

PRELIMINARY RESULTS OF FISH TISSUE ANALYSIS IN THE MISSISSIPPI EMBAYMENT NAWQA PROGRAM

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INTRODUCTION

As a standard part of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program, biological tissues are collected from sites within each project area to determine the occurrence and distribution of trace elements and organochlorine compounds (Crawford and Luoma 1992). Tissue analysis is widely used to determine the occurrence of contaminants in the aquatic environment because the contaminants are often present in higher concentrations in the tissues than in the water due to bioaccumulation, tissue data provide a time-averaged assessment of the contaminants, and tissue data provide a direct assessment of bioavailability.

The Mississippi Embayment (MISE) NAWQA project area generally includes the Mississippi River alluvial floodplain between the confluence of the Mississippi and Ohio Rivers south to approximately Natchez, Mississippi, and includes the Mississippi Valley loess hills on the eastern border (Figure 1). The landuse of the floodplain is dominated by agriculture; cotton, soybeans and rice are the principal crops. The loess hills are about half agricultural land and half pine forest. The Mississippi Embayment project is one of more than 50 projects that are located throughout the United States. These projects will be undertaken sequentially; that is, 20 projects began in 1991 and have now been completed, 15 projects began in 1994 and are about midway through the field sampling phase; and 15 projects will begin in 1997.

This paper presents the preliminary fish tissue data collected as part of the Mississippi Embayment NAWQA project. Additional sites will be sampled during the remaining 2 years of the Mississippi Embayment project in to provide a more complete geographic coverage of the project area.

METHODS

Fish were collected by electrofishing at 17 locations throughout the Mississippi Embayment NAWQA study area (Figure 1) during the low flow period of fall 1995 and fall 1996. At all but one site, a tissue sample consisted of an eight-fish composite of the livers from common carp (*Cyprinus carpio*) for trace element analysis and an additional eight-fish whole fish composite for

organochlorine analysis. No carp were collected at the Wolf River site; instead largemouth bass (*Micropterus salmoides*) were sampled. At two sites, spotted gar (*Lepisosteus oculatus*) was sampled in addition to the carp. Each fish was weighed, standard and total length were measured, sex was determined, and scales were removed for age determinations. Several samples of the liver were taken from each of the eight fish designated for trace element analysis. The liver parts were placed in an acid-washed glass jar, frozen, and shipped to the laboratory on dry ice. The whole fish designated for organochlorine analysis were individually wrapped in aluminum foil, frozen, and shipped.

Analysis of the samples was performed by the U.S. Geological Survey National Water-Quality Laboratory. The liver composites collected for trace element analysis were dried, digested, and analyzed using inductively coupled plasma emission spectrophotometry, inductively coupled plasma mass spectrometry, and cold vapor atomic absorption for total mercury (Crawford and Luoma 1992). Analytical methods for organochlorine pesticides and PCBs included homogenization and subsampling of the fish composite, Soxhlet extraction, fractionation, and analysis by dual capillary column GC/ECD (Leiker et al. 1995). The data presented in this paper were not lipid normalized due to the primary use of a single species.

RESULTS AND DISCUSSION

Trace Element Analysis

Fish livers were selected as the target for the NAWQA program because many trace elements are known to concentrate in liver. A principal objective of the program was to define the occurrence and distribution of trace elements in the aquatic environment. Fish livers provide a high probability of detection of these elements. However, because few other agencies analyze liver concentrations, it is difficult to find data for comparison. Currently, the best data available for comparison are data collected from other NAWQA project areas that represent 20 major drainage basins across the United States.

Generally, concentrations of trace elements in the water, sediments, and tissues in the Mississippi Alluvial Plain are relatively low. This is primarily due to the low concentration

of industrial and municipal sources of trace elements, the low population density, and the pH of the environment which makes the compounds less bioavailable. The Mississippi Embayment NAWQA data are summarized in Table 1. Personal communications with scientists working in other NAWQA project areas indicate that arsenic and mercury are the primary compounds which have concentrations at the high end of the range found in other NAWQA study units. Potential sources of arsenic in the basin include arsenate-based herbicides and fungicides. The mean mercury level is high, primarily because of high levels found in a gar sample collected at the Yazoo River site.

