

**U.S. Fish and Wildlife Service
Region 3
Contaminants Program**

**Mingo National Wildlife Refuge
Contaminants Survey Results**

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Abstract

Fishes and turtles were collected from Stanley and Linn Creeks, Ditches 1 and 2, and Mingo Ditch of Mingo National Wildlife Refuge (MNWR) near Puxico, Stoddard and Wayne Counties, Missouri. Whole fish samples and turtle livers were analyzed for various metal and organic contaminants to determine if concentrations were elevated in the biota located on the refuge. Results were compared to the literature and potential contaminant problems were recognized.

Concentrations of mercury and copper either exceeded or were the same as concentrations in the literature where adverse effects to biota were reported. However, the limited number of samples collected at MNWR and differing tissue types analyzed may demonstrate the reason for the apparent concentrations of concern. If concern is shown for populations of fish and wildlife resources using MNWR because of decreasing numbers or health, further investigations into these compounds should be initiated.

Introduction

The National Wildlife Refuge System was established to acquire, protect, restore, and manage a diversity of habitats across the United States for the benefit of important trust fish and wildlife resources. Even though refuges are managed specifically for fish and wildlife resources, the waters and land may be affected by contamination from offsite point and non-point sources of pollution. There is no direct evidence that contaminants are present in most refuge environments, but adjacent land uses may lead to the suspicion of contamination.

In 1987, a biological sampling program was initiated in Missouri on the four National Wildlife Refuges - Squaw Creek, Swan Lake, Mingo, and Clarence Cannon - and the National Fish Hatchery at Neosho to provide baseline characterization of contaminants in biological media collected. This program was conducted to determine if contaminant concentrations were elevated in biota on U.S. Fish and Wildlife Service (Service) lands and to identify potential sources.

Study Area

Mingo National Wildlife Refuge (MNWR) is located in southeast Missouri, near Puxico, in Wayne and Stoddard counties. Mingo National Wildlife Refuge lies within an abandoned channel and floodplain of the Mississippi River. The river shifted east approximately 18,000 years ago and a dense cypress and tupelo swamp developed in its place (Service 1988, Heitmeyer *et al.* 1989).

The area was exploited by settlers and by 1890 the bottomland hardwood forest was supporting a thriving lumber industry (Service 1988). Once the timber was removed, fifteen ditches were dug in the 1920's to drain the area for farming (Service 1988, Heitmeyer *et al.* 1989). The attempt was basically unsuccessful and in the late 1930's a move to purchase the area to develop a refuge had begun.

The purchase of refuge lands was initiated in 1945, and the area now encompasses 8,670.4 ha (21,676 a). Management of the land has restored most of the productivity of the former forested wetland (Service 1988). Mingo NWR is an important wintering ground for waterfowl along the Mississippi Flyway. The refuge is also an important nesting area for wood ducks and hooded mergansers.

Approximately 240 ha (600 a) are actively farmed on MNWR for wildlife food production. The main land use surrounding the refuge is agriculture. There are no large industries or known hazardous waste sites near MNWR.

Materials and Methods

Fish collections were conducted in July, 1987, at four sites along the MNWR boundary (Fig. 1). Sites were chosen in waterways entering and exiting the refuge to determine if contaminants were entering and collecting in the refuge environment. Fish were seined and gill netted until adequate samples were obtained. Species containing high fat content were chosen to be analyzed. Collections included bowfin (*Amia calva*), quillback (*Carpiodes cyprinus*), black buffalo (*Ictiobus niger*), and bigmouth buffalo (*I. cyprinellus*).

Each fish was weighed to the nearest 0.1 g and measured (total length) to the nearest millimeter. The fish were then individually wrapped in aluminum foil, labeled, and stored on ice in a cooler while in the field. Upon returning to the office, the samples were frozen in a locked chest-style freezer unit. The samples were shipped on dry ice to the respective analytical laboratories with instructions on the type of analyses to be conducted and specific sample information.

Red-eared turtles (*Chrysemys scripta elegans*) were incidentally caught in the nets while seining for fish. The turtles were transported on ice back to the office laboratory where the livers were dissected from the carcasses. Livers were placed in individual chemically-cleaned glass jars, frozen in the same freezer as the fish samples, and shipped with the fish samples for analyses.

Sample analyses were completed by two different contract laboratories. The Service's Patuxent Analytical Control Facility (Patuxent) awards the contracts based on quality assurance and quality control (QA/QC) results from analytical procedures conducted. Patuxent monitors the performance of the laboratories during the analyses and warrants the accuracy of the data. Laboratory quality control reports document the laboratories' performance on spikes, blanks, and duplicates.

The Environmental Trace Substances Research Center, Columbia, Missouri, conducted the analyses for metal residues in the samples. An atomic absorption spectrophotometer technique was conducted to measure levels of arsenic, mercury, and selenium residues. Levels of cadmium, copper, iron, lead, molybdenum, nickel, thallium, vanadium, and zinc were scanned using an inductively coupled plasma atomic emission spectrophotometer. Detection limits are included in Table 1. Results are reported in parts per million (ppm) dry weight unless otherwise stated.

