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Robert Conklin
Morningside College

Suzie Galles
Morningside College

Edward Shane
Morningside College

Rod Tondreau
Morningside College

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BIOCONCENTRATION OF HEAVY METALS

(Cu, Cr, Pb, and Zn)

IN THE MISSOURI RIVER

NEAR SIOUX CITY, IOWA

Principal Investigators

Robert Conklin
Suzie Galles

Faculty Advisors

Dr. Edward Shane
Rod Tondreau

Morningside College

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Abstract

The concentrations of the heavy metals- copper, chromium, lead, zinc- in the biota of the Missouri River were measured at a control site upstream of Sioux City and at a site downstream of the city. Bioconcentration factors for each of the metals were calculated for fish, periphyton, and invertebrates, and the concentrations of metals in the river sediments were measured.

Concentrations of the same metals were measured in the sediment, water, periphyton, invertebrates, zooplankton, and fish of Snyder's Bend Lake. Bioconcentration factors were calculated for each of the biological communities and were found to be very similar to those found for the Missouri River biota.

Introduction

Trace amounts of heavy metals are continually entering aquatic ecosystems through industrial and municipal effluents and agricultural runoff. These trace metals, some of which are toxic, may accumulate in the aquatic environment. With the possibility of bioconcentration, the trace metals may become concentrated enough to pose a health problem.

The purpose of this project is to study bioconcentration of copper, chromium, lead, and zinc in the Missouri River and Snyder's Bend Lake. This study is a continuation of three previous heavy metals projects (Conklin et al. 1986, Stevens et al. 1986, Weeber et al. 1986). The project incorporates new sample sites and samples that were not under investigation in the three previous studies.

Seven different samples from all levels of the food chain were chosen for analysis; water, sediment, aquatic plant, periphyton, invertebrates, zooplankton, and fish.

Experimental

Sample Location

Samples were selected from two different bodies of water. Two of the sites were located on the Missouri River, and three sample sites were located on Snyder's Bend Lake.

The Missouri River in the study area has been channelized with rock rip-rap to a typical channel width of 700-800 ft. Sample sites were located in the main channel border habitat, which is considered to be the most productive of the limited aquatic habitat available within the channelized river (Hey, Shane, Tondreau).

The north river site (Figure 1), located at river mile marker 735, is north of the mouth of the Big Sioux River and north of Sioux City, Iowa. This site acts as a control site for industrial and municipal effluents, other tributary inputs, and all other forms of runoff that occur within the Sioux City area.

The south river site (Figure 1), located at river mile marker 722, is south of the Sioux City area. The south site was selected to monitor all possible heavy metal contamination entering the river system in the Sioux City area. Possible contributing factors are: the Big Sioux River, Floyd River, industrial and municipal effluents, and agricultural runoff.

Snyder's Bend Lake (Figure 2), which corresponds to river mile marker 716, had three sample sites, the upper (north), middle, and lower (south) portions of the lake. Snyder's Bend, which is an oxbow lake created by the channelization of the Missouri River, obtains its water supply from the discharge of the Iowa Public Service Company Neal IV power plant, which is located north of Snyder's Bend on the Missouri River. The lake's outflow, located at the lower end of the lake, is then directed back into the Missouri River. The lake is a heavily used recreational area by the surrounding communities.

The surface area of the lake is approximately 300 acres, with an average depth of 8.25 feet (Corp of Engineers).

