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## METALS AND ORGANIC COMPOUNDS IN MISSOURI RIVER FISH IN 1988 Boyd County, Nebraska to Kansas City, Missouri

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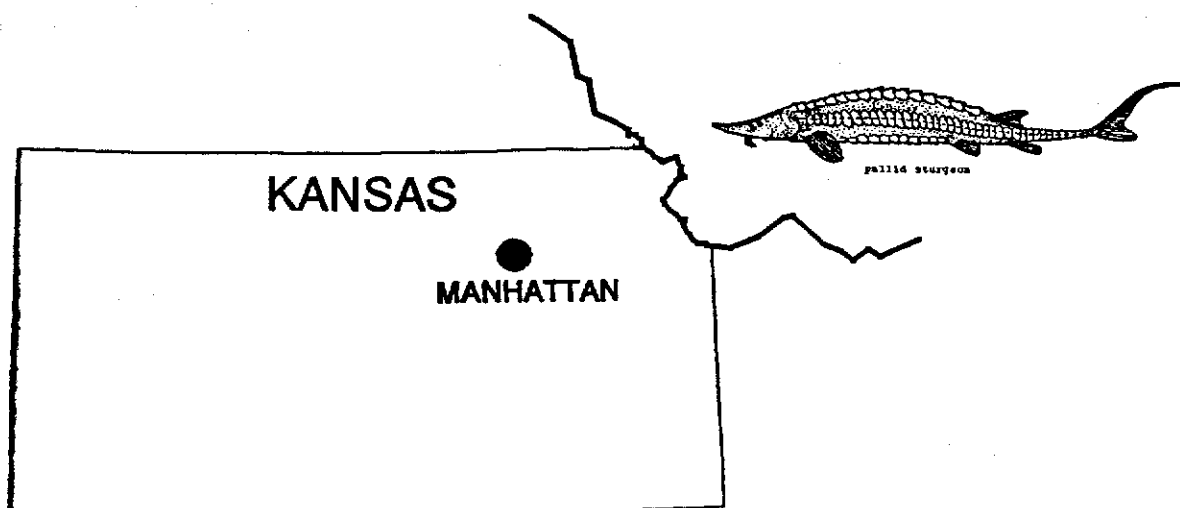


U.S. FISH & WILDLIFE SERVICE  
REGION 6



CONTAMINANTS PROGRAM

**METALS AND ORGANIC  
COMPOUNDS IN MISSOURI RIVER  
FISH IN 1988**



U.S. FISH AND WILDLIFE SERVICE  
Fish and Wildlife Enhancement  
315 Houston Street  
Manhattan, Kansas 66502

METALS AND ORGANIC COMPOUNDS  
IN MISSOURI RIVER FISH IN 1988  
Boyd County, Nebraska to Kansas City, Missouri

by

George T. Allen and R. Mark Wilson

U.S. Fish and Wildlife Service  
315 Houston Street  
Manhattan, Kansas 66502

October 1991

## ABBREVIATIONS AND CONVERSION FACTORS

### Conversions

parts per million .....	ppm
parts per billion .....	ppb
milligrams per liter .....	mg/l
micrograms per gram .....	$\mu\text{g/g}$
micrograms per liter .....	$\mu\text{g/l}$
not detected (i.e. below analytical detection limits) .....	ND
not analyzed (i.e. no test for this element or compound) .....	NA

### Conversions

milligrams per liter .....	ppm
micrograms per liter .....	ppb
micrograms per gram .....	ppm

## SUMMARY

We conducted this project to assess the concentrations of natural and anthropogenic contaminants in fish of the Missouri River from the Nebraska/South Dakota border to Kansas City, Missouri. We collected 45 composite samples of eight fish species from nine locations on the river. We were unable to collect all species at all locations, but the collections allowed us to compare concentrations within trophic levels and at different locations. Comparisons in this project are based on concentrations in composites of fish that may have been of different ages. Also, the comparisons of different species should be treated with caution because different species respond to contaminants in different ways and may have normal concentrations of metals or organic contaminants that differ from other species.

- Fish from seven of the nine locations were analyzed for arsenic, mercury, selenium, and 11 other metals, for organochlorine compounds, and for aliphatic hydrocarbons. Fish from two of the sampling locations were analyzed only for organochlorines.

- Aluminum, arsenic, cadmium, copper, manganese, and zinc concentrations in the fish samples were high enough to warrant further studies. Lead concentrations were high enough to warrant further study, especially downstream from Dakota City, Nebraska. Chromium and nickel concentrations were high relative to concentrations found in other locations. Beryllium, iron, mercury, selenium, and tellurium concentrations need not concern resource managers.

- Chlordane and heptachlor concentrations were well below the geometric means from the National Contaminant Biomonitoring Program (NCBP), but the total concentrations of those compounds exceeded the 1973 National Academy of Sciences and National Academy of Engineering (NAS/NAE) recommendation for protection of aquatic life in 14 of the 45 samples analyzed. Five of the samples were more than double the protection level. Most of the chlordane- and/or heptachlor-contaminated samples came from Blair, Nebraska or downstream. Half of the values exceeding the NAS/NAE recommendation were from Atchison, Kansas and Kansas City, Missouri.

- Thirteen of the fish composites exceeded the 1984 NCBP nationwide mean dieldrin concentration in fish. Concentrations in a paddlefish from Blair, Nebraska and in the channel catfish and shovelnose sturgeon composites from Rulo, Nebraska exceeded the NAS/NAE recommendation for dieldrin concentration. In addition, the presence of aldrin in the shovelnose sturgeon sample from Rulo suggests recent inputs of the banned chemical into the Missouri River.

► Total cyclodiene compound concentrations exceeded the NAS/NAE recommendation in 16 of the 45 samples.

► Ratios of DDT compounds in fish suggest recent inputs of DDT or pesticides containing DDT or of possible improper pesticide use, storage, or disposal. However, concentrations of DDT compounds in the fish we sampled were not high.

► The concentrations of Aroclor<sup>R</sup> 1254, one of the most persistent PCB compounds, or total PCBs were high. Many of the concentrations exceeded the mean from the latest NCBP and the recommendations for maximum total body concentration.

► Aliphatic hydrocarbon concentrations and ratios of aliphatic compounds in many samples indicated petroleum contamination of the river.

► Concentrations of some trace elements, cyclodiene compounds, PCBs, and petroleum hydrocarbons in fish from the study area warrant more detailed investigations.

#### ACKNOWLEDGMENTS

Larry Hesse and Gerald Mestl of the Nebraska Game and Parks Commission collected many of the fish analyzed for this project. John Lund and Steve Walker of the Nebraska Department of Environmental Control, Roger Wolfe of the Kansas Department of Wildlife and Parks, and Dick Ruelle, Dinae Laush, and Tim Fannin of the U.S. Fish and Wildlife Service also helped collect fish for this project. We also thank Dewey Caster, Ronel Finley, Darren Geimausaddle, and Gene Hansmann of the U.S. Fish and Wildlife Service for their help with this work. This report was much improved after very helpful reviews from Larry Hesse, Rod DeWeese, and Dick Ruelle.

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## INTRODUCTION

This report discusses preliminary sampling done to assess the concentrations of naturally-occurring elements and anthropogenic contaminants in fish of the Missouri River. The work was conducted primarily to assess the levels of chlordane, a mixture of heterocyclic chlorinated hydrocarbon compounds, in the Nebraska/Iowa/Kansas/Missouri reach of the Missouri River. Chlordane was widely used in the 1960s and the 1970s as an agricultural insecticide. It also has been used extensively for termite control in buildings. Chlordane, and especially some chlordane metabolites, are persistent and cumulative in terrestrial and aquatic environments (Cardwell et al. 1977). Chlordane is the highest priority aquatic contaminant concern of the Kansas Department of Wildlife and Parks.

Surveys of contaminants (especially chlordane, lead, and Aroclor<sup>R</sup> 1260) in fish from the Missouri River in the 1980s [U.S. Environmental Protection Agency (EPA) unpublished data, Bush 1989] indicated significant contamination in a number of commercial and sport fish species. Because of high chlordane compound concentrations, the Missouri Department of Health issued advisories against human consumption of fish taken from the Missouri River between Kansas City and St. Louis. However, the chlordane contamination of fishes upstream from Kansas City has been unknown. The reach includes DeSoto Bend National Wildlife Refuge. It is habitat for lake sturgeon (*Acipenser fulvescens*), paddlefish (*Polyodon spathula*), blue sucker (*Cycleptus elongatus*), sturgeon chub (*Hybopsis gelida*), and sicklefin chub (*Hybopsis meeki*), candidates for the federal endangered species list; for threatened piping plovers (*Charadrius melodus*); and for the endangered pallid sturgeon (*Scaphirhynchus platyrhynchus*), bald eagle (*Haliaeetus leucocephalus*), and interior least tern (*Sterna antillarum*). Many waterfowl and other migratory birds also use the river. Therefore, contaminants in the river are of concern to the U.S. Fish and Wildlife Service (Service) because of the large numbers of trust resources that use the river.

Although chlordane was the focus of this project, all fish samples were analyzed for other chlorinated hydrocarbon compounds. Most of the samples also were analyzed for metals and for aliphatic hydrocarbon compounds. Information from this project indicates present levels of many contaminants in fishes of the middle reach of the Missouri River and suggests locations for more detailed investigations.

## STUDY AREA AND METHODS

We collected fish samples from nine locations in the Missouri River from the South Dakota/Nebraska border to Kansas City, Missouri (Figure 1). Fish are often good indicators of metal contamination (Young and Blevins 1981), and upper trophic level fish are considered good indicators of organochlorine contamination (Niethammer et al. 1984). As food items for migratory, threatened, or endangered birds, they are of special concern to the Service. Sampling locations in Nebraska were in Boyd County, at Niobrara, at the tailwaters of Gavins Point Dam in Cedar County, at Dakota City, at Blair, at Omaha, and at Rulo. Samples also were collected at Atchison, Kansas and at Kansas City, Missouri.

Fish were collected from the nine sampling locations in April, May, and June 1988 by electroshocking or gill netting, or by purchasing them from commercial fishermen (Tables 1 and 2). We collected 45 fish composites. With the exception of two individual paddlefish collected at Blair, Nebraska, we composited fish of each species of approximately equal sizes. Most composites included five fish, but some included only three or four. We attempted to collect the same species in each location, but not all species were caught at all sites and at some sites few fish were caught. Walleye and sauger were combined for composites. Each fish was measured, weighed, and double wrapped in aluminum foil. All fish were kept on ice in the field. Thereafter, they were frozen until they were prepared for analysis. We considered aluminum contamination from wrapping samples in foil to be negligible. Samples were submitted to the analytical laboratories in September through November 1988. The last results of laboratory analyses were received in December 1989.

Laboratory analyses for total arsenic, mercury, and selenium were done using atomic absorption spectroscopy. Detection limits were 0.20  $\mu\text{g/g}$  for arsenic, 0.10  $\mu\text{g/g}$  for mercury, and 0.20  $\mu\text{g/g}$  for selenium. Inductively coupled plasma emission spectroscopy (ICP) with preconcentration at pH 6 was used to test for aluminum, beryllium, cadmium, chromium, copper, iron, lead, manganese, nickel, tellurium, and zinc. Detection limits were 0.30  $\mu\text{g/g}$  for aluminum, 0.01  $\mu\text{g/g}$  for beryllium, 0.02-0.03  $\mu\text{g/g}$  for cadmium, 0.10  $\mu\text{g/g}$  for chromium, 0.02-0.03  $\mu\text{g/g}$  for copper, 0.10  $\mu\text{g/g}$  for iron, 0.50  $\mu\text{g/g}$  for lead, 0.03  $\mu\text{g/g}$  for manganese, 0.10  $\mu\text{g/g}$  for nickel, and 0.03  $\mu\text{g/g}$  for zinc. For metals, results were reported as dry-weight concentrations. Wet weight concentrations were calculated by multiplying the dry weight by  $[1 - (\% \text{ moisture}/100)]$ .

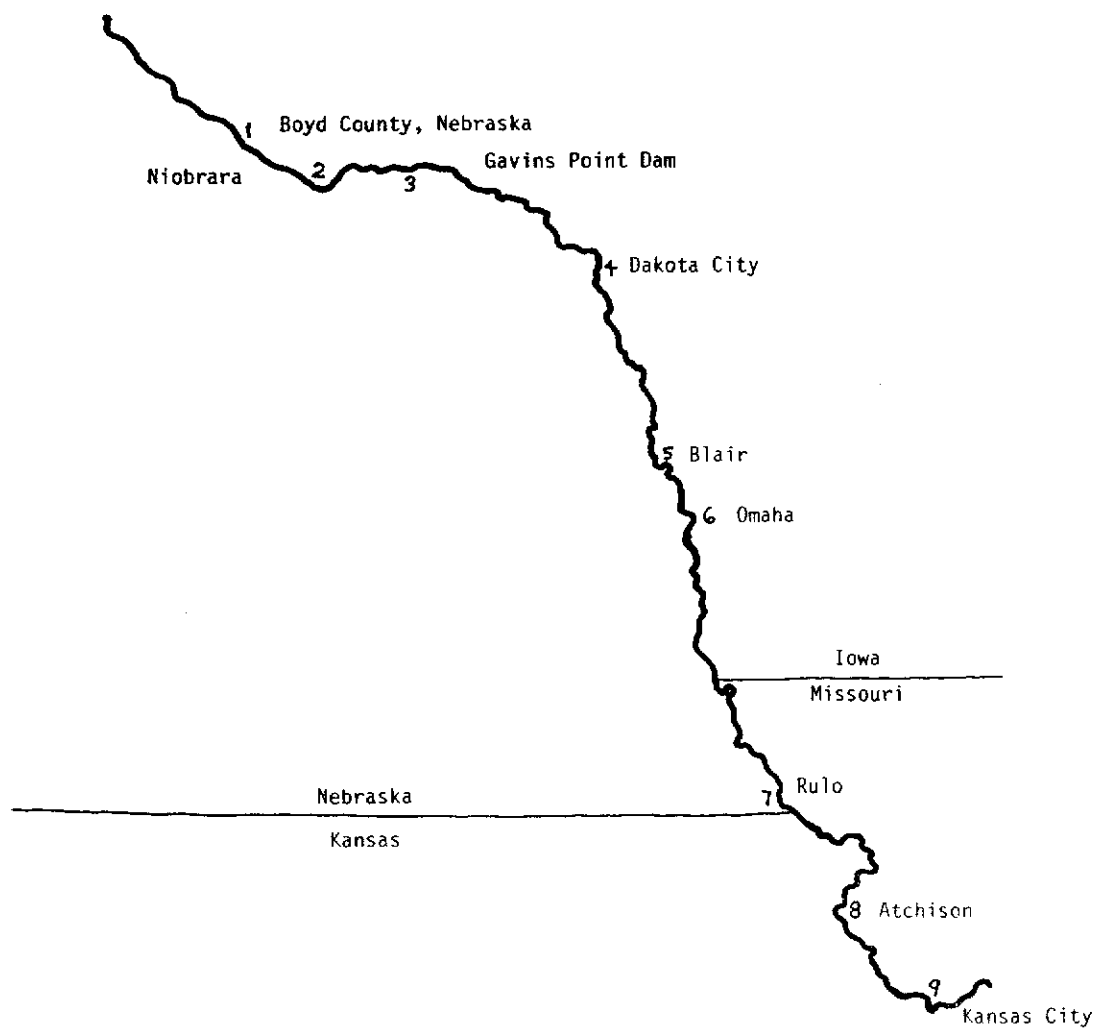


Figure 1. Sampling locations on the Missouri River in 1988.

Table 1. Fish species and collection locations from the Missouri River for contaminants analyses in 1988.

