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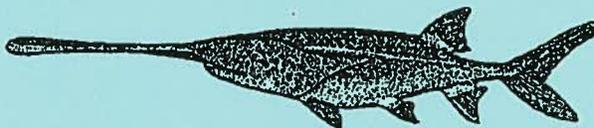


U.S. FISH & WILDLIFE SERVICE
REGION 6

CONTAMINANTS PROGRAM

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CONCENTRATIONS OF INORGANIC AND
ORGANIC CHEMICALS IN FISH AND
SEDIMENTS FROM MAJOR TRIBUTARIES
OF THE MISSOURI RIVER IN
NORTH DAKOTA, 1989-91



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U.S. FISH AND WILDLIFE SERVICE
Ecological Services
1500 Capital Avenue
Bismarck, North Dakota 58501

December 1993

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ABSTRACT

Fish and sediments from the Missouri River and its major tributaries in North Dakota were collected in 1989 and 1991 and analyzed for organochlorines, petroleum hydrocarbons, and elements. Concentrations of organochlorine pesticides and PCB's were generally below detection limits in fish and sediments. Sediment samples were not contaminated with petroleum. Indicators of petroleum contamination gave conflicting results. However, these conflicts probably resulted from inapplicability of several indicators rather than from petroleum contamination. Laboratory confirmation of the applicability of these indicators to freshwater fish would aid interpretation of tissue concentrations of aliphatic and aromatic hydrocarbons.

Concentrations of elements in fish were compared to national averages and percentiles available from the U.S. Fish and Wildlife Service's (Service) National Contaminant Biomonitoring Program (NCBP). Concentrations of arsenic, cadmium, and mercury were not elevated in the tributaries. However, arsenic and cadmium concentrations tended to be elevated in sediments. Zinc concentrations were not elevated except at sites where common carp were analyzed. Results of the NCBP indicate that carp tend to contain higher concentrations of zinc than most other freshwater fish species, so the elevated zinc levels in carp probably do not indicate environmental contamination.

Mercury concentrations in fish were elevated at Garrison Dam on the Missouri River, a result consistent with results of NCBP samples from that site. These concentrations were below levels associated with toxicity. Concentrations of copper, lead, and selenium were elevated in fish from several tributaries, but were also below levels associated with toxicity. These elevated concentrations are probably not due to point sources of contamination because few point sources exist along the western tributaries of the Missouri River in North Dakota. Non-point source contamination from energy development, agriculture, and erosion probably plays a larger role than point source contamination. Use of lead fishing gear may also contribute to elevated lead concentrations in fish from the tributaries. Energy development, agriculture, and other activities that may mobilize potentially toxic elements from soils in the watershed should be managed to minimize contamination of aquatic systems. This management need is greatest for selenium because the margin of safety between selenium concentrations in the fish samples and concentrations associated with toxicity was narrow.

INTRODUCTION

Concern for endangered species has led to increased emphasis by the U.S. Fish and Wildlife Service (Service) on identifying contaminant problems in the Missouri River and its tributaries. The pallid sturgeon (*Scaphirhynchus albus*), bald eagle (*Haliaeetus leucocephalus*), interior least tern (*Sterna antillarum*), piping plover (*Charadrius melodus*), peregrine falcon (*Falco peregrinus*), and whooping crane (*Grus americana*) are the federally listed threatened and endangered species found along the Missouri River in North Dakota. The blue sucker (*Cypleptus elongatus*), sturgeon chub (*Hybopsis gelida*), sicklefin chub (*H. meeki*), and paddlefish (*Polyodon spathula*) occur in the Missouri River and its tributaries and are category 2 candidates for listing as threatened or endangered species.

Declines in populations of endangered, threatened, and candidate species of fish in the Missouri River system may be primarily due to physical habitat alteration, but the hypothesis that chemical contaminants are partially responsible has not been ruled out. Little information is available to assess the degree of contamination of aquatic resources in the main tributaries of the Missouri River in North Dakota. These tributaries provide nutrients and water flows important to species endemic to the Missouri River system.

The objectives of this study were to determine baseline chemical concentrations in common bottom-feeding fish from major tributaries of the Missouri River in North Dakota, and to estimate from these data whether rare bottom-feeding fish are at risk of chemical contamination.

STUDY AREA

Tributaries of the Missouri River in North Dakota range from unnamed intermittent streams to large rivers. The U.S. Geological Survey monitors discharge rates and water quality of the largest tributaries, including 13 streams that have their confluence with the Missouri River within North Dakota (Table 1). The Yellowstone River is by far the largest of these tributaries, and was the subject of a previous contaminants study (Welsh 1992). The James River, a major tributary that originates in central North Dakota and has its confluence with the Missouri River in South Dakota, was also the subject of a previous report (USFWS 1989).

The five tributaries (Little Missouri River, Heart River, Cannonball River, Knife River, and Square Butte Creek) studied for this report drain into the Missouri River from the west and southwest (Figure 1). The combined flows of these tributaries equal only about 10 percent of the flow of the Yellowstone River, but drain an area of approximately 58,000 km². This drainage area includes almost all of southwestern North Dakota and portions of eastern Montana, northwestern South Dakota, and northeastern Wyoming. This drainage area includes most major oil and coal extraction areas in North Dakota, and also is utilized extensively for production of small grains and livestock.