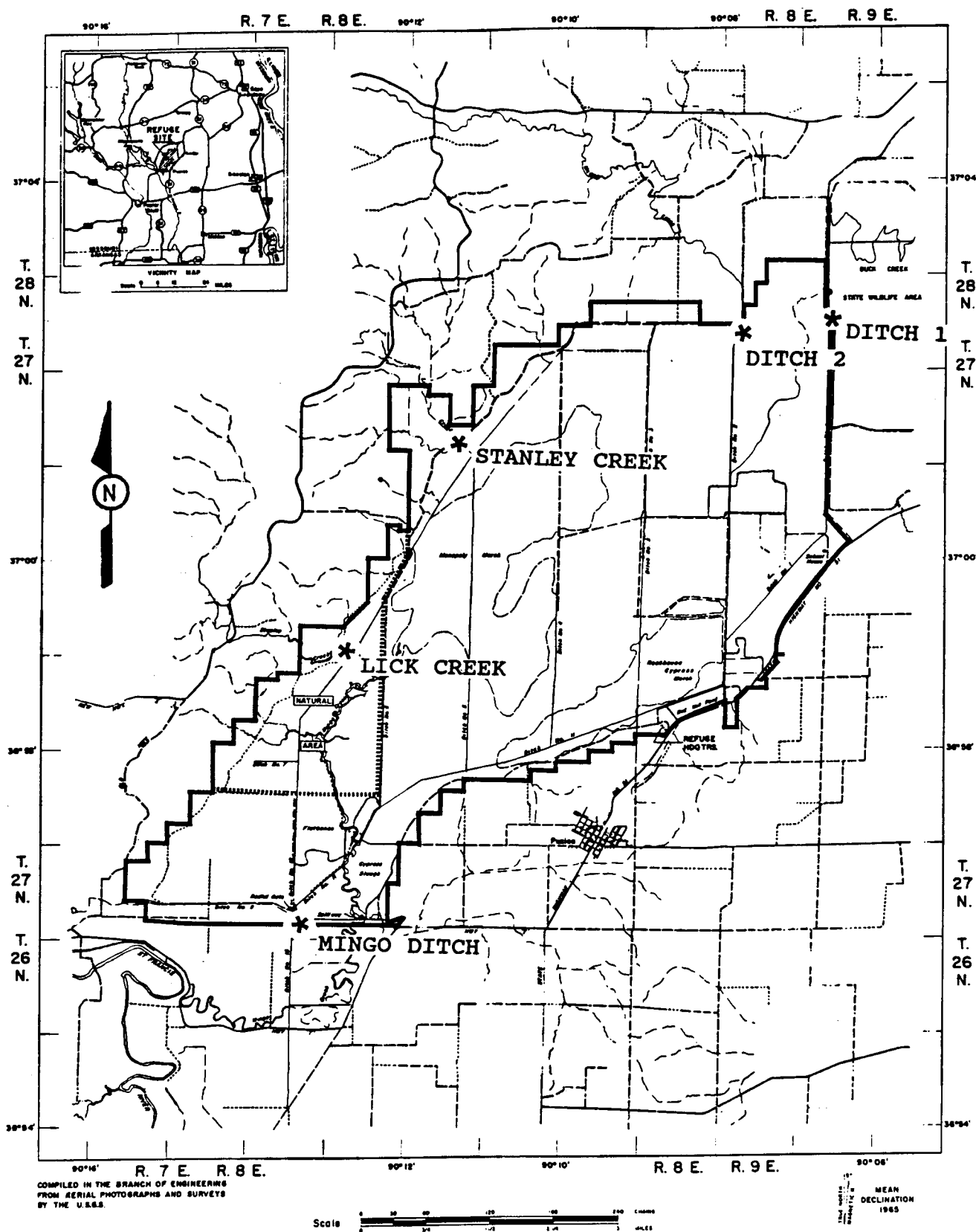


Figure 1. Approximate collection sites (*) at Mingo National Wildlife Refuge, Wayne and Stoddard Counties, Missouri.

Organochlorine and PCB residue analyses were conducted by The Mississippi State Chemical Laboratory, Mississippi State, Mississippi. Analyses were conducted using methods prescribed in Patuxent protocols for organochlorine and PCB residue scans using a gas chromatograph. Organochlorine residues analyzed included *p,p'* DDE, *p,p'* DDD, *p,p'* DDT, *o,p'* DDE, *o,p'* DDD, *o,p'* DDT, dieldrin, endrin, heptachlor epoxide, Γ -chlordane, α -chlordane, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, toxaphene, α -benzene hexachloride (BHC), β -BHC, Γ -BHC, γ -BHC, mirex, and hexachlorobenzene. Total chlordane is the summation of the compounds and by-products of chlordane that were analyzed. Results are reported in ppm wet weight unless otherwise stated. Detection limits are included in Table 4.

Results

Metal Contaminants

Nine of the 13 metals analyzed were found above the detection limit in fish collected from Mingo Ditch on MNWR (Table 1). No turtles were collected from Mingo Ditch. Copper concentrations ranged from 3.0 to 4.1 ppm, while iron ranged from 245 to 506 ppm. Mercury residue concentrations ranged from 1.3 to 2.8 ppm. The maximum concentration for nickel was 1.3 ppm, and for selenium, 2.6 ppm. Zinc concentrations ranged from 71.4 to 106 ppm.

Two of the 13 metals analyzed were found below the detection limit in all the samples, red-eared turtles and fish, collected from Ditches 1 and 2 (Table 2). All metal concentrations were lower in the black buffalo collected from Ditch 1 than the bowfin from Ditch 2, except zinc. The copper concentration in the bowfin was 8.13 ppm and red-eared turtle liver concentrations ranged from 4.5 to 15.6 ppm. Turtle livers contained a range of 1,070 to 1,730 ppm iron, while the bowfin contained 186 ppm iron. Mercury concentrations were higher in the fish sample (2.9 ppm) than the turtle liver samples (0.14 to 2.1 ppm). Concentrations of selenium in the bowfin was 2.1 ppm, while ranging from 0.67 to 1.9 ppm selenium in the turtle livers.

Red-eared turtles as well as fish were collected from Stanley Creek, but only one fish was collected from Lick Creek. Nine of the 13 metals analyzed were found above the detection limit (Table 3). Copper residue concentrations ranged from 1.7 to 2.3 ppm in fish and 10.6 to 13.0 ppm in turtle livers collected from Stanley Creek; 3.3 ppm copper was found in the bowfin from Lick Creek. Fish samples from Lick Creek (161 ppm iron) and Stanley Creek (127 to 338 ppm iron) contained less iron residue than turtle livers (1,000 to 2,180 ppm iron). Two fish samples from Stanley Creek had lead residue concentrations above the detection limit at 2.0 and 4.4 ppm, respectively. Bowfin collected from both creeks had high residue concentrations of mercury (2.9 ppm, Lick Creek; 5.51 ppm, Stanley Creek) when compared to other fish collected from Stanley Creek. Mercury concentrations in red-eared turtle livers were 2.8 and 7.46 ppm, respectively. Concentrations of zinc ranged from 42.5 to 58.5 ppm in fish from Stanley Creek; 45.9 to 54.1 ppm in turtle livers; and was 46.9 ppm in the fish from Lick Creek.

Table 1. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in bigmouth buffalo (*Ictiobus cyprinellus*) and a black buffalo (*I. niger*) collected from Mingo Ditch on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

Compound	Black Buffalo						Bigmouth Buffalo		Detection Limits (DW)
	DW	WW	DW	WW	DW	WW	DW	WW	
Arsenic	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02	0.1
Cadmium	0.22	0.04	0.08	0.02	<0.09	<0.02	0.24	0.04	0.06-0.09
Copper	3.0	0.57	3.2	0.68	3.2	0.61	4.1	0.65	0.04-0.05
Iron	326	62	506	107	245	47	425	67	0.2-0.3
Lead	2.0	0.38	<1.0	<0.2	<1.0	<0.2	2.0	0.32	0.9-1.0
Mercury	1.3	0.25	2.8	0.59	1.6	0.31	1.6	0.25	0.1
Molybdenum	<0.2	<0.04	<0.3	<0.06	<0.3	<0.06	<0.2	<0.03	0.2-0.3
Nickel	0.7	0.13	1.0	0.2	1.3	0.25	0.6	0.09	0.3-0.4
Selenium	2.6	0.49	0.88	0.19	1.4	0.27	1.4	0.22	0.2
Thallium	<1.0	<0.2	<1.0	<0.2	<1.0	<0.2	<1.0	<0.16	1.0
Vanadium	0.90	0.17	0.45	0.16	<0.07	<0.01	0.68	0.11	0.06-0.08
Zinc	71.4	13.5	75.8	16.0	78.8	15.1	106	16.7	0.05-0.06
% Moisture	81.1		78.9		80.9		84.2		

Table 2. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in a black buffalo (*Ictiobus niger*) from Ditch 1 and a bowfin (*Amia calva*) and liver samples from red-eared turtles (*Chrysemys scripta elegans*) collected from Ditch 2 on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

Compound	Ditch 1		Bowfin		RTL ¹		Ditch 2		RTL		RTL		RTL	
	Black Buffalo		DW	WW	DW	WW	DW	WW	DW	WW	DW	WW	DW	WW
	DW	WW												
Arsenic	<0.1	<0.03	0.54	0.14	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03
Cadmium	<0.06	<0.02	<0.07	<0.02	<0.07	<0.02	0.22	0.06	<0.07	<0.02	<0.07	<0.02	<0.07	<0.02
Copper	3.4	1.0	8.13	2.18	15.6	4.15	13.6	3.9	4.5	1.44	6.61	2.23	6.61	2.23
Iron	115	34	186	50	1730	460	1440	413	1390	445	1070	362	1070	362
Lead	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3
Mercury	1.1	0.32	2.9	0.78	0.57	0.15	2.1	0.6	0.28	0.09	0.14	0.05	0.14	0.05
Molybdenum	<0.2	<0.06	<0.2	<0.05	1.0	0.3	1.1	0.32	0.6	0.19	0.8	0.27	0.8	0.27
Nickel	0.6	0.18	1.4	0.38	0.6	0.16	0.5	0.14	0.5	0.16	<0.4	<0.14	<0.4	<0.14
Selenium	1.2	0.35	2.1	0.56	1.9	0.51	2.2	0.63	0.67	0.21	0.84	0.28	0.84	0.28
Thallium	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3	<1.0	<0.3
Vanadium	0.1	0.03	0.1	0.03	0.59	0.16	0.97	0.28	0.2	0.06	0.1	0.03	0.1	0.03
Zinc	46.2	13.5	40.7	10.9	51.3	13.6	47.3	13.6	36.3	11.6	37.6	12.7	37.6	12.7
% Moisture	70.8		73.2		73.4		71.3		68.0		66.2			

¹Red-eared turtle liver.