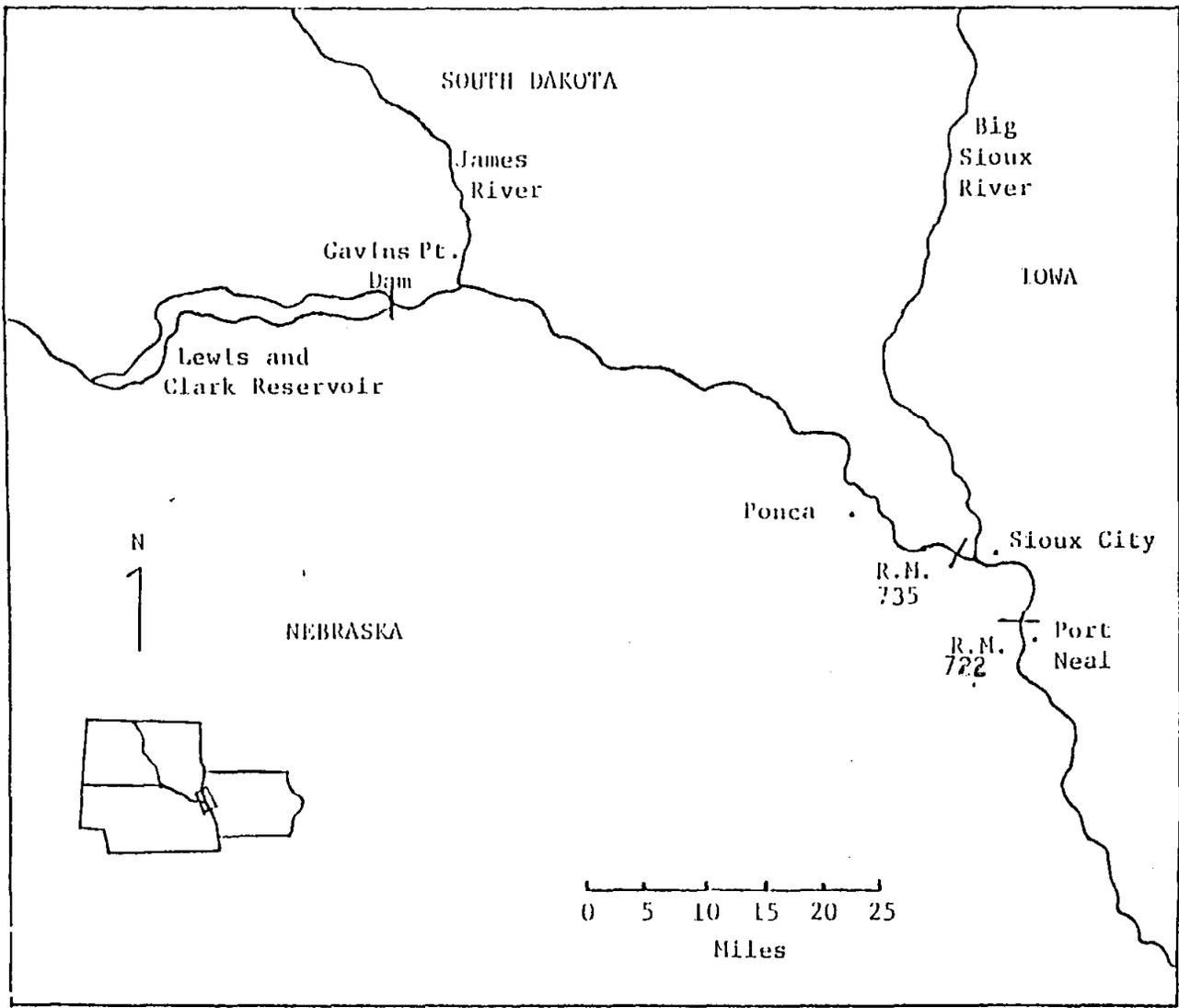
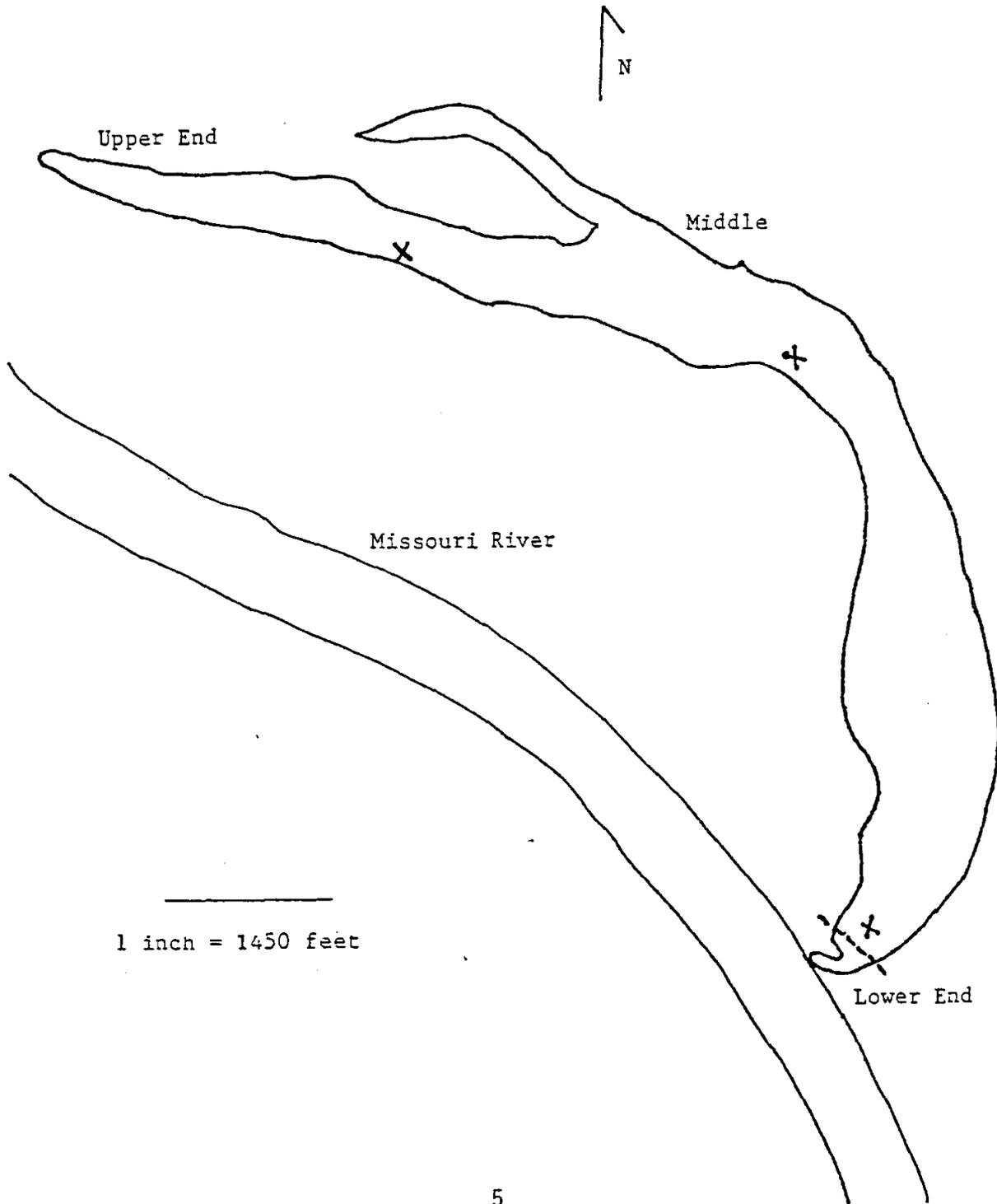


