CHLORINATED HYDROCARBON INSECTICIDE CONTAMINATION OF STREAMBED SEDIMENTS IN THE MISSISSIPPI RIVER DELTA

by

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ABSTRACT

The large amounts of chlorinated hydrocarbon insecticides previously applied to crops in the Mississippi River Delta have not created widespread, chronic contamination of the streambed sediments in the Mississippi River (detectable at 0.05 ppm) and its major tributaries (detectable at 0.01 ppm). On the tributaries, with one exception, DDT analogs and metabolites were the only residues originating from agricultural or urban sources. Significant contamination resulted from manufacturing operations in the Wolf River-Cypress Creek complex at Memphis, Tenn., and from a group of pesticide formulating plants in Mississippi. Concentrations of individual pesticides ranged from nondetectable to 24,000 ppm.

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INTRODUCTION

The Mississippi River Delta is a productive agricultural area where relatively large quantities of pesticides are used. In 1964 the Delta States (Mississippi, Louisiana, and Arkansas) used 21% (18.9 million pounds) of the total chlorinated hydrocarbon insecticides (89.8 million pounds) applied to croplands in the 48 contiguous states (Eichers et al., 1964). Toxaphene accounted for about 54% (10.2 million pounds) and DDT for about 36% (6.8 million pounds) of all the chlorinated hydrocarbon insecticides applied to croplands in the Delta States (Eichers et al., 1964). Several fish kills and apprehension about the extent of pollution of the lower Mississippi River by pesticides originating from land runoff and erosion, prompted investigations to determine the sources, and the extent and magnitude of streambed sediment contamination by chlorinated hydrocarbon insecticides.

Streambed sediment samples were collected by the USDA Sedimentation Laboratory, Oxford, Miss., in early summer 1964 and 1966 from the lower Mississippi River and several of its tributaries in Tennessee, Mississippi, Arkansas, and Louisiana (Figure 1). Sampling was done during low stages. A supplemental study of contamination of the Wolf River-Cypress Creek complex in Memphis, Tenn. was conducted in April 1967. A detailed report of these studies including site location maps and sampling procedures has been published (Barthel et al., 1969). Only the most recent data are summarized herein. It would have been informative to have the results of samplings done at other times of the year. Common names of the chlorinated hydrocarbon insecticides are used in the text; their respective chemical names are given in Table 1.

EXPERIMENTAL PROCEDURES

In 1966 the Mississippi River bed sediments were sampled at 132 places (11 sites) between Tiptonville, Tenn. and New Orleans, La. (Table 2 and Figure 1). At each site, samples were taken at three cross sections which were usually one or more stream widths apart. At each of the three cross sections, sampling was done at two water depths (2 feet and 7 feet below mean low water elevation) and on both sides of the river. Six or seven grab samples were mixed to obtain approximately 1 1/2 gallons of sediment for each sample.

One hundred fifty-four samples were collected from tributaries in Tennessee, Mississippi, Arkansas, and Louisiana (Figure 1). Samples were taken upstream and downstream from industrial and municipal sources to separate possible contributions of these sources from those of agriculture. Usually three cross sections were sampled at each site and a composited 1 1/2-gallon sample obtained from the low water perimeter at each cross section. A distance of several stream widths usually separated the sampled sections.

Table 1. Chemical Names of Chlorinated Hydrocarbon Insecticides.

Common Name	Chemical Name
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-exo-1,4:5,8-dimethanonaphthalene
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[1]	1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-exo-1,4:5,8-dimethanonaphthalene
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-endo 1,4:5,8-dimethanonaphthalene
Endrin keto	Structure uncertain
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Isodrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-endo-1,4:5,8-dimethanonaphthalene
Lindane	1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer
TDE(DDD)[2]	1,1-dichloro-2, 2-bis(p-chlorophenyl) ethane
Toxaphene	Chlorinated camphene containing 67% to 69% chlorine
X	1,2,3,4,7,7-hexachloro-2,5-norbornadiene
Y	1,2,3,4,6,7,7-heptachloro-2-norbornene

[1] Includes its isomers and dehydrochlorination products; technical DDT consists of a mixture of the p, p' - isomer and the o, p' - isomer in a ratio of 3 or 4 to 1.