<u>Species Collected and Food Preferences</u>	<u>Collection Location (Number of Fish Collected)</u>	<u>Weights of Individuals in Composite (g)</u>
Shovelnose Sturgeon <i>Scaphirhynchus platyrhynchus</i> omnivorous	Boyd County (5) Niobrara (3) Gavins Point Dam (5) Dakota City (5) Omaha (5) Rulo (4) Atchison (5)	730, 875, 930, 940, 980 640, 950, 960 540, 570, 620, 800, 1090 405, 520, 530, 540, 630 450, 550, 650, 800, 850 550, 550, 900, 950 610, 620, 640, 650, 1020
Paddlefish <i>Polyodon spathula</i> omnivorous	Blair (2 individual fish)	5850, 10000
Gizzard Shad <i>Dorosoma cepedianum</i> planktivorous	Gavins Point Dam (5) Dakota City (5) Blair (5) Rulo (5) Atchison (5)	144, 174, 202, 218, 235 250, 320, 340, 490, 560 160, 176, 186, 346, 354 150, 175, 200, 300, 300 105, 130, 170, 190, 200
Goldeye <i>Hiodon alosoides</i> omnivorous	Boyd County (4) Gavins Point Dam (5) Dakota City (5) Blair (5) Rulo (5) Atchison (5)	540, 690, 700, 850 270, 290, 330, 340, 360 260, 320, 340, 340, 420 242, 278, 310, 366, 424 100, 150, 250, 300, 350 100, 250, 250, 340, 490

Table 1 (continued). Fish species and collection locations from the Missouri River for contaminants analyses in 1988.

<u>Species Collected and Food Preferences</u>	<u>Collection Location (Number of Fish Collected)</u>	<u>Weights of Individuals in Composite (g)</u>
Common Carp <i>Cyprinus carpio</i> omnivorous	Boyd County (5) Niobrara (5) Gavins Point Dam (5) Dakota City (5) Blair (5) Rulo (5) Atchison (5) Kansas City (5)	composite weight 5950 composite weight 8900 composite weight 7900 1750, 1900, 1950, 2050, 2050 950, 1575, 1700, 1950, 2100 composite weight 2400 500, 645, 660, 830, 1000 1045, 1050, 1110, 1270, 1270
Channel Catfish <i>Ictalurus punctatus</i> omnivorous	Boyd County (5) Niobrara (5) Gavins Point Dam (5) Dakota City (5) Blair (5) Rulo (5) Atchison (3) Kansas City (5)	675, 860, 910, 1120, 1480 composite weight 6000 230, 230, 240, 280, 300 120, 150, 160, 240, 450 200, 225, 245, 260, 1140 500, 650, 700, 1050, 2200 250, 790, 2050 312, 520, 592, 596, 620
Walleye/Sauger <i>Stizostedion</i> sp. piscivorous	Niobrara (5) Gavins Point Dam (5)	composite weight 5700 composite weight 3150
Freshwater Drum <i>Aplodinotus grunniens</i> omnivorous	Gavins Point Dam (5) Dakota City (5) Blair (5) Rulo (3) Kansas City (5)	composite wieght 3150 composite weight 4150 200, 225, 290, 400, 560 450, 500, 550 480, 504, 534, 574, 658

Table 2. Missouri River fish collection locations and species for contaminants analyses in 1988.

<u>Collection Location</u>	<u>Species Collected</u>
Boyd County, Nebraska (1)	Channel Catfish, Common Carp, Goldeye, Shovelnose Sturgeon
Niobrara, Nebraska (2)	Channel Catfish, Common Carp, Shovelnose Sturgeon, Walleye/ Sauger
Gavins Point Dam, Nebraska (3)	Channel Catfish, Common Carp, Freshwater Drum, Gizzard Shad, Goldeye, Shovelnose Sturgeon, Walleye/Sauger
Dakota City, Nebraska (4)	Channel Catfish, Common Carp, Freshwater Drum, Gizzard Shad, Goldeye, Shovelnose Sturgeon
Blair, Nebraska (5)	Channel Catfish, Common Carp, Freshwater Drum, Gizzard Shad, Goldeye, Paddlefish Shovelnose Sturgeon
Omaha, Nebraska (6)	Shovelnose Sturgeon
Rulo, Nebraska (7)	Channel Catfish, Common Carp, Freshwater Drum, Gizzard Shad, Goldeye, Shovelnose Sturgeon
Atchison, Kansas (8)	Channel Catfish, Common Carp, Gizzard Shad, Goldeye, Shovelnose Sturgeon
Kansas City, Missouri (9)	Channel Catfish, Common Carp, Freshwater Drum

Concentrations of chlorinated hydrocarbon compounds were determined using electron capture gas chromatography. Concentrations of aliphatic hydrocarbons were determined using capillary column flame ionization gas chromatography. Each sample collected was large enough for the laboratory to determine the total concentration at the limit of the analytical equipment. No anomalies were reported in the samples. For arsenic, mercury, selenium, and other metals, percent moisture and dry-weight concentration were reported by the laboratory. Wet weight concentrations were reported for chlorinated hydrocarbons and for aliphatic hydrocarbons. Lipid-normalization of organic compounds provides no improvement in data reporting (Huckins et al. 1988, Schmitt et al. 1990), so we did not use it.

Arsenic, mercury, selenium, and other metals in fish were analyzed by the Environmental Trace Substances Research Center (ETSRC) at the University of Missouri. Because of funding limitations, the fish from Rulo, Nebraska and from Blair, Nebraska were analyzed only for chlorinated hydrocarbon compounds by Weyerhaeuser Analytical and Testing Services (WATS). Samples from other locations were analyzed for chlorinated hydrocarbon compounds and for aliphatic hydrocarbons by The Mississippi State Chemical Laboratory (MSCL). The two laboratories analyzed for slightly different groups of chlorinated hydrocarbon compounds (Table 3).

Laboratory quality control was approved by the Patuxent Analytical Control Facility (PACF) of the Service. Precision and accuracy of the laboratory analyses were confirmed with procedural blanks, duplicate analyses, test recoveries of spiked materials, and reference material analyses. Round-robin tests among Service and contract analytical labs also were part of the quality control.

Duplicate analyses for arsenic, mercury, and selenium had a percent deviation of 16.7% ( $0.20 \mu\text{g/g}$ ) in one analysis for arsenic; others differed by less. Duplicate ICP analyses had a percent deviation of 8.5% or less for elements in low concentrations, but 49.9% in one sample for iron. Iron, manganese, and aluminum, which were always present in relatively high concentrations, had higher percent deviations in duplicate analyses. Spike recoveries for inorganics ranged from 95% to 112% for arsenic, mercury and selenium, and from 86% to 115% for ICP analyses. Residue values were not adjusted on the basis of these recoveries. Results from analyses of inorganic reference standards differed from the expected values by less than  $1 \mu\text{g/g}$  for elements in low concentrations, and by less than 14% of the expected value for copper, iron, and zinc, which were present in higher concentrations.

Duplicate organics analyses of samples we submitted differed by no more than  $0.11 \mu\text{g/g}$  (17%), with the exceptions of the analyses for aroclor 1254 (WATS,  $0.23 \mu\text{g/g}$ , 27%) and n-heptadecane (MSCL,  $0.5 \mu\text{g/g}$ ,



Table 3. Chlorinated hydrocarbons in Missouri River fish analyzed for by Weyerhaeuser Analytical and Testing Services (WATS) or by The Mississippi State Chemical Laboratory (MSCL).

Compound	Detection Limit ( $\mu\text{g/g}$ wet weight)	
	MSCL	WATS
alpha-BHC	0.01	0.01
beta-BHC	0.01	0.01
delta-BHC	0.01	0.01
gamma-BHC	0.01	0.01
Oxychlordane	0.01	0.01
cis-Chlordane	0.01	0.01
trans-Chlordane	0.01	0.01
cis-Nonachlor	0.01	0.01
trans-Nonachlor	0.01	0.01
Methoxychlor	0.01	0.01
Heptachlor	NA	0.01
Heptachlor Epoxide	0.01	0.01
Aldrin	0.01	0.01
Dieldrin	0.01	0.01
Endrin	0.01	0.01
Endosulfan I	0.01	0.01
Endosulfan II	0.01	0.01
Endosulfan Sulfate	0.01	0.01
o,p'-DDT	0.01	0.01
p,p'-DDT	0.01	0.01
o,p'-DDE	0.01	0.01
p,p'-DDE	0.01	0.01
o,p'-DDD	0.01	0.01
p,p'-DDD	0.01	0.01
Hexachlorobenzene	0.01	0.01
DCPA	0.01	0.01
Aroclor <sup>R</sup> 1016	NA	0.50
Aroclor <sup>R</sup> 1221	NA	0.05
Aroclor <sup>R</sup> 1232	NA	0.05
Aroclor <sup>R</sup> 1242	NA	0.05
Aroclor <sup>R</sup> 1248	NA	0.05
Aroclor <sup>R</sup> 1254	NA	0.05
Aroclor <sup>R</sup> 1260	NA	0.05
Total PCBs	0.05	NA
Toxaphene	0.05	0.50
Mirex	0.01	0.01
Dicofol	NA	0.01
Tetradifon	NA	0.01

$\mu\text{g/g}$ , 6%). Spike recoveries for chlorinated hydrocarbons at MSCL ranged from 87% to 100%, with the exception of hexachlorobenzene (HCB, 65%). Spike recoveries were not done at WATS. For aliphatic hydrocarbons, the detection limit was  $0.01 \mu\text{g/g}$ . Spike recoveries ranged from 37% for n-dodecane to 92% for n-eicosane. Organic compound analytical results were not adjusted to reflect spike recoveries.

Concentrations of contaminants in Missouri River fish were compared to concentrations found in published studies. We made no attempt to assess the interactions of various contaminants, even though many are known to affect the toxicity of other elements or compounds. We view this project as a basis for assessing the needs for contaminants monitoring in the Missouri River. Comparisons in this project are based on concentrations in composites of fish that may have been of different ages. In addition, comparisons between species should be treated with caution because different species respond to contaminants in different ways and may have normal concentrations of metals or organic contaminants that differ from other species.

#### CONCURRENT STUDIES

Two other Missouri River studies were conducted concurrent with this project. Christiansen et al. (1991) sampled channel catfish fillets from fish caught at 10 locations from Rulo, Nebraska upstream. Fillets were found to contain DDT compounds, PCBs, dieldrin, heptachlor, trifluralin, and chlordane compounds. Chlordane compound concentrations in fillets from catfish caught south of Omaha exceeded the U.S. Food and Drug Administration action level for chlordane ( $0.3 \mu\text{g/g}$  wet weight).

Monitoring of contaminant levels in eggs, fillets, and whole fish from the Missouri River in Missouri from 1984 through 1988 indicated that PCBs and chlordane compounds exceeded FDA action levels in some locations (Bush 1989). Dieldrin was found at low levels in many samples during the project. The data from 1988 samples indicated that although there appears to be a decrease in the number of areas of concern in the Missouri River, chlordane contamination continues to be a problem.

## RESULTS AND DISCUSSION

### METALS

#### Metals Analyzed by AAS

Arsenic, mercury, and selenium concentrations are shown in Table 4.

#### Arsenic

There are limited data available on the biological need for arsenic or on its properties that affect animal life. Arsenic usually is rapidly excreted after exposure (Eisler 1988a). At very low levels, arsenic or arsenic compounds may improve health and growth in animals, and inorganic arsenic can protect against harmful effects of inorganic selenium (Eisler 1988a). However, the different forms of arsenic are poisonous at low concentrations, although the relative toxicities differ (Eisler 1988a, Murphy 1981, Spehar et al. 1980). Further, the effects of arsenic may be intensified by exposure to cadmium or lead. Arsenic can be converted to organic forms by methylating bacteria (Hodson 1988). Methylated selenium compounds are made much more toxic by inorganic arsenic compounds. Exposure to arsenic, however, increases later tolerance to arsenic in many animals (Eisler 1988a). Phillips and Russo (1978) considered arsenic to have a low bioaccumulation tendency in freshwater fish muscle. Spehar et al. (1980), Wageman et al. (1978), and Winger et al. (1990) also considered arsenic to have low bioaccumulation and biomagnification potential in fish.

Background arsenic concentrations in freshwater aquatic biota normally are less than 1  $\mu\text{g/g}$  fresh weight (Eisler 1988a). Arsenic concentrations in common carp, channel catfish, and shovelnose sturgeon from Boyd County, Nebraska; in shovelnose sturgeon from Niobrara, Nebraska; and in gizzard shad from below Gavins Point Dam, Nebraska and from Atchison, Kansas were above the 85th percentile values from the National Contaminant Biomonitoring Program (NCBP) since 1976 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). The arsenic concentration in shovelnose sturgeon from Boyd County also was larger than the higher 85th percentile value from the NCBP in 1976-1977 (Walsh et al. 1977), and was comparable to some of the high values found in central and western U.S. fish. Concentrations of arsenic in whole fish from the U.S. have declined significantly since 1976-1977 (Schmitt and Brumbaugh 1990). The lower arsenic concentrations in other species collected from the river in Boyd County suggest that sturgeon may not eliminate arsenic readily or that they accumulate it from their food more easily than do the other species collected. The arsenic found in the Boyd County reach also might be from soils along the river upstream.

Table 4. Arsenic, mercury, and selenium concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Concentration ( $\mu\text{g/g}$ )					
		Arsenic		Mercury		Selenium	
		Dry Weight	Wet Weight	Dry Weight	Wet Weight	Dry Weight	Wet Weight
<u>Boyd County, Nebraska</u>							
Common Carp	73.6	1.5	0.40	0.19	0.05	5.1	1.35
Channel Catfish	69.3	1.2	0.37	0.13	0.04	1.8	0.55
Shovelnose Sturgeon	69.4	2.2	0.67	0.14	0.04	3.7	1.13
Goldeye	65.1	0.6	0.21	0.48	0.17	3.9	1.36
<u>Niobrara, Nebraska</u>							
Common Carp	73.8	0.3	0.08	0.16	0.04	7.9	2.07
Channel Catfish	73.3	ND	ND	0.16	0.04	4.2	1.12
Shovelnose Sturgeon	72.4	0.9	0.26	0.27	0.07	3.8	1.05
Walleye/Sauger	69.0	0.4	0.12	0.24	0.07	5.7	1.77
<u>Gavins Point Dam, Nebraska</u>							
Common Carp	69.7	0.5	0.15	0.15	0.05	3.4	1.03
Channel Catfish	71.9	0.2	0.06	0.13	0.04	2.9	0.81
Shovelnose Sturgeon	66.5	0.5	0.17	0.16	0.05	3.7	1.24
Walleye/Sauger	73.3	0.3	0.08	0.26	0.07	4.6	1.23
Freshwater Drum	72.9	0.4	0.11	0.45	0.12	3.6	0.98
Gizzard Shad	73.8	2.3	0.60	0.11	0.03	2.4	0.63
Goldeye	63.4	0.2	0.07	0.22	0.08	2.6	0.95

Table 4 (concluded). Arsenic, mercury, and selenium concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Concentration ( $\mu\text{g/g}$ )					
		Arsenic		Mercury		Selenium	
		Dry Weight	Wet Weight	Dry Weight	Wet Weight	Dry Weight	Wet Weight
<u>Dakota City, Nebraska</u>							
Common Carp	71.2	0.5	0.14	0.17	0.05	3.2	0.92
Channel Catfish	76.7	ND	ND	0.18	0.04	2.6	0.61
Shovelnose Sturgeon	72.1	0.6	0.17	0.19	0.05	4.1	1.14
Gizzard Shad	77.6	0.8	0.18	0.19	0.04	4.2	0.94
Goldeye	71.0	ND	ND	0.86	0.25	4.1	1.19
Freshwater Drum	75.4	ND	ND	0.57	0.14	3.5	0.86
<u>Omaha, Nebraska</u>							
Shovelnose Sturgeon	71.3	0.2	0.06	0.23	0.07	3.9	1.12
<u>Atchison, Kansas</u>							
Common Carp	74.3	ND	ND	0.18	0.05	2.7	0.69
Channel Catfish	70.7	ND	ND	0.16	0.05	1.7	0.50
Shovelnose Sturgeon	70.2	ND	ND	0.19	0.06	4.1	1.22
Gizzard Shad	77.9	1.2	0.27	0.13	0.03	2.6	0.57
Goldeye	69.3	ND	ND	0.22	0.07	4.3	1.32
<u>Kansas City, Missouri</u>							
Common Carp	72.3	0.2	0.06	0.26	0.07	3.3	0.91
Freshwater Drum	70.8	0.2	0.06	0.23	0.07	3.5	1.02
Channel Catfish	72.0	ND	ND	0.15	0.04	2.3	0.64

## Mercury

Mercury is a nonessential metal with extreme potential toxicity. It is a teratogen, a mutagen, and a carcinogen. Mercury has been used for different purposes in agriculture, but industrial processes are now probably the most important sources of mercury contamination. Newly constructed reservoirs also have led to increased mercury levels in fish because mercury is released from flooded soils to the water (Eisler 1987). However, reservoirs also may limit exposure of fish below them to mercury that is mobilized during flooding (Phillips et al. 1987). Elemental mercury and its organic forms may persist for many years after sources of pollution are stopped. Mercury can be bioconcentrated and biomagnified<sup>1</sup> in food chains (Eisler 1987, Elliott and Griffiths 1986, Jernelev and Lann 1971, Johnels et al. 1967, Phillips et al. 1980, Rudd and Turner 1983), processes that are increased by methylation (Hodson 1988). Methylmercury has a high potential for bioaccumulation and toxicity to fish and wildlife (Phillips and Russo 1978).