Figure 1. Map of Missouri River in the Study Area.

Snyder's Bend Lake
Figure 2



Sample Intervals

Water, sediment, aquatic plant, and fish had no definite sampling intervals. It was felt that these four samples would not change drastically in metals concentration through the course of the research project. Periphyton and invertebrates had a set sampling interval of three weeks on the river and four weeks on the lake to allow for proper colonization. Zooplankton was collected from the lake on two consecutive days. All samples that were collected had two sampling dates.

Sample Collection

All sample containers were cleaned with a 2% potassium permanganate-5% potassium hydroxide cleaning solution. The containers were then rinsed with an oxalic acid rinse, followed by a de-ionized water rinse.

River

Water:

Four "grab" samples of water were taken at both the north and south sites. Two of the samples from each site were used for hardness and alkalinity analysis, with the remaining two samples from each site being preserved with concentrated nitric acid (Standard Methods A.P.H.A.) for metals analysis.

Sediment:

Two sediment samples were taken from the north and south sites. The samples were collected from the rock rip-rap along the main channel border, placed in sample bottles, and preserved by refrigeration until analysis.

Periphyton:

Three artificial substrates, with six 3cm x 11cm plexiglass slides, were placed at both the north and south sites. The artificial substrates (Standard Methods A.P.H.A.) were secured to the wood pilings along the main channel border by two steel rods, each with a length of three feet. The substrates were connected to the rods and allowed to float up and down with the changing river stage. After the substrates had colonized, the slides were removed and placed in a sample jar, making sure the slides were not in contact with each other. Six new slides were placed in the substrate and put back in the water for the colonization period. The samples were preserved by refrigeration.

Invertebrates:

Three rock baskets (Standard Methods A.P.H.A.) of hexagonal shape, measuring 6in. wide x 12in. long, were placed at both the north and south sites. The rock baskets were tied to the wood pilings on the main channel border and submerged to a depth of about 3ft. It was preferred to keep the rock baskets on the rock bottom and not in the sandy bottom, to allow for proper colonization of the invertebrates. After colonization was complete, the baskets were taken out of the water and all visible invertebrates were collected and placed in a sample jar. The colonized rock was removed from the baskets and was replaced by new rock. The colonized rock was brought back to the lab and the invertebrates were

collected and placed in the sample jar. The samples were preserved in a 70% ethanol solution.

Fish:

Fifteen fish were collected from both the north and south sites with the use of a pulse D.C. electroshocking apparatus (Standard Methods A.P.H.A.). The fifteen fish consisted of three species, Buffalo, Carp, and Flathead Catfish, with five of each species being collected. After collection, all fish had weight and length measurements recorded. The fish were then filleted, keeping at least 8 oz. of the muscle tissue for analysis. Buffalo and Carp had scales removed from above the lateral line and Catfish had a pectoral spine removed to be used for age analysis. Once all field work was completed, the fillets were returned to the lab and frozen until sample preparation.

Lake

Water:

Four "grab" samples were taken at each of the three sites. The samples from each site were treated like the samples from the river.

Sediment:

Two sets of samples were taken from each of the three sites with the use of a Phleger core sampler (Standard Methods A.P.H.A.). Each set of samples contained a top sediment sample, a sediment sample 4" below the top, and a sediment sample 10" below the top. Each individual sample was placed in a sample bottle and preserved by refrigeration.