Organochlorines

The widespread use of synthetic organic compounds, such as organochlorine pesticides and polychlorinated biphenyls (PCBs) began in the mid-1940s. The use of many of these compounds was restricted or banned in the 1970s and 1980s. The persistence of these compounds has been documented in national surveys such as the National Contaminant Biomonitoring Program studies conducted by the U.S. Fish and Wildlife Service (Schmitt et al. 1990). Current organochlorine concentrations are not directly related to current land-use practices. However, occurrence of organochlorine concentrations in fish tissue reflects past usage in a basin, indicates patterns of persistence, may propose explanations for the composition of the fish community, and in extreme cases, may suggest cause for concern regarding human consumption of fish tissue.

Currently, data from the 20 NAWQA study units which began sampling in 1991 are available for comparison. Fish tissue from 230 sites within the 20 study units has been analyzed. Carp was the primary species collected at 40 of the 230 sites. Organochlorine data for the carp from the Mississippi Embayment study unit and the carp data from the other 40 sites from across the United States are summarized in table 2. **Mean values presented are the mean of all values above laboratory detection limits.** Percent detects give an indication of the geographic coverage over which positive detections were found. Constituents in the Mississippi Embayment study unit which had a significant divergence from the national values include mirex, DDT and its metabolites, and toxaphene.

Mirex. Although samples were analyzed for mirex from more than 230 sites across the United States, the only locations where mirex was above the detection level of $5\mu\text{g/kg}$ in fish tissue were in the Mississippi Embayment study unit. Mirex was detected in whole fish from Bayou Macon near Delhi, Louisiana, ($41\mu\text{g/kg}$) and in fish from the Tensas River at Tendal, Louisiana, ($96\mu\text{g/kg}$); concentrations just above detection limits were found in fish in the Skuna River, near Bruce (Figure2), Mississippi.

Mirex was used as an insecticide to control imported red fire ants (*Solenopsis invicta*) in the South and more widely as a flame retardant and polymerizing agent (Kaiser 1987). Although the concentrations found in this study unit are probably related to the use of mirex for fire ant eradication, it is not clear why concentrations are higher in Louisiana as compared to the rest of the study unit.

DDT and metabolites. DDT was used as an insecticide in the United States from the end of World War II until the use of DDT was banned in 1972. DDT use was commonly used as a customary part of cotton cultivation. DDT weathers into two metabolites, DDE and DDD. Figure 3 depicts the detection of DDT and its metabolites at sites throughout the Mississippi Embayment.

The current NAWQA national data base of 40 sites where carp were collected within 20 study units indicates that the percent detections, that is the number of times a compound was found at levels above the analytical detection limit, was about 41, 95, and 15 percent for *p,p'*-DDD, DDE, and DDT, respectively. In the Mississippi Embayment study unit, these compounds were found at levels above detection at 100, 100, and 53 percent of the sites, respectively. These values are indications of the widespread occurrence of DDT and its metabolites in the environment. The maximum total DDT, defined as the sum of *o,p'*- and *p,p'*-DDE, DDD, and DDT, for the more than 230 previously sampled NAWQA sites was $2,998\mu\text{g/kg}$. Samples from the Mississippi Embayment study unit yielded total DDT levels which exceeded the maximum value of $2,998\mu\text{g/kg}$ at 9 of 17 sampled sites, with a maximum level of $9,544\mu\text{g/kg}$ found in fish from Bayou Cassidy at Sumner, Mississippi.

Schmitt and others (1990) reported on fish collected in 1984 from 112 stations in major rivers throughout the United States. In that study, the highest total DDT levels in the country were reported from the Yazoo River near Redwood, Mississippi. This site was re-sampled as part of the NAWQA project, and although values remained high at the Yazoo River site, eight other locations within the study unit had total DDT levels higher than those at the Yazoo River site. Schmitt and others (1990) also calculated a national geometric mean of about $250\mu\text{g/kg}$, whereas the mean value in the Mississippi Embayment study unit was about $3,410\mu\text{g/kg}$.

Although whole fish contaminant data are inherently variable, there is some indication that there may be a decrease in total DDT values over time. Schmitt et al. (1990) reported that the geometric mean of the total DDT concentration in carp at the Yazoo River site was more than $5,600\mu\text{g/kg}$ for fish collected in 1984. The carp collected in 1995 at the same site yielded a total DDT concentration for the composite sample of slightly less than $2,200\mu\text{g/kg}$.