[2] Includes its isomers and dehydrochlorination products; technical TDE contains some o, p' - isomer also.

Table 2. Chlorinated hydrocarbon insecticide concentrations in streambed sediment samples from the lower Mississippi River - 1966.

Sampling Location	River Miles [1]	Pesticide Concentration Range (ppm)[2]			
		Isodrin	X	Y	Chlordane
Tiptonville, Tenn.	880				
Redman Bar, Tenn.	739				
Memphis, Tenn.	732	0.08--0.41	0.28--0.63	0.13--1.3	0.8--2.8
West Memphis, Ark.	725		0.08--0.16		
State Line-Miss.-Tenn.	714				
Helena, Ark.	669				
Greenville, Miss.	565				
Vicksburg, Miss.	430				
Natchez, Miss.	359		0.1--0.31		
Baton Rouge, La.	227		0.05--1.1		
New Orleans, La.	87				

1/ Approximate center of sampling site measured upstream from the Head of Passes on the Gulf of Mexico (Flood control and navigation maps of the Mississippi River; Cairo, Ill. to the Gulf of Mexico. U. S. Mississippi River Commission, Corps of Engineers, U. S. Army, Vicksburg, Miss. 1962; 30 ed.).

2/ Based on oven-dry sediment weight.

Sediment samples were immediately frozen, once ashore. The chlorinated hydrocarbon analyses were performed by the USDA Plant Protection Division's Pesticide Monitoring Laboratory at Gulfport, Miss.

Chlorinated hydrocarbon insecticides were extracted from the sediment samples using a mixed solvent of hexane:isopropanol (3:1). Recovery data were obtained using control samples fortified with the insecticides likely to be encountered in the sediment. Analyses were performed on standard gas chromatographs using electron affinity detectors and glass columns with column injection. Two separate columns were used: 3% DC-200 on Gas Chrom Q (180° C.) and 9% QF-1 on Diatoport S (166° C.). Sulfur interference was eliminated by using a column of 5% XE-60 on Chromosorb W (180° C.). Confirmation of specific residues was made by thin layer chromatography, p values and by conversion to other products. The recovery data obtained from the analyses of the control samples were used in computing the concentrations of pesticides. Concentrations are reported on a dry sediment weight basis (110° C.).

RESULTS AND DISCUSSION

Analyses of the streambed sediment samples indicate two major areas of non-DDT chlorinated hydrocarbon insecticide contamination — one in association with manufacturing operations in the Memphis-Wolf River-Cypress Creek complex (Figure 2) and the other in association with a group of formulating plants, located on other tributaries in Mississippi, that prepare the technical pesticides for agricultural use (Figure 3).

In the Memphis area complex, high concentrations of chlorinated hydrocarbon residues including aldrin, dieldrin, endrin, endrin keto, isodrin, chlordane, heptachlor, hexachloronorbornadiene (X), heptachloronorbornene (Y) and Z, were detected in bottom sediments, spoils, and flood plain deposits from Cypress Creek, downstream from a primary manufacturer of endrin and heptachlor (Figure 2). Concentrations in samples from the other tributaries in the area were lower. In general these results agree with the 1964 data (Barthel *et al.*, 1966).

Isodrin, X, and Y are intermediates in the manufacture of endrin. 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 byproducts 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. 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--see Table 2). Traces of X were found in sediments at Baton Rouge, La. about 500 river miles downstream from the source at Memphis. Excepting the contamination from Wolf River and Cypress Creek, there is no detectable buildup of chlorinated hydrocarbon insecticide residues in the sediments of the lower Mississippi River. Most of the Mississippi River samples downstream from West Memphis, Ark. showed no residues in tests sensitive enough to detect 0.05 ppm.