METHODS

1989

Between June 27 and July 25, fish were captured with gill nets or electrofishing gear from the Cannonball River, Heart River, Knife River, Square Butte Creek, and the tailrace area below Garrison Dam on the Missouri River (Figure 1). Electrofishing gear was used in the tailrace, and monofilament gill nets were used at the other sites. Fish were collected in the lower reaches of each tributary at sites between the confluence with the Missouri River and 3 to 7 km upstream.

Individual common carp (*Cyprinus carpio*) and river carpsuckers (*Carpionodes carpio*) selected as samples were weighed to the nearest gram, wrapped in labeled polyethylene bags or aluminum foil, and placed on ice in an insulated cooler during transport to a freezer. Channel catfish (*Ictalurus punctatus*) and blue suckers also were selected for analysis if insufficient numbers of carp or carpsuckers were captured. Samples were shipped frozen on dry ice to analytical laboratories.

Two sediment samples, one for organic analyses and one for inorganic analyses, were collected from each tributary near its confluence with the Missouri River. Each sample consisted of several subsamples collected with a stainless steel transplanter from exposed banks or sandbars.

Separate fish and sediment samples were submitted for organic and inorganic analyses. Organic analyses included organochlorines, aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAH). Organic analyses were done by the Mississippi State Chemical Laboratory. Quantitative analyses for organic chemicals were performed using capillary gas chromatography (CGC) with electron capture detector for pesticides and PCB's, CGC with a flame ionization detector for aliphatic hydrocarbons, and CGC with confirmation from a mass spectrometer for aromatic hydrocarbons.

Analyses for inorganics were done at Hazleton Laboratories America, Inc., Madison, Wisconsin. Atomic absorption spectrophotometry (AAS) was used to determine arsenic, mercury, molybdenum, and selenium concentrations. Concentrations of other elements were determined using inductively-coupled plasma emission spectrophotometry (ICP).

Both laboratories performed standard quality assurance/quality control (QA/QC) analyses of duplicate samples, spiked samples, standard reference materials, and procedural blanks. The accuracy of organic and inorganic analyses, as measured by spike recovery analysis, was acceptable for most analytes. Percent recovery of hexachlorobenzene (HCB) was low (60%) in spiked fish samples, and percent recovery of n-dodecane was low (45%) in spiked sediment. Analytical results cannot be considered quantitative for these analytes. The precision, as measured by duplicate sample analysis, was acceptable for all organic and inorganic analytes.

1991

River carpsuckers were collected from the Cannonball, Heart, Knife, and Little Missouri Rivers in 1991 (Figure 1). These fish were collected with gill nets or hoop nets between June 25 and August 14. Sampling sites were located in the lower reaches of the tributaries, 0.2 to 8.0 km upstream of their confluences with the Missouri River. Each fish was weighed to the nearest ten grams and measured for total length to the nearest millimeter (Table 2). All specimens were analyzed as individual whole-body samples.

Fish samples were analyzed by AAS for arsenic, mercury, and selenium, and by ICP scan for other elements at Research Triangle Institute, North Carolina. These samples were not analyzed for organic chemicals. The same QA/QC analyses performed in 1989 were performed in 1991. Results of analyses of spiked samples for aluminum were highly heterogeneous, so aluminum results from 1991 are not included in this report.

RESULTS AND DISCUSSION

Organic Analyses, 1989

A) Organochlorine Pesticides and PCBs

Since 1967, the National Contaminant Biomonitoring Program (NCBP) has monitored concentrations of organochlorines, arsenic, cadmium, copper, lead, mercury, selenium, and zinc in fish from major rivers throughout the United States and in the Great Lakes (Walsh et al. 1977; Schmitt et al. 1981, 1985; Schmitt and Brumbaugh 1990). The NCBP documents temporal and geographic trends in concentrations of contaminants and identifies potential toxic threats to fish and wildlife (Schmitt and Brumbaugh 1990). Concentrations of a potential contaminant are considered elevated when they exceed the 85th percentile (NCBP-85th) of the nationwide geometric mean (Lowe et al. 1985). The NCBP-85th percentile values are not based on toxicity levels or regulatory standards. However, they provide a frame of reference to help identify contaminants of potential concern.

Concentrations of most organochlorines were at or below detection limits in fish samples (Table 3). The main exception was *p,p'*-DDE, a metabolite of the pesticide DDT. This pesticide was banned from use in the United States in 1972, partly because of its adverse effects on wildlife reproduction (Fleming and Clark 1983). All fish samples contained detectable concentrations of *p,p'*-DDE, three samples contained detectable concentrations of *p,p'*-DDD, and one sample contained *p,p'*-DDT.

Because they are stable and lipophilic, DDT and its metabolites persist in biota. For example, the *p,p'* isomers of DDT, DDE, and DDD were detected in fish from 88, 98, and 97%, respectively, of the 112 stations sampled in the NCBP in 1984 (Schmitt et al. 1990). The nationwide geometric mean concentration of *p,p'*-DDE in fish from the NCBP in 1984 was 0.19 $\mu\text{g/g}$, wet-wt (Schmitt et al. 1990). In contrast, concentrations in fish from this study were only 0.01 to 0.10 $\mu\text{g/g}$.