Aquatic plant:

One sample was taken from the three sites. The sample consisted of the rooted aquatic plant, Potamogeton(Pondweed), and the sample was placed in a plastic bag and preserved by refrigeration.

Periphyton:

Three of the artificial substrates were placed at each of the three sites, upper, middle, and lower. They were secured by connecting the substrate to an anchor, which allowed them to float on the surface in the same location. After colonization, the samples were handled the same as the river samples.

Invertebrates:

Three of the rock baskets were placed at each of three sites. The rock baskets were also attached to the anchor used by the periphyton substrates and allowed to remain on the bottom of the lake. After colonization, the samples were handled the same as the river invertebrate samples. Because colonization of the rock baskets was unproductive, the Ponar dredge was also used for collection of samples (Standard Methods A.P.H.A.).

Zooplankton:

Two samples were taken from each of the three sites. The samples were taken by using a zooplankton net and a winch for a horizontal tow (Standard Methods A.P.H.A.). The samples were collected and placed in a sample jar filled with 70% ethanol for preservation.

Fish:

Fifteen samples were taken from the lake, with the majority of samples coming from the middle and lower portions of the lake. Three different species, Buffalo, Carp, and Largemouth Bass, were collected. Five of each species were collected for analysis. These samples were treated and handled the same as the fish from the river.

Sample Preparation

Water:

Samples from the lake and the river were digested using a Nitric Acid digestion with a sample volume of 100ml (Standard Methods A.P.H.A.). After digestion of the sample was complete, the samples were filtered with a 0.45 micron filtering apparatus (Standard Methods A.P.H.A.) and then diluted to a final volume of 100ml. All of the samples had duplicates prepared.

Sediment:

Samples were placed in drying dishes and put in an oven at 105 C for approximately 12 hrs to dry. The dried sample was then weighed out to approximately 1.0000g and digested in a nitric acid digestion (Weeber 1986). All of the samples were filtered and diluted to a final volume of 100ml. Duplicates were also prepared.

Aquatic Plant:

Samples had wet weight data collected on each individual sample. The sample was then placed in drying dishes and dried at 105 C for 12 hrs. Once dried, the samples were again weighed to obtain a dry weight/wet weight ratio. Approximately 1.0000g dried samples were weighed out and digested in a nitric acid digestion (Weeber 1986). The samples were filtered and diluted to a final volume of 100ml. Duplicates were prepared.

Periphyton:

The six plexiglass slides from each of the substrates were scraped to collect the sample. Each sample was placed in a drying dish, keeping each substrate separate, and dried at 85 C for approximately 12 hrs. After drying, a 1.0000g sample was weighed out and digested in a nitric acid/30% hydrogen peroxidedigestion (Stevens 1986). In some cases there was not enough sample to obtain 1.0000g; therefore, duplicates could not be prepared. The samples were filtered and diluted to a final volume of 50ml.

Invertebrates:

Samples were removed from the 70% ethanol preservative and placed in drying dishes. They were dried at 85 C for approximately 12 hrs. The dried samples were weighed and digested in the same manner as the periphyton. In the case of these samples, 1.0000g was desired; but due to poor colonization this weight could not be obtained. Duplicates could not be prepared.

Zooplankton:

The samples were brought into the lab and separated from the ethanol solution and other organisms by gravity flow sieves. The samples were then placed in drying dishes and dried at 85 C for 12 hrs. The samples had to be watched carefully to avoid over drying and degrading the sample. The dried samples were digested and filtered in the same manner as the plant and sediment samples and diluted to a final volume of 50ml. Zooplankton samples were too small to prepare duplicates.

Fish:

The samples were defrosted and a portion of the fillet was placed in a blender and homogenized. Remaining portions of the fillet were re-frozen. The homogenized samples were weighed wet and then placed in drying dishes to dry for 12-15 hrs at 85 C. Once dried, the samples were weighed again to obtain a dry weight/wet weight ratio. A 1.0000-2.0000g sample was weighed out and digested in a nitric acid/30% hydrogen peroxide digestion (Stevens 1986). The sample was filtered and diluted to a final volume of 50ml. Duplicates were prepared for all fish samples.

All sample sets had blanks prepared to account for contamination during the digestion procedure.

Sample Analysis

All samples were analyzed for the trace metals copper, chromium, lead, and zinc using a Perkin-Elmer model 403 Flame Atomic Absorption Spectrophotometer. Set-up and operation of the instrument was according to the Perkin-Elmer model 403 operations manual. Some precautionary measures were taken on the instrument to insure smooth operation. They included: regularly cleaning the aspirator line and burner head with a 10% nitric acid solution in the sonic vibrator, bleeding the air line to remove all condensation, and cleaning the nebulizer and mixing chamber to insure uniform mixing of the sample with the acetylene and air.