Table 3. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in a bowfin (*Amia calva*), a quillback (*Carpionodes cyprinus*), a black buffalo (*Ictiobus niger*), and liver from red-eared turtles (*Chrysemys scripta elegans*) collected from Stanley Creek and a bowfin from Lick Creek on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

Compound	Bowfin		Quillback		Stanley Creek Black Buffalo		Red-eared Turtle Liver				Lick Creek Bowfin	
	DW	WW	DW	WW	DW	WW	DW	WW	DW	WW	DW	WW
Arsenic	0.1	0.03	0.1	0.04	0.1	0.03	<0.1	<0.03	<0.1	<0.02	0.1	0.03
Cadmium	<0.06	<0.02	<0.07	<0.03	0.08	0.02	0.36	0.1	0.37	0.09	0.06	0.02
Copper	2.3	0.60	1.7	0.70	2.0	0.55	10.6	2.95	13.0	3.0	3.3	0.87
Iron	338	88	127	52	210	58	2180	606	1000	232	161	42
Lead	<1.0	<0.3	4.4	1.8	2.0	0.55	<1.0	<0.3	<1.0	<0.2	<1.0	<0.26
Mercury	5.51	1.43	0.61	0.25	0.29	0.08	7.46	2.07	2.8	0.65	2.9	0.76
Molybdenum	<0.3	<0.08	<0.3	<0.12	<0.2	<0.06	1.2	0.33	1.9	0.44	<0.2	<0.05
Nickel	1.0	0.26	0.6	0.25	0.8	0.22	0.8	0.22	0.8	0.19	2.2	0.58
Selenium	0.83	0.21	0.60	0.25	1.1	0.3	4.5	1.25	3.4	0.79	1.0	0.26
Thallium	<1.0	<0.3	<1.0	<0.4	<1.0	<0.3	<1.0	<0.3	<1.0	<0.2	<1.0	<0.26
Vanadium	0.09	0.02	0.09	0.04	0.2	0.06	2.9	0.81	1.6	0.37	0.1	0.03
Zinc	49.1	12.7	42.5	17.5	58.5	16.1	45.9	12.8	54.1	12.6	46.9	12.3
% Moisture	74.1		58.9		72.5		72.2		76.8		73.7	

Organochlorine Contaminants

Only one sample, a red-eared turtle liver from Stanley Creek, had a concentration above the detection limit for one compound out of all organic compounds analyzed (Tables 4 through 6). The Total DDT residue concentration found in the turtle liver was 0.08 ppm.

Discussion

Numerous tests have been conducted on the sensitivity of different species exposed to contaminants in water, but information is lacking on the concentrations of contaminants in animal tissue that will directly harm the organism, or cause stress, thus exposing the animal as easier prey. Information also is lacking for concentrations that will harm predators which may consume a contaminated organism. There are only a few established action and alert levels for tolerable tissue concentrations of contaminants that may protect fish and wildlife resources, but there are no uniformly accepted standards (Irwin 1988).

When comparing contamination levels, one must realize that some data are based on fillet samples (edible to humans) and some on whole-body samples. Also, different species and tissue types have different abilities in accumulating contaminants (e.g., fatty tissues accumulate organic contaminants, muscle tissues accumulate few contaminants)(Irwin 1988). Therefore, the data presented in this report have been conservatively compared to that in scientific literature, mainly from the Service's National Contaminant Biomonitoring Program (NCBP)(Schmitt and Brumbaugh 1990, Schmitt *et al.* 1990). Only those contaminants that were at concentrations above the detection limits are discussed below.

Metal Contaminants

Arsenic

Arsenic is a metalloid found both as a free element and as compounds. In surface waters arsenic is found as the anion, arsenate (Luh *et al.* 1973), with sodium arsenate being the most prevalent environmental form (Camardese *et al.* 1990). Arsenic in surface waters tends to absorb onto clays, iron oxides, manganese compounds, and organic material (from Life Systems, Inc. 1989a) and is stored in the sediment that may be released by aerobic and anaerobic microorganisms.

Most of the arsenic used in the United States is a by-product from gases of copper furnaces (Nebergall *et al.* 1980). Arsenic compounds are used for their poisonous character as weed killers, cattle and sheep dips, and insecticides. Other anthropogenic sources include poultry feed additives and pharmaceuticals, coal and petroleum, mine tailings and smelting, and detergents (Moore and Ramamoorthy 1984a).

Table 4. Residue concentrations of organic contaminants (part per million wet weight) found in a bigmouth buffalo (*Ictiobus cyprinellus*) and black buffalo (*I. niger*) collected from Mingo Ditch on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Mississippi State Chemical Laboratory, Mississippi State, Mississippi.

Compound	Bigmouth Buffalo		Black Buffalo		Detection Limit
Total DDT ¹	ND ²	ND	0.05	0.04	0.05
PCBs (total)	ND	ND	ND	0.05	0.10
Dieldrin	ND	ND	ND	ND	0.05-1.0
Endrin	ND	ND	ND	ND	0.05-1.0
Total Chlordane ³	(ND)	(ND)	(0.02)	(0.01)	(ND)
Heptachlor epoxide	ND	ND	ND	ND	0.05-1.0
α -Chlordane	ND	ND	0.01	ND	0.05-1.0
Γ -Chlordane	ND	ND	ND	ND	0.05-1.0
cis-Nonachlor	ND	ND	ND	ND	0.05-1.0
trans-Nonachlor	ND	ND	0.01	0.01	0.05-1.0
Oxychlordane	ND	ND	ND	ND	0.05-1.0
Toxaphene	ND	ND	ND	ND	0.51
α -Benzene hexachloride (BHC)	ND	ND	ND	ND	0.05
β -BHC	ND	ND	ND	ND	0.05
Γ -BHC	ND	ND	ND	ND	0.05
γ -BHC	ND	ND	ND	ND	0.05
Hexachlorobenzene	ND	ND	ND	ND	0.05
Mirex	ND	ND	ND	ND	0.05
% Moisture	84.4	80.2	80.4	81.6	
% Lipid	0.22	0.37	1.19	0.41	

¹Sum of *p,p'*- and *o,p'*-homologs of DDT.

²ND indicates at or below the detection limit.

³Sum of the components (indented compounds) which comprise chlordane.

Table 5. Residue concentrations of organic contaminants (part per million wet weight) found in a black buffalo (*Ictiobus niger*) from Ditch 1 and a bowfin (*Amia calva*) and liver samples from red-eared turtles (*Chrysemys scripta elegans*) collected from Ditch 2 on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Mississippi State Chemical Laboratory, Mississippi State, Mississippi.

