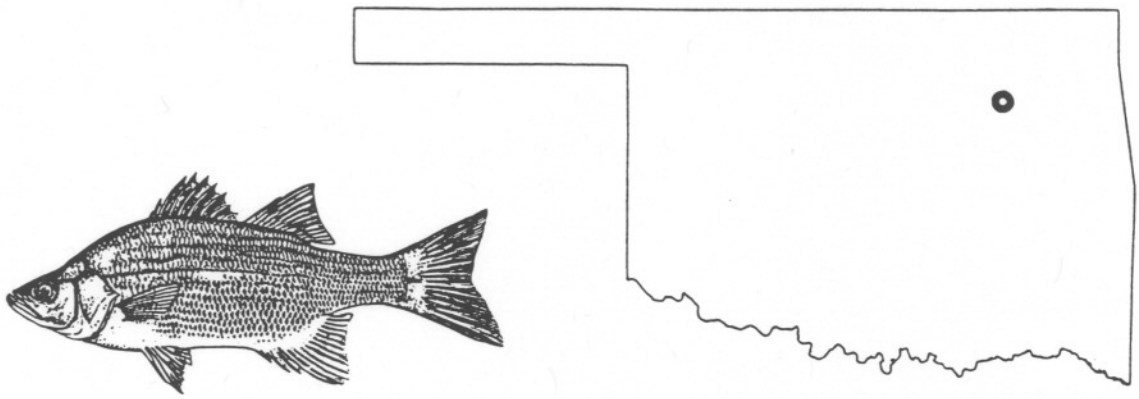
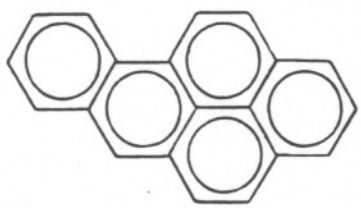
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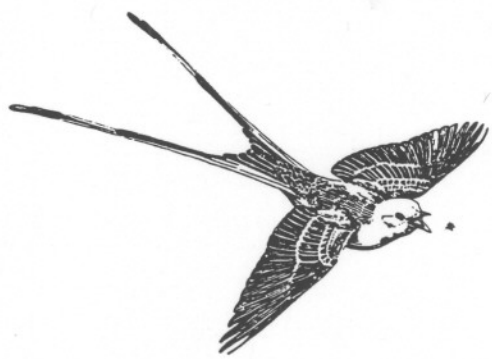
FISH AND WILDLIFE ENHANCEMENT CONTAMINANTS REPORT

TULSA ECOLOGICAL SERVICES FIELD OFFICE 1992

A PRELIMINARY SURVEY OF CONTAMINANTS IN FISH AND SEDIMENT FROM THE ARKANSAS RIVER IN THE VICINITY OF TULSA, OKLAHOMA







FISH AND WILDLIFE SERVICE

U.S. DEPARTMENT OF THE INTERIOR

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By

Dan B. Martin

U.S. Department of the Interior
Fish and Wildlife Service
Ecological Services
222 South Houston, Suite A
Tulsa, Oklahoma 74127

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INTRODUCTION

The middle reach of the Arkansas River in Oklahoma, between Keystone Dam and the mouth of the Verdigris River, is an important resource area for two federally listed endangered species. This section of the river (Figure 1) has been designated essential habitat for the recovery of the interior least tern (Sterna antillarum). Breeding and nesting sites for this bird are found on islands and sand bars along the river from Tulsa to Muskogee. The bald eagle (Haliaeetus leucocephalus) utilizes this area during the winter months. An eagle preserve, managed by the U.S. Army Corps of Engineers, is located directly below Keystone Dam, and a number of other perch and roost sites are scattered downstream along the riparian corridor.

Fish from the Arkansas River comprise the entire diet of interior least terns and constitute a significant portion of the food base for wintering bald eagles. In order to insure the well-being of these two endangered species along this portion of the Arkansas River, it will be necessary to maintain adequate numbers of fish in the river, and these fish must be free from harmful quantities of chemical contaminants.

The middle Arkansas River flows through Tulsa County, one of the most populated and industrialized areas in Oklahoma. Municipal sewage, industrial waste, and storm water runoff enter the river and its tributaries in the Tulsa vicinity. Two Superfund sites - an abandoned land fill, and an abandoned petrochemical plant - are also located adjacent to the river and may contribute to the overall contaminant loading.

The U.S. Fish and Wildlife Service has embarked on a long-term, three-phase program (Figure 2) to insure that chemical contaminants do not contaminate and/or eliminate the food supply for interior least terns and bald eagles along the middle Arkansas River. Phase One of the program consists of compiling a complete list of contaminant sources to the river. This inventory includes such things as NPDES permits, Superfund sites, and storm water discharge sites. Phase Two seeks to determine the fitness of the Arkansas River and its tributaries for aquatic life, and to evaluate the health of resident populations and communities. This approach utilizes bioassays and other bioindicators. Phase Three of the project is to determine the concentration of contaminants in key components of the aquatic ecosystem. Collectively, these three lines of effort will provide a database for a continuing assessment of the contaminant status of the middle Arkansas River and can be used to identify areas and/or sources for remediation.

The U.S. Fish and Wildlife Service began work on this program in the summer of 1989 by collecting fish and sediment from the Arkansas River in Tulsa for chemical analysis. The purpose of this report is to describe the 1989 study, present the results, and to briefly discuss their significance.

The author would like to acknowledge J. K. Andreasen, whose study proposal resulted in the funding for the 1989 project, and K.D. Collins, S.L. Hensley, L.A. Hill, D.W. McQuiddy, and J.A. Ratzlaff for their assistance in the collection of fish samples.