Like DDT, PCBs can persist in the environment for 20 to 30 years after a release. Prior to a nationwide ban on PCB use in 1979, primary uses of PCBs included transformer fluids, gas turbine lubricants, hydraulic fluids, and plasticizers. PCBs include over 200 closely related compounds, and are classified by the trade name Aroclor followed by a numerical code indicating, in part, the percent contribution of chlorine to the molecular weight of the compound (e.g., Aroclor 1248 is 48 percent chlorine).

Aroclors 1248, 1254, and 1260 were detected in fish from 42.9, 65.2, and 86.6 percent, respectively, of the stations sampled in the NCBP in 1984 (Schmitt et al. 1990). Total PCBs (all Aroclors combined) were detected in fish from 91.1 percent of the NCBP stations in 1984. The nationwide geometric mean concentration of total PCBs in 1984 was $0.39 \mu\text{g/g}$, wet-wt. Only one fish sample from this study contained detectable PCBs, and total PCBs in that sample were less than the national geometric mean.

With the exception of the sample from the Heart River, no organochlorine pesticides or PCBs were detected in sediment samples. The sample from Heart River contained $0.01 \mu\text{g/g}$, wet-wt *p,p'*-DDE, but did not contain detectable concentrations of other organochlorines. In summary, neither sediment nor fish samples were highly contaminated with organochlorines.

B) Aliphatic and Aromatic Hydrocarbons

Interpretation of tissue hydrocarbon residues is difficult and often yields conflicting results due to the variety of chemicals in petroleum products, the many similar compounds that occur naturally in animal tissues, and the ability of many animals to metabolize and excrete hydrocarbons (Hall and Coon 1988). However, indicators of exposure to petroleum hydrocarbons include:

- 1) High total aliphatic hydrocarbon concentrations
- 2) Low ratios of odd-numbered aliphatic hydrocarbons to even numbered hydrocarbons
- 3) High ratios of phytane to pristane
- 4) Low ratios of n-C17 to pristane and n-C18 to phytane
- 5) The presence of aromatic compounds

Concentrations of hydrocarbons can be as much as 10-fold greater in tissues of animals exposed to oil than in unexposed controls (Hall and Coon 1988). Total aliphatic hydrocarbon (C-10 to C-30) concentrations in cutthroat trout (*Salmo clarki*) negatively affected by crude oil were $4.63 \mu\text{g/g}$, wet-wt (Woodward et al. 1981). With one exception, total unbranched aliphatic hydrocarbon (C-12 to C-20) concentrations in fish from tributaries of the Missouri River were 3 to 20 times greater than $4.63 \mu\text{g/g}$ (Table 4). The only sample under $4.63 \mu\text{g/g}$ was the catfish sample from the Cannonball River at $0.81 \mu\text{g/g}$. In contrast to the catfish, river carpsuckers from the Cannonball River contained $85.4 \mu\text{g/g}$ total aliphatic hydrocarbons. These results suggest that fish from all of the tributaries and Garrison Dam had recently been exposed to petroleum. However, aliphatic hydrocarbon concentrations in sediment samples were low and do not indicate existence of point sources of petroleum contamination in the vicinity of sample collection sites (Table 5).

Total aliphatic hydrocarbon (C-12 to C-20) concentrations in Missouri River fish from Kansas and Nebraska ranged from 0.59 to 28.82 $\mu\text{g/g}$ (Allen and Wilson 1991). In that study, total aliphatic hydrocarbon concentrations varied widely between species collected at the same site. For example, concentrations in fish samples from Gavins Point Dam, Nebraska, ranged from 0.69 $\mu\text{g/g}$ in channel catfish to 28.82 $\mu\text{g/g}$ in common carp. The seemingly high concentrations of total aliphatic hydrocarbons in the fish samples from North Dakota may be due to species differences in natural levels of biogenically produced hydrocarbons rather than to contamination with petroleum.

Aliphatic hydrocarbons with odd numbers of carbon atoms (C-13, C-15, C-17, and C-19) occur naturally in plant and animal tissues, but even-numbered aliphatics are rare in uncontaminated tissue samples. In contrast, petroleum products typically contain approximately equal ratios of odd and even numbered aliphatic hydrocarbons (Farrington et al. 1973). Odd-numbered aliphatics predominated in our fish samples, suggesting that hydrocarbons were natural components of fish tissue and contamination with petroleum was not a problem (Table 4).

Phytane and pristane are branched aliphatics that occur frequently in petroleum products and are metabolized less readily than straight-chain aliphatics (Hall and Coon 1988). Pristane is a common biogenic hydrocarbon in biota and sediments, whereas phytane is rare in un-oiled matrices (Malins 1977a,b; National Research Council 1985). High ratios of pristane to phytane may indicate an un-oiled sample, and low ratios of pristane to phytane may indicate contamination with oil. High ratios of pristane to n-C17 and phytane to n-C18 may indicate chronic exposure to petroleum because pristane and phytane are metabolized less readily than the straight chain compounds (Farrington et al. 1973, Anderson et al. 1978, Hall and Coon 1988).

Phytane was detected in all of the fish samples (Table 4). However, pristane concentrations were below detection limits ($<0.01 \mu\text{g/g}$) in 8 of 10 samples, making it impossible to calculate most pristane:phytane ratios. The preponderance of phytane over pristane in all but one sample suggests that fish in these samples had been exposed to oil. Pristane also was not detected in many whole-body fish samples from the Savannah River drainage (Winger et al. 1990), so it may not be common in all species of fish. The ratios of phytane to n-C18 ranged from 0.12 to 2.27. Phytane concentrations exceeded n-C18 concentrations in 4 of 10 samples, suggesting possible petroleum contamination of the Knife, Cannonball, and Little Missouri Rivers.