It is difficult to assess quantitatively the extent and magnitude of the chlorinated hydrocarbon deposits associated with the manufacturing operations in the Memphis area. The principal problem is in obtaining samples that are representative of the deposits in the area. Three factors contribute to this sampling problem: (1) the variability in the nature of the deposits, (2) continuing dredging operations, and (3) unknown locations of industrial sewage outfalls. There is no evidence that pesticide manufacturing wastes are now being discharged directly into Cypress Creek or the Wolf River. However, the analyses indicate the presence of a variety of chlorinated hydrocarbon residues (in 84% of the samples), 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, intense flood flows in Cypress Creek or in the Wolf River may flush contaminated sediment from the bed and banks into the Mississippi River. Transportation and deposition of these pollutants are then functions of the hydraulic conditions of streamflow. During natural sediment routing, contaminated sediments may concentrate as channel deposits. Subsequent transport of contaminated sediments by high velocity flow may produce critical chlorinated hydrocarbon insecticide concentrations downstream.

Industrial pollution of tributary streams in Mississippi is indicated by the variety of chlorinated hydrocarbon residues detected in close proximity to formulator plants at five locations: Sunflower River at Clarksdale and Indianola, Horseshoe Bayou and Fish Lake at Greenville, and Jones Bayou at Cleveland (Figures 1 and 3).

One hundred twenty-two 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 (Figures 4 and 5) and were the only contaminants in 33 of the 122 tributary samples. Twenty-five samples were contaminated with non-DDT residues; 19 of these samples were collected from only two locations--near formulator plants at Clarksdale and Greenville, Miss. (Figure 3).

Residues of DDT analogs and metabolites originating from nonindustrial sources, i.e., urban spray programs or agricultural use, were found in several streams in Mississippi, Louisiana, and Arkansas (Figure 5). With one exception (St. Francis River, Lee County, Ark.; Figure 3) DDT analogs and metabolites were the only residues originating from nonindustrial sources.

The absence of contamination in samples from several streams is especially significant. 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 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, detectable chronic contamination of streambed materials.

Acknowledgments

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Trade names and company names are included for the benefit of the reader and do not infer any endorsement or preferential treatment of the product listed by the U. S. Department of Agriculture.

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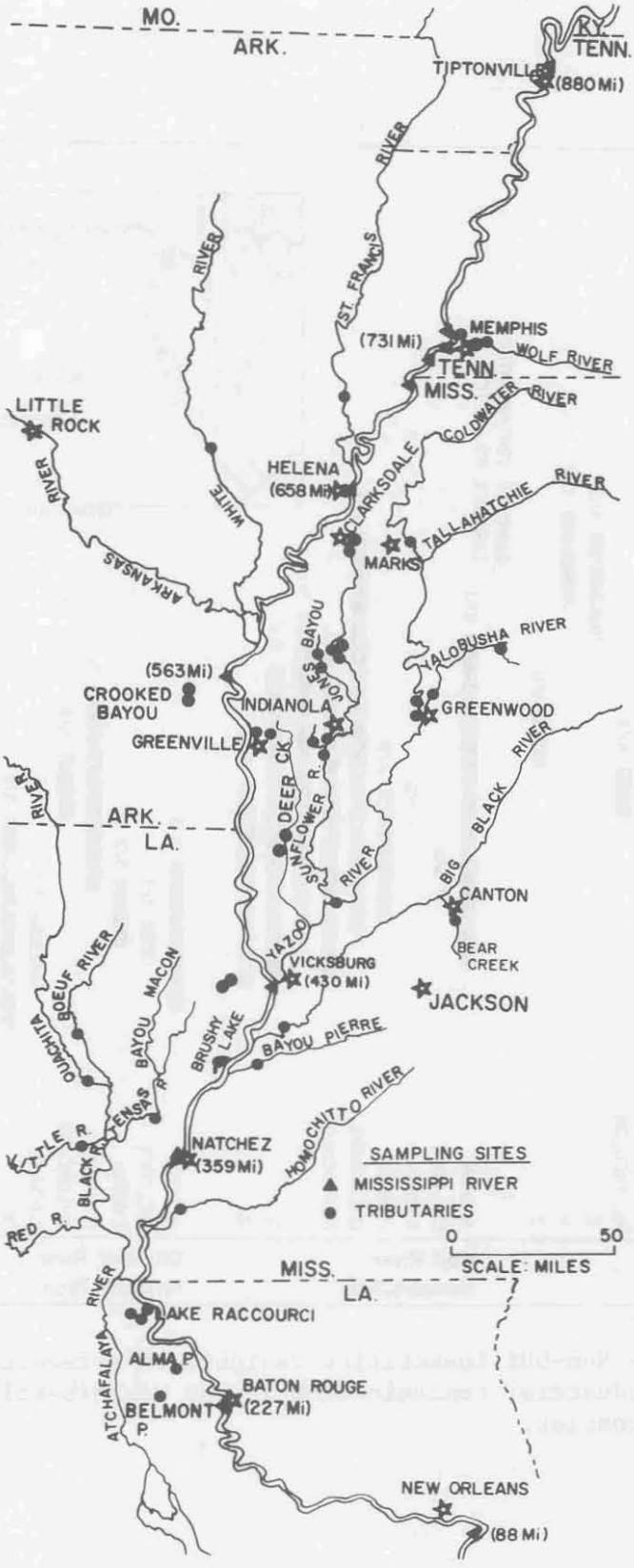