Analysis by AAS is only as accurate as the calibration of the instrument and the preparation of the calibration standards. The preparation of the standards (Standard Methods A.P.H.A.) for each metal is very crucial in the accuracy of the final results. The range in which the instrument is calibrated is also very critical. The calibration points for each metal are as follows:

Copper standards

120 ppb
80 ppb
40 ppb
20 ppb

Chromium Standards

500 ppb
200 ppb
100 ppb
50 ppb

Lead Standards

1000 ppb
800 ppb

Zinc Standards

2000 ppb
1500 ppb

400 ppb
200 ppb

1000 ppb
500 ppb
300 ppb

Samples were run on the calibrated instrument, with three concentration readings taken, using the 100 average mode. An average of the three readings was made. A least squares fit of the calibration points was prepared and all of the averaged sample readings were corrected from this curve. Once determined from the curve, all samples had the corresponding blank average subtracted to account for contamination introduced from sample preparation.

The final step in the analysis of the data is to convert the corrected machine readings to ppm units. For the water samples, this was done by dividing the value by 1000. For the remaining samples, a conversion (eq 1) was done.

$$(X \times Y)/Z \qquad \text{Eq 1}$$

where X is the corrected concentration reading in ppb, Y is the final diluted volume of the sample, and Z is the weight of the sample used.

RESULTS

Literature (EPA reports) on the bioconcentration of metals has suggested that there is a connection between bioconcentration and the hardness/alkalinity/pH of the water. Two high school research assistants analyzed hardness, alkalinity, and pH of the Missouri River and Snyder's Bend Lake. Their results are summarized in Table 5.

The major emphasis of this research is the bioconcentration of the heavy metals- copper, chromium, lead, and zinc. For the Missouri River, Tables 1 and 2 summarize the concentrations of the four metals in sediment, water, periphyton, invertebrates, and fish. Each of the values reported in the table represents the average and standard deviation for a number of samples collected on two sampling dates between May 1987 and July 1987. The approximate number of samples for each of the north and south river sites analyzed is: sediment (6 samples), water (4 samples), periphyton (6 samples), invertebrates (6 samples), and fish (10 samples with 2 replicates of each sample).

For Snyder's Bend Lake, Tables 3 and 4 summarize the concentrations of the four metals in lake bottom sediment (three depths- top, four inches depth, and ten inches depth), water, aquatic plant, periphyton, invertebrates, zooplankton, and fish. The values reported represent the average and standard deviations for several analysis. The approximate number of samples analyzed for each of the three lake sites are: sediment (four samples for each depth), water (four samples), plant (four samples), periphyton (five samples), invertebrates (three samples), zooplankton (four samples), and fish (ten samples with two replicates of each).

The aquatic plant collected for analysis was pond weed (Genus Potamogeton). River and lake periphyton consisted primarily of diatoms and smaller numbers of filamentous green algae. Invertebrate groups present included mayflies, caddisflies, chironomids, and dragonflies/damselflies. Zooplankton samples from Snyder's Bend Lake were composed primarily of Crustaceans, Cladocerans, Rotifers, and Protozoans. Fish species collected from both study areas included Carp, Buffalo(Bigmouth and Smallmouth species), Flathead catfish (river only) and Largemouth Bass (lake only).

Table 1
Missouri River
Cu and Cr Concentrations

| Site(Sample) | [Cu] ppm | [Cr] ppm |
|---------------------|-------------|--------------|
| North River | | |
| Water | .007 ± .004 | .0095 ± .006 |
| Sediment | 14.3 ± 3.7 | 12.6 ± 2.8 |
| Periphyton | 19.0 ± 1.9 | 13.0 ± 5.6 |
| Invertebrates | 32.0 ± 7.0 | 10.6 ± 5.4 |
| Buffalo sp. | 2.28 ± 0.22 | 0.76 ± 0.35 |
| Carp | 2.40 ± 1.1 | 0.76 ± 0.43 |
| Flathead Catfish | 2.20 ± 1.0 | 0.61 ± 0.22 |
| South River | | |
| Water | .007 ± .003 | .018 ± .011 |
| Sediment | 12.9 ± 4.5 | 11.7 ± 2.4 |
| Periphyton | 25.7 ± 7.4 | 14.8 ± 3.0 |
| Invertebrates | 27.0 ± 3.0 | 4.5 ± 1.3 |
| Buffalo sp. | 2.15 ± 0.46 | 0.34 ± 0.30 |
| Carp | 2.96 ± 0.84 | 0.33 ± 0.20 |
| Flathead Catfish | 2.10 ± 0.35 | 0.27 ± 0.21 |