Compound	Ditch 1	Ditch 2				
	BB ¹	BF	TL	TL	TL	TL
Total DDT ²	0.03	0.01	ND ³	0.01	0.02	0.01
PCBs (total)	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND
Total Chlordane ⁴	(0.02)	(ND)	(ND)	(ND)	(ND)	(ND)
Heptachlor epoxide	ND	ND	ND	ND	ND	ND
α -Chlordane	0.01	ND	ND	ND	ND	ND
Γ -Chlordane	ND	ND	ND	ND	ND	ND
cis-Nonachlor	ND	ND	ND	ND	ND	ND
trans-Nonachlor	0.01	ND	ND	ND	ND	ND
Oxychlordane	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND
α -Benzene hexachloride (BHC)	ND	ND	ND	ND	ND	ND
β -BHC	ND	ND	ND	ND	ND	ND
Γ -BHC	ND	ND	ND	ND	ND	ND
γ -BHC	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND	ND
% Moisture	72.0	72.6	76.0	72.0	71.0	68.0
% Lipid	10.4	4.66	10.9	7.62	15.4	19.4

¹BB=black buffalo, BF=bowfin, TL=turtle liver

²Sum of *p,p'*- and *o,p'*-homologs of DDT.

³ND indicates at or below the detection limit. The detection limit for all compounds was 0.05 ppm, except toxaphene, which was 0.50 ppm.

⁴Sum of the components (indented compounds) which comprise chlordane.

Table 6. Residue concentrations of organic contaminants (part per million wet weight) found in a bowfin (*Amia calva*), a quillback (*Carpionodes cyprinus*), a black buffalo (*Ictiobus niger*), and liver from red-eared turtles (*Chrysemys scripta elegans*) collected from Stanley Creek and a bowfin from Lick Creek on Mingo National Wildlife Refuge, Missouri. Analyses were conducted by the Mississippi State Chemical Laboratory, Mississippi State, Mississippi.

Compound	Stanley Creek					Lick Creek
	BF ¹	QB	BB	TL	TL	BF
Total DDT ²	0.03	0.05	0.02	0.08	ND ³	0.01
PCBs (total)	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND
Total Chlordane ⁴	(ND)	(0.02)	(ND)	(ND)	(ND)	(ND)
Heptachlor epoxide	ND	ND	ND	ND	ND	ND
α -Chlordane	ND	ND	ND	ND	ND	ND
Γ -Chlordane	ND	0.01	ND	ND	ND	ND
cis-Nonachlor	ND	ND	ND	ND	ND	ND
trans-Nonachlor	ND	0.01	ND	ND	ND	ND
Oxychlordane	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND
α -Benzene hexachloride (BHC)	ND	ND	ND	ND	ND	ND
β -BHC	ND	ND	ND	ND	ND	ND
Γ -BHC	ND	ND	ND	ND	ND	ND
γ -BHC	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND	ND
% Moisture	73.0	61.8	73.8	76.5	79.5	73.8
% Lipid	2.68	18.3	7.55	10.5	7.33	3.3

¹BF=bowfin, QB=quillback, BB=black buffalo, TL=turtle liver

²Sum of *p,p'*- and *o,p'*-homologs of DDT.

³ND indicates at or below the detection limit. The detection limit for all compounds was 0.05 ppm, except toxaphene, which was 0.50 ppm.

⁴Sum of the components (indented compounds) which comprise chlordane.

Arsenic can be sorbed by organisms from water (Faust and Aly 1981), but the primary source of the metal is from food resources (from Moore and Ramamoorthy 1984a). However, biomagnification along the aquatic food chain is not significant (from Eisler 1988a, from Life Systems, Inc. 1989, Moore and Ramamoorthy 1984a).

In the freshwater system arsenic is not a threat to aquatic resources, except when there is extreme pollution (Moore and Ramamoorthy 1984a). Sorenson et al. (1980) collected green sunfish (*Lepomis cyanellus*) from a contaminated lake and found damage to the fishes'

hepatic tissue. Rainbow trout (*Salmo gairdneri*) exhibited reduced growth, avoided food, and failed to metabolize food efficiently when fed diets containing 120 ppm arsenic (as As^{+3} or As^{+5}) (from Eisler 1988). LC_{50} values range widely due to effects by temperature, pH, organic content, arsenic speciation, duration of exposure and age and species tested (Eisler 1988, Moore and Ramamoorthy 1984a).

Arsenic does not accumulate in fish tissues during waterborne laboratory exposures to the extent that other metals do (Spehar et al. 1980). Body distribution of arsenic was measured in black bass (*Micropterus salmoides*) from Florida, Georgia, Alabama, and Texas. Arsenic was found to concentrate in the oily fraction of the liver in these fish (from Faust and Aly 1981), hence reducing the residue level measured when evaluating the whole fish (e.g. 0.66 ppm in whole body versus 40.51 ppm in liver oil). Fish excrete arsenic rapidly from the whole body, indicating that using the whole fish for monitoring arsenic in freshwaters may be of little value (Weiner et al. 1984).

Background concentrations of arsenic in organisms are usually <1 ppm fresh weight (Eisler 1988). The average residue value of arsenic as As_2O_3 was 0.71 ppm wet weight in freshwater fish caught in Florida, Georgia, Alabama, and Texas (from Faust and Aly 1981). The geometric mean of arsenic found in fish collected for the NCBP was 0.14 ppm wet weight (Schmidt and Brumbaugh 1990). Tissue residues of 1.35 ppm arsenic fresh weight in juvenile bluegill (*Lepomis macrochirus*) and 5 ppm in adults were considered hazardous (from Eisler 1988). Arsenic residue concentrations found at MNWR were the same as the NCBP geometric mean (0.14 ppm wet weight) and are below tissue residue concentrations considered hazardous. Therefore, arsenic pollution does not seem to be a problem at the refuge.

Cadmium

Cadmium is a silvery, crystalline metal, most commonly found in nature as the sulfide, greenockite, or as an impurity in zinc, copper, and lead ores. Once obtained as a by-product from smelting these ores, cadmium is used in electroplating, pigments, batteries, and as plastic stabilizers. Burning of fossil fuels or incineration of municipal waste and sewage sludge is the largest source of cadmium release to the environment (Life Systems, Inc. 1989b). Air emissions from zinc, lead, or copper smelters may also contain cadmium.

Precipitation removes cadmium from the atmosphere into surface waters (Moore and Ramamoorthy 1984a). Freshwater levels of cadmium range from 0.00001 to 0.0005 ppm (from Moore and Ramamoorthy 1984a). Fish flesh samples collected from relatively nonpolluted areas contained concentrations from 0.001 to 0.100 ppm cadmium (Life Systems, Inc. 1989b). Many plant and animal tissues have around 1 ppm cadmium (Faust and Aly 1981).

All organisms accumulate cadmium from both food and water. The metal accumulates mainly in the kidneys, liver, pancreas, and thyroid of animals (Callahan *et al.* 1979, Faust and Aly 1981). Cadmium is not essential or beneficial biologically. In fact, it is known to be teratogenic, carcinogenic, and probably mutagenic (Eisler 1985a). Cadmium is very similar to zinc and may displace it in different enzymes, disrupting normal metabolic function (Callahan *et al.* 1979, Moore and Ramamoorthy 1984a, Eisler 1985a).

Cadmium is extremely toxic to aquatic organisms causing acute and chronic poisoning. Concentrations of 0.0008 to 0.0099 ppm cadmium in water were lethal to aquatic insects, crustaceans, and teleosts (Eisler 1985a). Sublethal effects to aquatic species include decreased growth, inhibited reproduction, and population alterations (Eisler 1985a).