Aromatic hydrocarbons are usually not detected in tissues of animals that have not been exposed to petroleum (Hall and Coon 1988). Concentrations of the 13 aromatic compounds included in analyses of fish and sediment samples were usually at or below 0.01 $\mu\text{g/g}$, the detection limit of the analytical technique (Table 4). Naphthalene was the most commonly detected aromatic compound in fish and sediments. Phenanthrene and benzo(a)pyrene were also detectable in several fish samples, and fluoranthrene, pyrene, and benzo(a)pyrene in several sediment samples. All detectable concentrations of aromatics were at or only slightly above the detection limit and do not indicate contamination with petroleum.

The high ratios of odd to even numbered aliphatics and near absence of aromatic compounds indicate that fish and sediment were not contaminated with petroleum. However, this conclusion is weakened by high total aliphatic hydrocarbon concentrations and pristane:phytane ratios indicative of exposure to petroleum. The validity of these techniques for interpreting tissue hydrocarbon concentrations should be evaluated in the laboratory with common fish of the Missouri River system. Most of the guidelines for interpreting hydrocarbon residues in animals come from studies of marine animals, and their applicability to freshwater fish is questionable. Controlled laboratory studies in which Missouri River fish are exposed to petroleum and analyzed for aliphatic and aromatic hydrocarbons would help resolve this uncertainty. These laboratory studies would be useful references for the Service's Environmental Contaminants Specialists, especially those tasked with conducting natural resource damage assessments following oil spills in inland waters.

Inorganic Analyses, 1989 and 1991

A) Fish

Results of inorganic analyses are presented on a wet-weight basis for comparison to the NCBP and on a dry-weight basis for comparison to other published literature (Tables 6 and 7). Mean concentrations of arsenic, cadmium, and mercury were below the NCBP-85th percentile concentrations in fish from the tributaries (Table 6). These results suggest that the lower reaches of the tributaries do not contain elevated concentrations of these elements.

The mercury concentration in the carp sample from the Garrison Dam tailrace exceeded the NCBP-85th percentile. The tailrace is one of the NCBP sampling sites in North Dakota, and this result is consistent with past NCBP data from this site. Mercury concentrations in fish from the tailrace have typically been among the highest in the NCBP.

Copper, lead, and selenium concentrations were elevated in fish from several of the tributaries in one or more years (Table 6). Copper is a fairly common element in soils and sediments but is usually present at low concentrations in vertebrates due to homeostatic regulation (Hill 1977). Maximum copper concentrations in fish from the NCBP have been as high as 38.7 $\mu\text{g/g}$, wet-wt, but concentrations are usually below 1.0 $\mu\text{g/g}$. Mean copper concentrations were elevated (>1.0 $\mu\text{g/g}$, wet-wt) in fish from the Cannonball River, Knife River, and Square Butte Creek in one or both years. However, these means were only slightly above the NCBP-85th percentile value and do not indicate a contaminants problem.

Detection limits of lead analyses were too high (0.3 $\mu\text{g/g}$, wet-wt) to allow comparison of 1989 data with NCBP results. Lead concentrations were elevated in fish from the Cannonball, Heart, Knife, and Little Missouri Rivers in 1991 (Table 6). Lead also was identified as a contaminant of concern in the Missouri River system after a preliminary survey of contaminants in shovelnose sturgeon (*Scaphirhynchus platorhynchus*) collected from the confluence of the Yellowstone and Missouri Rivers in 1988 indicated elevated (>10 $\mu\text{g/g}$, wet-wt)

concentrations of lead (Welsh 1992). However, a more detailed study involving sturgeon and other species of fish did not indicate lead contamination at that site in 1990 (Welsh 1992).

Lead has no physiological role in animals, and is highly toxic. Toxicity of lead includes effects on the hematopoietic, vascular, nervous, renal, and reproductive systems (Eisler 1988). The primary sources of lead in the environment are mining and smelting, hunting and fishing, manufacture and combustion of leaded gasoline, and manufacture and recycling of batteries (Eisler 1988). Sediments of lakes, rivers, and oceans are the ultimate sink for lead in the environment (Eisler 1988). In recent years, lead content of gasoline has been reduced and use of lead shot by waterfowl hunters has been banned. However, many areas still contain sediments contaminated with lead, and bottom feeding fish are likely to be exposed to contaminated sediment.

The source of lead contamination of fish from Missouri River tributaries is unknown. The nearest lead smelters are over 600 miles west in Helena, Montana. Potential sources of lead in the Missouri River system include lead shot, fishing weights, and refineries. The only active refinery in North Dakota is the Amoco Refinery along the Missouri River in Mandan.

The Amoco Refinery has a North Dakota Pollutant Discharge Elimination System (NDPDES) permit to discharge water from an aerobic wastewater treatment lagoon to the Heart River. Between 1954 and 1978, effluent from this lagoon was discharged directly into the Heart River. Routine permitted discharges from the lagoon now go to the Missouri River, and the Heart River discharge point is used only for overflow water. Overflow discharges are infrequent and probably do not cause elevated lead concentrations in fish from the Heart River. Few other potential point sources of lead exist in the Cannonball, Heart, Knife, or Little Missouri River watersheds.