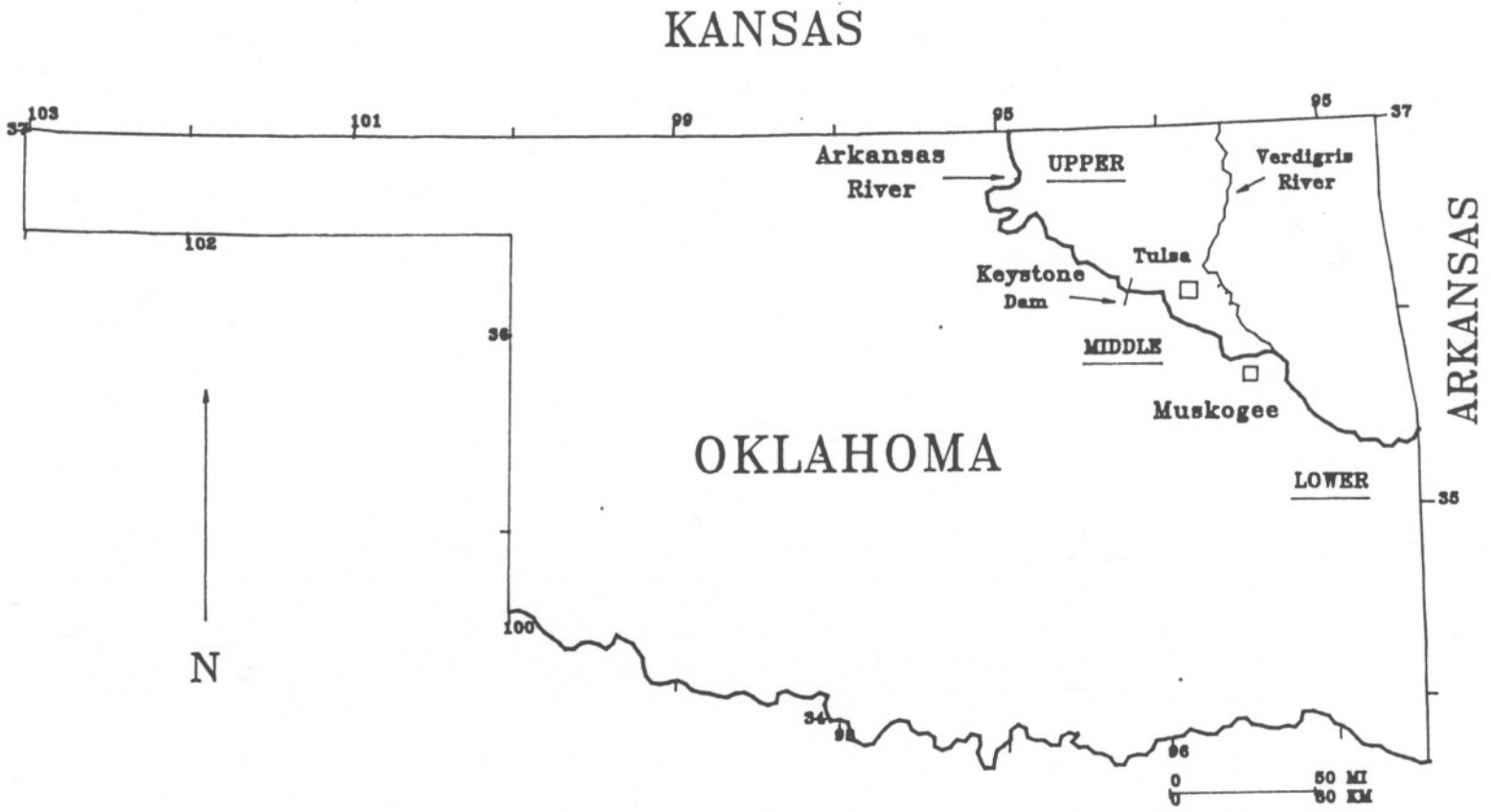


Figure 1. The Arkansas River in Oklahoma: Upper-Kansas border to Keystone Dam; Middle-Keystone Dam to Verdigris River; Lower-Verdigris River to Arkansas border.