Cadmium concentrations in fish collected from MNWR were approximately the same as the geometric mean (0.03 ppm wet weight cadmium) determined for the NCBP. The concentrations from MNWR were in the range (0.001 to 0.100 ppm cadmium) of fish flesh concentrations reported earlier collected from nonpolluted areas. Therefore, cadmium contamination is not likely a problem at MNWR.

Copper

Copper, an essential element in life processes, is a reddish metal that occurs naturally in the air, water, sediment, rock, and soil (SRC 1990). Copper is used in a wide range of products because of its physical properties including high thermal and electrical conductivity, low corrosion rate, alloying ability, and appearance (Moore and Ramamoorthy 1984a, SRC 1990). Copper is extensively mined and processed in the United States and is used in electrical wiring, sheet metal, pipe, and the U.S. coinage. Copper is mixed with other metals to produce alloys such as bronze, brass, gun metal, and sterling silver. Copper compounds are used in water treatment, and preservatives for wood, leather, and fabrics.

As a natural constituent in soil, copper is naturally discharged into the environment by wind-blown dust and runoff from the natural weathering of rock and soil (Moore and Ramamoorthy 1984a, SRC 1990). The major discharges of copper are anthropogenic sources such as production of nonferrous metals, wood combustion, iron and steel production, waste incineration, nonferrous metal mining, phosphate fertilizer manufacture, and domestic wastewater discharges (Moore and Ramamoorthy 1984a, SRC 1990).

Copper and copper compounds are priority pollutants as defined by the U.S. Environmental Protection Agency (EPA)(see 40 CFR 401.15). EPA has determined that the level of copper in surface waters should not exceed 1 ppm for protection of human health. This limit takes into account ingestion of copper

through water and contaminated aquatic organisms (SRC 1990). Copper concentrations in relatively uncontaminated surface waters range from 0.0005 to 0.001 ppm, and can increase to ≥ 0.002 ppm in urban areas (Moore and Ramamoorthy 1984a). Sediment concentrations of copper tend to be high because the metal is absorbed to the sediments rapidly depending on the type of clay/sediment, pH, and competing cations (Moore and Ramamoorthy 1984a).

The toxicity of copper to fish is usually higher than any other metal except mercury (Moore and Ramamoorthy 1984a). The LC_{50} ranges from 0.017 to 1.0 ppm copper, with acute toxicity depending on water hardness and different susceptibilities among species. Chronic toxicity of copper can reduce survival, growth, and rate of reproduction in fish (Moore and Ramamoorthy 1984a).

Residue concentrations of copper in invertebrates collected in polluted surface waters range from 5 to 200 ppm in soft tissues (Moore and Ramamoorthy 1984a). There is no accumulation of copper through the food chain, but contaminated food is probably the most important source of the metal when compared to water (Moore and Ramamoorthy 1984a). Muscle tissue residues in fish collected from metal-contaminated lakes near Sudbury, Ontario ranged from 0.5 to 1.4 ppm copper wet weight (Bradley and Morris 1986). While muscle tissue residue concentrations of copper tend to be low, high concentrations may be found in livers of fish (Moore and Ramamoorthy 1984a, SRC 1990). Thus, liver tissue is a better indicator of copper contamination than whole fish samples.

Five of the ten fish samples collected from MNWR contained copper residue concentrations greater than the NCBP geometric mean of 0.65 ppm wet weight (Schmitt and Brumbaugh 1990). However, none of the sample concentrations exceeded the maximum of 23.1 ppm wet weight copper.

Copper concentrations found in fish samples from MNWR are in the same range as, and in one case (bowfin from Ditch 2) greater than, concentrations in fish collected from metal-contaminated lakes near Sudbury, Ontario. A direct comparison is difficult since only muscle tissue of fish was analyzed by Bradley and Morris versus whole-body samples from MNWR. Heavy metals tend to accumulate in the liver and those residue concentrations would not be evidenced in muscle tissue samples. There may be a copper contamination problem at MNWR, but the chance is minimal with only one sample above comparable tissue concentrations from contaminated waters.

Iron

Although iron is the second most abundant metal and fourth among all elements in the earth's crust, pure iron is not common in the natural environment (Nebergall *et al.* 1980). Iron can be found in almost all rocks, minerals, soils, plants, and animals. Iron is an essential element in most animals, present in the hemoglobin of blood which acts as an oxygen carrier.

Iron-bearing ores are the common form of iron found in the environment, including hematite, magnetite, limonite, lodestone, taconite, and pyrite. Steels, such as carbon steel and stainless steel, are produced using iron and

other metal alloys.

Iron is corroded (i.e., oxidizes) when exposed to air and water. The resulting ions may constitute pollutants in surface waters (McKee and Wolf 1963). Other sources of iron pollutants are iron-bearing industrial wastes such as those from pickling operations and acid-mine drainage (McKee and Wolf 1963).

Concentrations of iron are purposely limited in public drinking water because of the objectionable taste, staining of plumbing fixtures, spotting of laundry, and accumulation in pipes (NAS/NAE 1972).

Iron salts (e.g. ferric chloride, ferrous sulfate) dissociate in water and the resulting ferric or ferrous ions combine with hydroxyl ions and precipitate. The addition of iron salts in surface water that is not strongly buffered may lower the pH to a toxic level (McKee and Wolf 1963). The precipitated iron hydroxides may deposit on the gills of fish causing irritation and blockage of respiratory channels (McKee and Wolf 1963). Also, heavy deposits of ferric hydroxide can smother fish eggs.

Iron was not analyzed in the fish collected for the NCBP (Schmitt and Brumbaugh 1990). Iron concentrations in edible tissues of fish collected from streams contaminated by lead mining ranged from 0.3 to 25.0 ppm wet weight (Schmitt and Finger 1987). Residue concentrations of iron (34 to 107 ppm wet weight) from MNWR fish samples were greater than those reported by Schmitt and Finger (1987). This may be due to the type of sample analyzed, whole fish versus edible tissue. Heavy metals tend to accumulate in the liver and those residue concentrations would not be evidenced in edible tissue samples. No reference data could be found to determine if residue concentrations of iron found in the fish collected at MNWR could cause any adverse effects to the fish population or predators.

Lead

Lead is widely distributed in the earth's crust and is found in trace amounts in water, plants, animals, and air. Galena is the sulfide form in which lead usually exists in nature. The nation's largest lead producing area is southeastern Missouri (ATSDR 1986, Eisler 1988b).

The metal has been used by man since medieval times for piping, building materials, solders, paint, ammunition, and castings (Moore and Ramamoorthy 1984a). Some of these products still use lead today, but recent uses include storage batteries, gasoline additives, paints, ceramics, sheet lead, cable covering, and for radiation-shielding against gamma rays in nuclear-powered reactors, ships, and submarines (Faust and Aly 1981, Moore and Ramamoorthy 1984a, ATSDR 1986, Eisler 1988b). The primary method for disposal of lead is recycling (ATSDR 1986).

Anthropogenic emissions to the atmosphere are the primary source of lead to both soils and surface waters (Faust and Aly 1981, Moore and Ramamoorthy 1984a, ATSDR 1986, Eisler 1988b). Other sources include mining, non-ferrous metal production (Moore and Ramamoorthy 1984a), wastewaters from industrial

and manufacturing operations (Faust and Aly 1981), and urban runoff (ATSDR 1986).

The toxicity of lead to aquatic biota varies due to physicochemical characteristics of water such as temperature, dissolved oxygen concentrations, pH, water hardness (Faust and Aly 1981, Eisler 1988b), and the chemico-physical state of lead (Merlini and Pozzi 1977). Toxicities are also influenced by biotic species, age of the organisms, and length of exposure (Eisler 1988b).