The confluence areas of the tributaries with the Missouri River are used for sport fishing, and lead fishing gear is deposited in the rivers as a result. The bioavailability of this lead and its importance as a source of elevated lead concentrations in fish are unknown. Additional studies will be necessary before effects of lead fishing gear can be separated from effects of energy development, agriculture, erosion and other potential nonpoint sources of lead in the watersheds.

Selenium concentrations were not elevated in any fish samples from 1989 (Table 6). However, mean selenium concentrations exceeded the NCBP-85th percentile (0.73 $\mu\text{g/g}$, wet-wt) in fish from the Cannonball, Heart, Knife, and Little Missouri Rivers in 1991. Selenium is an essential trace element in the diet of fish, but excessive amounts can be toxic. Toxic effects of selenium in fish include reproductive impairment and mortality of juveniles and adults (Lemly and Smith 1987). Fish that contain selenium concentrations greater than 2 to 3 $\mu\text{g/g}$, wet-wt may suffer reproductive impairment, including malformations or death of embryos during development (Baumann and May 1984, Lemly 1985, Gillespie and Baumann 1986, Lemly and Smith 1987, Hermanutz et al. 1992).

Although mean concentrations of selenium exceeded the NCBP-85th percentile in 1991, all mean concentrations were below the 2-3 $\mu\text{g/g}$ associated with the onset of toxicity. With one exception, maximum concentrations of selenium also were below toxic concern levels. The exception was a carpsucker from the Heart River that contained 2.3 $\mu\text{g/g}$ selenium. This concentration is at the low end of the range of concentrations associated with the onset of toxicity in sensitive species of fish.

Selenium sensitivity of carpsuckers and most other native species of fish in the Missouri River is unknown, and could be greater or lesser than sensitivity of commonly studied species. The results of this study indicate that fish from North Dakota tributaries of the Missouri River contain elevated but subtoxic concentrations of selenium. Depending on their sensitivity to selenium, native species may have a narrow margin of safety with regard to selenium toxicity. Therefore, activities that have the potential to mobilize selenium in the watersheds of these rivers should be carefully managed to minimize selenium contamination of fish.

The remaining 12 elements included in the ICP scan were not included in the NCBP, and few guidelines are available to aid in interpretation of tissue residue data. Allen and Wilson (1991) reported on element concentrations in several species of fish from the Missouri River in Kansas and Nebraska. In that study, ranges of element concentrations ($\mu\text{g/g}$, dry-wt) in whole-body samples of bottom-feeding fish were as follows: aluminum, 16-363; beryllium, <0.01-0.05; chromium, 0.39-8.2; iron, 69-1770; manganese, 8.1-166; nickel, 0.3-6.7.

Mean concentrations of several elements in fish from North Dakota tributaries of the Missouri River exceeded the ranges from Allen and Wilson's study. These elevated mean concentrations included aluminum at Square Butte Creek in 1989 (385 $\mu\text{g/g}$, dry-wt), chromium at Cannonball River in 1991 (9.06 $\mu\text{g/g}$, dry-wt), and nickel at Knife River in 1989 (8.93 $\mu\text{g/g}$, dry-wt). Nickel concentrations in fish from the Knife River in 1989 also exceeded the 2.0 $\mu\text{g/g}$, wet-wt concentration considered normal for fish from unpolluted locations (Jenkins 1980). However, results from 1991 did not indicate problems with nickel contamination.

Eisler (1986) considered dry weight concentrations of 4.0 $\mu\text{g/g}$ or higher to be evidence of chromium contamination. The 4.0 $\mu\text{g/g}$ guideline was exceeded in fish from the Cannonball and Knife Rivers in 1991, but not in 1989. Chromium concentrations of 14 to 17 $\mu\text{g/g}$ (dry-wt) have been reported in fish of various species from locations in the Great Plains, but the health of these fish was not assessed (Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988). Chromium concentrations may be elevated in bottom-feeding fish from the Cannonball and Knife Rivers. Alternatively, normal background concentrations of chromium may be higher in carpsuckers than in other fish. More studies such as this one and that of Allen and Wilson (1991) should help establish background element concentrations in indigenous Missouri River fish.

B) Sediment

Wiener et al. (1984) determined concentrations ($\mu\text{g/g}$, dry-wt) of arsenic, cadmium, mercury, lead, and manganese in sediments from the upper Mississippi River. Overall means (with minima and maxima) from that study were as follows:

Arsenic	2.58	(0.63-6.24)
Cadmium	2.20	(0.04-15.1)
Mercury	0.048	(0.001-0.198)
Lead	13.0	(0.37-85.8)
Manganese	535	(134-1320)

Arsenic concentrations in sediments from the Missouri River and its tributaries were 2 to 15 times higher than in sediments from the upper Mississippi River (Table 8). With the exception of the sample from the Little Missouri River, sediments from the Missouri River and its tributaries contained higher cadmium concentrations than the mean for the upper Mississippi. Mercury concentrations were below detection limits except in the sample from the Little Missouri River. Manganese concentrations were in the same range as in sediments from the upper Mississippi. Lead concentrations of sediments from the Missouri River and its tributaries tended to be lower than in sediments from the upper Mississippi.

