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A CONTAMINANTS EVALUATION OF THE BIG BLUE RIVER IN SOUTHEASTERN NEBRASKA

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u.s. FISH & WILDLIFE SERVICE REGION 6

CONTAMINANTS PROGRAM

BY

Brent J. Esmoil, Kirk D. Schroeder, and Timothy E. Fannin

u.s. FISH AND WILDLIFE SERVICE Ecological Services Grand Island, Nebraska 1994

A CONTAMINANTS EVALUATION OF THE BIG BLUE RIVER IN SOUTHEASTERN NEBRASKA

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by

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ABBREVIATIONS AND CONVERSION FACTORS

Proposed Control Ave.

Abbreviations

micrograms per gram = μ g/g

parts per million = ppm

not detected (below analytical detection limits) = ND

Conversions

1 microgram per gram = 1 part per million

Wet weight = Dry weight $[100-(\text{%Moj}$ oisture/100)]

ACKNOWLEDGMENTS

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Project Numbers Covered Under This Report:

92-6-6F12

SUMMARY

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Protestant contract and contract

- o We collected three composite fish and three composite sediment samples from the Big Blue River in southeastern Nebraska to determine the presence of agricultural chemicals or other contaminants. Inorganic analyses consisted of individual analyses for arsenic, selenium, and mercury, as well as an ICP scan for other elements. Organic analyses included organochlorines, polynuclear aromatic hydrocarbons, organophosphate and carbamate pesticides, and chlorphenoxy acid herbicides.
- o Arsenic was detected in the sediment samples, but not in the fish samples.
- o Selenium was detected in one of three sediment samples and in all fish samples.
- o Mercury was not detected in sediment samples, but was detected in all fish samples.
- o Organic compounds detected in composite fish samples include BHC compounds, chlordane compounds, DDT and its metabolites, and anthracene.
- o outside of oil and grease, organic compounds were not detected in any sediment sample.

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INTRODUCTION

Production America

Previously, the u.s. Fish and wildlife Service (Service) had not investigated environmental contaminants in the Big Blue River or their possible effects on fish and wildlife resources in the area. The Big Blue River Basin (Basin) encompasses less than 6 percent of the total area in Nebraska (Nebraska Natural Resources Commission 1976). Riparian areas within the Basin provide nesting, migrating, and wintering habitat for bald eagles *(Haliaeetus leucocephalus)* , osprey *(Pandion haliaetus)* , and numerous other species of raptors and songbirds. The Basin also serves as an important staging and nesting area for migratory waterfowl. The Big Blue River is also considered a "Highestvalued fishery resource" by the Nebraska Game and Parks Commission.

The Big Blue River and its tributaries are strongly associated with agricultural lands throughout the entire watershed. Within the Basin there are approximately 2,796,000 acres of land suitable for agricultural purposes. Approximately two million acres in the Basin are suitable for irrigation (Nebraska Natural Resources Commission 1976). The loess soils that predominate the Basin are relatively impermeable soils and can facilitate rapid runoff from agricultural fields during periods of high precipitation and/or irrigation.

Stream gauge readings on the Big Blue River vary greatly, with peak discharges usually occurring during the months of March through June. Daily minimum and maximum flows have varied from 32 to 45,700 cubic feet per second, respectively at Barneston, Nebraska over the last 20 years (Dave Schwartz, USGS, pers. comm.) .

The primary crops produced in the Basin are corn, sorghum, wheat, soybeans, and alfalfa. In an attempt to increase yields,

croplands in the area are treated with insecticides and/or herbicides. Many insecticides used include organophosphates and carbamates, which are considered to be highly toxic to waterfowl and to other migratory birds. There is a high potential for agricultural chemicals to be transported via wind and water from adjacent fields into the river system and to impact fish and wildlife resources.

We initiated this survey to gather baseline information on environmental contaminants potentially impacting fish and wildlife which utilize the Big Blue River system. Through repeat sampling we hope to assess changes in contaminant concentrations after a five-year period.