The National Academy of Science and Engineering (NAS/NAE 1972) reported 96-h LC_{50} values of lead in soft water for rainbow trout at 1.0 ppm, brook trout (*Salvelinus fontinalis*) at 4.0 to 5.0 ppm, and fathead minnows (*Pimephalas promelas*) at 5.0 to 7.0 ppm. When tested in hard water, 96-h LC_{50} values were 442 ppm for brook trout and 482 ppm for fathead minnows (NAS/NAE 1972). Davies (1973) conducted bioassays on rainbow trout in hard water testing total lead and dissolved lead. He reported a 96-h LC_{50} of 471 ppm for total lead and 1.38 ppm for dissolved lead. Davies (1973) also conducted an 18-d test using soft water and determined the LC_{50} to be 0.14 ppm lead for rainbow trout.

Although lead is found in almost all biological organisms, it is not considered an essential element to life (Faust and Aly 1981) and in fact can be harmful. When lead is absorbed in excessive amounts it can be mutagenic and teratogenic (Eisler 1988b). Lead has carcinogenic properties, impairs reproductive, liver, and thyroid functions, and interferes with resistance to infectious diseases (from Eisler 1988b). Lead is one of the metals which causes increased mucus formation on fish which coagulates over the whole fish, particularly the gill area, causing death by anoxia (from Eisler 1988b).

In a review of the literature, Moore and Ramamoorthy (1984a) found that residues in muscle tissue are only slightly lower than concentrations in specific organs so comparisons can be easier made between studies. Common carp (*Cyprinus carpio*) collected from the upper Mississippi River had concentrations of lead at 3 ppm, while bluegill contained 0.4 ppm lead (Wiener *et al.* 1984). The geometric mean of lead in fish collected for the NCBP was 0.11 ppm wet weight (Schmitt and Brumbaugh 1990). Catostomids collected upstream from a mine site on the Big River in southeastern Missouri contained <0.1 ppm fresh weight lead, while catostomids collected downstream contained 0.4 to 0.8 ppm fresh weight lead (Schmitt *et al.* 1984). Longear sunfish (*L. megalotis*) and black redhorse (*Moxostoma duquesnei*) collected from the same site downstream had residue concentrations of 18 and 15 ppm fresh weight lead, respectively. Bluegill from a mine tailings pond in Missouri contained 128 ppm dry weight lead, while bluegill collected 1 km downstream contained 23 ppm lead and 65 km downstream, 5 ppm lead (from Eisler 1988b).

Concentrations of lead in fish collected from MNWR were significantly less than concentrations found in fish from polluted sites reported above. Eisler (1988b:48) states that "fish had comparatively elevated Pb [lead] concentrations when collected near industrialized areas, ponds with high numbers of Pb shot, urban areas, Pb mines, and tailings ponds". Because concentrations of lead in fish from MNWR are low when found above the detection limit, there apparently is not a lead contamination problem on the

refuge.

Mercury

Mercury is the only metal found in liquid form at normal ambient temperatures and is distributed throughout the environment. The largest industrial use for mercury is in electrolytic preparations of chlorine and caustic soda (Faust and Aly 1981). Mercury also is used in thermometers, barometers, manometers, batteries, high-intensity street lamps, fluorescent lights, insecticides, fungicides, bactericides, pharmaceuticals, dental preparation, and employed as a shield against atomic radiation (Faust and Aly 1981, Moore and Ramamoorthy 1984a, Clement Associates 1989a).

The Study Group on Mercury Hazards (1971:26) states that "decontamination through natural processes is extremely slow and, considering the large volumes of mercury contained in some bottom sediments, it is quite conceivable that some waters will remain contaminated for 100 years or more". Mercury is constantly released into the air from ore deposits and soil surfaces because it is highly volatile (Moore and Ramamoorthy 1984a). Anthropogenic sources contribute more mercury into the environment than natural sources. These sources include burning of fossil fuels, smelting operations of mercury-containing ores, operation of chloralkali plants, incineration of municipal sludges, and disposal of batteries and fluorescent lamps (Faust and Aly 1981, Moore and Ramamoorthy 1984a, from Eisler 1987).

Toxic concentrations of mercury range from 0.15 to 0.20 ppm (96-h LC_{50}) for juvenile rainbow trout and 0.03 ppm (10-d LC_{50}) for channel catfish (*Ictalurus punctatus*) embryo-larvae (from Eisler 1987). Mercury as mercuric chloride was lethal to bivalve larvae at 0.027 ppm (from NAS/NAE 1972). Mercury as mercuric sulfate caused severe deformities in developing salmon (*Oncorhynchus nerka* and *O. gorbuscha*) at concentrations exceeding 0.003 ppm mercury. Flaring of gill covers, loss of equilibrium and sluggishness are signs of acute mercury poisoning (from Eisler 1987).

Chronic mercury poisoning causes emaciation, brain lesions, cataracts, inability to capture food, and abnormal motor coordination in different fish species (from Eisler 1987). Sublethal poisoning in fish also can cause inhibition of enzymes and protein synthesis in liver, kidney, and brain, reduction in sperm viability and survival of second generation fry, and reduction in fin regeneration time (Moore and Ramamoorthy 1984a). These symptoms reduce the ability of fish to survive in the natural environment.

Mercury has no known normal metabolic function in living organisms. The majority of the mercury found in fish is methylmercury (from Faust and Aly 1981, Moore and Ramamoorthy 1984a). Faust and Aly (1981) stated that alkylmercurials cumulate in the food chain and are concentrated by aquatic organisms. In fish from relatively unpolluted sites, the average concentrations of mercury is <0.2 ppm (Clement Associates 1989a).

In a review of the literature, Eisler (1987) found that concentrations of mercury in biotic samples collected from areas not directly impacted by man were usually <1.0 ppm fresh weight. However, samples collected in the

vicinity of point and nonpoint sources of mercury contained concentrations exceeding 1.0 ppm fresh weight, sometimes significantly. Muscle tissue of channel catfish collected in Lake Erie had mercury residue concentrations of 0.3 to 1.8 ppm fresh weight; from Lake St. Clair, 0.5 to 2.0 ppm fresh weight; and from Texas, 0.2 to 2.5 ppm fresh weight (from Eisler 1987).

Common carp and bluegills collected from the upper Mississippi River were analyzed as whole body samples; liver samples also were analyzed from the carp. Mercury concentrations in the whole fish samples ranged from 0.179 to 1.43 ppm dry weight in carp and 0.158 to 0.325 ppm dry weight in bluegill (Weiner *et al.* 1984). Carp liver samples ranged from 0.092 to 7.91 ppm dry weight mercury (Weiner *et al.* 1984).

Mercury concentrations in fish collected from the NCBP had a geometric mean of 0.10 ppm wet weight, with a maximum concentration of 0.37 ppm wet weight in a largemouth bass from Pee Dee River, South Carolina (Schmitt and Brumbaugh 1990). Concentrations of mercury in individual fish depends on the waterbody in which it lives, species, age, and size of the fish (Murray 1978).

All but one of the ten fish samples from MNWR were greater than the 85th percentile of 0.17 ppm wet weight mercury determined for the NCBP (Schmitt and Brumbaugh 1990). Of those, three exceeded the maximum level of 0.37 ppm wet weight reported above. Also, concentrations of mercury found in MNWR fish were at the higher end or above the range of concentrations found in fish from areas of potential mercury contamination reported above. There may be a mercury contamination problem in the fish on MNWR.