Martin and Hartman (1984) studied arsenic, cadmium, lead, mercury, and selenium in sediments from wetlands in the North Central United States, including impounded riverine sites along the Des Lacs, Souris, James, and Missouri Rivers in North Dakota. The overall mean concentrations of these elements in north-central riverine wetlands were 2.4, 0.26, 6.6, 0.03, and 0.52 $\mu\text{g/g}$, dry-wt, respectively. Compared to results of that study, sediments from the Missouri River and its tributaries contained relatively high concentrations of arsenic and cadmium and low concentrations of selenium (Table 8). The lead concentration of sediments from the Heart, Knife, and Missouri Rivers and Square Butte Creek were lower than in Martin and Hartman's study, but lead concentrations were slightly higher at the other two sites. Detection limits for mercury differed between the two studies, so comparisons are not possible.

The U.S. Department of Interior recently completed a series of studies of the impacts of irrigation drainwater on fish and wildlife in the western United States (e.g. Knapton et al. 1988, Lambing et al. 1988, Peterson et al. 1988). Numerous sediment samples were analyzed in those studies. The standard to which element concentrations in sediments from the drainwater studies were compared was the survey by Shacklette and Boerngen (1984), in which means and baseline ranges (the 95 percent confidence intervals of the means) were reported for 13 elements in soils of the western United States (Table 9). Concentrations of these 13 elements in sediment samples from the Missouri River and its tributaries were generally within the baseline range or lower, indicating that the concentrations were not elevated. The only exception was arsenic, which was elevated in the sample from the Knife River.

The elements that were present at elevated concentrations in fish samples (copper, lead, mercury, and selenium) were not elevated in sediments, and the elements that were elevated in sediments (arsenic, and cadmium) were not elevated in fish. Sampling effort may not have been adequate to provide a representative sample of sediments from each tributary, and this alone could explain the lack of correspondence between fish and sediment data. However, biological processes, such as homeostatic regulatory mechanisms and bioaccumulation, may be partly responsible.

Homeostatic regulatory mechanisms are known to control concentrations of many elements in fish tissues. Therefore, fish may be able to regulate internal concentrations of arsenic and cadmium despite elevated concentrations in the environment. Mercury and selenium are known to bioaccumulate in organisms to levels higher than their concentrations in the environment. Bioaccumulation is a complex process that is affected by physiological processing of contaminants (absorption, distribution, metabolism, and excretion), trophic status, health, and nutrition. Therefore, concentrations of contaminants in fish may not always correspond to concentrations in sediments. Future efforts to monitor contaminants in the Missouri River system should include analysis of fish tissues because sampling abiotic components of the environment may be insufficient to determine potential risks to fish from chemicals that are homeostatically regulated or bioaccumulate.

CONCLUSIONS

- Sediments and fish did not contain elevated concentrations of organochlorine pesticides or PCBs compared to national averages.
- Indicators of hydrocarbon contamination were negative for sediments, but gave conflicting results for fish.
- Guidelines for interpretation of hydrocarbon concentrations should be validated with experiments on freshwater fish.
- Copper, lead, and selenium concentrations were elevated in fish from several of the tributaries in one or both years, but were below toxic concentrations.
- Mercury concentrations were elevated in fish from the tailrace of Garrison Dam on the Missouri River, a result consistent with findings of the Service's National Contaminant Biomonitoring Program.

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Figure 1. Major tributaries of the Missouri River in North Dakota.