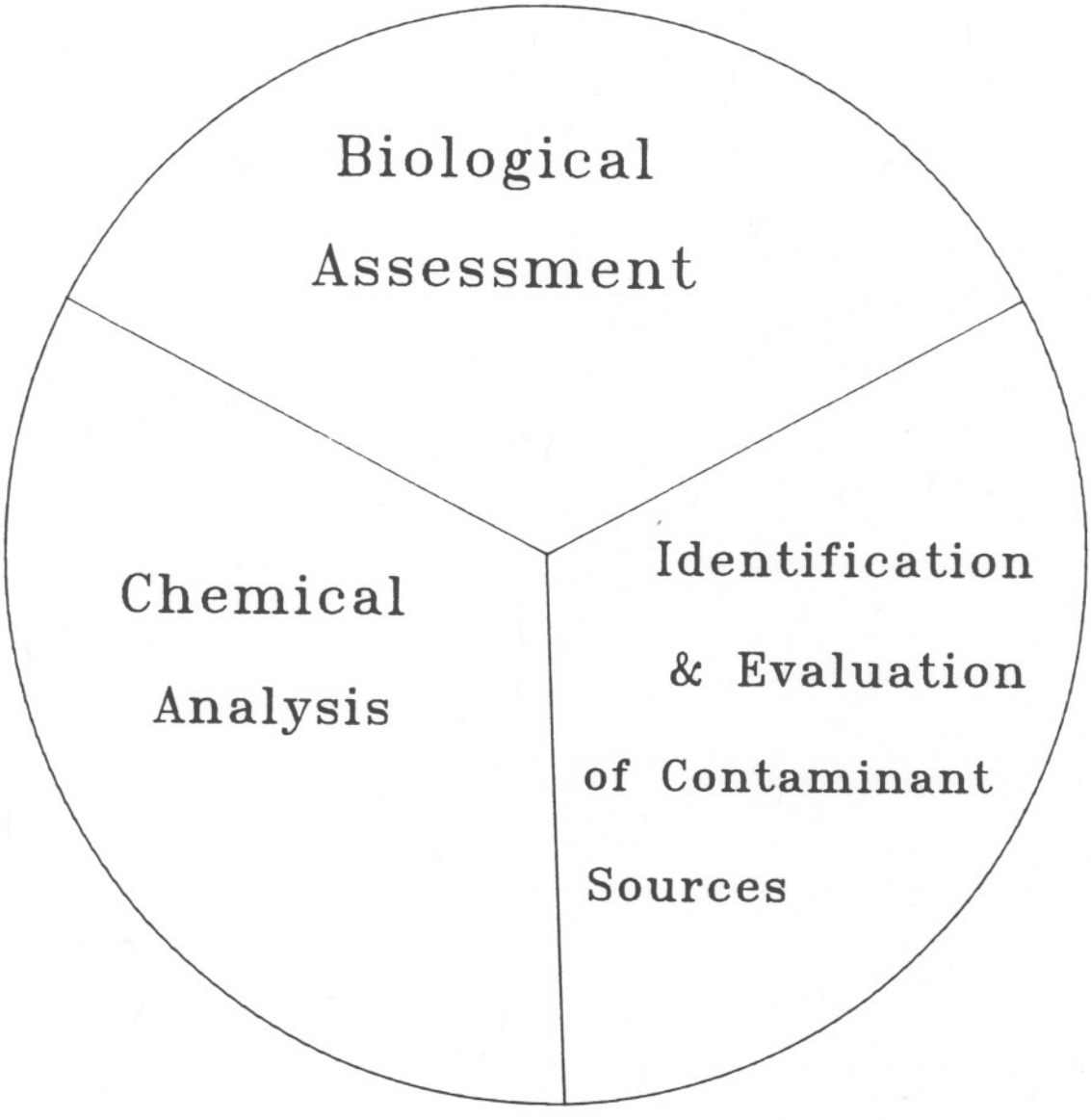


Figure 2. Three phased program employed by U.S. Fish and Wildlife Service for determining the contaminant status of the middle Arkansas River in relation to the interior least tern and bald eagle.

METHODS

The middle Arkansas River, which extends from Keystone Dam downstream about 80 miles to the mouth of the Verdigris River, has been divided into eight segments for U.S. Fish and Wildlife Service contaminant studies (Figure 3). In the latest study, sediment and small fish were collected for chemical analysis from segments M1 through M5 (Table 1) on August 7 and 8, 1989. Fish were collected with a seine and immediately wrapped in aluminum foil and placed on ice for transport and storage in the field. Upon returning to the laboratory, fish were sorted into composite samples. Each composite sample consisted of all the individuals of a particular species taken from within a given segment of the river. Small fish that could be captured by seine were scarce. Only one species, the inland silverside (Menidia beryllina), was collected from each of the five segments. Two other species, gizzard shad (Dorosoma cepedianum) and red shiner (Notropis lutrensis) were sufficiently abundant to obtain samples from one or two segments. Fish in each composite sample were counted and the total weight of the sample was taken. Maximum and minimum total lengths were also obtained for the fish in each composite sample. Composite fish samples were wrapped in aluminum foil and frozen.

Sediment samples were collected by hand from depositional areas in the river by sampling the surface of the substrate (1 - 2 cm) and placing it into a glass jar. Approximately one liter (1400 - 1700 g) of sediment was collected, placed on ice in the field, and frozen upon returning to the laboratory.

Fish and sediment samples were packed in dry ice and shipped to U.S. Fish and Wildlife Service contract laboratories in September 1989 for analyses. At the analytical laboratories, sediment samples were homogenized and composite fish samples were ground and homogenized prior to digestion, extraction, and analysis.

Sediments were analyzed for organochlorine pesticides, total polychlorinated biphenyls, aliphatic hydrocarbons, polynuclear aromatic hydrocarbons, and several elements. Fish were analyzed for the same constituents except for polynuclear aromatic hydrocarbons.

RESULTS

Nearly all of the fish sampled in this study represented individuals that would be taken as food by interior least terns. Inland silversides from all segments ranged between 2.8 and 11.0 cm while red shiners were between 2.5 and 6.1 cm in length (Table 2). In general, the chemical composition of these samples should characterize the contaminants present in the diet of interior least terns along this reach of the river. It probably is not valid to use these samples of inland silversides to compare contaminants in various segments of the river, since each composite sample contains a different age class mixture of individuals ranging from young-of-year to at least 3 years. This is illustrated by the fact that the mean weight of silversides in composite samples ranged between 0.6 g in segment M3 to 1.6 g in segment M2 (Table 2).

The fish in the two gizzard shad samples were too large to represent tern food, but they were within the size range taken by bald eagles. Since these were young of the year gizzard shad, they represent the most abundant age-class of this species available to bald eagles in winter. However, more species of large fish need to be analyzed to adequately characterize the dietary intake of contaminants by bald eagles.