Figure 1 -- Streambed sampling locations on the Mississippi River and its tributaries.

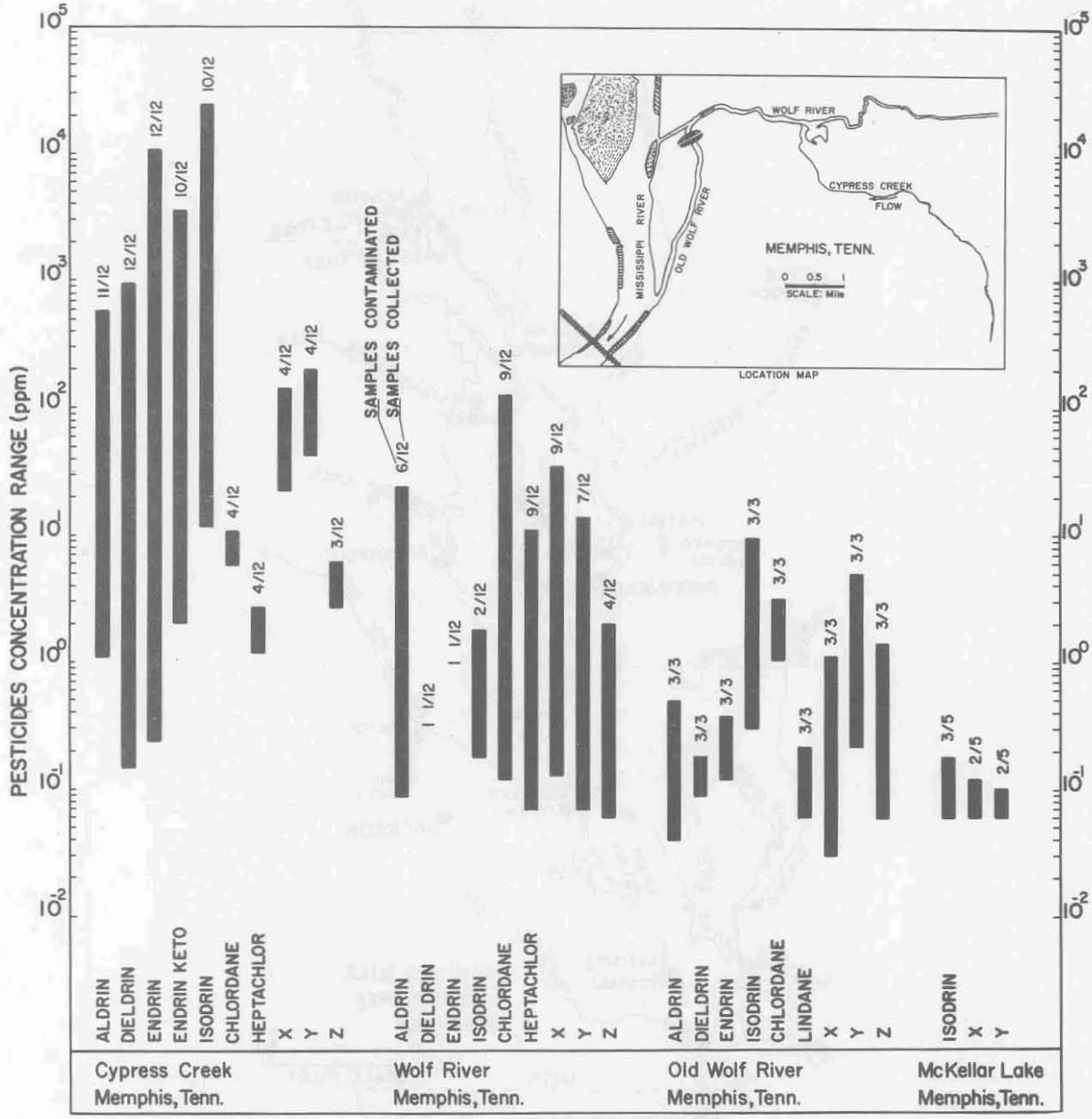

Figure 2 -- Non-DDT insecticide residues in streambed sediments from industrial contamination in the