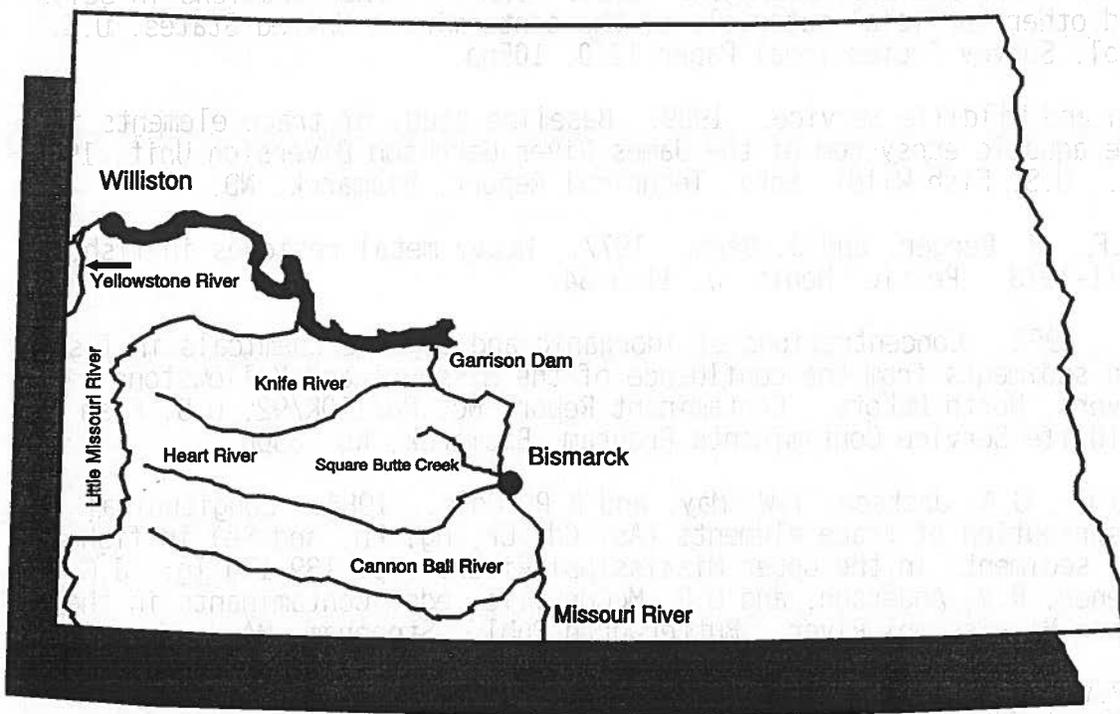


Table 1. Drainage areas and annual mean discharges of the Missouri River and its tributaries in North Dakota¹.

Stream	Drainage Area		Annual Mean Discharge		Water Year
	mi ²	km ²	ft ³ /s	L/s	
Missouri River (Garrison Dam)	181,400	469,800	23,000	651,300	1970-91
Yellowstone River (Sidney, MT)	69,100	179,000	12,790	362,200	1912-91
Little Missouri River (Watford City)	8,310	21,520	552	15,630	1935-91
Heart River (Mandan)	3,310	8,570	256	7,250	1924-91
Cannonball River (Breien)	4,100	10,620	243	6,880	1934-91
Knife River (Hazen)	2,240	5,800	172	4,870	1929-91
Little Muddy River (Williston)	875	2,270	39	1,100	1954-91
Apple Creek (Menoken)	1,680	4,350	32	906	1946-91
Painted Woods Creek (Wilton)	427	1,110	13	368	1983-90 ²
Square Butte Creek (Center)	146	378	11	311	1965-91
Burnt Creek (Bismarck)	108	280	8	226	1968-91
Bear Den Creek (Mandaree)	74	192	7	198	1966-91
Beaver Creek (Linton)	765	1,980	7	198	1990-91
Turtle Creek (Washburn)	350	906	5	142	1987-91

¹ Harkness et al. 1992

² During these years, Missouri River water was diverted into Painted Woods Creek for wildlife habitat management. Prior to diversion of Missouri River water (1958-1981) annual mean discharge was approximately 8 ft³/s.

Table 2. Lengths, weights, and moisture contents of fish collected from the Missouri River and its major North Dakota tributaries and analyzed for inorganics.

Stream/Species	Date	n	Length (mm) mean(min-max)	Weight (g) mean(min-max)	Moisture (%) mean(min-max)
<u>Cannonball</u>					
Channel Catfish	6/27/89- 6/30/89	4	---	1672 (743-3849)	76 (74-79)
River Carpsucker	7/25/91	5	397 (368-438)	790 (600-1050)	64 (58-69)
<u>Heart</u>					
River Carpsucker	6/27/89- 6/30/89	5	---	777 (521-1060)	70 (64-73)
Blue Sucker	6/27/89- 6/30/89	1	---	738	72
River Carpsucker	6/6/91	5	465 (398-566)	1340 (800-2000)	66 (63-71)
<u>Knife</u>					
River Carpsucker	7/12/89	6	---	1529 (1025-1975)	69 (65-72)
River Carpsucker	7/5/91	5	460 (398-488)	1230 (750-1550)	67 (62-72)
<u>Little Missouri</u>					
River Carpsucker	7/31/91	5	370 (360-380)	780 (750-850)	65 (62-69)
<u>Missouri</u>					
Common Carp	7/25/89	1	---	6075	75
<u>Square Butte</u>					
River Carpsucker	7/13/89	4	---	706 (475-950)	72 (67-77)
Common Carp	7/13/89	2	---	950 (800-1100)	71 (69-72)

Table 3. Concentrations ($\mu\text{g/g}$, wet-wt) of organochlorines in fish from the Missouri River and its major tributaries in North Dakota, 1989.

Stream	Species ²	Concentration ¹ ($\mu\text{g/g}$, wet-wt)						
		Aroclor-1254	Aroclor-1260	t-nonachlor	p,p'-DDE	p,p'-DDD	p,p'-DDT	dieldrin
Cannonball Downstream Upstream	RCS	ND	ND	ND	0.01	ND	ND	0.01
	CCF	ND	ND	0.01	0.07	0.02	ND	0.01
Heart Downstream Upstream	RHS	ND	ND	ND	0.01	ND	ND	ND
	RHS	ND	ND	ND	0.01	ND	ND	ND
Knife Downstream Upstream	Mix	0.31	0.13	ND	0.10	0.06	0.10	ND
	RHS	ND	ND	ND	0.02	ND	ND	0.01
Little Missouri Downstream	CAP	ND	ND	ND	0.03	0.01	ND	ND
	CAP	ND	ND	ND	0.05	ND	ND	ND
Square Butte Downstream Upstream	Mix	ND	ND	ND	0.01	ND	ND	ND
	RHS	ND	ND	ND	0.02	ND	ND	ND

¹ Concentrations of the following compounds were below detection limits ($0.01 \mu\text{g/g}$, wet-wt): hexachlorobenzene (HCB), α -benzene hexachloride (BHC), β -BHC, γ -BHC, δ -BHC, oxychlordanes, cis-nonachlor, heptachlor epoxide, α -chlordane, γ -chlordane, toxaphene, Aroclor-1242, Aroclor-1248, o,p'-DDE, o,p'-DDD, o,p'-DDT, endrin, mirex.

