91

[a] Arithmetic mean.
[b] Standard deviation of arithmetic mean.
[c] Geometric mean.
[d] Standard deviation of geometric mean.
NOTE: Residues are expressed as parts per million, dry weight. Expressions of residue values as ppm, dry weight, were 1.3 times the wet weight values for soil. T = Trace, <0.005 ppm, wet weight.

TABLE 3.—*Earthworms: organochlorine insecticides (ppm dry weight) in 67 fields*

Pesticide	No. of Fields	A.M.[a]	S.D.[b]	Range	Median	Ratio: Storage/ Exposure[c]	G.M.[d]	S.D.[e]	Ratio: Storage/ Exposure
DDE	67	2.66	7.705	T- 56.01	0.27	7.4	0.33	7.82	9.2
DDD	63	3.57	11.698	T- 82.77	0.092	8.3	0.27	8.35	7.3
DDT	67	6.28	20.483	T-140.74	0.36	10.6	0.43	10.79	10.5
DDD+DDT	67	9.64	25.824	T-153.07	0.543	9.7	0.86	9.59	9.6
DDE+DDD+DDT	67	12.30	30.031	T-159.26	0.953	9.0	1.3	9.12	10.0
Aldrin	7	0.10	0.043	T- 0.16	T	3.3	0.088	1.53	6.3
Dieldrin	51	0.99	3.223	T- 22.54	0.13	9.9	0.19	5.50	8.3
Aldrin+Dieldren	51	1.01	3.228	T- 22.54	0.13	9.2	0.19	5.55	7.3
Endrin	26	1.75	3.018	T- 11.04	0.38	3.6	0.44	5.72	5.6
Heptachlor	1	0.049	—	T	T	—	—	—	—
Hept. epoxide	9	0.09	0.058	T- 0.20	0.074	3.0	0.072	2.08	5.5
γ-Chlordane	7	0.10	0.176	T- 0.50	T	5.0	0.048	3.11	5.0
Hept.+H. epox.+γ-Chlordane	10	0.16	0.136	T- 0.50	0.107	4.0	0.12	2.11	5.7
	67	13.77	31.433	T-159.43	1.83	9.0	2.1	7.48	10.5

[a] Arithmetic mean.
[b] Standard deviation of arithmetic mean.
[c] Ratio of arithmetic means of residues in earthworms to residues in soils.
[d] Geometric mean.
[e] Standard deviation of geometric mean.
[f] Ratio of geometric means of residues in earthworms to residues in soils.
NOTE: Residues are expressed as parts per million, dry weight. Expressions of residue values as ppm, dry weight, were 5.8 times the wet weight values for earthworms. T = Trace, <0.015 ppm, wet weight.

TABLE 4.—*Coefficients of correlation between residues in soil and earthworm samples (ppm, dry weight) when arranged by crop type*

Crop Type	Chemical					
	DDE	DDD	DDT	DDE+DDD+DDT	Dieldrin	Total
Cotton	0.67[a] (20)	0.55[b] (20)	0.38 (20)	0.61[a] (20)	–0.06 (16)	0.66[a] (20)
Pasture	0.16 (16)	0.11 (16)	0.24 (16)	0.24 (16)	0.44 (11)	0.19 (16)
Corn	0.56[b] (13)	0.11 (14)	0.42 (13)	0.56[b] (13)	0.27 (12)	0.59[b] (13)
Apples	0.98[a] (5)	0.89[b] (5)	0.002 (5)	0.93[b] (5)	–0.06 (4)	0.92[b] (5)
Rice	0.95 (3)	0.40 (3)	0.96 (3)	0.99[b] (3)	0.96 (3)	0.90 (3)
Remaining Crops	0.95[a] (10)	0.87[a] (10)	0.82[a] (10)	0.95[a] (10)	0.43 (8)	0.96[a] (10)
Total	0.80[a] (67)	0.68[a] (67)	0.65[a] (67)	0.80[a] (67)	–0.08 (54)	0.79[a] (67)

[a] Significant at the 1% level.
[b] Significant at the 5% level.
NOTE: Numbers in parentheses indicate number of samples represented in each block.

TABLE 5.—*Coefficients of correlation between residues in soil and earthworm samples (ppm, dry weight) when arranged by soil type*

Soil Type	Chemical					
	DDE	DDD	DDT	DDE+DDD+DDT	Dieldrin	Total
Sandy loam	0.94 [a] (6)	0.87 [b] (6)	0.42 (6)	0.84 [b] (6)	−0.63 (4)	0.85 [b] (6)
Silt loam	0.75 [a] (18)	0.64 [a] (18)	0.46 (18)	0.76 [a] (18)	0.67 [a] (16)	0.75 [a] (18)
Clay loam	0.90 [a] (20)	0.86 [a] (20)	0.84 [a] (20)	0.90 [a] (20)	0.30 (17)	0.86 [a] (20)
Clay	0.92 [a] (7)	0.47 (7)	0.83 [b] (7)	0.89 [a] (7)	0.09 (6)	0.80 [b] (7)
Total	0.84 [a] (51)	0.74 [a] (51)	0.47 [a] (51)	0.82 [a] (51)	0.25 (43)	0.80 [a] (51)

[a] Significant at the 1% level.
[b] Significant at the 5% level.
NOTE: Numbers in parentheses indicate number of samples represented in each block.

APPENDIX

Chemical Names of Compounds Mentioned in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,-8-dimethanonaphthalene
BHC	1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers
γ-CHLORDANE	1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane, gamma isomer
DDD (TDE)	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDD contains some *o,p'*-isomer also.
DDE	1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene
DDT (including its isomers and dehydrochlorination products)	1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in a ratio of about 3 or 4 to 1)
DIELDRIN	Not less than 85% of 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-dimethano=naphthalene
ENDRIN	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,*endo-endo*-5,8-dimethanonaphthalene
HEPTACHLOR	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methonoindan
LINDANE	1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer
MALATHION	diethyl mercaptosuccinate, *S*-ester with *0,0*-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane
METHYL PARATHION	*0,0*-dimethyl *0-p*-nitrophenyl phosphorothioate
TOXAPHENE	chlorinated camphene containing 67% to 69% chlorine

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