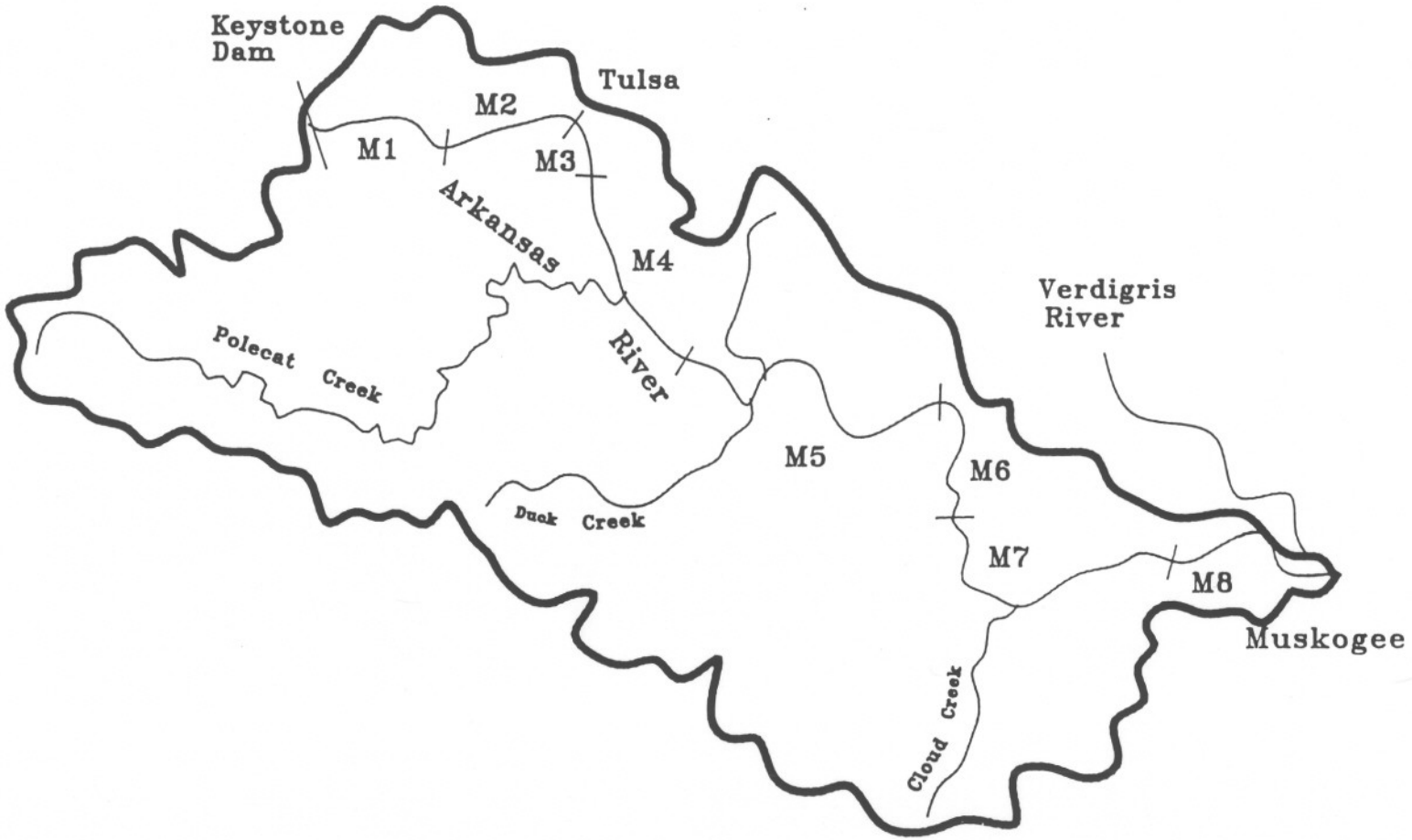


Figure 3. The middle Arkansas River watershed in Oklahoma. The river has been divided into eight segments (M1 - M8) for contaminant studies.

Table 1. Hydrologic divisions of the Arkansas River in Oklahoma used to describe U.S. Fish and Wildlife Service contaminant studies.

Reach	Segment	Location
Upper	U1	Kansas border to Kaw Dam
	U2	Kaw Dam to Salt Fork Arkansas River
	U3	Salt Fork Arkansas River to Red Rock Creek
	U4	Red Rock Creek to Salt Creek
	U5	Salt Creek to Black Bear Creek
	U6	Black Bear Creek to Hwy 99 Bridge
	U7	Hwy 99 Bridge to Keystone Dam
Middle	M1	Keystone Dam to Hwy 97 Bridge
	M2	Hwy 97 Bridge to Union Avenue
	M3	Union Avenue to Low Water Dam (28th Street)
	M4	Low Water Dam (28th Street) to Hwy 64 Bridge
	M5	Hwy 64 Bridge to Hwy 72 Bridge
	M6	Hwy 72 Bridge to Hwy 104 Bridge
	M7	Hwy 104 Bridge to Pecan Creek
	M8	Pecan Creek to Verdigris River
Lower	L1	Verdigris River to Hopewell Park
	L2	Hopewell Park to Webber Falls Lock & Dam
	L3	Webber Falls Lock & Dam to Hwy I-40 Bridge
	L4	Hwy I-40 Bridge to Downstream Boundary, Sequoyah National Wildlife Refuge (NWR)
	L5	Downstream Boundary, Sequoyah NWR to Robert S. Kerr Lock & Dam
	L6	Robert S. Kerr Lock & Dam to W.D. Mayo Lock & Dam
	L7	W.D. Mayo Lock & Dam to Arkansas Border

Table 2. Characteristics of fish samples taken in 1989 from the middle Arkansas River for chemical analysis.