STUDY AREA

The Big Blue River system of southeastern Nebraska is comprised of two main river channels, the Big Blue River, and its main tributary, the West Fork of the Big Blue River. These rivers originate near the towns of Chapman and Hastings, respectively. The confluence of these rivers is approximately six miles north of Crete. From the confluence, the river flows southerly into Kansas where it joins the Little Blue River near Blue Rapids. Numerous small rivers and creeks drain into the two main river channels throughout the entire reach of the river.

FANCISCH SET

The Big Blue River is approximately 468 miles long and drains approximately 4,558 square miles in southeastern Nebraska (Nebraska Game and Parks Commission 1983). Numerous small hydroelectric dams were once scattered along the mainstem of the river. The last dam was removed from service in the early 1970's. The remnants of these dams still have the potential to trap silt from adjacent agricultural fields, and sediment samples from the areas likely contain contaminants which could impact natural resources of the area.

OBJECTIVES

The objective of this study was to evaluate Big Blue River sediments and fish and to determine if agricultural chemicals or other contaminants are present in concentrations which could pose a threat to bald eagles, migratory waterfowl, and other fish and wildlife resources that utilize the area.

MATERIALS AND METHODS

We collected composite sediment and fish samples from the Big Blue River near the towns of staplehurst, Crete, and Holmesville. The sampling sites at Crete and Holmesville were located where hydroelectric dams were once present. These dams may have had the potential to trap sediment containing environmental contaminants.

Two sediment samples were collected from each sampling site by scooping the top 2.5 cm of sediment with an acetone and distilled water rinsed stainless steel spoon. Sediments were placed in

pre-cleaned glass sample jars with teflon-lined lids. We collected approximately 800 g of sediment per sample. Composite fish samples of common carp *(cyprinus carpio)* were collected at each of the sampling sites via electrofishing. Each fish was weighed and double-wrapped in aluminum foil. All samples were placed on ice in the field, and later frozen until shipment to the analytical laboratory. Because of small sample size, the composite fish sample from staplehurst (bf1c) was aliquoted for both organic and inorganic analyses. Samples were first shipped to the inorganics laboratory, analyzed, and remaining sample contents were shipped to the organics laboratory for completion of analyses. All other samples had sufficient weight for organic and inorganic analyses, and therefore aliqots were not required. No anomalies were reported in the samples.

Laboratory quality control was reviewed by the U.S. National Biological Survey's Patuxent Analytical Control Facility (PACF). **Precision and accuracy of the laboratory analyses were confirmed** with procedural blanks, duplicate analyses, test recoveries of spiked materials, and reference material analyses. Standard reference materials and spiked samples were analyzed to verify the accuracy of analytical techniques. Duplicate samples were analyzed to verify the precision of analytical methods.

INORGANICS

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Inorganic analyses for fish and sediment samples were conducted by the Geochemical & Environmental Research Group at Texas A&M University. Mercury concentrations were determined by cold vapor atomic absorption spectrometry. Arsenic, selenium, cadmium, and lead concentrations were determined using graphite furnace atomic absorption spectrometry (AAS). Concentrations of the other elements analyzed were determined by atomic emission using an argon plasma. All results are presented here as $\mu q/q$. Detection limits for arsenic in fish ranged from 0.122 to 0.156, and 0.225

to 0.351 in sediments. Detection limits for selenium in fish ranged from 0.122 to 0.156, and 0.450 to 0.703 in sediments. Detection limits for mercury in fish ranged from 0.024 to 0.031, and 0.045 to 0.070 in sediments. Analyses of spiked samples of mercury, arsenic, and selenium in sediment yielded 101, 122, and 124 percent recovery, respectively. Spiked samples of mercury, arsenic, and selenium in fish yielded 93, 96, and 123 percent recovery, respectively.

ORGANICS

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Organophosphate and carbamate pesticide scans in fish and sediment were conducted by PACF. Mississippi State Chemical Laboratory conducted analyses in fish and sediment for the following: organochlorines in fish and sediment, polynuclear aromatic hydrocarbons in fish, chlorophenoxy acid herbicides in sediment, and oil and grease in sediment. All organic compound concentrations are given in wet weight throughout this report.