Schmitt et al. also noted that nationally, during the period from 1976-81, the composition of the DDT mixture was about 70 percent *p,p'* - DDE, 20 percent *p,p'* - DDD, and 10 percent *p,p'* - DDT. By 1984, the proportion of DDE increased to 73 percent indicating an overall continued weathering of DDT. In the 1995 NAWQA data set, the proportions for the entire Mississippi Embayment study unit were 77 percent *p,p'* - DDE, 20 percent *p,p'* - DDD, and only 3 percent *p,p'* - DDT, suggesting further weathering of the compound.

Toxaphene. After the ban of DDT in 1972, toxaphene became a very widely used insecticide, particularly for cotton farming, until its registration was canceled for most uses in 1982 (USEPA 1982). Concentrations of toxaphene detected in the Mississippi Embayment study sites are shown in Figure 4. Considering the NAWQA national data base, toxaphene was detected at only 1.1 percent of the 230 sites sampled in the United States, at a maximum value of 2,000 $\mu\text{g/kg}$. In the Mississippi Embayment study unit, toxaphene was detected at 53 percent of the sites, at a maximum value of 12,000 $\mu\text{g/kg}$.

Schmitt et al. (1990) documented that the Yazoo River near Redwood was also the site with the highest reported toxaphene concentrations in the United States with a geometric mean of about 4,800 $\mu\text{g/kg}$, compared to a national geometric mean of about 200 $\mu\text{g/kg}$ in 1984. In the 1995 NAWQA study, the composite carp sample at the Yazoo River site had a toxaphene concentration of 1,600 $\mu\text{g/kg}$, again indicating a potential decrease during the 11-year period between samples, but there were six sites in the Mississippi Embayment which had higher values.

CONCLUSIONS

Concentrations of most of the trace elements found in fish liver in the Mississippi Embayment study unit, with the exception of arsenic and mercury, appear to be within ranges found at other NAWQA sites, although the data base for trace elements in fish livers is limited. Concentrations of many organochlorines in fish tissue collected from Mississippi Embayment study unit appear to be similar to concentrations found in other parts of the United States. However, the concentrations of DDT and toxaphene,

pesticides that were primarily used in the cultivation of cotton, have persisted in the aquatic environment at levels considerably higher than those found elsewhere in the United States. The detection of these materials is not surprising, in light of the application rates in the basins studied; however, the persistence of the compounds at relatively high levels 15 to 25 years after the discontinuation of their use may be considered noteworthy.

REFERENCES

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Table 1. Mean, minimum and maximum trace element concentrations (dry weight) in the Mississippi Embayment NAWQA fish liver samples. The mean value represents the mean of all samples reported above the detection limit.

METAL	MISSISSIPPI EMBAYMENT NAWQA (µg/g)		
	Mean	Minimum	Maximum
Aluminum	27	1.8	248
Antimony	---	> 0.1	>0.2
Arsenic	0.6	> 0.2	1.8
Barium	0.4	> 0.1	1.3
Beryllium	---	> 0.1	> 0.2
Boron	0.7	0.3	1.2
Cadmium	3.9	0.7	8.7
Chromium	0.6	> 0.5	0.8
Cobalt	0.32	> 0.1	1.3
Copper	81	6.8	125
Iron	776	269	1530
Lead	0.18	> 0.1	0.4
Manganese	6.8	2.9	19.8
Mercury	0.68	0.18	4.2
Molybdenum	1.15	0.6	1.9
Nickel	0.64	0.10	3.5
Selenium	6.6	3.8	8.8
Silver	0.38	0.2	0.7
Strontium	1.12	0.1	10.1
Uranium	0.16	0.1	0.2
Vanadium	2	0.7	4.7
Zinc	502	76	794

Table 2. Summary of mean organochlorine concentrations (wet weight) and percent detections for carp from 17 sites within the Mississippi Embayment (MISE) and for carp at 40 sites from other NAWQA projects in the U.S. The mean value is the mean of all samples above the detection limit.