Memphis-Wolf River-Cypress Creek complex.

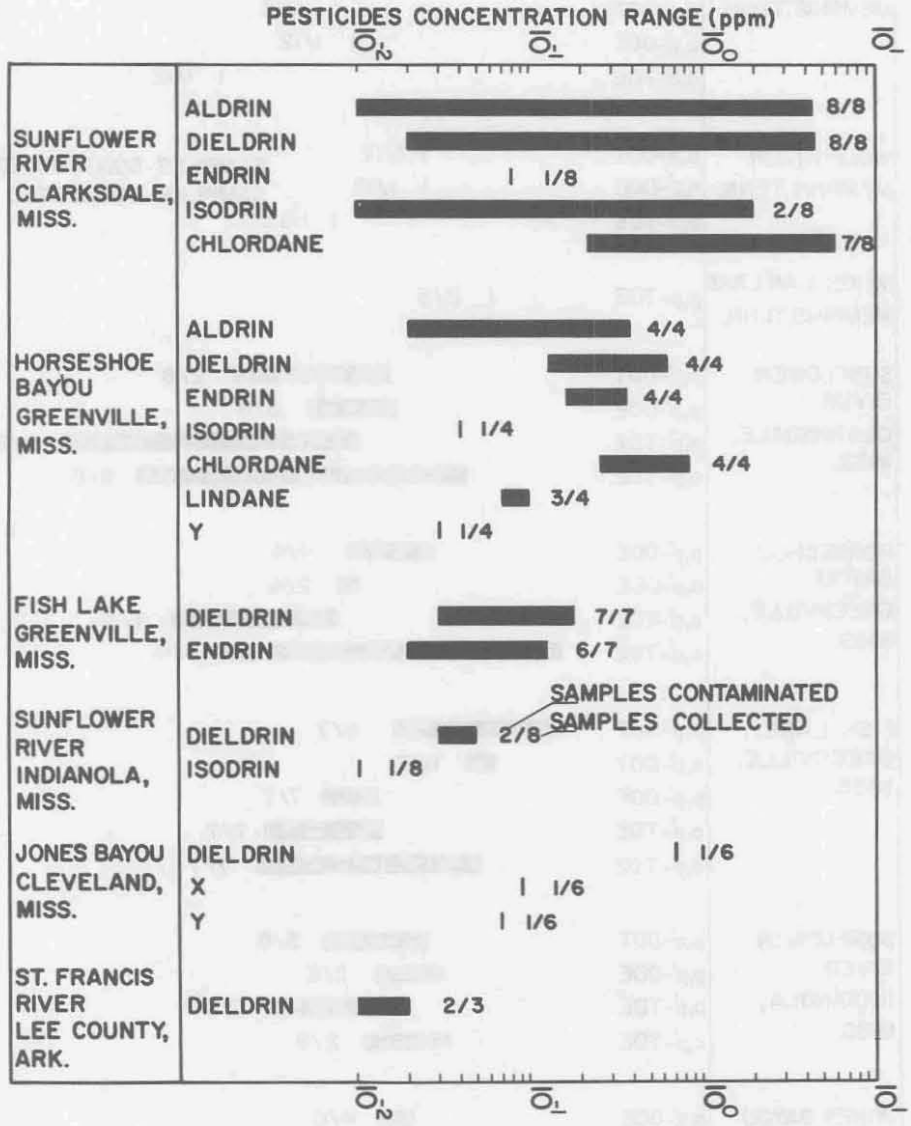

Figure 3 -- Non-DDT insecticide residues in streambed sediments from industrial contamination (exception: St. Francis River, Lee County, Ark.).