Table 2
Missouri River
Pb and Zn Concentration

| Site(Sample) | [Pb] ppm | [Zn] ppm |
|------------------|-------------|--------------|
| North River | | |
| Water | 0.0 - 0.2 | 0.8 ± 0.05 |
| Sediment | 8.0 - 19.6 | 60.0 ± 5.0 |
| Periphyton | 41.0 ± 14.0 | 62.0 - 129.0 |
| Invertebrates | 41.0 ± 27.0 | 233.0 ± 45.0 |
| Buffalo species | 5.40 ± 3.00 | 17.9 ± 3.50 |
| Carp | 5.20 ± 2.60 | 25.4 ± 5.60 |
| Flathead Catfish | 5.60 ± 2.10 | 22.7 ± 1.90 |
| South River | | |
| Water | 0.0 - 0.1 | 0.01 - 0.13 |
| Sediment | 10.0 - 24.0 | 58.0 ± 21.0 |
| Periphyton | 41.7 ± 17.0 | 36.0 - 113.0 |
| Invertebrates | 24.0 ± 20.0 | 233.0 ± 60.0 |
| Buffalo species | 4.30 ± 1.30 | 22.0 ± 1.20 |
| Carp | 5.00 ± 1.50 | 28.6 ± 8.40 |
| Flathead Catfish | 5.10 ± 1.70 | 25.6 ± 9.80 |

TABLE 3
Snyder's Bend Lake
Cu and Cr Concentrations

| Site (Sample) | [Cu] ppm | [Cr] ppm |
|-----------------|-------------|-------------|
| Water | | |
| Upper | .007±.004 | .006±.006 |
| Middle | .005±.005 | .001±.001 |
| Lower | .002±.001 | .005±.004 |
| Sediment | | |
| Upper Top | 11.7 ± 1.5 | 9.5 ± 1.0 |
| Upper 4" | 10.1 ± 6.2 | 10.9 ± 5.3 |
| Upper 10" | 10.9 ± 1.5 | 11.2 ± 2.0 |
| Middle Top | 3.9 ± 1.6 | 4.1 ± .8 |
| Middle 4" | 5.3 ± 4.9 | 4.1 ± .8 |
| Middle 10" | 1.6 ± .6 | 5.1 ± 1.4 |
| Lower Top | 16.5 ± 5.2 | 11.4 ± 4.0 |
| Lower 4" | 14.4 ± 2.6 | 14.4 ± 3.1 |
| Lower 10" | 14.2 ± 2.7 | 14.3 ± 2.7 |
| Plant | | |
| Upper | 11 ± 2.6 | 4.0 ± 2.9 |
| Middle | 7.1 ± 5.7 | 1.5 ± 1.2 |
| Lower | 7.0 ± 1.8 | 1.3 ± .74 |
| Periphyton | | |
| Upper | 15 ± 5 | 9.7 ± 1.6 |
| Middle | 10 ± 8 | 10.3 ± 4.3 |
| Lower | 14 ± 2 | 13.2 ± 5.1 |
| Invertebrates | | |
| Upper | 23 ± 7 | .3 ± .3 |
| Middle | 22 ± 5 | 0 - 54 |
| Lower | 27 | 0 |
| Zooplankton | | |
| Upper | 50 ± 9 | 4.6 ± .3 |
| Middle | 70 ± 9 | 7.2 ± 1.0 |
| Lower | 24 ± 6 | 5.2 ± 1.5 |
| Fish | | |
| Buffalo species | 1.19 ± .21 | .32 ± .14 |
| Carp | 1.88 ± .85 | .44 ± .17 |
| Largemouth Bass | 1.64 ± .50 | .43 ± .19 |

Table 4
Snyder's Bend Lake
Pb and Zn Concentrations

| Site (Sample) | [Pb] ppm | [Zn] ppm |
|----------------------|-------------|-------------|
| Water | | |
| Upper | 0 - .04 | .044 ± .035 |
| Middle | 0 | .031 ± .020 |
| Lower | 0 | .016 ± .011 |
| Sediment | | |
| Upper Top | 12.7 ± 7.9 | 46 ± 8 |
| Upper 4" | 21.4 ± 5.9 | 38 ± 10 |
| Upper 10" | 23.9 ± 7.5 | 41 ± 3 |
| Middle Top | 26.9 ± 6.6 | 22 ± 3 |
| Middle 4" | 24.4 ± 5.2 | 20 ± 3 |
| Middle 10" | 17.8 ± 3.6 | 18 ± 2 |
| Lower Top | 18.8 ± 11.4 | 57 ± 6 |
| Lower 4" | 16.7 ± 12.3 | 54 ± 11 |
| Lower 10" | 26.4 ± 10.4 | 46 ± 13 |
| Plant | | |
| Upper | 19 ± 2 | 33 ± 7 |
| Middle | 15 ± 4 | 30 ± 13 |
| Lower | 14 ± 5 | 38 ± 9 |
| Periphyton | | |
| Upper | 37 ± 7 | 74 ± 28 |
| Middle | 48 ± 22 | 129 ± 40 |
| Lower | 40 ± 7 | 104 ± 12 |
| Invertebrates | | |
| Upper | 25 ± 12 | (275 - 579) |
| Middle | 43 ± 12 | (421 - 650) |
| Lower | 15 | (730 - 300) |
| Zooplankton | | |
| Upper | 39 ± 29 | 198 ± 32 |
| Middle | 76 ± 31 | 275 ± 82 |
| Lower | 47 ± 19 | 52 ± 5 |
| Fish | | |
| Buffalo species | 3.18 ± 1.03 | 16.3 ± 2.3 |
| Carp | 2.39 ± 1.05 | 23.4 ± 6.2 |
| Largemouth Bass | 2.86 ± 1.25 | 22.1 ± 2.8 |