COMPOUND	MISE NAWQA INFORMATION		NATIONAL NAWQA INFORMATION	
	Mean ($\mu\text{g/kg}$)	Percent Detects	Mean ($\mu\text{g/kg}$)	Percent Detects
Aldrin	0	0	0	0
Alpha-BHC	0	0	0	0
Beta - BHC	5	7	0	0
<i>Cis</i> -Chlordane	14	33	16	28
<i>cis</i> -Nonachlor	13	33	9	16
DCPA	5	7	28	10
Delta-BHC	8	15	0	0
Dieldrin	19	79	32	41
Endrin	0	0	0	0
Heptachlor	11	7	0	0
Heptachlorepoxyde	0	0	8	5
Hexachlorobenzene	0	0	9	13
Mirex	32	29	0	0
<i>o,p'</i> - DDD	70	53	12	13
<i>o,p'</i> - DDE	25	54	11	5
<i>o,p'</i> - DDT	46	22	43	11
<i>o,p'</i> Methoxychlor	50	11	0	0
Oxychlordane	79	13	13	3
<i>p,p'</i> - DDD	661	100	29	47
<i>p,p'</i> - DDE	2458	100	199	95
<i>p,p'</i> - DDT	51	73	79	15
PCB's	132	65	3647	44
Pentachloranisol	11	7	0	0
<i>p,p'</i> -Methoxychlor	0	0	0	0
<i>trans</i> -Chlordane	14	20	12	26
Toxaphene	3748	56	0	0
<i>trans</i> -Nonachlor	11	69	19	31