Molybdenum

Molybdenum is not found naturally in its elemental form, but occurs with sulfur, tungsten, lead, uranium, iron, magnesium, cobalt, vanadium, bismuth, or calcium. Molybdenum is a rare element used primarily in steel alloys for aircraft and weapon industries (Eisler 1989). The metal also is used in the production of spark plugs, x-ray tubes, electrodes, pigments, chemical reagents, and in fertilizers for leguminous crops (McKee and Wolf 1963, Eisler 1989).

Anthropogenic sources of molybdenum contamination in the environment include the combustion of fossil fuels, and smelting, mining and milling for steel, copper, uranium, and molybdenum (Eisler 1989). In Missouri, clay pit mine erosion containing molybdenum caused industrial molybdenosis in domestic cattle in 1970 to 1972 (Eisler 1989).

Aquatic biota are relatively resistant to molybdenum. Eisler (1989) noted that adverse effects on growth and survival were not witnessed until waters were at 50 ppm molybdenum or higher. Bluegill tested in molybdenum contaminated water had a 96-h LC_{50} of 1,320 ppm, while fathead minnows in soft water had a 96-h LC_{50} of 70 ppm and in hard water, 360 ppm (from Eisler 1989). LC_{50} s (96-h) for rainbow trout with a mean length of 20 mm were 800 ppm molybdenum and with a mean length of 55 ppm, 1,320 ppm molybdenum (from Eisler 1989).

Molybdenum is found in all plant and animal tissues and is an essential micronutrient for life (from Eisler 1989). However, there is no evidence that molybdenum deficiency can be detrimental to animal health (Eisler 1989). Concentrations of molybdenum are low in biota, except in terrestrial plants. Aquatic invertebrates contain about 4 ppm molybdenum fresh weight and whole fish samples have molybdenum residue concentrations of 2 ppm fresh weight (Eisler 1989).

Molybdenum was not measured in the samples collected for the NCBP. Red-eared turtle livers dissected from turtles from MNWR contained molybdenum residue concentrations above the detection limit; however, all the fish samples collected were below the detection limit. Information on residue concentrations in turtles is lacking. Therefore, molybdenum is not likely a problem at MNWR.

Nickel

Nickel is not found in its elemental form in nature. It is present in many ores, minerals, and soils. Nickel has good thermal and electrical conductivity and is highly magnetic. Nickel is used in coinage, electroplating and in more than 3,000 different alloys such as stainless steel and cast iron. The different alloys are used in instruments for electrical transmission and reproduction of sound, electrical heating units, industrial equipment, manufacture of automobiles, heavy machinery and armaments, magnetic components in electrical equipment, nickel cadmium batteries, solar energy equipment, and dyes in ceramics and fabrics (NAS/NAE 1972, Nebergall et al. 1980, Moore and Ramamoorthy 1984a).

Surface water nickel contamination may result from eroded soil particles, industrial applications, fertilizer production, mine wastes and deposition from the atmosphere due to automobile combustion, waste incineration, and wood and coal combustion (NAS/NAE 1972, Moore and Ramamoorthy 1984a).

Nickel ions can be toxic depending on species, water hardness, and synergism with other metallic ions (NAS/NAE 1972). Even though nickel is toxic, it is one of the least toxic of the heavy metals. The LC_{50} (48 to 96-h) for invertebrates ranges from 0.5 to 20 ppm nickel (Moore and Ramamoorthy 1984a). The LC_{50} (96-h) for fathead minnows ranges from 5 ppm nickel in soft water to 43 ppm nickel in hard water (NAS/NAE 1972). The lethal limit of nickel for sticklebacks (Gasterosteidae) has been reported at 0.8 ppm (from McKee and Wolf 1963). Moore and Ramamoorthy (1984a) reported LC_{50} s (48- to 96-h) for adult fish ranging from 5 to 100 ppm nickel, with lower values reported for immature stages. Chronic effects have not been investigated fully, although there may be a reduction in fecundity and egg survival in fish.

Nickel contamination in invertebrates may occur at site specific points (Moore and Ramamoorthy 1984a). Nickel tends to accumulate in tissues with high metabolic activity, not in muscle tissue. Residue concentrations also vary seasonally due to reproductive activities and changing water temperature (Moore and Ramamoorthy 1984a). Moore and Ramamoorthy (1984a:171) suggest that "biomonitoring and impact assessment programs should not be based on muscle residue data".

Data on residue concentrations of nickel in fish is limited. Concentrations in fish collected from lakes and rivers near Sudbury, Ontario, an area heavily contaminated with metals, ranged from 9.5 to 13.8 ppm nickel wet weight (Hutchinson et al. 1975). Nickel residue concentrations in fish from other industrialized areas of the world seldom exceed 1 ppm wet weight.

Nickel concentrations in the fish collected from MNWR are well below the concentrations reported for contaminated areas. Nickel was not measured in the fish collected for the NCBP (Schmitt and Brumbaugh 1990). In comparison to other sites sampled in Missouri, Clarence Cannon NWR had the highest maximum residue concentration of nickel (23.8 ppm dry weight). There does not seem to be a nickel contamination problem on MNWR.

Selenium

Selenium, an essential element to living organisms, is naturally occurring and widely, but unevenly distributed. Selenium is most commonly found in sedimentary rock. There are no significant deposits of selenium to mine; therefore, the majority of selenium used is produced from copper refinery slimes. The element selenium is used for photoelectric cells, xerographic copying machines, in the manufacture of glass and ceramics, in pigments to color plastics, paints and enamels, and in agriculture as a prevention of selenium deficiency in livestock and poultry (NAS/NAE 1972, Faust and Aly 1981, Clement Associates, Inc. 1989).

The weathering of natural rock is the major environmental source of selenium. Anthropogenic activities which contribute to selenium concentrations are the combustion of coal, coal fly ash, mining and milling operations, and selenium refining factories (Faust and Aly 1981, Clement Associates, Inc. 1989).

Dietary selenium is essential for living organisms; however, selenium in excess is toxic and can cause death (NAS/NAE 1972). Goldfish (*Carassius auratus*) tested in softwater with pH ranging from 6.4 to 7.3 survived 10 ppm sodium selenate for only 98 to 144 h. (from NAS/NAE 1972). In a review of the literature, Eisler (1985b) listed 96-h LC₅₀s for selenium contamination to various species, including the common carp at 35 ppm, mosquitofish (*Gambusia affinis*) at 12.6 ppm, channel catfish at 13.6 ppm, bluegill at 28.5 ppm, and rainbow trout ranging from 4.2 to 12.5 ppm. Signs of selenium poisoning in fish include, but are not limited to, loss of equilibrium, lethargy, muscle spasms, protruding eyes, and swollen abdomen (from Eisler 1985b).

Sublethal effects of selenium were noted in green sunfish from a North Carolina lake contaminated with selenium from fly-ash wastes. Reproduction failed and the population decreased (Sorensen et al. 1984). Other noted sublethal effects are growth reduction of green algae and rainbow trout fry, shifts in species composition of algal communities, and avoidance response in goldfish (Eisler 1985b).

Selenium is accumulated through the food chain and is modified by water temperature, age of the organisms, mode of administration (Eisler 1985b) and species of fish (Faust and Aly 1981). Selenium concentrations were higher in the kidney and liver than muscle tissue in carp (Sato et al. 1980).

Concentrations of selenium in whole carp and bluegill from the upper Mississippi River ranged from 0.7 to 1.4 ppm dry weight; livers of carp contained 2.2 to 5.2 ppm dry weight (Wiener et al. 1984). Whole fish samples collected nationwide for the NCBP contained a geometric mean of 0.42 ppm wet weight selenium, with the highest level of 2.3 ppm wet weight from a carp collected in the Colorado River in Arizona (Schmitt and Brumbaugh 1990).