Missouri River fish concentrations were not elevated compared to those in fish collected for the NCBP (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). Only the concentrations in Goldeye from Boyd County, Nebraska and in freshwater drum from Atchison, Kansas were above the nationwide geometric means from the NCBP.

## Selenium

Selenium is an essential trace nutrient for terrestrial and freshwater organisms. However, proper selenium levels in animals fall within narrow ranges, and the acute and chronic effects of organic and inorganic forms of selenium differ on aquatic and terrestrial plants and animals (EPA 1987). Selenium deficiency can produce a variety of symptoms, as can selenium toxicosis. Many of the symptoms are the same (Marier and Jaworski 1983). Numerous cases of selenium poisoning of fish, mammals, and birds have been documented (e.g. Clark 1987, Cumbie and Van Horn 1978, EPA 1987, Hoffman et al. 1988, Lemly 1987, Ohlendorf et al. 1986a,b, 1988, Saiki and Lowe 1987). In contrast, selenium can reduce the toxic effects of arsenic, mercury, and some other environmental contaminants (EPA 1987).

Habitat variables play a large role in selenium availability (Lemly and Smith 1987). Selenium bioaccumulation occurs in some settings

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<sup>1</sup> Bioconcentration is the accumulation of an element or compound by an aquatic organism directly from the water. Bioaccumulation is accumulation from water and from food. Biomagnification refers to increases in body burden of an element or compound in successively higher trophic levels (Beyer 1986, Biddinger and Gloss 1984, Hall and Burton 1982, Macek et al. 1979, Rand and Petrocelli 1985). Wren et al. (1983) considered bioaccumulation in fish to be increasing concentration of an element or compound with fish age or size.

(Cherry and Guthrie 1977, DuBow 1989, Lemly 1985, 1987, Lemly and Smith 1987, Saiki 1986), and concentrations may be progressively greater in organisms higher in the food chain. However, Adams and Johnson (1977) and Kay (1984) believed that selenium biomagnification does not occur. Phillips and Russo (1978) considered selenium to have a low bioaccumulative tendency. Besser et al. (1989) found that the form of selenium had a great effect on bioaccumulation and toxicity. Organic selenomethionine had a greater toxic effect, a finding also reported by others (e.g. Eisler 1985a, Kleinow and Brooks 1986). Hodson (1988) reported that dietary selenium is much more toxic than waterborne selenium to fish. Cumbie and Van Horn (1978) found that size and age make little difference in selenium concentrations in common carp, which accumulate selenium only moderately (e.g. Cumbie and Van Horn 1978, Baumann and May 1984).

Nationwide geometric means for selenium concentration in fish collected for the NCBP ranged from 0.48  $\mu\text{g/g}$  wet weight in 1978-1979 to 0.42  $\mu\text{g/g}$  in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). Comparable 85th percentile concentrations were 0.70, 0.71, and 0.73  $\mu\text{g/g}$ . Most samples collected for this project were above the NCBP 85th percentile values, but in only 1 sample was the 2  $\mu\text{g/g}$  wet weight level of concern suggested by Baumann and May (1984) exceeded. Dry-weight concentrations were well below the 12  $\mu\text{g/g}$  dry-weight whole-body concentration of concern (Gillespie and Baumann 1986, Lemly 1985, Lemly and Smith 1987).

#### Metals Analyzed by ICP

Metal concentrations determined with ICP are shown in Table 5. Tellurium was not detected in any sample.

#### Aluminum

Aluminum is abundant in the earth's crust, but normally is found in water at concentrations less than 1  $\mu\text{g/l}$ . However, toxicity is greatly affected by its complex chemistry, its form in water, water chemistry (especially pH), and life stage of the organism being studied (e.g. Baker and Schofield 1982, Hunter et al. 1980, Hunn et al. 1987, Palawaski et al. 1989, Palmer et al. 1989). Hall et al. (1985) suspected that high aluminum concentrations and water softness in a Chesapeake Bay tributary contributed to mortality of larval striped bass. Aluminum has a high tendency to bioaccumulate (Phillips and Russo 1978).

There are limited published data for whole-body concentrations of aluminum in fish (e.g. Brumbaugh and Kane 1985, Guthrie and Cherry 1979, Wells et al. 1988). Berg and Burns (1985) and Brumbaugh and Kane (1985) reported differences in aluminum concentrations in different tissues.

Table 5. ICP scan sample concentrations in fish collected from the Missouri River in 1988.

Species	Element Concentration ( $\mu\text{g/g}$ )									
	Aluminum		Beryllium		Cadmium		Chromium		Copper	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Boyd County, Nebraska</u>										
Common Carp	320	434	0.03	0.04	1.20	1.63	8.20	11.10	6.58	8.94
Channel Catfish	211	304	0.02	0.03	0.23	0.33	1.70	2.50	2.00	2.89
Shovelnose Sturgeon	244	351	0.05	0.07	0.87	1.25	5.80	8.40	3.82	5.50
Goldeye	8.8	13.5	ND	ND	0.17	0.26	0.60	0.90	1.50	2.30
<u>Niobrara, Nebraska</u>										
Common Carp	268	363	ND	ND	0.53	0.72	0.73	0.99	5.74	7.78
Channel Catfish	176	240	ND	ND	0.14	0.19	0.47	0.64	3.13	4.27
Shovelnose Sturgeon	136	187	ND	ND	1.00	1.38	0.70	0.97	3.62	5.00
Walleye/Sauger	6.0	8.7	ND	ND	0.05	0.07	ND	ND	2.55	3.70
<u>Gavins Point Dam, Nebraska</u>										
Common Carp	239	343	ND	ND	0.47	0.67	1.60	2.30	4.81	6.90
Channel Catfish	91.3	127.0	ND	ND	0.11	0.15	2.60	3.62	1.70	2.36
Shovelnose Sturgeon	62.5	94.0	ND	ND	0.38	0.57	1.70	2.56	3.47	5.28
Walleye/Sauger	5.2	7.1	ND	ND	0.08	0.10	ND	ND	1.60	2.18
Freshwater Drum	16.0	21.9	ND	ND	0.16	0.22	1.50	2.06	1.30	1.78
Gizzard Shad	1210	1639	0.03	0.04	0.11	0.15	8.80	11.92	21.70	29.40
Goldeye	20.0	31.5	ND	ND	0.06	0.09	0.20	0.30	1.10	1.74



Table 5 (continued). ICP scan sample concentrations in fish collected from the Missouri River in 1988.

Species	Element Concentration ( $\mu\text{g/g}$ )									
	Aluminum		Beryllium		Cadmium		Chromium		Copper	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Dakota City, Nebraska</u>										
Common Carp	353	496	0.02	0.03	0.49	0.69	0.91	1.28	4.73	6.64
Channel Catfish	232	302	0.02	0.03	0.14	0.18	3.80	4.95	1.90	2.48
Shovelnose Sturgeon	88.3	122.5	0.01	0.01	0.70	0.97	0.61	0.85	3.73	5.17
Freshwater Drum	27.0	35.8	0.01	0.01	0.14	0.19	1.50	1.99	2.78	3.69
Gizzard Shad	1570	2023	0.07	0.09	0.09	0.12	8.30	10.70	4.56	5.86
Goldeye	26.0	36.6	ND	ND	0.13	0.18	0.20	0.28	1.70	2.39
<u>Omaha, Nebraska</u>										
Shovelnose Sturgeon	31.0	43.5	ND	ND	0.20	0.28	0.44	0.62	2.91	4.08
<u>Atchison, Kansas</u>										
Common Carp	226	304	ND	ND	0.26	0.35	0.71	0.96	5.21	7.01
Channel Catfish	130	184	ND	ND	0.11	0.16	0.43	0.61	2.00	2.83
Shovelnose Sturgeon	72.8	103.7	ND	ND	0.25	0.36	0.43	0.61	2.00	2.85
Gizzard Shad	2540	3261	0.10	0.13	0.15	0.19	12.30	15.79	4.66	5.98
Goldeye	47.2	68.1	0.01	0.01	0.08	0.12	0.30	0.43	1.60	2.31
<u>Kansas City, Missouri</u>										
Common Carp	363	502.1	0.02	0.03	0.12	0.17	2.70	3.73	3.54	4.90
Channel Catfish	114	158	0.01	0.01	0.08	0.12	0.39	0.54	1.80	2.50
Freshwater Drum	99.3	140.3	ND	ND	0.13	0.18	1.10	1.55	2.00	2.83

Table 5 (continued). ICP scan sample concentrations in fish collected from the Missouri River in 1988.

Species	Element Concentration ( $\mu\text{g/g}$ )									
	Iron		Lead		Manganese		Nickel		Zinc	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Boyd County, Nebraska</u>										
Common Carp	1710	2323	0.9	1.2	135	183.4	6.2	8.4	304	413
Channel Catfish	636	918	ND	ND	73.8	106.5	2.0	2.9	47.8	69.0
Shovelnose Sturgeon	1770	2550	1.0	1.4	166	239	6.7	9.7	73.1	105.3
Goldeye	90.8	139.5	ND	ND	5.11	7.9	0.3	0.5	77.9	119.7
<u>Niobrara, Nebraska</u>										
Common Carp	330	447	ND	ND	34.1	46.2	0.5	0.7	309	418.7
Channel Catfish	289	394	ND	ND	29.9	40.8	0.3	0.4	59.4	81.0
Shovelnose Sturgeon	349	482	ND	ND	27.3	37.7	0.71	0.98	80.0	110.5
Walleye/Sauger	35.5	51.4	ND	ND	9.77	14.16	ND	ND	42.6	61.7
<u>Gavins Point Dam, Nebraska</u>										
Common Carp	267	383.1	ND	ND	32.0	45.9	0.93	1.3	247	354.4
Channel Catfish	124	172.5	ND	ND	43.1	59.9	1.5	2.1	75.7	105.3
Shovelnose Sturgeon	200	300.8	ND	ND	18.9	28.4	1.9	2.9	82.7	124.4
Walleye/Sauger	44.6	60.8	ND	ND	11.5	15.7	ND	ND	44.9	61.3
Freshwater Drum	69.2	94.9	ND	ND	25.7	35.3	0.79	1.08	63.5	87.1
Gizzard Shad	1350	1829.3	ND	ND	197	267	4.6	6.2	37.4	50.7
Goldeye	56.1	88.5	ND	ND	8.62	13.6	ND	ND	70.3	110.9

Table 5 (concluded). ICP scan sample concentrations in fish collected from the Missouri River in 1988.

Species	Element Concentration ( $\mu\text{g/g}$ )									
	Iron		Lead		Manganese		Nickel		Zinc	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
<u>Dakota City, Nebraska</u>										
Common Carp	400	562	1.0	1.4	26.1	36.7	0.7	1.0	252	354
Channel Catfish	324	422	ND	ND	19.5	25.4	2.8	3.7	74.8	97.5
Shovelnose Sturgeon	225	312	0.5	0.7	14.4	20.0	0.6	0.9	80.6	111.8
Freshwater Drum	86.8	115.1	ND	ND	31.0	41.1	1.5	2.0	61.2	81.2
Gizzard Shad	1440	1856	0.7	0.9	79.7	102.7	5.1	6.6	72.6	93.6
Goldeye	123	173	1.4	2.0	6.25	8.80	0.3	0.4	88.2	124.2
<u>Omaha, Nebraska</u>										
Shovelnose Sturgeon	120	168	0.6	0.8	11.9	16.7	0.3	0.4	72.0	101.0
<u>Atchison, Kansas</u>										
Common Carp	264	355	0.5	0.7	20.2	27.2	0.6	0.9	209	281
Channel Catfish	179	253	1.0	1.4	13.6	19.2	0.4	0.6	47.8	67.6
Shovelnose Sturgeon	155	221	0.9	1.3	12.8	18.2	0.37	0.53	57.3	81.6
Gizzard Shad	1820	2336	ND	ND	128	164	6.3	8.09	72.7	93.3
Goldeye	115	166	0.9	1.3	7.35	10.61	0.3	0.43	71.1	102.6
<u>Kansas City, Missouri</u>										
Common Carp	394	545	0.6	0.83	19.9	27.5	1.5	2.1	259	358
Channel Catfish	169	235	0.5	0.69	8.1	11.3	0.39	0.54	56.6	78.6
Freshwater Drum	129	182	ND	ND	22.5	31.8	0.66	0.93	47.3	66.8

Concentrations in most fish samples from the Missouri River were comparable to the values reported by Brumbaugh and Kane (1985) for smallmouth bass (*Micropterus dolomieu*), by Guthrie and Cherry (1979) for mosquitofish (*Gambusia affinis*), and by Wells et al. (1988) in Texas. An exception is gizzard shad from Gavins Point Dam, from Dakota City, and from Atchison. Brumbaugh and Kane (1985) reported that aluminum concentrations in gut contents of fish analyzed add much variability to whole-body aluminum analyses and can produce large differences in the concentrations measured. However, we have no explanation for the high concentrations in the samples from the Missouri River. Analyses of additional samples from more locations and with greater analytical precision would be required to determine if the aluminum concentration in gizzard shad normally is high, if concentrations are larger in shad from locations further downstream, or if there is a source of aluminum contamination of the river.

#### Beryllium

There is little information in the published literature about whole-body concentrations of beryllium in fish. Beryllium has low solubility in water, and a low bioaccumulative tendency (Phillips and Russo 1978).

The low concentrations in fish we collected are comparable to the concentrations found in several U.S. Department of the Interior (DOI) studies in the western U.S. (Knapp et al. 1988, Lambing et al. 1988, Peterson et al. 1988, Radtke et al. 1988, Stephens et al. 1988). Beryllium does not appear to be an element of concern in the reach of the river that we sampled.

#### Cadmium

Cadmium usually is present in water as a result of discharges from human activities (Eisler 1985, Pratrapp et al. 1989). Its subsequent availability to aquatic biota apparently is dependent on a variety of physical conditions (Kent and Johnson 1979, Pita and Hyne 1975, Wiener and Giesy 1979.) Lodénus and Autio (1989) and Wiener and Giesy (1979) found that cadmium is more available at low pH levels.

Cadmium is a biologically nonessential teratogen, carcinogen, and probable mutagen. Freshwater biota are especially sensitive to cadmium, with concentrations of 0.8 to 9.9  $\mu\text{g/l}$  known to be lethal to insects, crustaceans, or teleosts (Eisler 1985b). Many researchers have suggested that uptake through the gills is the common source of cadmium contamination, but Dallinger and Kautzky (1985) and Klaverkamp et al. (1983) suggested that supply through food may be a more important source of cadmium (and other metal) contamination for rainbow trout than gill uptake. Cadmium availability to biota differs little between hard water and soft water conditions (Wiener and Giesy 1979). Phillips and Russo

(1978) believed that cadmium has a low tendency to bioaccumulate, but Spehar et al. (1978) found that concentrations in invertebrates can be as much as 30,000 times as high as concentrations in their water.