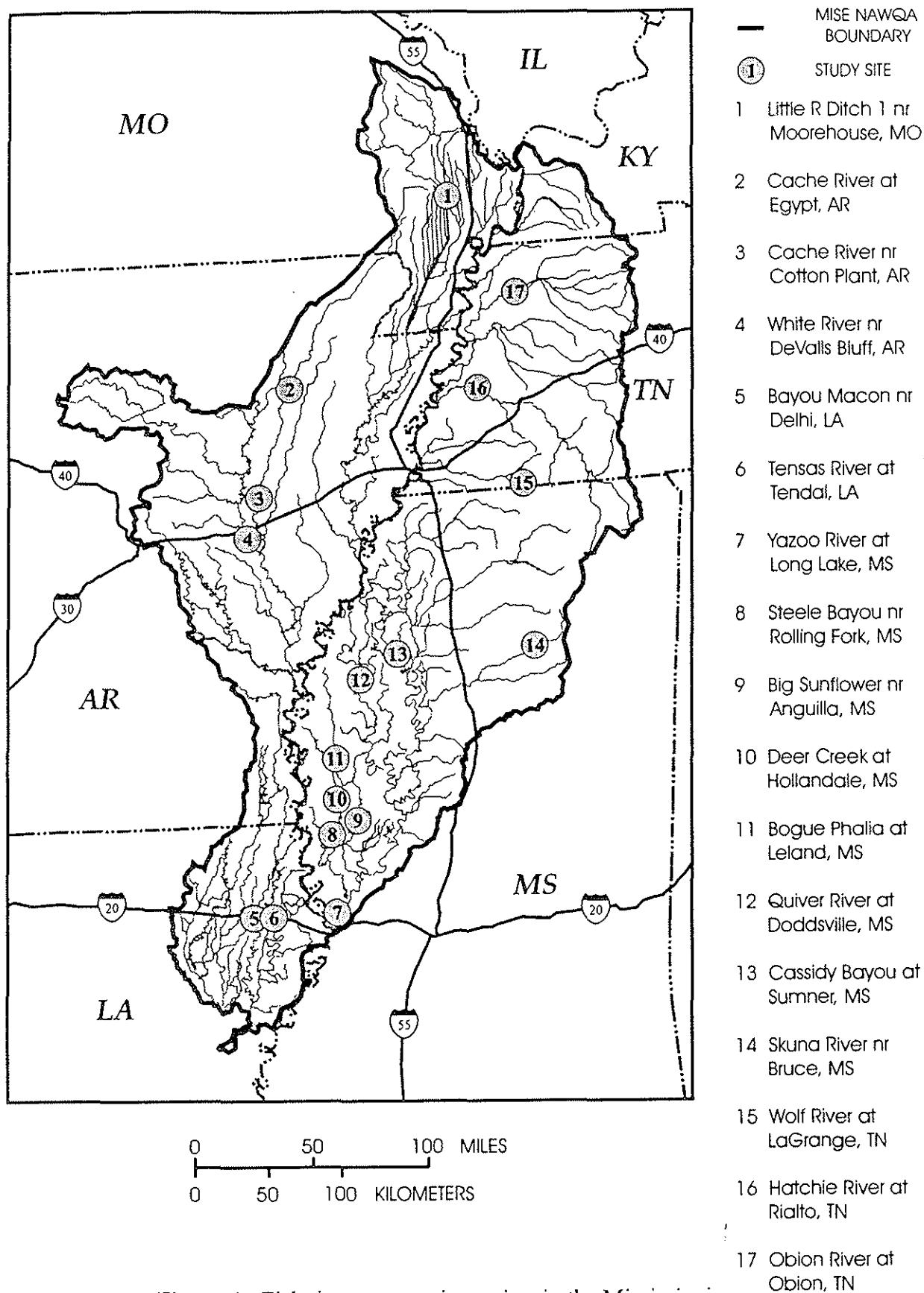


Figure 1. Fish tissue contaminant sites in the Mississippi Embayment NAWQA.