Two of the 10 fish samples collected at MNWR were only slightly higher than the NCBP geometric mean (Schmitt and Brumbaugh 1990). All of the fish samples were below the 85th percentile of 0.73 ppm wet weight selenium. There does not seem to be a selenium contamination problem at MNWR.

Vanadium

Elemental vanadium is not found naturally; however, vanadium is found in many minerals such as chileite and vanadinite. Vanadium is used in the manufacture of steel to increase hardness. Salts of vanadium are used in glass, photography, and in dyeing and printing fabrics (McKee and Wolf 1963).

A source of environmental vanadium is through the combustion of fossil fuels, because the metal was concentrated by marine organisms at the geological time of the formation of oil-bearing strata (NAS/NAE 1972). The other main release of vanadium is from the manufacture processes of products containing the metal.

Surface waters have been known to contain vanadium concentrations up to 0.3 ppm (from NAS/NAE 1972). Trace amounts of vanadium have been reported in animal tissues (McKee and Wolf 1963). Vanadium has not been known to be an essential element for living organisms, however, evidence demonstrates it has beneficial biological functions such as lowering serum cholesterol and reducing coronary heart disease in humans (from McKee and Wolf 1963).

The toxicity of vanadium has been tested on some fish species. The 96-h LC_{50} of vanadium to fathead minnows was 4.8 ppm in soft water and 30 ppm in hard water. When bluegill were tested, the 96-h LC_{50} was 6 ppm vanadium in soft water and 55 ppm in hard water (NAS/NAE 1972).

Vanadium was not measured in fish collected for the NCBP (Schmitt and Brumbaugh 1990). For comparative purposes, however, samples collected from Clarence Cannon and Squaw Creek National Wildlife Refuges and Neosho National Fish Hatchery indicated maximum values in a carp containing 2.9 ppm vanadium and a gizzard shad (*Dorosoma cepedianum*) containing 4.46 ppm vanadium. No reference data could be found to determine if residue concentrations of vanadium found in fish collected at MNWR could cause any adverse effects to fish populations or predators.

Zinc

Rocks and ores containing zinc are mined and refined into pure zinc. Pure zinc is then used for galvanizing, in the production of noncorrosive alloys, brass, U.S. coinage, and for electrical purposes. Zinc salts are used in paint pigments, pharmaceuticals, cosmetics, and insecticides.

Zinc compounds are found naturally in the air, water, soil, and all living organisms. Anthropogenic sources, which contribute 96% of the zinc discharged into the environment, include non-ferrous metal production, waste incineration, electroplating, drainage from active and inactive mining operations, domestic and industrial sewage effluents, combustion of fossil fuels, road surface runoff, and erosion of agricultural soils (Moore and Ramamoorthy 1984a, Clement Associates 1989c, from Eisler 1993).

Zinc is an essential element for living organisms, but in excess zinc can be toxic. The susceptibility of fish to zinc contamination depends on species, age, and health of the fish, water hardness, pH, and temperature (McKee and Wolf 1963, NAS/NAE 1972, Moore and Ramamoorthy 1984a). In an overview of the literature, Moore and Ramamoorthy (1984a) found that the LC_{50} (48 to 96-h) for fish ranged from 0.5 to 5.0 ppm zinc, with an extension of the range from 0.09 to >100 ppm zinc due to physio-chemical and biological factors. The toxic action of zinc is thought to be caused through formation of insoluble compounds within the mucous covering the gills, damage to the gill epithelium, or possibly as an internal poison (from McKee and Wolf 1963, Moore and Ramamoorthy 1984a).

Fish exposed to sublethal concentrations of zinc exhibit reproductive impairment, significant alterations in blood and serum chemistry, liver enzyme activity, cholesterol, RNA, and proteins (from Eisler 1993), decrease in growth, maximum size and fecundity, and alteration in schooling and reproductive behaviors (Moore and Ramamoorthy 1984a).

Zinc residue concentrations in fish tissue are elevated at point sources and decrease further away from the source (from Eisler 1993). Zinc is obtained by organisms through their diet (Eisler 1993). In a review of the literature, Moore and Ramamoorthy (1984a) found that muscle tissue from yellow perch (*Perca flavescens*), bluegill, and black crappie (*Pomoxis nigromaculatus*) collected from recreational and industrial river zones contained 106, 108, and 103, 100, and 109, 101 ppm zinc dry weight, respectively. Muscle tissue collected from omnivorous and carnivorous fish from industrial and agricultural areas of the lower Great Lakes contained 16 to 88 and 3 to 9 ppm zinc wet weight, respectively (Brown and Chow 1977). Concentrations of zinc in edible tissue collected from fish inhabiting streams contaminated by lead mining in Missouri ranged from 4.0 to 24.0 ppm wet weight (Schmitt and Finger 1987). Whole fish analyzed from the NCBP contained a geometric mean of 21.7 ppm zinc wet weight (Schmitt and Brumbaugh 1990). The maximum concentration was 118.4 ppm wet weight zinc in a carp collected from Lake St. Clair, Michigan.

Residue concentrations of zinc found in fish collected from MNWR did not exceed the NCBP geometric mean (Schmitt and Brumbaugh 1990). Zinc concentrations found at MNWR were at the lower end of the range or below concentrations found at contaminated areas. There apparently is not a zinc contamination problem at the refuge.

Organochlorine Contaminants

1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane (DDT)

Technical DDT is a mixture of up to 14 analogs and isomers (Moore and Ramamoorthy 1984b). The white, amorphous powder is persistent once in the environment, is transported long distances in the air and water, and is extremely lipophilic. DDT was used as an insecticide for the control of mosquitoes and other insect pests in agriculture. In 1972, EPA restricted the use of DDT for insecticidal use. It was only to be used in case of a public health emergency (Clement Associates 1989b).

DDT does not occur naturally in the environment, so all releases are from its production, use as an insecticide, and runoff from agricultural lands into streams and lakes. Due to the extensive past use of DDT and its persistence, the insecticide and its metabolites are found at low concentrations in most living organisms (Clement and Associates 1989b). DDT bioaccumulates in fish (Moore and Ramamoorthy 1984b, Clement Associates 1989b) and is known to cause eggshell thinning in fish-eating avian species (Haseltine *et al.* 1975).

The geometric mean residue concentrations in fish collected for the NCBP was 0.26 ppm total DDT (Schmitt *et al.* 1990). Because only one sample is above the detection limit for DDT, and is not at a significant concentration to cause adverse effects to fish, there is not a problem with DDT contamination at MNWR.

Recommendations

There are potential contamination problems from mercury and possibly copper on MNWR, according to the data discussed in this report. The major source of these compounds is unknown.

If there is concern that populations of fish and wildlife using MNWR are decreasing or do not seem healthy there should be further investigations into the above metals. First, an intensive survey of possible sources of these contaminants should be conducted in the watersheds which drain into the refuge. Then further sampling should be completed to include water, sediment, and biota of several trophic levels. The biotic organisms also should be necropsied to check for any abnormalities.

The reason whole fish were analyzed for this report is that top fish and wildlife predators consume whole fish. However, data are limited for comparison of the significance of whole fish concentrations to predator populations, and even to the prey species themselves. Therefore, separate tissues or organs should be analyzed as reported in the literature (*i.e.*, fatty tissue for organics, liver for metals). This approach may result in more solid conclusions concerning the possible significance of contamination levels of the listed compounds found in samples from MNWR.

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