Documentation of cadmium body burdens in wildlife and fish and effects of long-term exposure are lacking. According to Eisler (1985b), 5.0 ppm fresh (wet) weight should be considered life-threatening in whole animals. Cadmium concentrations in whole fish from DOI studies in the western United States were very low (Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988, Radtke et al. 1988, Schroeder et al. 1988, Stephens et al. 1988, Wells et al. 1988). Maximum whole body wet weight concentrations in fish collected for the NCBP were 1.04  $\mu\text{g/g}$  in 1976-1977, 0.41  $\mu\text{g/g}$  in 1978-1979, 0.35  $\mu\text{g/g}$  in 1980-1981, and 0.22  $\mu\text{g/g}$  in 1984. The comparable geometric means and 85th percentile values were 0.07 and 0.11, 0.04 and 0.09, 0.03 and 0.06, and 0.03 and 0.05 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977).

Cadmium concentrations in several samples collected for this project exceeded the maximums in fish collected for the NCBP. Cadmium levels in common carp in the Boyd County to Gavins Point Dam section of the river and in shovelnose sturgeon from the Boyd County, Niobrara, and Gavins Point Dam sampling sites were especially high. Although common carp and shovelnose sturgeon are bottom feeders, cadmium was sufficiently concentrated in all species and in all locations to warrant further investigations of the sources of the cadmium contamination in the river.

### Chromium

Relatively little is known about effects of environmental chromium on organisms, but at high ambient levels chromium is a mutagen, a teratogen, and a carcinogen. The chemistry of chromium in aquatic settings is not well understood, and can be modified by a variety of environmental factors. Chromium is a trace nutrient for some animals, but its requirement in fish has not been established.

Chromium is not known to be biomagnified in food webs, and concentrations are usually greatest in the lowest trophic levels (Eisler 1986a). Knoll and Fromm (1960) indicated that  $\text{Cr}^{5+}$  is not accumulated in significant amounts by fish exposed to 2.5 mg/l. Phillips and Russo (1978) stated that chromium has a low bioaccumulation tendency. Hamilton and Reash (1988) believed that bone development of creek chubs (*Semotilus atromaculatus*) was affected by high concentrations of chromium and zinc in two streams in Ohio. A whole-body chromium concentration of 4.0  $\mu\text{g/g}$  dry weight or more was considered by Eisler (1986a) to be evidence of chromium contamination. However, according to Buhler et al. (1977), Giesy and Wiener (1977), and Tong et al. (1974),

fish usually contain less than 0.4  $\mu\text{g/g}$  dry weight.

Chromium concentrations in whole fish from DOI studies in the western U.S. were variable. Common carp from the lower Colorado River contained up to 1.9  $\mu\text{g/g}$  wet weight (Radtke et al. 1988). Most species from the study of the Lower Rio Grande and Laguna Atascosa NWR (Wells et al. 1988) contained 1.1  $\mu\text{g/g}$  or less, wet weight. *Tilapia* spp., however, contained 3.4  $\mu\text{g/g}$  wet weight, or 14  $\mu\text{g/g}$  dry weight. A sample of forage fish from Benton Lake NWR in Montana contained 17  $\mu\text{g/g}$ , and yellow perch from the Sun River Irrigation Project contained 14  $\mu\text{g/g}$  dry weight (Knapton et al. 1988). White sucker (*Catostomus commersoni*) from Nelson Reservoir in northeastern Montana contained 17  $\mu\text{g/g}$  dry weight (Lambing et al. 1988). Common carp from a reservoir in central Wyoming contained 16  $\mu\text{g/g}$  dry weight, and fathead minnows (*Pimephales promelas*) from the same site contained 14  $\mu\text{g/g}$  dry weight (Peterson et al. 1988). Whole-body chromium concentrations in fish from the southern San Joaquin valley in California ranged from 1.8 to 8.4  $\mu\text{g/g}$  dry weight (Schroeder et al. 1988).

Chromium concentrations in common carp and shovelnose sturgeon from Boyd County, and in gizzard shad from below Gavins Point Dam, from Dakota City, in from Atchison were above the 4.0  $\mu\text{g/g}$  dry-weight level that Eisler (1986a) believed denoted chromium poisoning. Fish from other locations in the western United States contained higher concentrations, but we suggest that the concentrations in fish of the Missouri River should be further assessed.

#### Copper

Copper is a minor nutrient for plants and animals. In unpolluted waters it is usually found at concentrations less than 1 mg/l. Copper availability depends on water hardness in many settings (Hodson 1988). Hill (1977) did not consider copper toxicosis a serious threat to terrestrial organisms because copper is handled well by the liver and is seldom encountered in problematic concentrations. Copper concentrations in fish usually are homeostatically controlled (Cross et al. 1973, Giesy and Wiener 1977, Goodyear and Boyd 1972, Wiener and Giesy 1979). However, there are numerous documented cases of deleterious effects of copper in aquatic and terrestrial organisms, usually due to anthropogenic activities (e.g. Chupp and Dalke 1964, Clausen and Wolstrup 1978, Imlay and Winger 1983, McKim and Benoit 1971, Sprague et al. 1965).

In western United States DOI studies, whole-body wet weight copper concentrations in fish ranged from below the detection limit to 5.3  $\mu\text{g/g}$  in rainbow trout collected from the North Platte River in central Wyoming (Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988, Radtke et al. 1988, Schroeder et al. 1988, Stephens et al. 1988, Wells et al. 1988). The 5.3  $\mu\text{g/g}$  wet weight was equivalent to 22.0  $\mu\text{g/g}$  dry

weight.

Mean whole-body wet weight copper concentrations in fish collected for the NCBP were 0.82 in 1978-1979, 0.65 in 1980-1981, and 0.65 in 1984 (Lowe et al. 1985, Schmitt and Brumbaugh 1990). Corresponding 85th percentile values were 1.1, 0.9, and 1.0  $\mu\text{g/g}$ . The associated maximum values were 38.7, 24.1, and 23.1  $\mu\text{g/g}$ . Nationwide, fish have relatively low whole-body copper burdens, but fish in some locations apparently are exposed to large concentrations.

All copper concentrations in fish collected for this project were above the 85th percentile values from the NCBP. Gizzard shad collected from below Gavins Point Dam had a higher copper concentration than the maximum recorded for the NCBP in 1980-1981 and 1984.

### Iron

Iron is necessary for metabolic processes and especially for hemoglobin in fish, and can be expected to be found in higher concentrations than most other elements. Iron also has a high tendency to bioaccumulate, but large doses may cause serious problems. Fish accumulate large concentrations in the gills, but concentrations do not appear to change with age (Phillips and Russo 1978).

Radtke et al. (1988) and Schroeder et al. (1988) found relatively consistent iron concentrations between sampling locations, whereas Peterson et al. (1988), Stephens et al. (1988), and Wells et al. (1988) found greater variation in their whole fish samples. Their results indicate that iron concentrations differ between locations and between species. Concentrations in fish from the Missouri River were within the ranges reported in the DOI studies.

### Lead

Lead is biologically nonessential, and has long been recognized as a cumulative poison. The chemistry of lead introduced into aquatic systems is complex, and its availability to aquatic organisms varies (Eisler 1988b). Much lead entering fresh waters is precipitated, but decreasing pH increases lead availability. The toxicity and bioconcentration of lead in aquatic organisms are increased by methylation (Hodson 1988), but unmethylated lead has a low tendency to bioaccumulate (Phillips and Russo 1978). Lead poisoning in birds has been especially well studied, and effects in aquatic systems also have been well documented in many areas (Demayo et al. 1982, Wong et al. 1978).

Normally, little or no lead is available to aquatic systems. However, lead has been demonstrated to be at high levels in areas of metal mining (Benson et al. 1976, Chupp et al. 1964, Czarnecki 1985,

Dwyer et al. 1988, Harwood et al. 1987, Knowlton et al. 1983, Niethammer et al. 1985, Roberts and Johnson 1978, Schmitt and Finger 1987) and metal smelting (Beyer 1988, Beyer et al. 1985, Dmowski and Karolewski 1979, Johnson et al. 1978). Wiener and Giesy (1979) found that lead was less available to aquatic biota in soft water systems. Much evidence suggests that often lead is not bioconcentrated (Eisler 1988b, Wong et al. 1978).

In freshwater fish in the United States, geometric mean lead concentrations were 0.28  $\mu\text{g/g}$  wet weight in 1976-1977, 0.19  $\mu\text{g/g}$  in 1978-1979, 0.17  $\mu\text{g/g}$  in 1980-1981, and 0.11  $\mu\text{g/g}$  in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990, Walsh et al. 1977). This is a significant decline ( $P \leq 0.01$ ), and appears to represent a drop in environmental lead levels (Schmitt and Brumbaugh (1990). Corresponding 85th percentile values and maximum lead concentrations were 0.44  $\mu\text{g/g}$  and 4.93  $\mu\text{g/g}$  in 1976-1977, 0.32  $\mu\text{g/g}$  and 6.73  $\mu\text{g/g}$  in 1978-1979, 0.25  $\mu\text{g/g}$  and 1.94  $\mu\text{g/g}$  in 1980-1981 (with the station normally having the highest concentrations not reporting), and 0.22  $\mu\text{g/g}$  and 4.88  $\mu\text{g/g}$  in 1984.

Lead concentrations in some fish composites from the Missouri River were above the 85th percentile values of the NCBP and above the values for fish collected in the western U.S. DOI studies. Lead was not detected in fish from Niobrara or Gavins Point Dam, Nebraska. However, lead concentrations in fish from Boyd County, Nebraska, and downstream from Dakota City, Nebraska suggest that a search for sources of lead contamination of the river may be warranted.

#### Manganese

We have very little information on normal concentrations of manganese in biota. Manganese levels in fish are apparently well regulated under most conditions (Cross et al. 1973, Giesy and Wiener 1977, Goodyear and Boyd 1972, Wiener and Giesy 1979), and manganese has a low bioaccumulative tendency (Phillips and Russo 1978).

Many of the manganese concentrations in fish from the Missouri River were higher than the highest values in fish collected in the western United States (Knapton et al. 1988, Lambing et al. 1988, Schroeder et al. 1988, Radtke et al. 1988, Peterson et al. 1988, Stephens et al. 1988., Wells et al. 1988). The manganese concentrations in common carp, channel catfish, and shovelnose sturgeon from Niobrara, in common carp and channel catfish, from Gavins Point Dam, and in common carp and freshwater drum from Dakota City were high. Concentrations in common carp, channel catfish, and shovelnose sturgeon from Boyd County and in gizzard shad from Gavins Point Dam, Dakota City, and Atchison were high. We do not know the effects of the high concentrations on the fish in the river.



## Nickel

Nickel has been found in most aquatic organisms, but concentrations in whole fish from unpolluted locations should be less than 2.0  $\mu\text{g/g}$  wet weight (Jenkins 1980). Nickel concentrations in many locations have been greatly altered as a result of mining and smelting operations, many industrial processes, and fossil fuel combustion. However, nickel has been considered less problematic than many other heavy metals. Nickel was considered by Phillips and Russo (1978) to have a low tendency to bioaccumulate. However, it is bioaccumulated by at least some fish species (Tjalve et al. 1988). We have little comparative information on background nickel concentrations in fish. However, bluegills and common carp collected by Saiki and May (1988) in the San Joaquin River and some of its tributaries in California had a maximum mean nickel concentration of 0.495  $\mu\text{g/g}$  wet weight.

Nickel concentrations in common carp and shovelnose sturgeon from the Missouri River at Boyd County, Nebraska were elevated relative to concentrations in most fish collected for DOI studies (Knapton et al. 1988, Lambing et al. 1988, Schroeder et al. 1988, Radtke et al. 1988, Peterson et al. 1988, Stephens et al. 1988., Wells et al. 1988) and from the Savannah River (Winger et al. 1990), and may warrant further investigation.

## Zinc

Zinc is a required trace element for most organisms, but it is toxic at high concentrations (Holcombe et al. 1979, Taylor et al. 1982), and in some instances at relatively low concentrations (Bengtsson 1974). Zinc is a relatively mobile metal in natural settings, but zinc concentrations in many locations have been greatly increased by human activities (e.g. Beyer et al. 1985, Johnson et al. 1978, Niethammer et al. 1985, Roch et al. 1985, Sileo and Beyer 1985). Zinc availability and toxicity are affected by pH and by water hardness (Phillips and Russo 1978).

Zinc concentrations are well controlled metabolically in most organisms, and bioaccumulation or bioconcentration of zinc are highly dependent on location, feeding habits, and life stage of the organism being studied (Beyer et al. 1982, Beyer 1986, Giesy and Wiener 1977, Marshall et al. 1983, Murphy et al. 1978, O'Grady and Abdullah 1985, White and Cromartie 1985, Wiener and Giesy 1979).

Zinc and copper in water are synergistic at high concentrations, and affected rainbow trout and immature Atlantic salmon (*Salmo salar*) more than simple additive effects of the two metals would suggest (Lloyd 1961, Sprague 1964). Concentrations and toxicity to fish may vary with migration or preparation for spawning (Fletcher et al. 1975, Fletcher and King 1978, O'Grady 1981), and with water chemistry and fish size

(Bradley and Sprague 1985). Bone development of creek chubs in two streams in Ohio was thought to have been affected by high concentrations of chromium and zinc (Hamilton and Reash 1988). Zinc has a low bioaccumulative tendency, according to Phillips and Russo (1978).

Maximum wet weight zinc concentrations in whole fish collected for the NCBP were 168.1  $\mu\text{g/g}$  in 1978-1979, 109.2  $\mu\text{g/g}$  in 1980-1981, and 118  $\mu\text{g/g}$  in 1984. Corresponding mean and 85th percentile concentrations were 23.8 and 46.3  $\mu\text{g/g}$  in 1978-1979, 21.4 and 40.1  $\mu\text{g/g}$  in 1980-1981, and 21.7 and 34.2  $\mu\text{g/g}$  in 1984 (Lowe et al. 1985, May and McKinney 1981, Schmitt and Brumbaugh 1990). High zinc concentrations in whole fish were found in DOI studies in California (Schroeder et al. 1988), Texas (Wells et al. 1988), Utah (Stephens et al. 1988), Wyoming (Peterson et al. 1988), and Montana (Knapton et al. 1988).

Zinc concentrations in Missouri River common carp from all locations except Omaha were well in excess of the highest values reported for the NCBP. Zinc concentrations in goldeye from Boyd County, Gavins Point Dam, and Dakota City and in shovelnose sturgeon from Boyd County, Niobrara, Gavins Point Dam, and Dakota City also were high. Zinc is easily mobilized from soils (Taylor et al. 1982), and the observed concentrations may be the norm for the Missouri River. However, we believe that the possibility of anthropogenic introductions of zinc to the Missouri River should be investigated.

#### Further Study Needs

The toxic effects of metals in aquatic systems are difficult to assess. Metal and metalloid elements and compounds may interact to produce synergistic effects or they may counteract each other. In addition, toxic effects of metals in water "range from a complete loss of biota to subtle effects on rates of population reproduction, growth, and mortality" (Hodson 1988). Further, our analyses indicated only the total in the fish composite of each element for which analyses were done; the laboratory analyses did not indicate the forms of the elements that were present. Therefore, this project gives only preliminary indications of further studies that may be needed.

Aluminum, arsenic, cadmium, copper, manganese, and zinc concentrations in the fish samples were high enough to warrant further studies. Lead concentrations also were high enough to warrant further study, especially downstream from Dakota City, Nebraska. Chromium and nickel concentrations were high relative to concentrations found in other locations. Beryllium, iron, mercury, selenium, and tellurium concentrations in fish we sampled were below the levels of concern to resource managers.

## CHLORINATED HYDROCARBON COMPOUNDS

Use of organochlorine compounds has been restricted in the United States, but because of their persistence they still are found in many biota. Results of chlorinated hydrocarbon analyses of the fish composites are shown in Table 6. The following compounds were not detected in any sample in which analyses for the compound were completed: endrin, alpha, beta, gamma, and delta benzene hexachloride (BHC), endosulfan sulfate, mirex, dicofol, tetradifon, toxaphene, and aroclors 1016, 1221, 1232, 1242, 1248, and 1260.