RESULTS AND DISCUSSION

organophosphate and carbamate pesticides were not detected in any composite fish or sediment sample. Chlorphenoxy acid herbicides were not detected in any sediment sample. Metals analyzed by AAS are shown in Table 1. Concentrations of oil and grease in sediments are shown in Table 2. Metals analyzed by ICP are shown in Table 3. Organic analyses are shown in Table 4.

METALS

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Metals Analyzed by AAS

Arsenic

While arsenic is found widely in nature, it is not known to be an essential plant or animal nutrient. Background levels are typically less than 1 $\mu q/q$ fresh weight in aquatic biota. Adverse effects emerge on freshwater fish at residue levels of 1.3 to 5 μ q/q wet weight. Arsenic can be bioconcentrated, but is not biomagnified (Eisler 1988a). It is designated as a toxic pollutant under both the Clean Water Act and the Clean Air Act. Arsenic was not detected in any fish sample (Table 1). Levels of arsenic found in sediment in this study were below those found in northern Great Plains soils (Severson and Tidball 1979), and below levels of concern.

Mercury

There are many sources of mercury into the environment, but agriculture and industry are typically identified as the most significant. since 1970, industry-related mercury contamination of water sourceS has been reported in 26 states. Sources of mercury include combustion of fossil fuels, gold mining, pesticide compounds, batteries, sewage treatment plants, and electrical switches (Eisler 1987a). Seeds treated with organomercury fungicides have been used in agriculture throughout the world, including the northern Great Plains (Swanson et al. 1972) .

Animals take up mercury from industrial sources, contaminated water, and contaminated food (Jenkins 1981). Mercury is a nonessential carcinogen, mutagen, and teratogen with no metabolic function. Mercury is bioconcentrated and biomagnified, and

produces only harmful effects with no useful physiological functions in fish and wildlife (Eisler 1987a). Concentrations of mercury ranged from 0.25 to $0.3 \mu q/q$ dry weight in Blue River fish. These concentrations were less than the values recommended for protection of fish by Eisler (1987a), and below the NCBP means reported by Schmitt and Brumbaugh (1990). Mercury was not detected in any of the composite sediment samples (Table 1).

Selenium

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At high concentrations, selenium is toxic to wildlife. While selenium is an essential trace element, non-toxic concentrations fall within narrow ranges (Lemly and smith 1987). Irrigation return flows are a potential source of selenium, and have been implicated in wildlife mortalities at Kesterson National wildlife Refuge in California (Ohlendorf 1989). Other sources of selenium include sewage sludge, emmissions from coal-fired power plants (Eisler 1985a), production of stainless steel, fungicides, lubricants, electronic devices, insecticides, and veterinary medicine (U.s. EPA 1980). Selenium is bioaccumulated and biomagnified in some locations, and therefore should be monitored in fish, wildlife, and their habitats (Allen and wilson 1990).

Prior to the 1980's, few studies of selenium toxicity in wildlife were conducted (Ohlendorf 1989). Eisler's (1985a) documentation of selenium hazards to fish, wildlife, and invertebrates served as a catalyst for additional quantitative information on selenium toxicosis.

In this study selenium was detected in the sediment sample from Crete at a concentration well below the 4 μ g/g dry weight level of concern in sediment recommended by Lemly and smith (1987) for protection of fish and wildlife. The former hydroelectric dam at the site could have trapped sediment containing slightly elevated selenium concentrations.

Concentrations of selenium exceeding 12 μ g/g dry weight are often associated with reproductive failure in fish (Lemly and smith 1987). Concentrations in samples we collected were below this reference value. Additional samples of fish from this area do not appear to be warranted.

Metals Analyzed by ICP

Aluminum

Response Links

Aluminum was detected in all fish and sediment samples. Much of the available literature addresses the toxicity of dissolved aluminum to fish as related to pH and hardness (e.g., Baker and Schofield 1982; Hunn et al. 1987; Palmer et al. 1989). In general, aluminum toxicity to fish is inversely correlated to pH (Albers and Camardese 1993). Brumbaugh and Kane (1985) **discovered extreme variation in aluminum concentrations in organs** and whole bodies of smallmouth bass *(Micropterus dolomieui)* due to inclusion of gastrointestinal tract contents. Concentrations of aluminum in whole body analyses of common carp in this study ranged from 15.89 $\mu q/q$ to 157.42 $\mu q/q$ dry weight. Several factors influence our interpretation of aluminum concentrations found in fish. First, we did not collect information on pH from any of the sites, and therefore cannot address the aluminum/pH relationship to fish toxicity. Second, small sample sizes of composite fish confounds accurate interpretation. And third, because of inherent variability induced by whole body analyses, it would likely be advantageous to conduct separate analyses of gut contents and whole bodies.