River Segment	Species[1]	No.	Length Range (cm)	Mean Weight (g)	Lipid %	Moisture[2] %	Moisture[3] %
M1	IS	539	2.8-11	1.5	2.6	75.4	75.0
M1	GS	13	14-16	26	1.3	80.5	80.7
M2	IS	200	3.8-7.6	1.6	2.4	74.1	75.0
M3	IS	500	3.0-6.9	0.6	1.7	77.8	78.0
M4	IS	220	3.8-7.6	1.4	2.0	74.2	76.1
M4	IS	410	4.0-8.0	1.2	2.4	77.5	75.3
M4	GS	7	12-17	25	2.6	77.7	74.5
M5	IS	126	4.0-7.4	1.1	3.0	75.9	74.2
M5	RS	600	2.5-6.1	0.6	5.3	74.8	74.9

[1] IS=Inland silversides; GS=Gizzard shad; RS=Red shiner
[2] Moisture determinations for organic analyses, Geochemical & Environmental Research Group, Texas A&M University.
[3] Moisture determinations for inorganic analyses, Hazleton Laboratories America, Inc.

Elements

Concentrations of twenty elements were reported from the analyses that were performed on sediments and fish. Fifteen of these elements - aluminum, antimony, barium, beryllium, boron, iron, magnesium, manganese, molybdenum, nickel, silver, strontium, thallium, tin, and vanadium - are not discussed in this report because: (a) they are not considered to be contaminants with toxic or deleterious effects, (b) their concentrations were for the most part below detection limits, or (c) the significance of their reported concentrations are unknown.

Cadmium in fish exceeded the minimum detection limit of 0.05 ppm wet weight in only one sample, that being gizzard shad from segment M4 (Table 3). The National Contaminants Biomonitoring Program (NCBP) 85th percentile value for cadmium is 0.05 ppm (Schmitt and Brumbaugh 1990), which indicated that the analytical method used in this study is not sufficiently sensitive for discerning variations in cadmium concentrations in the majority of whole-body fish samples nationwide. The method is however, probably sensitive enough to be used as a screening technique, and it would appear that none of the samples representing interior least tern food would be considered seriously contaminated. Cadmium concentrations in sediment ranged from below the detection limit (0.3 ppm dry weight) in segments M1 and M3 to 1.4 ppm dry weight in segment M5 (Table 4). These values are substantially lower than the Effects Range-Low (ER-L) concentrations suggested by Long and Morgan (1990). It does not appear that sediments in this reach of the Arkansas River are seriously contaminated with cadmium.

Chromium concentrations were fairly uniform in tern food samples, ranging between 1.0 and 1.6 ppm wet weight (Table 3). Gizzard shad from segment M4 were slightly higher at 2.3 ppm. Chromium concentrations in sediment ranged from 4.6 to 10 ppm dry weight, well below either the ER-L value of 80 ppm or the EPA (1977) "nonpolluted" limit of 25 ppm dry weight. On the basis of these samples, chromium would not appear to be a contaminant problem for least terns.

Copper concentrations in inland silversides ranged from 0.52 to 0.69 ppm wet weight, values that were comparable to the NCBP geometric mean (Table 3). Copper concentrations in red shiners and gizzard shad ranged from 1.0 to 2.2 ppm, values that were equal to or slightly in excess of the NCBP 85th percentile. Sediment copper, which ranged between 1.9 and 4.7 ppm dry weight, fell below both the ER-L concentration and the EPA "nonpolluted" guideline of 70 and 25 ppm, respectively (Table 4). These samples do not indicate that copper is a contaminant problem.

Lead concentrations were below the detection limit of 0.30 ppm wet weight in all of the fish samples except for gizzard shad from segment M4 (Table 3). As with cadmium, the method used in this study apparently is not sensitive for lead, given the fact that the limit of detection is above the NCBP 85th percentile concentration of 0.22 ppm. The gizzard shad sample from segment M4 raises some question as to whether or not there is significant lead contamination in this section of the Arkansas River. Sediment concentrations of lead were highest above the low water dam (Segment M3) but all segments were below the ER-L and EPA "nonpolluted" guidelines of 35 and 40 ppm, respectively. The gizzard shad sample from segment M4 may have been accidently contaminated during collection, handling, or analysis. Additional lead analyses, to include more of the fish utilized by bald eagles, would seem appropriate.

Table 3. Concentrations of selected elements (ppm wet weight) in whole fish samples from different segments of the middle Arkansas River in Oklahoma. Geometric mean and 85th percentile concentrations from the 1984 National Contaminant Biomonitoring Program (Schmitt and Brumbaugh, 1990) are shown for comparison.

River Segment	Species[1]	Cadmium	Chromium	Copper	Lead	Zinc
M1	IS	--	1.6	0.65	--	52
M1	GS	--	1.3	1.2	--	32
M2	IS	--	1.3	0.52	--	50
M3	IS	--	1.0	0.66	--	58
M4	IS	--	1.4	0.61	--	54
M4	IS	--	1.5	0.69	--	52
M4	GS	0.07	2.3	2.2	2.9	43
M5	IS	--	1.2	0.69	--	54
M5	RS	--	1.1	1.0	--	78
NCBP Geometric Mean		0.03	--	0.65	0.11	22
NCBP 85th Percentile		0.05	--	1.0	0.22	34

[1] IS=Inland silversides; GS=Gizzard shad; RS=Red shiner

Table 4. Concentrations of selected elements (ppm dry weight) in sediment samples from different segments of the middle Arkansas River in Oklahoma. The Effects Range-Low (ER-L) and Effects Range-Median (ER-M) values reported by Long and Morgan (1990) and the EPA (1977) guidelines for pollutional classification of Great Lakes harbor sediments are shown for comparison.