The following compounds are grouped for discussion:

- Cyclodiene compounds,
- Chlordane/Heptachlor compounds,
- Aldrin and Dieldrin; and
- Endosulfan I and Endosulfan II;
- DDT compounds; and
- Aroclor<sup>®</sup> 1254 and Total PCBs.

### Cyclodiene Compounds

#### Chlordane Compounds

Chlordane is a complex mixture of compounds. Components of chlordane may include cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, chlordanes, and heptachlor, as well as other compounds (Cardwell et al. 1977, National Research Council of Canada 1974). Oxychlordane is a metabolite of chlordane or heptachlor components. Cis- and trans-nonachlor and cis-chlordane are more readily stored than are other chlordane components (Cardwell et al. 1977, Winger et al. 1984).

Chlordane formerly was used for control of a variety of soil insects, including termites and agricultural pests. It is now used less for agricultural pests, and Arruda et al. (1987) suggested that the main sources of chlordane contamination of aquatic systems are urban areas. Chlordane is very persistent and highly toxic to aquatic organisms and birds. Detrimental effects of chlordane components or metabolites on birds have been demonstrated by Blus et al. (1983) and Stickel et al. (1979, 1983). Heptachlor has been used for controlling insects in seeds and for control of fire ants. It is also a constituent of chlordane, so it is difficult to separate the sources of heptachlor and heptachlor epoxide, a more toxic metabolite of heptachlor (Schmitt et al. 1990). Heptachlor has been demonstrated to be long-lasting (Beyer and Krynsky 1989, Gish and Hughes 1982) and to have detrimental effects on birds (Blus et al. 1984, 1985, Ferguson 1964, Henny et al. 1983, 1984, Rosene

Table 6. Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Percent Lipid	Concentration ( $\mu\text{g/g}$ wet weight)			
			cis- chlordane	trans- chlordane	cis- nonachlor	trans- nonachlor
<u>Boyd County, Nebraska</u>						
Common Carp	73.8	4.11	ND	ND	ND	ND
Channel Catfish	69.8	14.10	0.01	0.01	ND	0.01
Shovelnose Sturgeon	69.8	8.44	0.01	0.01	ND	0.01
Goldeye	64.0	15.50	0.02	ND	ND	0.02
<u>Niobrara, Nebraska</u>						
Common Carp	74.2	4.51	ND	ND	ND	ND
Channel Catfish	73.0	9.02	0.01	0.01	ND	0.01
Shovelnose Sturgeon	69.6	9.00	0.02	0.01	ND	0.02
Walleye/Sauger	69.2	7.67	0.01	ND	ND	0.01
<u>Gavins Point Dam tailwaters, Nebraska</u>						
Common Carp	68.8	7.16	0.02	0.01	ND	0.03
Channel Catfish	71.6	4.73	ND	ND	ND	ND
Shovelnose Sturgeon	67.8	9.84	0.02	0.02	ND	0.03
Walleye/Sauger	71.6	4.74	ND	ND	ND	ND
Freshwater Drum	73.2	6.10	0.03	0.01	ND	0.05
Gizzard Shad	70.4	4.98	ND	ND	ND	ND
Goldeye	66.2	12.10	0.01	ND	ND	0.01

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Percent Lipid	Concentration ( $\mu\text{g/g}$ wet weight)			
			cis- chlordane	trans- chlordane	cis- nonachlor	trans- nonachlor
<u>Dakota City, Nebraska</u>						
Common Carp	72.0	5.17	0.02	0.01	ND	0.01
Channel Catfish	76.8	2.55	0.01	ND	ND	0.01
Shovelnose Sturgeon	73.4	9.16	0.02	0.01	ND	0.02
Freshwater Drum	74.2	4.16	0.01	0.01	ND	0.02
Gizzard Shad	77.0	1.60	0.01	ND	ND	0.01
Goldeye	69.6	6.79	0.03	0.01	ND	0.04
<u>Blair, Nebraska</u>						
Common Carp	60.7	3.00	ND	ND	ND	0.01
Channel Catfish	72.0	4.60	0.03	0.03	ND	0.05
Shovelnose Sturgeon	71.8	4.60	0.03	0.03	ND	0.05
Freshwater Drum	73.6	5.70	ND	0.02	0.01	0.02
Gizzard Shad	69.0	2.20	ND	ND	ND	0.01
Goldeye	62.3	3.90	ND	ND	ND	ND
Paddlefish	69.7	16.90	0.09	0.16	0.01	0.07
Paddlefish	71.7	5.80	0.01	0.01	ND	0.01
<u>Omaha, Nebraska</u>						
Shovelnose Sturgeon	70.2	9.46	0.06	0.05	ND	0.07

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Percent Lipid	Concentration ( $\mu\text{g/g}$ wet weight)			
			cis- chlordane	trans- chlordane	cis- nonachlor	trans- nonachlor
<u>Rulo, Nebraska</u>						
Common Carp	75.2	1.80	ND	0.01	ND	ND
Channel Catfish	69.7	10.20	0.01	0.02	ND	0.02
Shovelnose Sturgeon	57.2	8.10	0.06	0.06	0.01	0.07
Freshwater Drum	76.6	4.80	0.01	0.01	ND	0.02
Gizzard Shad	68.2	0.40	ND	ND	ND	ND
Goldeye	68.9	2.20	ND	ND	ND	ND
<u>Atchison, Kansas</u>						
Common Carp	75.0	4.20	0.02	0.02	ND	0.02
Channel Catfish	69.6	11.30	0.04	0.03	ND	0.05
Shovelnose Sturgeon	71.0	10.60	0.08	0.08	0.03	0.11
Gizzard Shad	76.0	1.11	ND	0.01	ND	0.01
Goldeye	68.2	10.60	0.02	ND	ND	0.03
<u>Kansas City, Missouri</u>						
Common Carp	73.0	4.78	0.14	0.10	0.06	0.12
Channel Catfish	71.2	9.23	0.06	0.04	0.02	0.06
Freshwater Drum	69.0	9.43	0.05	0.03	0.02	0.07

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)							
	Oxychlor- dane	Methoxychlor	Heptachlor	Hept. Epoxide	Chlordane Total	Dieldrin	Aldrin	Cyclodiene Total <sup>a</sup>
<u>Boyd County, Nebraska</u>								
Common Carp	ND	NA	NA	ND	ND	NA	0.01	0.01
Channel Catfish	ND	NA	NA	ND	0.03	NA	0.02	0.05
Shovelnose Sturgeon	ND	NA	NA	ND	0.03	NA	0.01	0.04
Goldeye	ND	NA	NA	ND	0.04	NA	0.01	0.05
<u>Niobrara, Nebraska</u>								
Common Carp	ND	NA	NA	ND	ND	NA	0.01	0.01
Channel Catfish	ND	NA	NA	ND	0.03	NA	0.01	0.04
Shovelnose Sturgeon	ND	NA	NA	ND	0.05	NA	0.01	0.06
Walleye/Sauger	ND	NA	NA	ND	0.02	NA	0.01	0.03
<u>Gavins Point Dam tailwaters, Nebraska</u>								
Common Carp	ND	NA	NA	ND	0.06	NA	0.01	0.07
Channel Catfish	ND	NA	NA	ND	ND	NA	0.02	0.02
Shovelnose Sturgeon	ND	NA	NA	ND	0.07	NA	0.01	0.08
Walleye/Sauger	ND	NA	NA	ND	ND	NA	0.01	0.01
Freshwater Drum	0.01	NA	NA	0.01	0.11	NA	0.08	0.30 <sup>b</sup>
Gizzard Shad	ND	NA	NA	ND	ND	NA	0.01	0.01
Goldeye	ND	NA	NA	ND	0.02	NA	0.01	0.03

<sup>a</sup> Cyclodiene total includes endosulfan compounds, not shown in table

<sup>b</sup> Exceeds NAS/NAE 0.1  $\mu\text{g/g}$  recommendation for cyclodiene compounds.

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)							
	Oxychlor- dane	Methoxychlor	Heptachlor	Hept. Epoxide	Chlordane Total	Dieldrin	Aldrin	Cyclodiene Total <sup>a</sup>
<u>Dakota City, Nebraska</u>								
Common Carp	0.01	NA	NA	0.01	0.06	NA	0.02	0.08
Channel Catfish	ND	NA	NA	ND	0.02	NA	0.02	0.04
Shovelnose Sturgeon	0.01	NA	NA	ND	0.06	NA	0.02	0.08
Freshwater Drum	ND	NA	NA	ND	0.04	NA	0.03	0.07
Gizzard Shad	ND	NA	NA	ND	0.02	NA	0.01	0.03
Goldeye	0.01	NA	NA	0.01	0.10	NA	0.04	0.14 <sup>b</sup>
<u>Blair, Nebraska</u>								
Goldeye	ND	ND	ND	ND	ND	ND	0.01	0.01
Gizzard Shad	ND	0.02	ND	ND	0.03	ND	0.01	0.04
Freshwater Drum	0.02	ND	ND	0.01	0.07	ND	ND	0.07
Shovelnose Sturgeon	0.02	ND	0.01	ND	0.14	ND	0.04	0.18 <sup>b</sup>
Channel Catfish	0.02	ND	ND	ND	0.13	ND	0.06	0.19 <sup>b</sup>
Common Carp	ND	ND	ND	ND	0.01	ND	0.01	0.02
Paddlefish	0.01	ND	0.02	0.01	0.36	ND	0.14	0.52 <sup>b</sup>
Paddlefish	ND	0.02	ND	ND	0.05	ND	0.01	0.06
<u>Omaha, Nebraska</u>								
Shovelnose Sturgeon	0.02	ND	NA	0.02	0.22	NA	0.11	0.33 <sup>b</sup>

<sup>a</sup> Cyclodiene total includes endosulfan compounds, not shown in table

<sup>b</sup> Exceeds NAS/NAE 0.1  $\mu\text{g/g}$  recommendation for cyclodiene compounds.



Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)							
	Oxychlor- dane	Methoxychlor	Heptachlor	Hept. Epoxide	Chlordane Total	Dieldrin	Aldrin	Cyclodiene Total <sup>a</sup>
<u>Rulo, Nebraska</u>								
Common Carp	ND	ND	ND	ND	0.01	ND	0.02	0.03
Channel Catfish	0.01	0.02	ND	0.01	0.09	ND	0.11	0.21 <sup>b</sup>
Shovelnose Sturgeon	0.02	0.03	ND	0.01	0.25	0.01	0.10	0.36 <sup>b</sup>
Freshwater Drum	0.02	0.01	ND	0.01	0.08	ND	0.06	0.14 <sup>b</sup>
Gizzard Shad	ND	ND	ND	ND	ND	ND	ND	ND
Goldeye	ND	ND	ND	ND	ND	ND	0.01	0.02
<u>Atchison, Kansas</u>								
Common Carp	0.03	ND	NA	0.03	0.12	NA	0.02	0.14 <sup>b</sup>
Channel Catfish	0.02	ND	NA	0.02	0.16	NA	ND	0.16 <sup>b</sup>
Shovelnose Sturgeon	0.03	ND	NA	0.03	0.33	NA	0.09	0.42 <sup>b</sup>
Gizzard Shad	ND	ND	NA	ND	0.02	NA	0.01	0.03
Goldeye	0.02	ND	NA	0.04	0.11	NA	0.04	0.15 <sup>b</sup>
<u>Kansas City, Missouri</u>								
Common Carp	0.02	ND	NA	0.03	0.41	NA	0.03	0.44 <sup>b</sup>
Channel Catfish	0.03	ND	NA	0.02	0.21	NA	0.07	0.28 <sup>b</sup>
Freshwater Drum	0.03	ND	NA	0.02	0.20	NA	0.08	0.28 <sup>b</sup>

<sup>a</sup> Cyclodiene total includes endosulfan compounds, not shown in table

<sup>b</sup> Exceeds NAS/NAE 0.1  $\mu\text{g/g}$  recommendation for cyclodiene compounds.

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)						
	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	DDT Total
<u>Boyd County, Nebraska</u>							
Common Carp	ND	0.01	ND	ND	ND	ND	0.01
Channel Catfish	ND	0.01	ND	ND	ND	ND	0.01
Shovelnose Sturgeon	ND	0.09	ND	ND	ND	ND	0.09
Goldeye	ND	0.05	ND	0.02	ND	ND	0.07
<u>Niobrara, Nebraska</u>							
Common Carp	ND	0.01	ND	ND	ND	ND	0.01
Channel Catfish	ND	0.02	ND	ND	ND	ND	0.02
Shovelnose Sturgeon	ND	0.16	ND	0.03	ND	ND	0.19
Walleye/Sauger	ND	0.02	ND	ND	ND	ND	0.02
<u>Gavins Point Dam tailwaters, Nebraska</u>							
Common Carp	ND	0.06	ND	0.03	ND	ND	0.09
Channel Catfish	ND	0.02	ND	ND	ND	ND	0.02
Shovelnose Sturgeon	ND	0.10	ND	0.04	ND	ND	0.14
Walleye/Sauger	ND	0.01	ND	0.01	ND	ND	0.02
Freshwater Drum	ND	0.07	ND	0.02	ND	ND	0.09
Gizzard Shad	ND	0.01	ND	ND	ND	ND	0.01
Goldeye	ND	0.04	ND	0.01	ND	ND	0.05

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)						
	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	DDT Total
<u>Dakota City, Nebraska</u>							
Common Carp	ND	0.04	ND	ND	ND	ND	0.04
Channel Catfish	ND	0.03	ND	ND	ND	ND	0.03
Shovelnose Sturgeon	ND	0.07	ND	0.02	ND	ND	0.09
Freshwater Drum	ND	0.03	ND	ND	ND	ND	0.03
Gizzard Shad	ND	0.02	ND	ND	ND	ND	0.02
Goldeye	ND	0.08	ND	0.03	ND	ND	0.11
<u>Blair, Nebraska</u>							
Common Carp	ND	ND	ND	0.02	0.01	ND	0.03
Channel Catfish	ND	0.11	ND	0.02	ND	0.03	0.16
Shovelnose Sturgeon	ND	0.11	ND	0.02	0.04	0.04	0.21
Freshwater Drum	ND	0.06	ND	0.02	ND	0.02	0.10
Gizzard Shad	ND	0.02	ND	0.01	ND	0.01	0.04
Goldeye	ND	0.05	0.01	0.01	ND	ND	0.07
Paddlefish	0.05	0.02	0.06	ND	ND	ND	0.08
Paddlefish	ND	0.04	0.01	ND	0.01	ND	0.06
<u>Omaha, Nebraska</u>							
Shovelnose Sturgeon	ND	0.15	ND	0.04	ND	0.05	0.24

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)						
	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	DDT Total
<u>Rulo, Nebraska</u>							
Common Carp	ND	0.01	ND	ND	ND	0.01	0.02
Channel Catfish	ND	0.05	ND	0.02	0.02	0.01	0.10
Shovelnose Sturgeon	ND	0.1	ND	0.03	0.05	0.03	0.21
Freshwater Drum	ND	0.05	ND	0.02	0.02	0.02	0.11
Gizzard Shad	ND	ND	ND	ND	ND	0.02	0.02
Goldeye	ND	0.01	ND	0.01	ND	ND	0.02
<u>Atchison, Kansas</u>							
Common Carp	ND	0.07	ND	0.03	ND	0.01	0.11
Channel Catfish	ND	0.06	ND	0.03	ND	ND	0.09
Shovelnose Sturgeon	ND	0.18	ND	0.06	ND	0.07	0.31
Gizzard Shad	ND	0.01	ND	ND	ND	ND	0.01
Goldeye	ND	0.12	ND	0.04	ND	ND	0.16
<u>Kansas City, Missouri</u>							
Common Carp	ND	0.11	ND	0.10	ND	0.01	0.22
Channel Catfish	ND	0.07	ND	0.03	ND	0.02	0.12
Freshwater Drum	ND	0.08	ND	0.03	ND	0.02	0.13