Concentrations of aluminum in sediment ranged from $2,923 \mu g/g$ to 5,651 μ q/q dry weight, well below the maximum background concentration of 12,000 μ g/g dry weight found by Harms et al.

(1990) in the western united states. Aluminum concentrations were below levels known to adversely affect fish and wildlife.

Cadmium

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Cadmium is a biologically nonessential trace element which has been implicated as a teratogen, carcinogen, and probable mutagen. Acute toxicity was observed in aquatic insects, crustaceans, and teleosts when concentrations of cadmium in water ranged from 0.8 to 9.9 $\mu q/l$ (Eisler 1985b). All cadmium compounds are potentially toxic (Jenkins 1981). Sources of cadmium input into the environment include zinc smelting, electroplating, municipal wastewater discharge, and the manufacturing of batteries (Eisler 1985b) .

Cadmium concentrations in composite fish samples from this study ranged from 0.13 to 0.47 $\mu q/q$ dry weight. Concentrations exceeding $0.47 \mu q/q$ were associated with decreased standing crop, reduced growth, reproductive inhibition, and population alterations (Eisler 1985b). Eisler (1985b) further stated that cadmium concentrations exceeding 3.0 μ g/g are potentially hazardous to aquatic biota and concentrations near 1.0 μ q/q are cause for concern in waters with low alkalinity. The movement of cadmium in the soil profile is strongly influenced by soil acidity. In dredging operations, adequate rainfall and acidic soil conditions facilitate leaching into underlying sulfidic material, which makes cadmium and other metals less available to wildlife (Beyer et al. 1990).

Concentrations of cadmium in sediment ranged from 0.24 to 0.41 μ g/g dry weight. The concentration of cadmium in the composite fish sample from Staplehurst may warrant further investigation. However, we do not believe cadmium concentrations detected in this study pose a hazard to fish or wildlife resources. Should

additional samples be collected, it would be beneficial to gain information on water alkalinity.

Chromium

Robert Marine Liberies

Chromium was listed as one of the 14 most noxious contaminants by Jenkins (1981). At high concentrations chromium is considered a carcinogen, mutagen, and teratogen. Chromium may be transported in aquatic systems through suspended particulates, though most chromium in soil and sediment is unavailable to living organisms (Eisler 1986). Sources of chromium include metal plating facilities, tanneries, sewage sludge and outfalls, and municipal landfills (Eisler 1986). Plants take up chromium from ground and surface water, soil, sewage sludge, fertilizers, and air pollution. Animals take it up as it becomes available from food or industrial processing (Jenkins 1981). Jenkins (1981) considered plants to be the best medium for monitoring chromium **in the environment.**

Chromium was detected in only one composite fish sample at a concentration of 0.89 μ g/g dry weight. Opinions differ as to concern levels of chromium in fish. Walsh et al. (1977) recommended a concentration of $0.20 \mu q/q$ dry weight, while Eisler (1986) recommended 4.0 μ g/g dry weight level of concern. Our data slightly exceed the recommendation made by Walsh et al. (1977), and is well below Eisler's (1986) recommendation. Further monitoring of chromium concentrations in fish do not appear to be warranted.

Chromium concentrations in sediment samples from this study ranged from 4.7 to 7.71 μ g/g dry weight. The geometric mean concentration found in northern Great Plains soils was 45 μ g/g dry weight (Severson and Tidball 1979). The geometric mean chromium concentration found in western and conterminous U.S. soils were 41 and 37 $\mu q/q$ dry weight, respectively (Shacklette

and Boerngen 1984). Based on our data, chromium concentrations do not appear elevated in the Blue River system.