River Segment	Cadmium	Chromium	Copper	Lead	Zinc
M1	--	7.1	3.4	--	14
M2	0.76	10	2.9	3.6	27
M2	0.53	5.8	1.9	4.1	17
M3	--	5.1	4.7	26	31
M4	1.2	4.6	2.5	11	27
M5	1.4	9.0	2.2	5.0	17
ER-L	5.0	80	70	35	120
ER-M	9.0	145	390	110	270
EPA Nonpolluted	--	<25	<25	<40	<90
Moderately Polluted	--	25-75	25-50	40-60	90-200
Heavily Polluted	>75	>75	>50	>60	>200

Zinc concentrations exceeded the NCBP 85th percentile value in all of the fish samples except for gizzard shad from segment M1 (Table 3). Zinc concentrations in inland silversides were uniform throughout the study area, ranging between 50 and 58 ppm wet weight. Zinc concentrations in gizzard shad were lowest (32-43 ppm) while zinc concentrations in red shiners were markedly higher than the other species. Zinc concentrations in sediment ranged from 14 ppm dry weight in segment M1 to 31 ppm in (Table 4). These values were considerably lower than ER-L (120 ppm) or EPA "nonpolluted" (90 ppm) concentrations. Thus, it appears that fish from the middle Arkansas River are relatively high in zinc, while sediments are within normal background concentrations. Based on the data, one could speculate that the source of zinc in fish is probably dissolved pollution originating from somewhere within the Tulsa vicinity. This hypothesis should be verified by analyzing fish from above Keystone Dam.

Organochlorine Pesticides

Twenty four organochlorine pesticides and related compounds were reported in all fish and sediment samples taken in this study. The lower limit of detection in both sediment and fish was 0.01 ppm wet weight for all of the compounds except toxaphene which was 0.10 ppm. No organochlorine pesticides or their metabolites were detected in any of the samples of fish or sediment. Results of one duplicate analysis performed on the sediment sample from segment M3 were identical to the original; and additions of 2.0 to 2.3 ug of individual organochlorine pesticides to this same sample were recovered at rates ranging from 4 to 130 percent. All of the recoveries, except for three of the minor compounds (Alpha-BHC, Beta-BHC, and HCB), were greater than 90%. Thus, it appears that lack of recovery was not a factor in the failure to detect organochlorine pesticides in any of these samples. Sources for organochlorine pesticides may be limited in the portion of the Arkansas River sampled. Agricultural activities are minimal, and past use of organochlorines was probably restricted primarily to household, horticultural, and industrial pest control.

Food for interior least terns does not appear to be seriously contaminated with organochlorine pesticides in this section of the Arkansas River. Young-of-year gizzard shad do not appear to be contaminated, but older fish and additional species need to be analyzed in order to adequately address the question of organochlorine pesticide contamination in regard to bald eagles.

Polychlorinated Biphenyls (PCBs)

Total PCBs are included as part of the organochlorine compound scan that was performed on all fish and sediment samples taken in this study. The lower limit of detection for total PCB compounds in both fish and sediment was stated as 0.10 ppm wet weight by the laboratory performing the analyses. Total PCB concentrations in all samples of fish and sediment were reported as less than 0.10 ppm wet weight. One duplicate analysis performed on the sediment sample from segment M3 yielded less than 0.10 ppm; and the recovery of 2.1 ug total PCB added to this same sample averaged 113 percent.

It is a little surprising that detectable concentrations of PCBs were not found in at least some of the samples from this study. PCBs have become ubiquitous contaminants, and are nearly always encountered in at least trace quantities in aquatic environments that receive significant amounts of urban and industrial runoff. The absence of detectable PCB concentrations in sediment may

be due to the fact that Arkansas River substrates are predominately coarse grained with a high proportion of sand and little organic matter. PCBs are very insoluble in water and are known to be associated primarily with sediment organic matter and finer, clay-sized particles. The physical characteristics of the sediment collected in this study are unknown, and may be largely responsible for the apparently low concentrations of PCBs encountered. Fish bioconcentrate PCBs from water and also bioaccumulate PCBs from lower organisms in the food chain. Since the quantity taken up through either of these two pathways is partially influenced by the age of the fish involved, one normally expects older fish in a particular setting to contain higher residues of PCBs. It may be suggested that the fish samples submitted for analysis in this study were predominately young fish (i.e., individuals that had not had sufficient time to accumulate detectable residues of PCBs). This seems to be supported by consideration of the time of year that the samples were collected and the size of the fish in the composite samples.

These data do not indicate that PCBs are a serious contaminant in the food supply of interior least terns. Young-of-year gizzard shad, an important food item for wintering bald eagles, are also not contaminated with PCBs, but samples of additional species, made up of older age classes, would be necessary to more adequately evaluate their food supply.