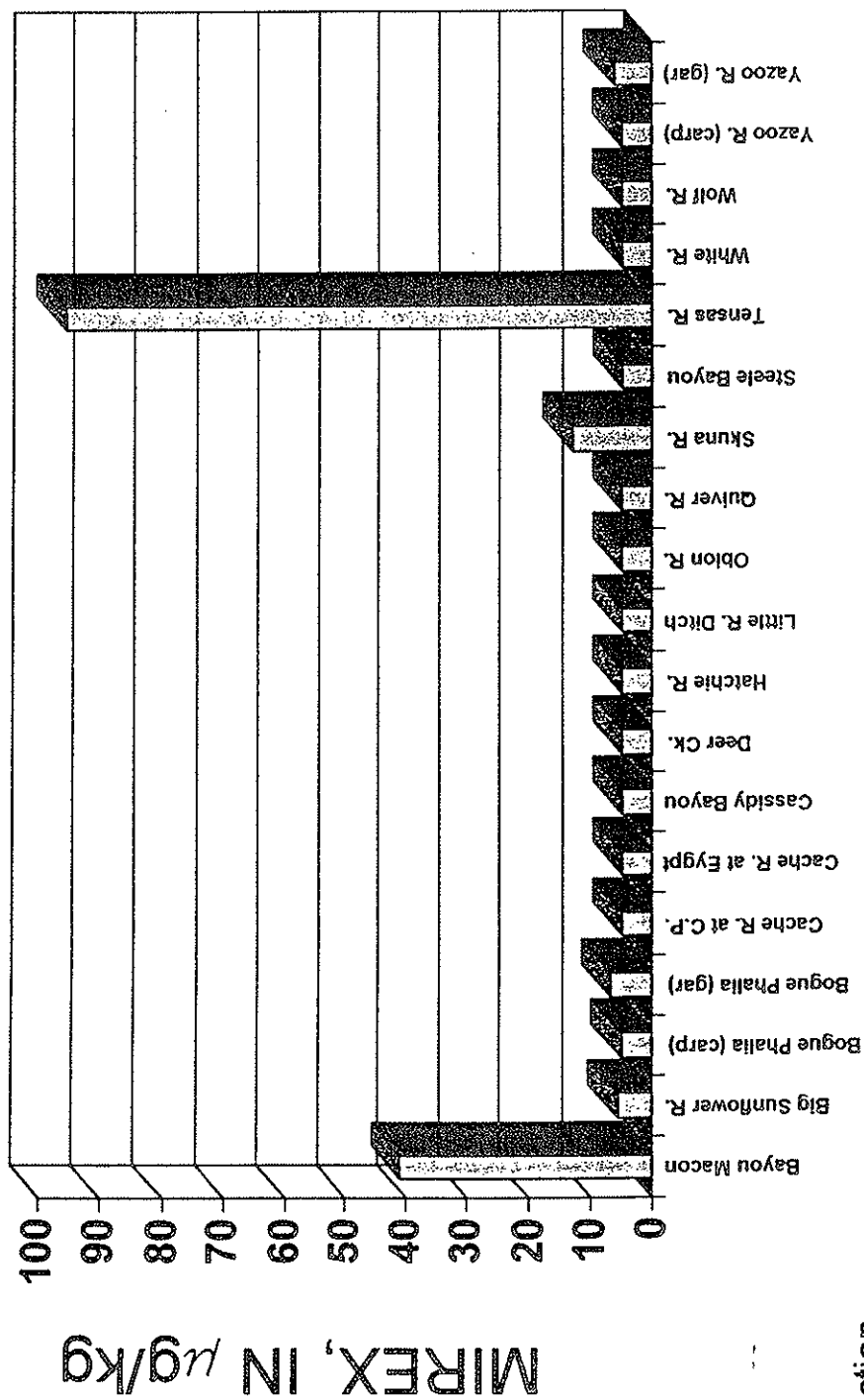
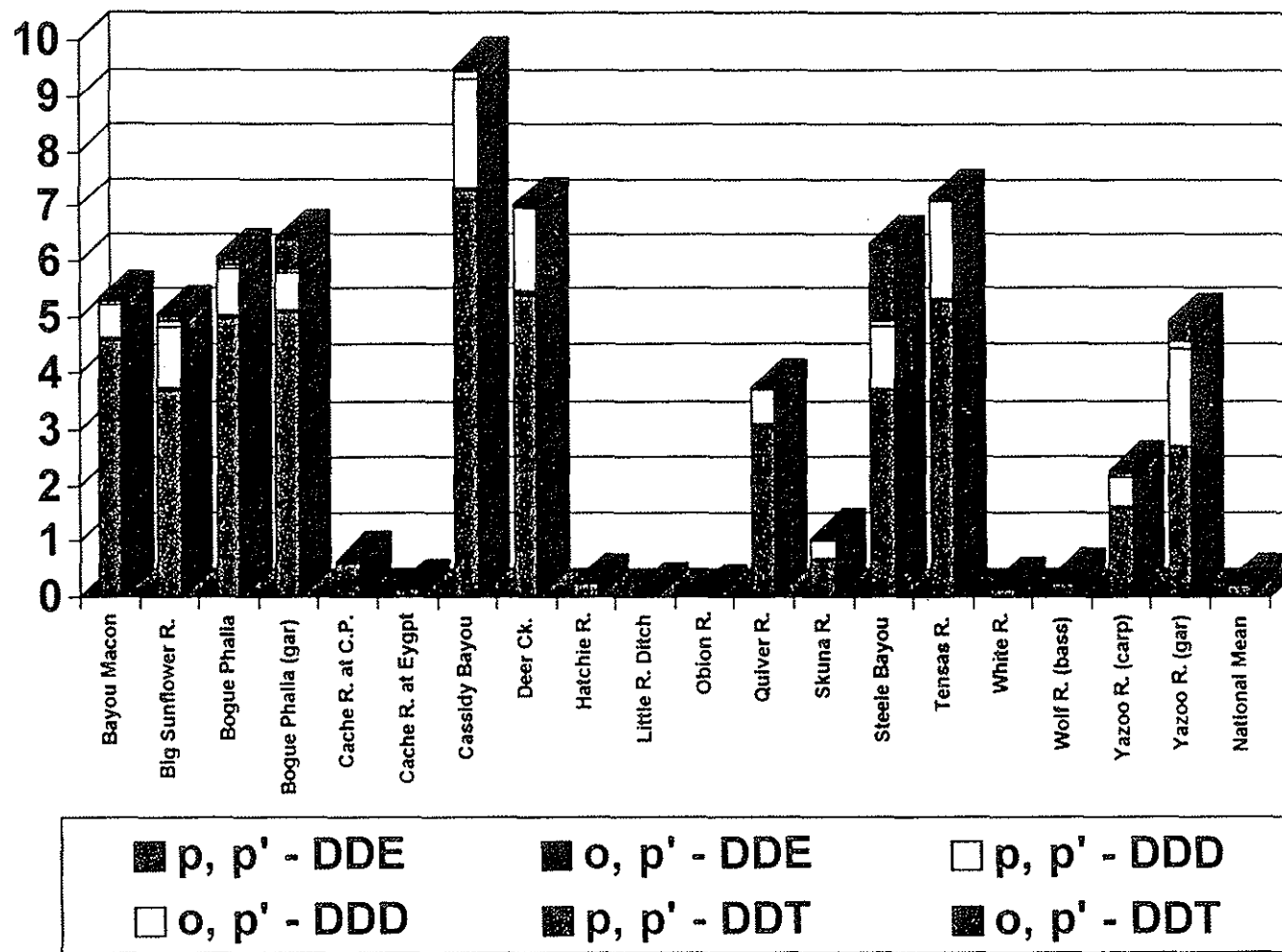


Figure 2. Mirex concentrations at 17 sites within the Mississippi Embayment study unit.