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)			Total PCBs
	Hexachlorobenzene	DCPA	Aroclor <sup>®</sup> 1254	
<u>Boyd County, Nebraska</u>				
Common Carp	ND	ND	NA	ND
Channel Catfish	ND	ND	NA	ND
Shovelnose Sturgeon	ND	ND	NA	ND
Goldeye	ND	ND	NA	ND
<u>Niobrara, Nebraska</u>				
Common Carp	ND	ND	NA	ND
Channel Catfish	ND	ND	NA	ND
Shovelnose Sturgeon	ND	ND	NA	ND
Walleye/Sauger	ND	ND	NA	ND
<u>Gavins Point Dam tailwaters, Nebraska</u>				
Common Carp	ND	ND	NA	ND
Channel Catfish	ND	ND	NA	ND
Shovelnose Sturgeon	ND	ND	NA	0.24
Walleye/Sauger	ND	ND	NA	ND
Freshwater Drum	ND	ND	NA	0.38
Gizzard Shad	ND	ND	NA	ND
Goldeye	ND	ND	NA	ND

Table 6 (continued). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)			
	Hexachlorobenzene	DCPA	Aroclor <sup>H</sup> 1254	Total PCBs
<u>Dakota City, Nebraska</u>				
Common Carp	ND	ND	NA	0.06
Channel Catfish	ND	ND	NA	ND
Shovelnose Sturgeon	ND	ND	NA	0.35
Freshwater Drum	ND	ND	NA	0.13
Gizzard Shad	ND	ND	NA	0.07
Goldeye	ND	ND	NA	0.65
<u>Blair, Nebraska</u>				
Common Carp	0.02	ND	0.29	NA
Channel Catfish	ND	0.01	0.96	NA
Shovelnose Sturgeon	ND	ND	1.20	NA
Freshwater Drum	ND	ND	0.48	NA
Gizzard Shad	ND	ND	0.47	NA
Goldeye	ND	ND	0.62	NA
Paddlefish	0.01	0.02	0.82	NA
Paddlefish	ND	ND	0.75	NA
<u>Omaha, Nebraska</u>				
Shovelnose Sturgeon	ND	ND	NA	0.65

Table 6 (concluded). Chlorinated hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)			Total PCBs
	Hexachlorobenzene	DCPA	Aroclor <sup>®</sup> 1254	
<u>Rulo, Nebraska</u>				
Common Carp	ND	0.01	0.15	NA
Channel Catfish	ND	ND	0.81	NA
Shovelnose Sturgeon	ND	ND	1.50	NA
Freshwater Drum	ND	ND	0.64	NA
Gizzard Shad	ND	ND	0.29	NA
Goldeye	0.02	ND	0.54	NA
<u>Atchison, Kansas</u>				
Common Carp	ND	ND	NA	ND
Channel Catfish	ND	ND	NA	0.30
Shovelnose Sturgeon	ND	ND	NA	0.70
Gizzard Shad	ND	ND	NA	ND
Goldeye	ND	ND	NA	0.72
<u>Kansas City, Missouri</u>				
Common Carp	ND	ND	NA	0.55
Channel Catfish	ND	ND	NA	0.33
Freshwater Drum	ND	ND	NA	0.62

1965, Stickel et al. 1965, Wright 1965) and mammals (Clark et al. 1980, Clawson and Clark 1989, Rosene 1965).

Chlordane compounds were not in most western U.S. drainwater studies (Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988, Radtke et al. 1988, Stephens et al. 1988, Wells et al. 1988). However, Schroeder et al. (1988) found chlordane compounds in common carp from two of three locations sampled for the Tulare Lake Bed Area study in the San Joaquin Valley in California. Individual chlordane and nonachlor compounds were found in carp composites at up to 0.15  $\mu\text{g/g}$  wet weight.

Nationwide, the decreasing concentrations of chlordane and the increasing proportions of trans-nonachlor, the most persistent component of chlordane, in fish collected for the NCBP indicate that the input of chlordane to aquatic systems in the U.S. may be declining (Schmitt et al. 1990, Table 7). In general, the highest chlordane compound concentrations reported from the NCBP came from the midwest and from Hawaii (Schmitt et al. 1990).

Table 7. Geometric mean chlordane/heptachlor compound concentrations from the NPMP and the NCBP ( $\mu\text{g/g}$  wet weight).

Compound	Collection Period			
	1976-1977	1978-1979	1980-1981	1984
heptachlor <sup>a</sup>	0.01	0.02	0.01	0.01
<u>cis</u> -chlordane	0.06	0.07	0.03	0.03
<u>trans</u> -chlordane	0.02	0.02	0.02	0.02
<u>cis</u> -nonachlor	0.01	0.03	0.02	0.02
<u>trans</u> -nonachlor	0.03	0.05	0.04	0.03
oxychlordane	NA	0.01	0.01	0.01
total <sup>b</sup>	0.12	0.20	0.13	0.12

<sup>a</sup> Heptachlor epoxide plus traces of heptachlor

<sup>b</sup> Does not include methoxychlor

Chlordane/heptachlor compound concentrations in Missouri River fish were well above the corresponding mean values from the NCBP from 1976 through 1984. The National Academy of Sciences and National Academy of Engineering [(NAS/NAE) 1973] recommended that to protect aquatic life, the whole-body wet weight concentration of all cyclodiene compounds together should not exceed 0.1  $\mu\text{g/g}$ . Although no chlordane/heptachlor compounds were detected in eight of the samples, 16 of the 45 composites exceeded the NAS/NAE criterion. Five of the samples contained more than double the protection level. Fourteen of the 16 values over 0.1  $\mu\text{g/g}$



were at or below Blair, Nebraska, although at Rulo only the shovelnose sturgeon composite exceeded  $0.1 \mu\text{g/g}$ . Seven of the values exceeding the NAS/NAE recommendation were from Atchison, Kansas and Kansas City, Missouri. The highest concentration of chlordane/heptachlor compounds was  $0.41 \mu\text{g/g}$  in the common carp sample from Kansas City.

#### Aldrin and Dieldrin

Aldrin and dieldrin are insecticides once supplied in many formulations primarily for use on soil insects. In addition, dieldrin is the primary metabolite of aldrin in animals. Aldrin and/or dieldrin have been found to be detrimental to fish (Anderson and Fenderson 1970, Johnson and Finley 1980), birds (e.g. Hill 1982, Jones et al. 1978, Labisky and Lutz 1967, McEwen and Brown 1966, Newton and Bogan 1978, Wiemeyer et al. 1986), frogs (Mayer and Ellersieck 1986), snakes (Flickinger and King 1972), turtles (Flickinger and Mulhern 1980), and bats and other mammals (Blus 1978, Clark 1983, 1988, Clark et al. 1978, 1980, 1983, Clark and Prouty 1984).

Nationwide, geometric mean dieldrin concentrations in fish collected for the NPMP in the early 1970s were little different from the means from the NCBP in the late 1970s and early 1980s. Wet weight mean concentrations were  $0.08 \mu\text{g/g}$  in 1970,  $0.07 \mu\text{g/g}$  in 1971 and 1972,  $0.05 \mu\text{g/g}$  in 1973, and  $0.09 \mu\text{g/g}$  in 1974 (Schmitt et al. 1981). The geometric mean wet weight residues of dieldrin in fish did not change significantly from 1976 through 1984. They were  $0.06 \mu\text{g/g}$  in 1976-1977,  $0.05 \mu\text{g/g}$  in 1978-1979, and  $0.04 \mu\text{g/g}$  in 1980-1981 and 1984 (Schmitt et al. 1983, 1985, 1990).

Thirteen of the Missouri River fish composites exceeded the 1984 NCBP nationwide mean. Most of the composites from locations upstream from Blair, Nebraska contained low concentrations of dieldrin, as did most of the fish from the Blair collection. The concentration in one of the paddlefish from Blair and in the channel catfish and shovelnose sturgeon samples from Rulo, Nebraska exceeded the NAS/NAE recommendation for cyclodienes. The paddlefish and sturgeon are long-lived species, and may represent concentrations from earlier periods of cyclodiene use. However, the data support the suggestion that dieldrin residues in soils still threaten fish and wildlife in the midwest (Clark et al. 1983, Schmitt et al. 1990). In addition, the presence of aldrin in the shovelnose sturgeon sample from Rulo suggests recent aldrin inputs into the Missouri River.

#### Endosulfan I and Endosulfan II

Endosulfan insecticides were analyzed only in the samples from Blair and from Rulo, Nebraska. One paddlefish from Blair contained  $0.01 \mu\text{g/g}$  wet weight endosulfan I, and  $0.01 \mu\text{g/g}$  endosulfan II. Endosulfan I was found at  $0.01 \mu\text{g/g}$  in the channel catfish and goldeye composites

from Rulo. Neither compound was detected in any other composite. Although considered a priority pollutant by the EPA, endosulfan has not been reported in many studies. The concentrations in fish from Rulo and Blair did not change the proportion of samples exceeding the NAS/NAE recommendation for total cyclodiene concentration.

#### Total Cyclodiene Compounds

Residues of all cyclodiene compounds exceeded the NAS/NAE (1973) recommendation in 16 of the 45 fish composites from the Missouri River (Figure 2).

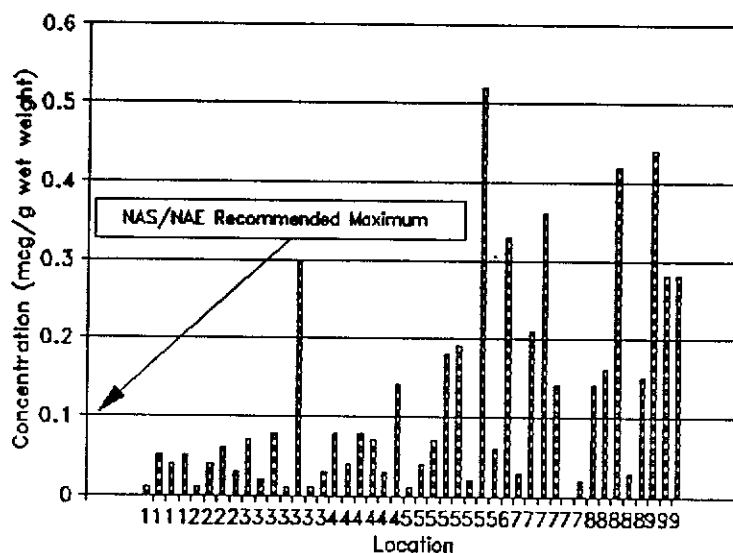


Figure 2. Total cyclodiene compound concentrations in Missouri River fish in 1988.

#### DDT Compounds

DDT and its metabolites are probably the most studied organochlorine contaminants. Although banned in 1972, DDT compounds are very persistent. In addition, dicofol acaricide may be contaminated with DDT, and is a possible source of DDE (Hunt et al. 1986, Risebrough et al. 1985, Schmitt et al. 1985, White and Krynitsky 1986). DDT compounds have been shown to have a variety of detrimental effects, especially reduced recruitment in birds (e.g. Blus et al. 1977, Henny and Herron 1989, Henny et al. 1984, Hickey and Anderson 1968, Longcore et al. 1971, Lundholm 1987, Newton and Bogan 1978, Ratcliffe 1967, Wiemeyer et al. 1986). Effects on fish, frogs, and bats also have been

documented (e.g. Berlin et al. 1981, Burdick et al. 1964, Clark 1988, Geluso et al. 1976, Kirk 1988, Sanders 1970).

DDT is metabolized to DDE and DDD by most fish species, so the ratio of DDT to its metabolites usually is indicative of time elapsed since introduction (Aguillar 1984). In addition, the ratios of ortho-para (o,p') DDT and metabolites to the para-para (p,p') forms are indicative of the sources of contamination. The o,p'- compounds are shorter-lived than their p,p'- analogs, and technical grade DDT contains less than 20% of the o,p'- compound (Fry and Toone 1981, Schmitt et al. 1985, 1990). Therefore, high concentrations of the o,p'- forms of DDT or its metabolites indicate "relatively recent inputs and pollution sources other than insecticides - e.g., pesticide manufacturing and formulation sites or chemical waste dumps" (Schmitt et al. 1985).

In the north-central U.S., fish from National Wildlife Refuge wetlands sampled by Martin and Hartman (1985) contained lower organochlorine residues than fish from most other parts of the country. The maximum concentration found in their study was 0.51  $\mu\text{g/g}$  DDE wet weight in a Rio Grande chub (*Gila nigrescens*) sample from Monte Vista NWR in Colorado. Fish from Lake Poinsett, South Dakota in 1967-1968 contained low levels of DDT compounds. The maximum concentration detected in any sample was 0.21  $\mu\text{g/g}$  wet weight in channel catfish (Hannon et al. 1970). In Tuttle Creek Lake in 1970-1971, Klaassen and Kadoum (1975) found low total DDT concentrations in fish they analyzed. Although 98 percent of the fish samples analyzed contained DDT compounds, most total DDT concentrations were less than 0.10  $\mu\text{g/g}$  wet(?) weight. The highest concentration observed was 0.57  $\mu\text{g/g}$  in a freshwater drum sample. In the same lake in 1985, Arruda et al. (1988) found p,p'-DDE and p,p'-DDD in 15 of 16 common carp samples. However, mean concentrations were all less than 0.1  $\mu\text{g/g}$  wet weight.

In western U.S. DOI studies, DDT and DDT homolog concentrations were variable. Wells et al. (1988) found p,p'-DDE at up to 9.9  $\mu\text{g/g}$  wet weight in fish from the lower Rio Grande River. The median concentration, however, was 0.38  $\mu\text{g/g}$ . In the lower Colorado River drainage, common carp samples from a few locations contained less than 0.1  $\mu\text{g/g}$  p,p'-DDE wet weight, all but two samples contained less than 0.2  $\mu\text{g/g}$  (Radtke et al. 1988). The Tulare basin study in the San Joaquin valley in California (Schroeder et al. 1988) documented p,p'-DDD, -DDE, and -DDT in mosquitofish, common carp, and yellow bullhead. Geometric means ranged from below the detection limit in 1/3 of the samples to 0.32  $\mu\text{g/g}$  wet weight p,p'-DDE in mosquitofish from one location. In that study, the high ratios of DDT to DDE and DDD indicated recent inputs of DDT to the system. In Montana, individual DDT compound concentrations in whole fish were below 0.03  $\mu\text{g/g}$  wet weight (Knapton et al. 1988). In limited samples from Utah, DDT compounds were below the detection limits (Stephens et al. 1988).

Mean DDT compound concentrations in fish collected for the NPMP and the NCBP declined in the 1970s, but did not change during the early 1980s. However, concentrations of p,p'-DDT did decline, and apparent inputs into most aquatic systems have diminished (Schmitt et al. 1990). Nationwide wet weight geometric means for total DDT (p,p'- forms) from the NCBP were 6.54  $\mu\text{g/g}$  in 1976-1977, 10.62  $\mu\text{g/g}$  in 1978-1979, 6.50  $\mu\text{g/g}$  in 1980-1981, and 9.08  $\mu\text{g/g}$  in 1984 (Schmitt et al. 1983, 1985, 1990). Data from the NCBP support the indications in the literature that, in general, DDT compound concentrations in the midwest are lower than those found in many other parts of the country.

DDT compound concentrations in Missouri River fish were low. However, in our analyses, the high proportion of o,p'-DDT and p,p'-DDT in samples from Blair, Nebraska suggests recent inputs of DDT to the Missouri River. The relative proportions of DDT to its metabolites downstream from Blair also indicate recent use or disposal of DDT. The concentrations of o,p'-DDT compounds in the Blair and Rulo areas suggest contamination through improper use, storage, disposal, or handling of DDT in those areas. Although DDT compound concentrations are relatively low overall, our sampling suggests that there may be a source of continuing DDT contamination of the Missouri River.

#### Hexachlorobenzene

Hexachlorobenzene (HCB) is a fungicide used primarily for protection of seeds and is an industrial intermediate in the production of other compounds. HCB is widespread in the environment (Zell and Ballschmiter 1980), but is less toxic to fish and more volatile than most other organochlorine compounds (Schmitt et al. 1990).