Aliphatic Hydrocarbons

Aliphatic hydrocarbons (alkanes), in the range of 12 to 20 carbons, were present in all fish and sediment samples (Tables 5 and 6). There appeared to be marked species differences in alkane concentrations. Total alkanes ranged between 1.7 and 6.2 ppm wet weight in inland silversides, while in gizzard shad and red shiners, the range was 22 to 26 ppm. Odd-numbered carbon molecules were predominant in all fish samples, comprising between 86 and 96 percent of the total. According to some authors (Farrington 1973; Giger et al 1974), the predominance of odd-numbered carbon compounds indicates hydrocarbons of recent biological origin. Petroleum hydrocarbons supposedly have approximately equal amounts of even-numbered and odd-numbered carbon compounds. Some authors have used the pristane/N-C17 and phytane/N-C18 ratios in birds to indicate chronic exposure to petroleum pollutants (Hall and Coon 1988). In fish samples from this study, both the pristane/N-C17 and the phytane/N-C18 ratios were less than 1.0, suggesting little bioaccumulation of pristane or phytane in tissues.

In sediment, odd-numbered and even-numbered carbon molecules were about equally present in samples from segments M1, M2, and M3. Odd-numbered molecules were dominant in segments M4 and M5. The pristane/N-C17 ratio was also substantially higher is segments M4 and M5 than in the three upstream segments, M1, M2, and M3. These factors suggest that perhaps aliphatic hydrocarbons in segments M4 and M5 have a different origin than those farther upstream.

More work needs to be done to elucidate the source and the biological significance of aliphatic hydrocarbons in this portion of the Arkansas River. It is apparent that alkanes are present in the sediment and that they are accumulating in fish tissue. This indicates that interior least terns and bald eagles are ingesting pollutant oil and that their food supply might be impacted as well. Further studies, designed to answer specific questions, are needed.

Table 5. Concentrations of aliphatic hydrocarbons (ppm wet weight) in whole fish samples from different segments of the middle Arkansas River in Oklahoma.

Alkane	M1[1] IS[2]	M1 GS	M2 IS	M3 IS	M4 IS	M4 IS	M4 GS	M5 IS	M5 RS
N-C12	0.02	0.03	0.03	0.04	0.02	0.06	0.02	0.03	0.04
N-C13	0.02	0.06	0.03	0.14	0.03	0.06	0.03	0.44	1.7
N-C14	0.03	0.08	0.04	0.06	0.02	0.07	0.06	0.03	0.06
N-C15	0.43	7.8	0.33	0.86	0.42	0.55	2.8	0.56	4.5
N-C16	0.04	0.43	0.06	0.14	0.07	0.11	0.71	0.10	0.61
N-C17	0.96	13	1.2	4.2	1.9	2.7	19	2.5	17
PRIST	--	--	0.02	0.03	0.03	0.07	0.03	0.03	0.04
N-C18	0.04	0.19	0.05	0.12	0.07	0.12	0.35	0.10	0.36
PHYT	0.03	0.04	0.04	0.06	0.05	0.10	0.11	0.05	0.10
N-C19	0.15	0.19	0.16	0.48	0.24	0.36	0.25	0.45	1.8
N-C20	0.02	0.05	0.02	0.05	0.03	0.04	0.12	0.04	0.12
Total	1.7	22	2.0	6.2	2.9	4.2	23	4.3	26

[1] River segment
[2] IS=Inland silverside; GS=Gizzard shad; RS=Red shiner

Table 6. Concentrations of aliphatic hydrocarbons (ppm wet weight) in sediment samples from different segments of the middle Arkansas River in Oklahoma.

Alkane	M1	M2	M2	M3	M4	M5
N-C12	0.01	0.01	0.01	0.04	0.01	0.01
N-C13	0.01	0.01	0.01	0.05	--	0.01
N-C14	0.02	0.02	0.02	0.04	0.01	0.02
N-C15	0.05	0.02	0.02	0.14	0.22	0.25
N-C16	0.02	0.02	0.02	0.05	0.03	0.03
N-C17	0.03	0.11	0.10	0.21	0.60	0.44
PRIST	0.03	0.03	0.03	0.07	0.02	0.02
N-C18	0.02	0.02	0.02	0.04	0.03	0.04
PHYT	0.03	0.04	0.03	0.08	0.02	0.02
N-C19	0.02	0.02	0.02	0.04	0.03	0.02
N-C20	0.02	0.03	0.02	0.04	0.03	0.02
Total	0.26	0.33	0.30	0.80	1.0	0.88

Table 7. Concentrations of polynuclear aromatic hydrocarbons (ppm dry weight) in sediment samples from different segments of the middle Arkansas River in Oklahoma.

Compound	M1	M2	M2	M3	M4	M5
naphthalene	--	--	--	0.28	--	--
1-methyl naphthalene	--	--	--	0.20	--	0.01
2-methyl naphthalene	0.01	0.01	--	0.97	--	0.01
2,6-dimethyl naphthalene	0.01	0.01	0.01	0.21	--	0.01
2,3,4-trimethyl naphthalene	0.01	0.01	0.01	0.05	--	--
anthracene	--	--	--	0.04	0.02	--
benz(a)anthracene	--	--	--	0.10	0.11	0.01
dibenzanthracene	--	--	--	0.03	0.04	--
phenanthrene	--	0.01	--	0.35	0.13	0.01
1-methyl phenanthrene	--	--	--	0.11	0.01	--
fluorene	--	--	--	0.01	0.01	--
pyrene	--	0.01	--	0.24	0.22	0.01
benzo(a)pyrene	--	--	0.01	0.09	0.18	0.01
benzo(e)pyrene	--	0.01	0.01	0.14	0.17	0.01
indenopyrene	--	--	--	0.03	0.16	0.01
fluoranthrene	--	--	--	0.09	0.29	0.01
benzo(b)fluoranthrene	--	--	--	0.05	0.18	0.01
benzo(k)fluoranthrene	--	0.02	--	0.05	0.19	0.01
perylene	--	--	--	0.02	0.05	0.01
benzo(g,h,i)perylene	--	--	--	0.05	0.13	0.01
chrysene	--	0.01	0.01	0.16	0.15	0.01
biphenyl	--	--	--	0.04	--	--
acenaphthene	--	--	--	0.01	0.01	--
acenaphthylene	--	--	--	--	--	--
Total	0.03	0.09	0.05	3.32	2.05	0.15

Table 8. Effects Range Low (ER-L) and Effects Range Median (ER-M) concentrations of polynuclear aromatic hydrocarbons (Long and Morgan 1990).