Copper

Pressure and Alaska

Copper is a U.S. Environmental Protection Agency priority pollutant (Keith and Telliard 1979). Copper concentrations in unpolluted freshwaters are usually less than 2 μ g/l. Copper concentrations in fish samples from the Big Blue River slightly exceeded the National contaminant Biomonitoring Program (NCBP) 85th percentile concentration, which ranged from 0.9 μ g/g wet weight in 1980-1981 to 1.1 μ g/g wet weight in 1978-1979. Maximum NCBP concentrations during these same periods ranged from 24.1 to 38.7 µq/q wet weight (Schmitt and Brumbaugh 1990). Concentrations of copper in sediments (Table 3) were less than the means for western U.S. sediments.

Iron

Iron is one of the most common elements in the earth's crust. Iron concentrations ranged from 0.4 to 6.3 percent in western U.S. drainwater study area sediments (Severson et al. 1987). Severson and Tidball (1979) found mean iron concentrations at 2.1 percent in northern Great Plains soils. Iron concentrations in biotic and abiotic samples from this study do not appear to warrant concern.

Manganese

We found manganese concentrations in fish ranging from 4.52 to 11.27μ g/g wet weight. We are unaware of potential adverse effects caused by these concentrations of manganese in fish. Concentrations of manganese in sediment ranged from 153.77 to 394.71μ g/g wet weight in this study. Manganese concentrations

in sediment ranged from 66 to 4,500 μ g/g in western U.S. irrigation drainwater study areas (Severson et al. 1987)

Nickel

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Sources of nickel into the environment include mining, smelting, and fossil fuel combustion. The geometric mean nickel concentration in U.S. soils was 13 $\mu q/q$ (Severson et al. 1987). Concentrations as high as 170 μ g/g were detected in sediments of u.S. irrigation drainwater study areas. Nickel concentrations in respective composite fish and sediments samples ranged from 0.26 to 1.83 $\mu q/q$ and 5.55 to 8.62 $\mu q/q$ wet weight. We do not consider nickel concentrations to be elevated in this study.

Lead

Lead is biologically nonessential and all measured effects appear to be adverse (i.e. non-beneficial). Input of lead into the environment is widespread and includes, but is not limited to ammunition, leaded gasoline, smelters, and metal finishing industries (Eisler 1988b).

Lead was detected in only one composite fish sample from Holmesville. This lead concentration was far below the 85th percentile reported by Schmitt and Brumbaugh (1990). Lead concentrations in sediments ranged from 8.7 to 14.35 μ g/g dry weight. The geometric mean lead concentration for northern Great Plains soils was 16 μ g/g (Severson and Tidball 1979). Our sediment samples were below this reported concentration, as well as those reported by Shacklette and Boerngen (1984).

$Zinc$

Zinc is a priority pollutant often associated with urban runoff (U.S. EPA 1980). While zinc is an essential trace element for

all living organisms, toxicity is reported at high concentrations (Eisler 1993). As with many other metals, the concentration and bioavailability of zinc is often influenced by the pH of the water (Albers and Camardese 1993).

concentrations of zinc in Big Blue River composite fish samples ranged from 56.08 to 86.91 μ g/g wet weight (179.65 to 297.67 μ g/g dry weight). The maximum wet weight concentration of zinc in whole fish from the NCBP was 168.1 μ g/g in 1978-1979, 109.2 μ g/g in 1980-1981, and 118.4 μ q/q in 1984. Respective 85th percentiles were 46.3 $\mu q/q$, 40.1 $\mu q/q$, and 34.2 $\mu q/q$. Fish samples taken in this study were elevated in comparison to these 85th percentile values. We are unaware of potential adverse effects caused by these concentrations.

Zinc concentrations in sediments samples we collected ranged from 25.57 to $48.04 \mu q/q$ dry weight. Severson and Tidball (1979) reported a geometric zinc concentration of 63 μ q/q. Our sample concentrations were below those detected in western U.S. soils (Shacklette and Boerngen 1984).

ORGANICS

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Organochlorines

concentrations of organochlorine compounds in fish and sediment are shown in Table 4. No organochlorine compounds were detected in sediment. The greatest number of organochlorine compounds were detected in the composite fish sample taken from Crete. Most of the fish samples contained either DDT or chlordane constituents and metabolites, and a few had detectable concentrations of individual compounds.