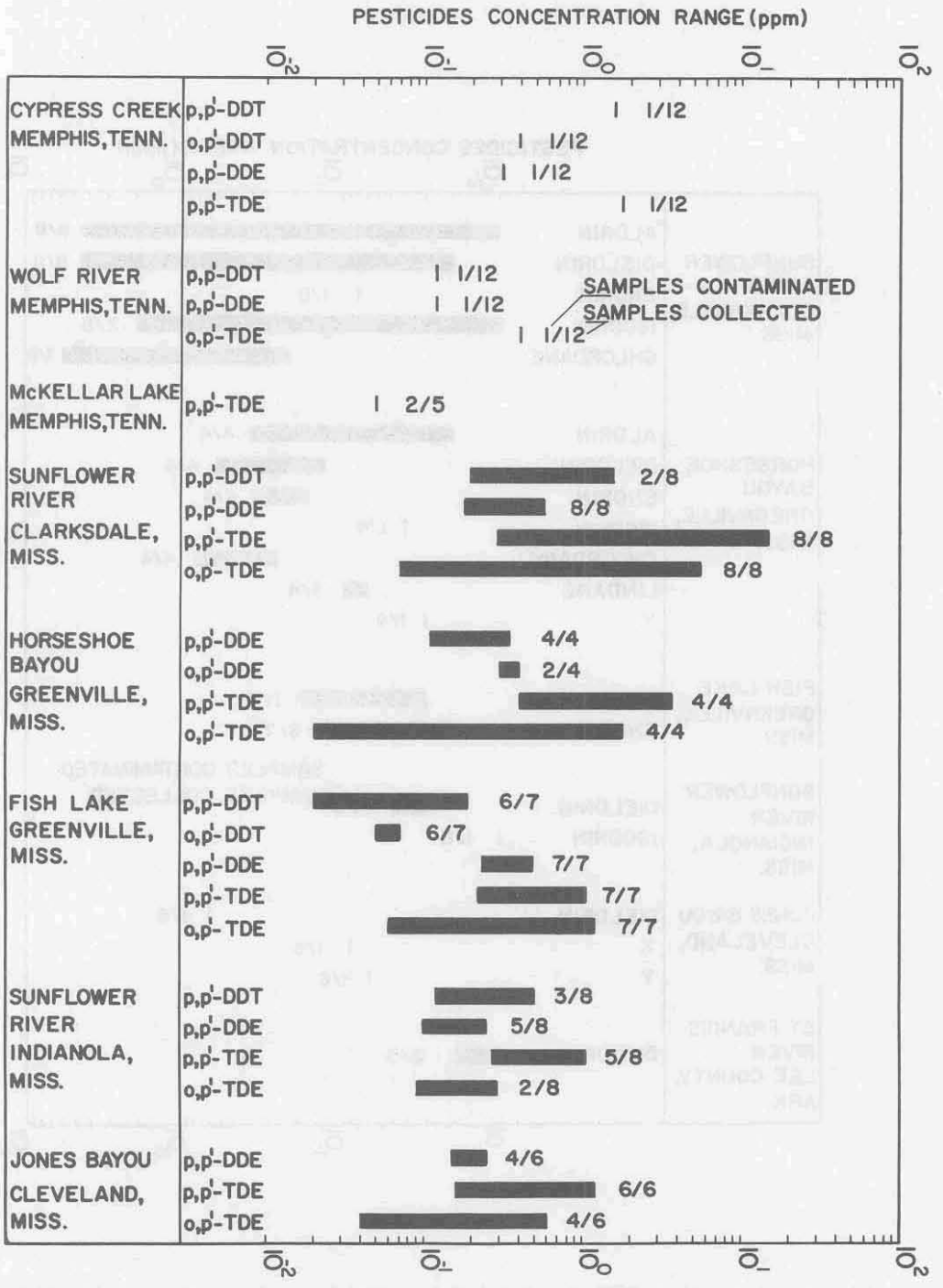

Figure 4 -- DDT residues in streambed sediments from industrially contaminated areas.