Compound	ppm (dry weight)	
	ER-L	ER-M
Acenaphthene	0.15	0.65
Anthracene	0.08	0.96
Benzo(a)anthracene	0.23	1.6
Benzo(a)pyrene	0.40	2.5
Chrysene	0.40	2.8
Dibenz(a,h)anthracene	0.06	0.26
Fluoranthene	0.60	3.6
Fluorene	0.04	0.64
2-methylnaphthalene	0.06	0.67
Naphthalene	0.34	2.1
Phenanthrene	0.22	1.4
Pyrene	0.35	2.2
Total PAHs	4.0	35

Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAHs) are derived from a variety of sources, including new and used petroleum products, industrial activities, and combustion processes. Used motor oil is a common source of PAHs which often make their way into aquatic habitats via storm water runoff. The heavier PAHs, such as benzo(a)pyrene, are potent carcinogens, while some of the lighter compounds, such as naphthalene are more acutely toxic. Because most PAHs are readily metabolized by fish, they do not tend to bioaccumulate. This is the reason that fish in the present study were not analyzed for PAH compounds. Metabolic degradation of PAHs proceeds more slowly in sediment environments, particularly those that are low in oxygen and sunlight.

PAH concentrations varied greatly in sediment from different segments of the Arkansas River in Tulsa (Table 7). The upstream segments (M1 and M2) contained only a few compounds at relatively low concentrations. The semi-impounded segment (M3), directly above the low water dam, contained the greatest number of compounds and the highest total PAH concentration. Segment M4, directly below the low water dam, had slightly fewer compounds and a slightly lower total PAH concentration than M3. Farther downstream (segment M5), the number of compounds remained high, but concentrations were markedly reduced.

The relationship between PAHs in sediment and cancer in fish has been noted. In Puget Sound sediments, concentrations of total PAHs above 1.0 ppm dry weight had positive correlations with the incidence of liver cancer in fish (Malins et al 1985 and 1987). Sediments from the Buffalo River, New York, with concentrations of total carcinogenic PAHs as low as 1.0 ppm dry weight induced tumors in brown bullhead catfish (Eisler 1987). These results suggest that sediments from segments M3 and M4 of the Arkansas River may be potentially carcinogenic to fish. Long and Morgan (1990) included an evaluation of several individual PAH compounds in their analysis of biological effects (Table 8). ER-L values ranged from a low of 0.04 ppm for fluorene to 0.60 ppm for fluoranthene. The ER-L value for total PAHs was 4.0 ppm. Total PAH concentrations in sediment from segments M3 and M4 of the Arkansas River were slightly below the 4.0 level; however, phenanthrene in segment M3 exceeded the ER-L concentration while 2-methylnaphthalene in segment M3 exceeded the ER-M value. The occurrence and biological significance of PAH compounds need to be more fully understood in this portion of the Arkansas River.

SUMMARY AND CONCLUSIONS

Small fish, representative of prey taken by interior least terns, did not appear to be contaminated by organochlorine pesticides or PCBs. Likewise, concentrations of these organochlorine compounds were below detection limits in sediment samples from each of the five segments of the river sampled. Heavy metals in these same fish samples were, for the most part, below concentrations of concern. Cadmium and lead were below detection limits, although admittedly these limits are equal to or slightly greater than the NCBP 85th percentile concentration for these two elements. Chromium and copper were in the range of "normal" background concentrations. Only zinc appeared to be significantly elevated in small fish samples. Without exception, zinc concentrations in these samples were 1.5 to 2.3 times higher than the NCBP 85th percentile concentration. Sediments did not appear contaminated with any of the heavy metals considered, as concentrations were substantially below both the EPA (1977) "nonpolluted" guidelines and Long and Morgan's (1990) suggested Effects Range-Low (ER-L) concentrations.

Pollution from petroleum and petroleum-based products was clearly evident in both fish and sediment samples. Aliphatic hydrocarbons were present in all fish, and marked species differences in concentrations were noted. Sediment samples suggested a definite spatial pattern, with higher concentrations downstream. Polynuclear aromatic hydrocarbons (PAHs) were not measured in fish, since these compounds are normally metabolized. However, substantial quantities of PAHs were present in sediment samples from Zink Lake (segment M3) and directly below Zink Lake (segment M4).

The findings from this study can be used to direct further investigations on contaminants in the middle Arkansas River. First, the question of zinc, both as a toxicant to fish and as a dietary toxicant to birds, should be investigated in the literature. Second, it is evident that fish are being exposed to aliphatic hydrocarbons and that fish eating birds are ingesting these compounds regularly. The literature should be reviewed to determine the significance of these two facts. Third, it is evident that portions of the river are contaminated with PAHs. The significance of these compounds in the environment is known. They are toxic, mutagenic, and carcinogenic. Further investigations are needed to determine the source and distribution of PAHs in the river, and to determine if biological effects of present concentrations can be demonstrated.

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