Table 5
 Hardness, Alkalinities and pH
 of the Missouri River
 and Snyder Bend Lake
 Summer 1987

Alkalinities

| <u>Date</u> | <u>Site</u> | <u>Hardness</u> | <u>Carb.</u> | <u>Bicarb.</u> | <u>Total</u> | <u>pH</u> |
|-------------|-------------|-----------------|--------------|----------------|--------------|-----------|
| 06/21 | Upper Lake | 267 | 1.3 | 163 | 164 | 8.3 |
| 06/21 | Middle Lake | 238 | 0.0 | 151 | 151 | 8.2 |
| 06/21 | Lower Lake | 218 | 8.6 | 132 | 140 | 8.8 |
| 06/21 | Lake Ave. | 246 | 3.3 | 149 | 152 | 8.4 |
| 07/15 | Upper Lake | 271 | 3.0 | 168 | 171 | n/a |
| 07/15 | Middle Lake | 240 | 1.0 | 153 | 154 | n/a |
| 07/15 | Lower Lake | 227 | 4.5 | 145 | 149 | n/a |
| 07/15 | Lake Ave | 246 | 2.8 | 155 | 158 | n/a |
| 06/22 | North River | 261 | 1.6 | 158 | 160 | 8.4 |
| 06/22 | South River | 276 | 2.4 | 168 | 170 | 8.4 |
| 07/14 | North River | 271 | 5.0 | 161 | 166 | n/a |
| 07/14 | South River | 278 | 3.0 | 172 | 175 | n/a |

Discussion

Missouri River

In the 1986 summer SEURP study (Stevens) of the Missouri River, differences were noted between the north (control) and the south sites with the south site showing higher metal concentrations in invertebrates and periphyton. In this study the much larger number of samples allowed a thorough statistical comparison of the north and south river sites. The current data suggests that there is no difference between the two sites for any of the metals. This was true for all of the samples mentioned, i.e. sediment, water, periphyton, invertebrates, and fish. The summer 1986 study (Stevens) also detected no north/south differences for fish, but this was expected since fish have a very large range compared to the simpler organisms. In this study no difference was found in metal concentrations between the three fish species studied- Buffalo, Carp, and Flathead Catfish- even though these species have very different feeding habits.

Snyder's Bend Lake

The lake was sampled in its upper, middle, and lower regions. A comparison by site of the data in Tables 3 and 4 showed no site differences in metal concentrations for water, periphyton, plant, invertebrates, or zooplankton. Metal concentrations of copper, chromium, and zinc were significantly lower in sediment samples collected at the middle lake site. Sediment samples taken at the surface of the lake bottom sediment and at depths of four inches and ten inches showed no variation with depth for any of the metals. Fish were collected from the entire lake so no site-to-site comparison could be made. A comparison of the three fish species- Buffalo, Carp, and Largemouth Bass- showed no variation of metal concentrations between species even though the three species have different feeding habits.

Missouri River/Snyder's Bend Lake Comparison

The samples taken from the river and the lake had very similar metal concentrations for most of the communities monitored. No differences were observed for sediment and periphyton samples. For invertebrates, chromium and zinc were lower in the lake, although the difference was not substantial. For fish the only statistically significant differences appear in Buffalo, which had a lower copper level for lake. The averages for lead, chromium, and copper for the lake were consistently lower than the river, but there was no statistically significant difference. (Two samples were determined to be statistically different if the ranges, defined as the standard deviation, about the average did not overlap. For example, two readings of 4 ± 1 and 7 ± 1 would have been statistically different while readings of 4.5 ± 1.5 and 6.0 ± 2.0 would have been statistically identical.)

Hardness, Alkalinity, and pH

Values for hardness and alkalinity were slightly higher for the river than the lake. One exception was the values observed at the upper lake site, which

is influenced by the incoming Missouri River water. River versus lake values at this site were nearly identical. pH levels were similar for both lake and river.

As stated in the literature, the toxicity of copper, chromium, lead, and zinc decreases with increasing water hardness and pH (U.S. E.P.A.). This is due in part to the tendency of metal ions to precipitate out of the water solution when more carbonate ions are available. Hardness values are now used when determining the ambient water quality criteria for each respective metal.

The observed hardness and pH/alkalinity values from this study are at the high range of values reported in the literature. At these levels the toxic effects of these heavy metals is considered to be less severe.