With the exception of data from the NCBP, we have little information on HCB concentrations in other studies. The nationwide mean HCB concentration in fish collected for the NCBP in 1976-1977 was 0.01  $\mu\text{g/g}$  wet weight. The mean in more recent collections has been below the detection limit of 0.01  $\mu\text{g/g}$  (Schmitt et al. 1983, 1985, 1990). HCB was detected at low concentrations in two samples from Blair and in one from Rulo, Nebraska. Although actual concentrations may have been higher than found because of the relative volatility, HCB does not appear to be a serious contaminant of the section of the Missouri River that we studied.

#### DCPA

DCPA is a common name for Dacthal<sup>R</sup> broad-spectrum herbicide. In the San Joaquin Valley, Saiki and Schmitt (1986) found DCPA in common carp at concentrations from below the detection limit to 0.054  $\mu\text{g/g}$  wet weight. The maximum concentration in bluegills was 0.01  $\mu\text{g/g}$ . In many other studies of specific locations, DCPA has not been detected. DCPA

was found at very low concentrations in only three Missouri River samples. The collection locations with the highest DCPA concentrations in fish collected for the NCBP in 1984 were scattered across the U.S. (Schmitt et al. 1990), indicating widespread use. However, DCPA concentrations were generally low. Geometric mean concentrations from the NCBP were 1.22  $\mu\text{g/g}$  wet weight in 1978-1979, 0.40  $\mu\text{g/g}$  in 1980-1981, and 0.45  $\mu\text{g/g}$  in 1984 (Schmitt et al. 1983, 1985, 1990).

#### Aroclor<sup>R</sup> 1254 and Total PCBs

Polychlorinated biphenyls are compounds formerly used in a variety of commercial applications. Although a ban on U.S. manufacture and processing of PCBs went into effect in the 1970s, the pool of sources of PCB compounds is large enough to assure continued introduction of PCBs into the environment (Eisler 1986b). Aroclor<sup>R</sup> is the most common trade name for PCBs in the United States, but other trade names may be encountered. In most cases, the last two numbers in the Aroclor<sup>R</sup> names refer to the percent chlorine by weight in the molecule.

PCB compounds are some of the most ubiquitous environmental contaminants. They are very slow to degrade, and long range transport of PCBs has been well documented. They have been found in most environments throughout the world (e.g. Aguilar 1983, Bowes and Lewis 1974, Hidaka et al. 1983, Knap and Jickells 1983, Muir et al. 1988, Solbakken et al. 1984, Weber 1983). PCB compounds are relatively insoluble in water, but most are very soluble in biological lipids. In addition, PCBs are strongly adsorbed on aquatic sediments (Eisler 1986b). Therefore, although PCBs may be anaerobically degraded (Huckins et al. 1988, Rhee et al. 1989), benthic organisms are at special risk from PCBs (Dunnivant et al. 1989, Fry and Fisher 1990, Stainken 1984).

Effects of PCBs include a variety of maladies in many animals (e.g. Eisler 1986b, Hoffman et al. 1986, Hogan and Brauhn 1975, Koval et al. 1987, Linzey 1987, Mauch et al. 1978, Mayer et al. 1985, Newton and Bogan 1978, Stendell 1976, White and Cromartie 1977, Wren et al. 1987b). PCBs also may alter the effects of other contaminants (Bills et al. 1981, Wren et al. 1987a). PCBs are bioaccumulated and biomagnified in the environment, although which of these is more important has been debated (e.g. Crossland et al. 1987, Hunter et al. 1980, Macek et al. 1979, Thomann 1981). The bioconcentration factor for Aroclor<sup>R</sup> in freshwater invertebrates can be as high as 47,000 (Eisler 1986b). In addition, impurities in PCBs such as polychlorinated dibenzo-furans may be extremely toxic.

The EPA criteria for protection of aquatic life (EPA 1980) state that the whole-body fresh weight concentration of PCBs should be less than 0.4  $\mu\text{g/g}$ . However, that criterion was based on protection of human health, based on research using striped bass. Whole-body PCB

concentrations of 0.4  $\mu\text{g/g}$  fresh weight were associated with reproductive toxicity in rainbow trout (EPA 1980). The criterion probably should be lower for nonmigratory benthic species (Eisler 1986b).

Few Aroclor<sup>R</sup> compounds were found in the analyses done by WATS. Therefore, this discussion and comparison will focus on the Aroclor<sup>R</sup> 1254 found in many samples and on the total PCB analyses done by MSCL. However, the two are not equivalent. The high partition coefficient and high steric effect (related to positioning of chlorine atoms on the biphenyl rings) of Aroclor<sup>R</sup> 1254 mean that it is among the most readily accumulated of the PCB compounds (Eisler 1986b).

In the north-central United States, Martin and Hartman (1985) found PCB concentrations in few of the whole fish samples they analyzed. A mixed species sample from Alamosa NWR in Colorado contained 1.2  $\mu\text{g/g}$  wet weight, two samples from other locations contained less than 1  $\mu\text{g/g}$ , and 23 other samples from various refuges did not contain detectable PCB concentrations. In analyses of fish collected for the NPMP, total wet weight PCB concentrations ranged from below the detection limit to 75.0  $\mu\text{g/g}$  from 1970 through 1974 (Schmitt et al. 1981). Nationwide geometric means were 1.20, 1.03, 1.20, 0.78, and 0.95  $\mu\text{g}$  in 1970, 1971, 1972, 1973, and 1974, respectively. Separate PCBs were not analyzed before 1973, when the mean for Aroclor<sup>R</sup> 1254 was 0.58  $\mu\text{g/g}$ . In 1974 the nationwide mean was 0.82  $\mu\text{g/g}$  wet weight. Mean Aroclor<sup>R</sup> 1254 and total PCB concentrations were 0.47 and 0.87  $\mu\text{g/g}$  in 1976-1977, and 0.47 and 0.86  $\mu\text{g/g}$  in 1978-1979 (Schmitt et al. 1983). In 1980-1981, the values were 0.24 and 0.53  $\mu\text{g/g}$  (Schmitt et al. 1985). By 1984, the Aroclor<sup>R</sup> 1254 and total PCB mean concentrations nationwide had declined to 0.21 and 0.39  $\mu\text{g/g}$  wet weight, respectively. The maximum nationwide values in 1984 were 4.0  $\mu\text{g/g}$  and 6.7  $\mu\text{g/g}$ . Since 1976, both Aroclor<sup>R</sup> 1254 and total PCB mean concentrations have shown highly significant declines (Schmitt et al. 1990).

We observed no obvious association between PCB concentrations and fish species or percent lipid. PCBs were not detected in the Boyd County and Niobrara, Nebraska samples. Total PCB concentrations in fish from the collection location just below Gavins Point Dam were about equal to the nationwide geometric mean in 1984. However, at all locations from Dakota City downstream, PCB concentrations are of concern. Two of the total PCB concentration values from Dakota City exceeded the nationwide mean from 1984. All of the Aroclor<sup>R</sup> 1254 concentrations from Blair, Nebraska exceeded the 1984 NCBP mean, and most exceeded the 0.4  $\mu\text{g/g}$  wet weight level of concern of the EPA (1980) and Eisler (1986b). The total PCB concentration in shovelnose sturgeon from Omaha exceeded the 1984 nationwide mean, as did concentrations in two samples from Atchison, Kansas and two samples from Kansas City, Missouri. However, PCBs were not detected in two of the samples from

Atchison. Most of the Aroclor<sup>R</sup> 1254 concentrations in fish from Rulo, Nebraska exceeded both the NCBP 1984 mean and the 0.4  $\mu\text{g/g}$  recommendation for freshwater fish. In most of our sampling locations PCB concentrations contrasted with the relatively pristine locations sampled by Martin and Hartman (1985).

#### Further Study Needs

Total concentrations of chlordane compounds exceeded the National Academy of Sciences and National Academy of Engineering [NAS/NAE (1973)] recommendation for protection of aquatic life in 14 of the 45 samples analyzed. Five of the samples were more than double the protection level. Thirteen of the fish composites exceeded the 1984 NCBP nationwide mean dieldrin concentration in fish. In addition, the presence of aldrin in the shovelnose sturgeon sample from Rulo suggests recent inputs of the banned chemical into the Missouri River. Total cyclodiene compound concentrations exceeded the NAS/NAE recommendation in 16 of the 45 samples. The concentrations of Aroclor<sup>R</sup> 1254, one of the most persistent PCB compounds, or total PCBs were high. Many of the concentrations exceeded the mean from the latest NCBP and the recommendations for maximum total body concentration. These results indicate that continued monitoring of chlordane compounds, cyclodienes, and PCBs in the Missouri River are warranted. However, although ratios of DDT compounds in fish suggest recent inputs of DDT or pesticides containing DDT and of possible improper pesticide storage or disposal, concentrations of DDT compounds in the fish we sampled were low.

#### ALIPHATIC HYDROCARBON COMPOUNDS

Aliphatic, naphthenic, and aromatic hydrocarbons of different molecular weights are present in varying amount in different crude and refined petroleum mixtures. Wildlife and fish are commonly exposed to petroleum pollutants, but assessments of petroleum hydrocarbon concentrations and their effects on wildlife are attempted infrequently, in part because the assessments often seem too difficult to make (Hall and Coon 1988). However, the effects of petroleum compounds on birds have been documented after oil spills, and effects on the survival of adults, eggs and young have been well studied (e.g. Albers 1980, Albers and Szaro 1978, Coon et al. 1979, Eastin and Hoffman 1979, Fleming et al. 1982, Hoffman 1979, Holmes et al. 1979, King and Lefever 1979, Miller et al. 1982, Patton and Dieter 1980, Szaro et al. 1978, 1980, Tarshis and Rattner 1982).

Aromatic hydrocarbons comprise 15 to 40% of refined oils (Korte and Boedefeld 1978), but are difficult to study because they are readily lost from aquatic systems. In addition, shorter and lighter weight aliphatic hydrocarbons are metabolized much quicker than are the longer

chain compounds (Hall and Coon 1988). Studies of the heavier-weight naphthenic and aliphatic components of crude and refined petroleum have been limited (Hellou et al. 1989). The sources of aromatic and aliphatic hydrocarbons in aquatic systems are generally considered to be combustion of fossil fuels, antifouling agents such as creosote, and spills or discharges (see Winger et al. 1990 and the citations therein).

Results of aliphatic hydrocarbon analyses of the fish composites are shown in Table 8. Total aliphatic hydrocarbons exceeded the concentrations found in cutthroat trout (*Salmo clarki*) negatively affected by crude oil ( $\geq 4.63 \mu\text{g/g}$  wet weight, Woodward et al. 1981) in 13 of the fish composites. The aliphatic concentrations suggest species differences in uptake or metabolizing of aliphatics. The concentration of aliphatics was high in the four samples of goldeye collected. Four of the six common carp samples exceeded  $6 \mu\text{g/g}$  wet weight, and the highest aliphatic concentration we found was in the common carp sample from below Gavins Point Dam. Two channel catfish composites, two gizzard shad composites, and one shovelnose sturgeon composite also exceeded  $5.0 \mu\text{g/g}$ . Woodward et al. (1983) studied effects of a petroleum refinery seepage on cutthroat trout, and found that body burdens associated with reduced fish health were  $2.7 \mu\text{g/g}$  for naphthalenes (which are aromatics), and  $0.971 \mu\text{g/g}$  for all aliphatics. Aromatics were the dominant compounds in the refinery seepage, and the naphthalenes were the most readily taken up by the trout.

We have no direct comparison to the fish species that we studied, but the aliphatic hydrocarbon concentrations suggest that petroleum compounds may be affecting Missouri River fish. Other comparisons provide additional information about the aliphatics in Missouri River fish. The relative abundance of low and high molecular weight compounds can indicate how recently fish were exposed to the hydrocarbons. The proportions of 12, 13, and 14 carbon compounds to heavier compounds in the fish we collected are difficult to interpret. However, the increase in n-dodecane, n-tridecane, and n-tetradecane in channel catfish at Atchison and Kansas City (Table 8) suggest either poorer metabolism of hydrocarbons or recent exposure. The relatively high concentrations of n-pentadecane and heavier hydrocarbons suggest considerable exposure to aliphatic hydrocarbons.

Concentrations of pristane and phytane, branched hydrocarbons that occur frequently in pollutant oils, can be compared to straight-chain n-heptadecane (n-C17) and n-octadecane (n-C18) concentrations for an indication of chronic exposure to hydrocarbon contamination (Anderson et al. 1978, Farrington et al. 1973, Hall and Coon 1988). Pristane and phytane are metabolized less readily than the straight-chain compounds. Therefore, high ratios of pristane and phytane to n-C17 and n-C18, respectively, indicate chronic exposure to petroleum pollutants. In Missouri River fish, n-heptadecane to pristane ratios were never less than 1, and in many cases were very large (Table 8, Figure 3). However,



Table 8. Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Percent Lipid	Concentration ( $\mu\text{g/g}$ wet weight)			
			n-dodecane	n-tridecane	n-tetradecane	n-pentadecane
<u>Boyd County, Nebraska</u>						
Common Carp	73.80	4.11	0.01	0.04	0.02	0.32
Channel Catfish	69.80	14.10	0.01	0.02	0.04	0.37
Shovelnose Sturgeon	69.80	8.44	0.01	0.02	0.05	0.26
Goldeye	64.00	15.50	0.01	0.13	0.08	0.50
<u>Niobrara, Nebraska</u>						
Common Carp	74.20	4.51	0.01	0.05	0.02	0.24
Channel Catfish	73.00	9.02	0.01	0.18	0.02	0.25
Shovelnose Sturgeon	69.60	9.00	0.01	0.07	0.07	0.68
Walleye/Sauger	69.20	7.67	0.01	0.01	0.02	0.54
<u>Gavins Point Dam, Nebraska</u>						
Common Carp	68.80	7.16	0.01	0.56	0.03	0.35
Channel Catfish	71.60	4.73	0.01	0.01	0.02	0.07
Shovelnose Sturgeon	67.80	9.84	0.02	0.07	0.04	0.18
Walleye/Sauger	71.60	4.74	0.01	0.04	0.02	0.13
Freshwater Drum	73.20	6.10	0.03	0.03	0.04	0.12
Gizzard Shad	70.40	4.98	0.01	0.01	0.02	1.70
Goldeye	66.20	12.10	0.02	0.05	0.05	1.30

Table 8 (continued). Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Percent Moisture	Percent Lipid	Concentration ( $\mu\text{g/g}$ wet weight)			
			n-dodecane	n-tridecane	n-tetradecane	n-pentadecane
<u>Dakota City, Nebraska</u>						
Common Carp	72.00	5.17	0.02	0.08	0.05	0.52
Channel Catfish	76.80	2.55	0.01	0.28	0.01	0.09
Shovelnose Sturgeon	73.40	9.16	0.02	0.14	0.05	0.14
Gizzard Shad	77.00	1.60	0.01	0.07	0.05	1.10
Goldeye	69.60	6.79	0.02	0.10	0.03	0.29
Common Carp	74.20	4.16	0.01	0.01	0.01	0.05
<u>Omaha, Nebraska</u>						
Shovelnose Sturgeon	70.20	9.46	0.05	0.08	0.08	0.15
<u>Atchison, Kansas</u>						
Common Carp	75.00	4.20	0.01	0.02	0.04	0.17
Channel Catfish	69.60	11.13	0.23	0.31	0.24	0.62
Shovelnose Sturgeon	71.00	10.60	0.06	0.06	0.11	0.28
Gizzard Shad	76.00	1.11	0.01	0.01	0.01	0.82
Goldeye	68.20	10.60	0.02	0.29	0.09	0.74
<u>Kansas City, Missouri</u>						
Common Carp	73.00	4.78	0.12	0.20	0.23	0.41
Channel Catfish	71.20	9.23	0.42	0.85	0.58	1.20
Freshwater Drum	69.00	9.43	0.06	0.05	0.06	0.13