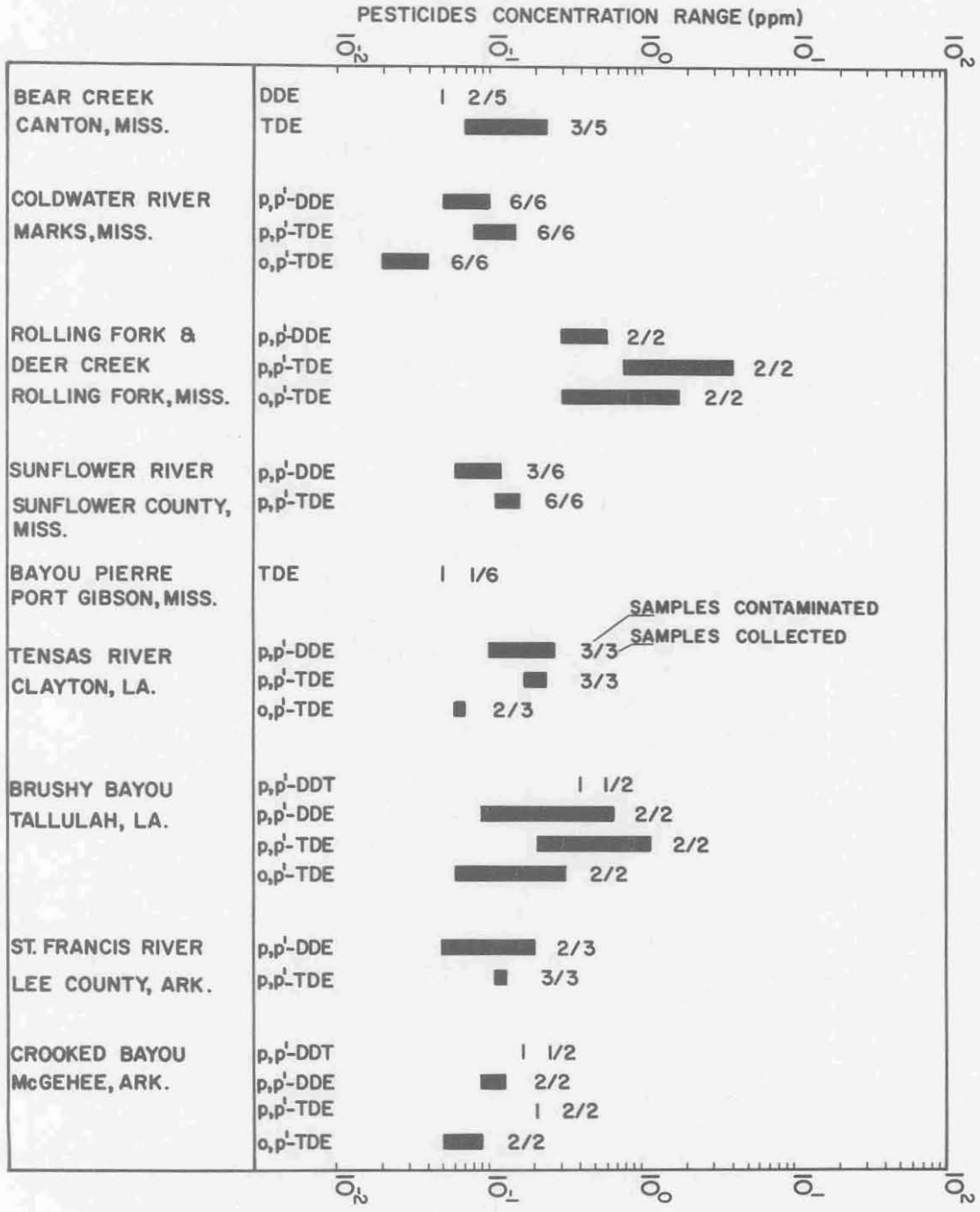

Figure 5 -- DDT residues in streambed sediments from nonindustrial sources.