Bioconcentration Factors

Bioconcentration factors (BCF's) were calculated by dividing the metal concentration of a given sample, e.g., river periphyton, by the metal concentration of the water. Bioconcentration factors for the Missouri River and Snyder's Bend Lake are listed in Table 6.

Although each metal had its own distinctive trend of bioconcentration through the biological communities, there were some general trends that should be noted. For Snyder's Bend Lake, the fish and aquatic plant consistently had the lowest BCF's. Zooplankton had either the largest or the next-to-largest BCF's for each of the metals. A summer 1986 SEURP study of metals in New Lake (Weeber) was more limited but showed similar trends. In that study, bioconcentration factors increased going from periphyton to zooplankton for copper, lead, and zinc. For chromium, Weeber found periphyton to have a higher BCF than zooplankton. The present study found this same trend. Weeber's results are summarized in Table 8 and are seen to be very similar to the values reported for this study.

For the Missouri River each metal had its own distinctive trend of bioconcentration through the biological communities. However, there were general trends common to all metals. Fish always had the lowest BCF's, but periphyton or invertebrates were equally likely to have the highest BCF's. (See Table 6). BCF's calculated from the summer 1986 SEURP study of the Missouri River (Stevens, Conklin) showed exactly the same trends and similar BCF's as compared with this study. BCF's calculated from summer 1986 data are summarized in Table 9.

An extensive review of the heavy metals literature was completed by the U.S. Environmental Protection Agency in 1984 (EPA Reports- Copper, Chromium, Lead, Zinc). Although much information is available on the toxicity of the metals, there is very little which is reported on BCF's for fresh water environments. Table 7 summarizes the literature results as found in the EPA reports. A comparison of our data with the EPA reports shows similar BCF's for periphyton and invertebrates. Our BCF's for fish and zooplankton are consistently higher than the literature values.

Table 6
 Bioconcentration Factors
 in the
 Missouri River and Snyder Bend Lake

| | Cu | Cr | Pb | Zn |
|-------|---|---|--|---|
| River | fish(340) peri(3200) inv.(4200) | fish(40) inv.(550) peri(1000) | fish(170) inv.(1100) peri(1400) | fish(530) peri(1100) inv.(5200) |
| Lake | fish(300) plant(1800) peri(2000) inv.(5000) zoo(10,000) | fish(100) inv.(170) plant(570) zoo(1400) peri(2800) | fish(140) plant(800) inv.(1400) peri(2100) zoo(2700) | fish(690) plant(1100) peri(3400) zoo(5800) inv.(16,000) |

peri = periphyton
 inv. = invertebrates
 zoo = zooplankton

Table 7
Literature Bioconcentration Factors

| Species | Metal | | | |
|---------------|-----------|---------|----------|----------|
| | Cu | Cr | Pb | Zn |
| Periphyton | 2000-4000 | | | |
| Invertebrates | 203 | | 499-1120 | 107-1130 |
| Fish | 1.0 | < 1-2.8 | 42-45 | 51-432 |
| Zooplankton | 471 | | | |

Table 8
 Summer 1986
 Bioconcentration for New Lake(Weeber)

Community (BCF)

| Cu | Cr | Pb | Zn |
|------------------------|-------------------------|------------------------|-------------------------|
| peri(600) zoo(8500) | zoo(3800) peri(6500) | peri(100) zoo(1500) | peri(1800) zoo(6400) |

Table 9
 Summer 1986
 Study of Bioconcentration Factors
 for the Missouri River(Stevens, Conklin).

Community (BCF)

| Cu | Cr | Pb | Zn |
|---|---|--|---|
| Carp(650) Buffalo(800) Catfish(600) | Carp(200) Buffalo(200) Catfish(200) | Carp(80) Buffalo(80) Catfish(80) | Carp(600) Buffalo(300) Catfish(400) |
| peri(3000) | inv(700) | peri(400) | peri(550) |
| inv(5000) | peri(1700) | inv(500) | inv(650) |

peri = periphyton
 inv = invertebrates

Conclusions

This study is an extension of the summer 1986 SEURP study. For the river study the numbers of samples of periphyton and invertebrates were increased. Sediment samples were taken for the first time and the number of fish species was reduced from five to three while the number of samples per species was increased to ten (with two replicates each). The limited data in the 1986 study had suggested that a north/south difference was present. With the increased number of samples in this study an improved statistical comparison of the north and south river sites was possible. No statistical differences were detected for any of the biological communities. The general trends of bioconcentration of the four metals through the food chain founds in the 1986 study were verified in this study.

The study of Snyder's Bend Lake was new. Sampling techniques that were tested on New Lake in 1986 were improved and the number of biological communities observed was expanded. A complete profile of bioconcentration of metals through the food chain of the lake was obtained.

The concentrations of the four metals in the waters of the River and Snyder's Bend Lake were found to be well below the federal water quality standards.

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