Table 8 (continued). Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)					
	octyl- cyclohexane	nonyl- cyclohexane	n-hexadecane	n-heptadecane	pristane	n-C17/ pristane
<u>Boyd County, Nebraska</u>						
Common Carp	0.01	0.01	0.08	5.10	0.01	1020.00
Channel Catfish	0.01	0.01	0.07	2.50	0.01	500.00
Shovelnose Sturgeon	0.03	0.01	0.03	0.41	0.01	82.00
Goldeye	0.01	0.01	0.24	21.00	0.01	4200.00
<u>Niobrara, Nebraska</u>						
Common Carp	0.01	0.01	0.08	4.50	0.01	900.00
Channel Catfish	0.01	0.01	0.06	1.50	0.01	300.00
Shovelnose Sturgeon	0.04	0.01	0.09	4.10	0.02	205.00
Walleye/Sauger	0.01	0.01	0.07	2.80	0.01	560.00
<u>Gavins Point Dam, Nebraska</u>						
Common Carp	0.01	0.01	0.21	23.00	0.03	766.67
Channel Catfish	0.01	0.01	0.03	0.38	0.02	19.00
Shovelnose Sturgeon	0.01	0.01	0.04	0.49	0.09	5.44
Walleye/Sauger	0.01	0.01	0.06	3.10	0.01	620.00
Freshwater Drum	0.01	0.01	0.06	1.10	0.03	36.67
Gizzard Shad	0.01	0.01	0.40	14.00	0.01	2800.00
Goldeye	0.01	0.01	0.25	11.00	0.16	68.75

Table 8 (continued). Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)					
	octyl- cyclohexane	nonyl- cyclohexane	n-hexadecane	n-heptadecane	pristane	n-C17/ pristane
<u>Dakota City, Nebraska</u>						
Common Carp	0.01	0.01	0.30	3.90	0.04	97.50
Channel Catfish	0.01	0.01	0.04	0.72	0.01	144.00
Shovelnose Sturgeon	0.01	0.01	0.04	0.65	0.07	9.29
Gizzard Shad	0.01	0.01	0.36	9.70	0.01	1940.00
Goldeye	0.01	0.01	0.23	8.70	0.12	72.50
Common Carp	0.01	0.01	0.02	0.32	0.03	10.67
<u>Omaha, Nebraska</u>						
Shovelnose Sturgeon	0.02	0.01	0.05	0.31	0.22	1.41
<u>Atchison, Kansas</u>						
Common Carp	0.01	0.01	0.09	1.00	0.02	50.00
Channel Catfish	0.01	0.08	0.41	3.60	0.34	10.59
Shovelnose Sturgeon	0.02	0.01	0.15	0.62	0.39	1.59
Gizzard Shad	0.01	0.01	0.22	4.40	0.01	880.00
Goldeye	0.01	0.04	0.98	12.00	0.93	12.90
<u>Kansas City, Missouri</u>						
Common Carp	0.04	0.07	0.40	0.83	0.22	3.77
Channel Catfish	0.10	0.27	1.10	4.20	0.49	8.57
Freshwater Drum	0.01	0.05	0.08	0.55	0.11	5.00

Table 8 (continued). Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)					
	n-octadecane	phytane	n-C18/ phytane	n-nonadecane	n-eicosane	total aliphatics
<u>Boyd County, Nebraska</u>						
Common Carp	0.24	0.03	8.00	2.70	0.16	8.71
Channel Catfish	0.02	0.02	1.00	0.06	0.01	3.13
Shovelnose Sturgeon	0.02	0.05	0.40	0.09	0.02	1.00
Goldeye	0.30	0.23	1.30	1.20	0.21	23.92
<u>Niobrara, Nebraska</u>						
Common Carp	0.37	0.13	2.85	2.20	0.54	8.15
Channel Catfish	0.03	0.06	0.50	0.08	0.02	2.22
Shovelnose Sturgeon	0.04	0.19	0.21	0.09	0.01	5.41
Walleye/Sauger	0.03	0.06	0.50	0.05	0.05	3.65
<u>Gavins Point Dam, Nebraska</u>						
Common Carp	0.52	0.35	1.49	3.30	0.45	28.82
Channel Catfish	0.02	0.03	0.67	0.06	0.04	0.69
Shovelnose Sturgeon	0.03	0.10	0.30	0.12	0.03	1.22
Walleye/Sauger	0.07	0.05	1.40	0.18	0.03	3.71
Freshwater Drum	0.10	0.07	1.43	0.09	0.05	1.73
Gizzard Shad	0.34	0.10	3.40	0.34	0.09	17.02
Goldeye	0.48	0.59	0.81	1.90	0.39	16.21

Table 8 (concluded). Aliphatic hydrocarbon concentrations in fish collected from the Missouri River in 1988.

Species	Concentration ( $\mu\text{g/g}$ wet weight)					
	n-octadecane	phytane	n-C18/ phytane	n-nonadecane	n-eicosane	total aliphatics
<u>Dakota City, Nebraska</u>						
Common Carp	0.65	0.18	3.61	1.00	0.42	7.18
Channel Catfish	0.07	0.03	2.33	0.10	0.06	1.42
Shovelnose Sturgeon	0.03	0.07	0.43	0.19	0.03	1.44
Freshwater Drum	0.03	0.03	1.00	0.05	0.03	0.59
Gizzard Shad	0.74	0.41	1.80	0.59	0.14	13.19
Goldeye	0.64	0.28	2.29	1.90	0.37	12.70
<u>Omaha, Nebraska</u>						
Shovelnose Sturgeon	0.03	0.17	0.18	0.06	0.04	1.26
<u>Atchison, Kansas</u>						
Common Carp	0.19	0.10	1.90	0.96	0.27	2.88
Channel Catfish	0.47	0.29	1.62	0.43	0.26	7.29
Shovelnose Sturgeon	0.09	0.25	0.36	0.15	0.06	2.24
Gizzard Shad	0.20	0.08	2.50	0.20	0.07	6.03
Goldeye	1.50	0.67	2.24	1.80	0.70	19.77
<u>Kansas City, Missouri</u>						
Common Carp	0.53	0.25	2.12	0.53	0.38	4.21
Channel Catfish	0.94	0.42	2.24	0.53	0.38	11.48
Freshwater Drum	0.11	0.10	1.10	0.12	0.04	1.47

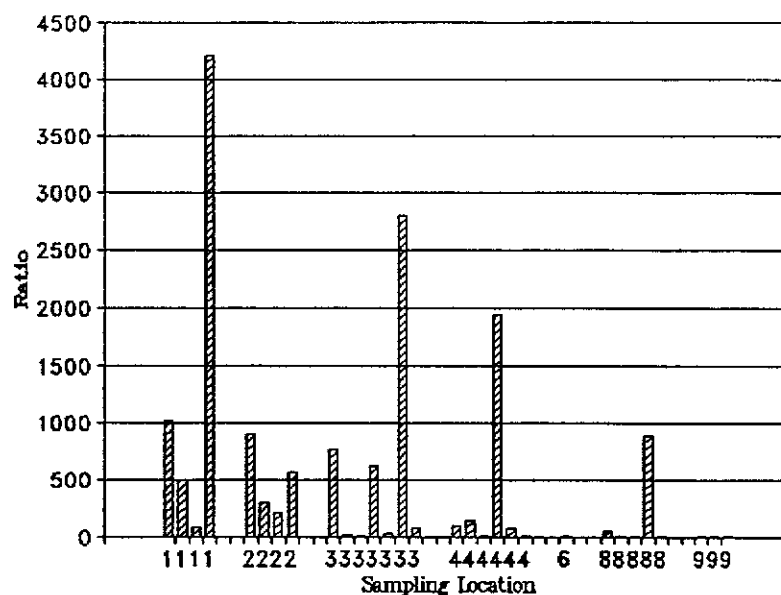


Figure 3. N-C17 to pristane ratios in Missouri River fish in 1988.

n-octadecane to phytane ratios were less conclusive (Table 8, Figure 4). In 10 of the 45 composites, the n-C18/phytane ratio was less than 1, which suggests chronic exposure to petroleum contamination.

Aliphatic hydrocarbons with odd numbers of carbon atoms are attributable to living organisms (Blumer et al. 1972, Woodward et al. 1988). Hall and Coon (1988), Winger et al. (1990), and other researchers associated n-heptadecane with petroleum contamination. However, Veith et al. (1979) indicated that "...heptadecane is thought to occur naturally, originating in benthic algae." Although many of the aliphatic hydrocarbon concentrations in Missouri River fish samples indicated petroleum contamination, the proportion of n-heptadecane relative to all other aliphatics (Table 8, Figure 5) suggests that n-heptadecane is naturally produced in the river.

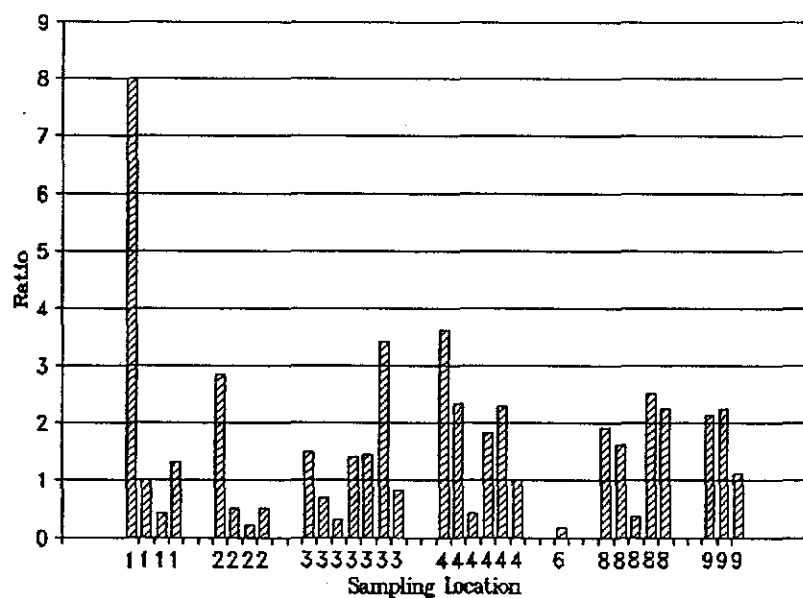


Figure 4. N-C18 to phytane ratios in Missouri River fish in 1988.

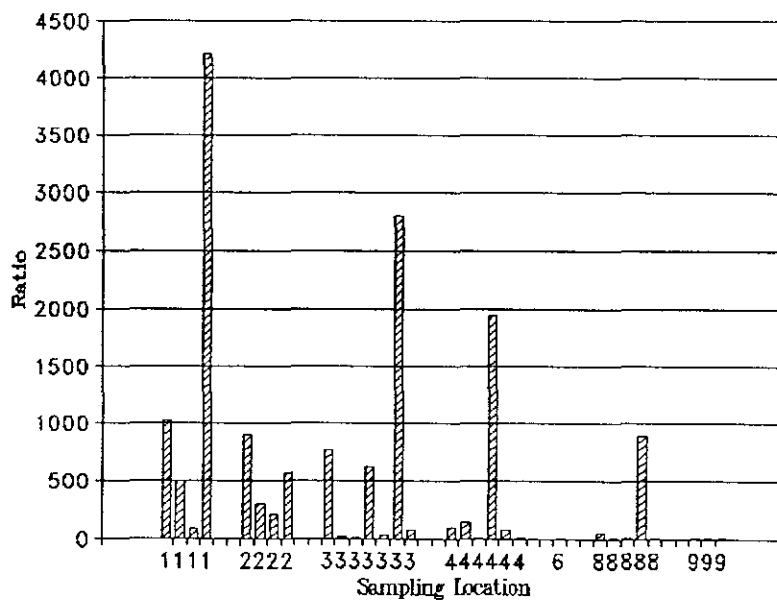


Figure 5. N-C17 to total hydrocarbons (less n-C17) ratios in Missouri River fish in 1988.



## CONCLUSIONS

This sampling showed that there may be contamination of Missouri River fish by metals and organic compounds (Figure 6). Problems from this contamination may affect not only the fish species and areas sampled, but also may affect trust resources that depend on the Missouri River. Therefore, more detailed investigations of the levels and sources of contamination of the river and anatomical and histopathological evaluations of river biota are warranted.

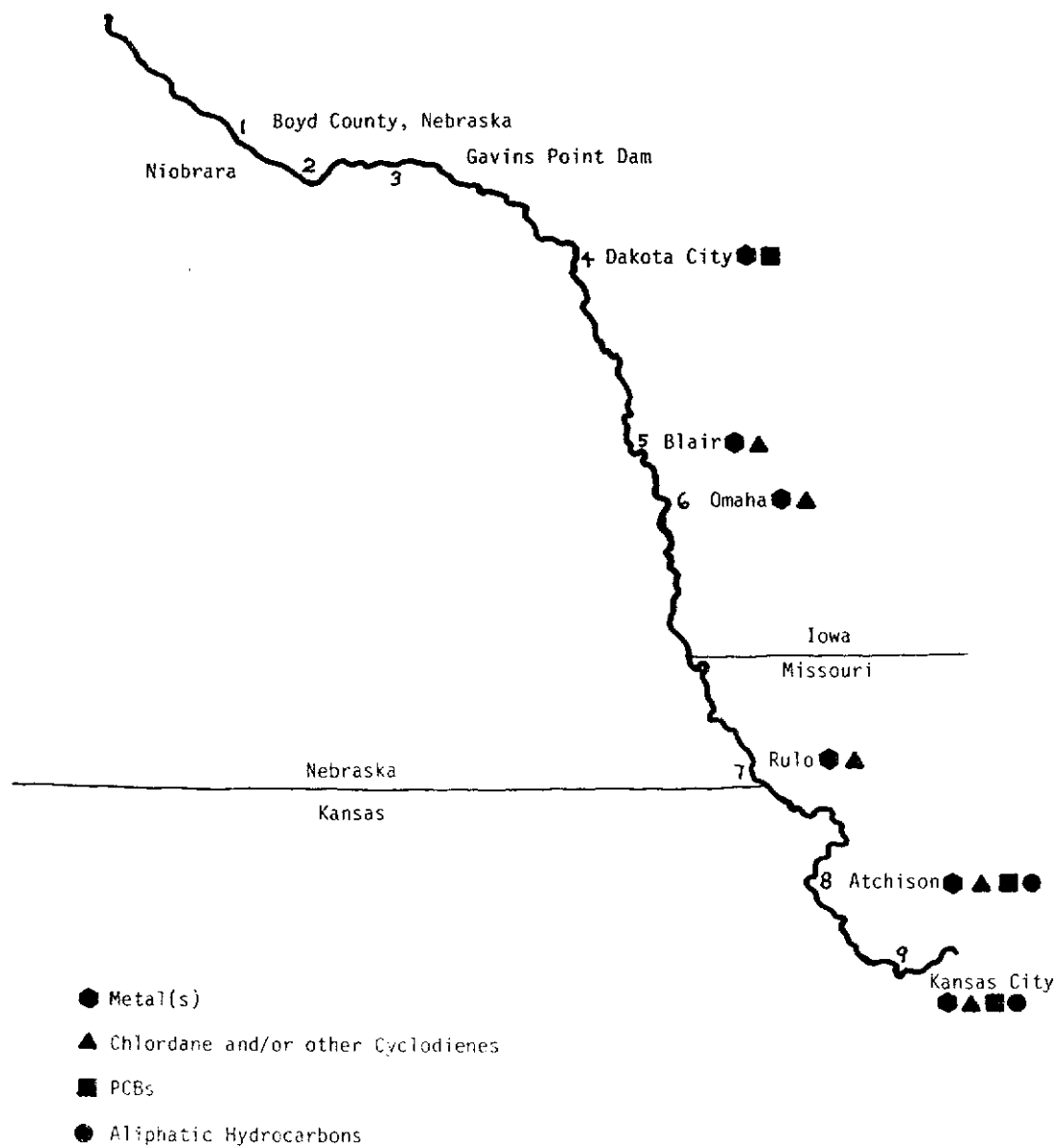


Figure 6. Project area contaminants problems.

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