Benzene hexachloride (BHC) was detected at relatively low concentrations in the fish sample from Crete. BHC is an insecticide which, in birds, can quickly produce signs of polydipsia (excessive drinking), regurgitation, hyperexcitability, and ataxia (muscular incoordination) (Hudson et al. 1984). We do not believe the concentrations of BHC detected in this study warrant concern. However, because of the intensive agricultural use of the Blue River Basin, future monitoring may be necessary to delineate changes and BHC inputs into the system.

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An extremely low concentration (0.01 μ q/q) of endrin was detected in the composite fish sample from Crete. Chlordane residues were also at low concentrations in fish from the Blue River. *Trans*nonachlor, one of the most persistant chlordane compounds, was detected at a very low concentration in the fish composite from Crete. Chlordane compounds are water-soluble and have a tendency to bind to sediment organic carbon and enter the food chain via benthic organisms (Wilcock et al. 1993). Chlordane was detected in more than 80 percent of the sites sampled in Kansas and served as the impetus for fish-consumption advisories for the Kansas River (Arruda et al. 1987). Eisler (1990) reported a "no observed effect level" (NOEL) for chlordane concentrations <0.1 μ q/q (fresh weight) in fish tissue. The highest concentration of heptachlor epoxide was $0.02 \mu g/g$ wet weight.

very few organic compounds have provided such exhaustive research as DDT and its metabolites. While DDT use has been banned, it is quite persistent in the environment and can produce adverse biological effects long after application. Adverse effects from DDT compounds have been reported in a number of studies (Wiemeyer et al. 1993, Blus and Prouty 1979, Beyer and Krynitsky 1989).

Concentrations of DDT compounds found in this study are shown in Table 4. Schmitt (1990) reported there has been little recent

influx of DDT to the aquatic environment. We suspect this contention is accurate as well for the Blue River system for a number of reasons: 1) the parent compound (p,p' DDT) was not detected in our samples, 2) the most persistent metabolite of DDT (DOE) was found at low concentrations, and 3) detected DDT compounds and its metabolites were present below concentrations of concern.

polynuclear Aromatic Hydrocarbons

make a service of

Polynuclear aromatic hydrocarbons (PAH) may enter aquatic environments via domestic and industrial sewage effluent, petroleum spills, and through atmospheric deposition (Eisler 1987b). Only the composite fish sample from Holmesville contained detectable concentrations of any polynuclear aromatic hydrocarbon (PAH); anthracene was present at 0.02 μ q/q wet weight. Anthracene consists of three linearly-fused benzene rings which possess significant acute toxicity in comparison with the higher molecular weight 4-7 ring aromatics. However, we believe that the detected anthracene concentration does not warrant concern. All other PAH analytes were undetected in this study.

CONCLUSIONS

From this study, environmental contaminants within the Blue River system do not appear elevated. However, the low concentrations of contaminants does not imply pristine conditions. The Blue River is dominated by agricultural production throughout its reach and is subjected to runoff after precipitation events such as rainfall and irrigation. Our sampling did not include data collection over an extended period, and therefore is merely a "snapshot" in time. Further problems are likely introduced through whole body, composite fish samples. Concentrations of

contaminants would likely differ had we analyzed individual fish. Sediment samples should be taken from additional areas, as we suspect contaminants often exceed concentrations detected in this study.

manager of the state

Slightly elevated concentrations of cadmium and zinc in fish may warrant further investigation. Future sampling should include replication rather than a single collection period. Based on our results and additional literature review, analyses should include inorganics and triazine herbicides. Concentrations of atrazine often exceed the maximum contaminant level (MCL) established by the Nebraska Department of Environmental Quality. We recommend sampling again in three to five years to ascertain possible changes in concentrations of environmental contaminants.

Table 1. Arsenic, **selenium,** and mercury concentrations and detection limits, in ppm wet Table 1.
weight.

Table 2. Concentrations in sediment of oil and grease in ppm.

Table 3. Concentrations of metals in fish and sediment in ppm dry weight.

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