Lab detection
limit 5.0 $\mu\text{g/kg}$

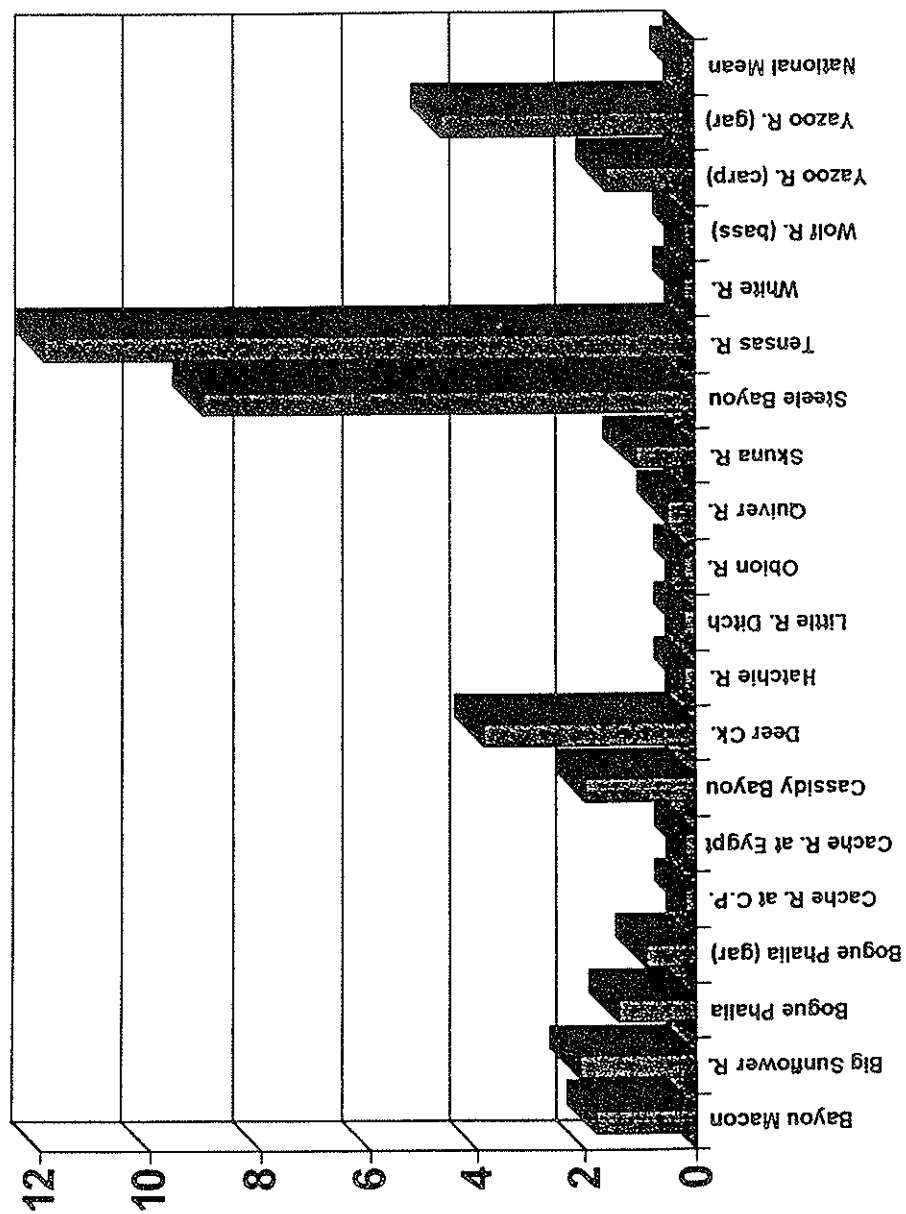
TOTAL DDT, IN mg/kg



Lab detection
limit 0.005 mg/kg

Figure 3. Concentrations for DDT and metabolites at 17 sites within the Mississippi Embayment study unit. National mean for comparison from Schmitt et al. (1990).

TOXAPHENE, IN mg/kg



Lab detection
limit 0.2 mg/kg

Figure 4. Toxaphene concentrations at 17 sites within the Mississippi Embayment study unit. National mean for comparison from Schmitt et al. (1990).