² RCS = river carpsucker, CCF = channel catfish, CAP = common carp, RHS = river redhorse, Mix = mixture of species.

Table 4. Concentrations ($\mu\text{g/g}$, wet-wt) of aliphatic and polycyclic aromatic hydrocarbons in fish from the Missouri River and its major tributaries in North Dakota, 1989.

Compound	Location ¹									
	C-D	C-U	GD	H-D	H-U	K-D	K-U	L-D	S-D	S-U
<u>Aliphatics</u>										
n-C12	<0.01	0.01	0.02	<0.01	<0.01	0.02	0.05	<0.01	0.02	0.10
n-C13	<0.01	0.03	0.02	<0.01	<0.01	0.22	<0.01	0.07	0.20	<0.01
n-C14	0.21	0.01	0.02	0.06	0.04	0.07	0.03	0.02	0.02	0.04
n-C15	5.10	0.08	0.33	<0.01	<0.01	3.20	<0.01	0.50	0.44	<0.01
n-C16	1.10	0.03	0.13	0.23	0.28	0.52	0.23	0.26	0.11	0.25
n-C17	75.00	0.43	8.20	19.00	22.00	11.00	21.00	14.00	11.00	18.00
pristane	<0.01	<0.01	<0.01	<0.01	<0.01	29.00	<0.01	0.28	<0.01	<0.01
n-C18	0.63	0.03	0.43	0.71	0.72	0.75	0.57	0.41	0.28	0.83
phytane	0.98	0.05	0.14	0.09	0.21	1.70	0.11	0.75	0.04	0.10
n-C19	2.90	0.14	2.90	9.30	6.50	4.90	8.10	3.70	3.80	14.00
n-C20	0.45	0.05	0.33	0.37	0.28	0.44	0.35	0.39	0.12	0.64
<u>Aromatics²</u>										
naphthalene	<0.01	0.02	0.01	0.01	<0.01	0.01	<0.01	0.01	0.01	<0.01
phenanthrene	<0.01	0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.03
benzopyrene	<0.01	<0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	<0.01

¹ C = Cannonball River, G = Garrison Dam on Missouri River, H = Heart River, K = Knife River, L = Little Missouri River, S = Square Butte Creek. D = confluence of tributary with Missouri River, U = 2 to 4 miles upstream of confluence of tributary with Missouri River.

² Concentrations of the following aromatic compounds were below detection limits ($0.01 \mu\text{g/g}$, wet-wt): fluorene, anthracene, fluoranthrene, pyrene, 1,2-benzanthracene, chrysene, benzo-(b)-fluoranthrene, benzo-(k)-fluoranthrene, 1,2,5,6-dibenzanthracene, benzo-(ghi)-perylene.

Table 5. Concentrations ($\mu\text{g/g}$, wet-wt) of aliphatic and polycyclic aromatic hydrocarbons in sediments from the Missouri River and its major tributaries in North Dakota, 1989.

	Location					
	Cannonball River	Missouri River	Heart River	Knife River	Little Missouri River	Square Butte Creek
<u>Aliphatics</u>						
n-C12	0.01	<0.01	0.01	<0.01	0.02	0.01
n-C13	0.01	<0.01	0.02	0.02	0.03	0.02
n-C14	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
n-C15	0.01	<0.01	0.02	0.03	<0.01	0.03
n-C16	<0.01	<0.01	0.01	0.01	0.01	0.01
n-C17	0.06	0.01	<0.01	0.08	0.05	0.20
pristane	0.01	<0.01	<0.01	0.01	<0.01	<0.01
n-C18	0.01	0.01	0.01	0.02	0.01	0.02
phytane	0.02	<0.01	0.02	0.03	<0.01	<0.01
n-C19	0.03	0.02	<0.01	0.03	<0.01	0.03
n-C20	<0.01	0.01	0.01	0.02	0.02	0.02
<u>Aromatics¹</u>						
naphthalene	0.02	0.01	<0.01	<0.01	0.02	0.01
fluoranthrene	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
pyrene	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
benzopyrene	<0.01	<0.01	<0.01	0.01	<0.01	0.01

¹ Concentrations of the following aromatic compounds were below detection limits ($0.01 \mu\text{g/g}$, wet-wt): fluorene, phenanthrene, anthracene, 1,2-benzanthracene, chrysene, benzo-(b)-fluoranthrene, benzo-(k)-fluoranthrene, 1,2,5,6-dibenzanthracene, benzo-(ghi)-perylene.

Table 6. Mean element¹ concentrations ($\mu\text{g/g}$, wet-wt) in fish from the Missouri River and its major North Dakota tributaries compared to the National Contaminants Biomonitoring Program.

Stream/Year	n	As	Cd	Cu	Pb	Hg	Se	Zn
Cannonball								
1989	4	<0.10	<0.05	0.49	<0.30	0.14	<0.50	16.20
1991	5	0.22	0.04	1.08	0.72	0.03	0.90	14.70
Heart								
1989	6	<0.10	<0.05	0.87	<0.30	0.13	<0.50	17.30
1991	5	0.14	<0.05	0.91	0.37	0.15	1.22	14.50
Knife								
1989	6	<0.10	<0.05	1.10	<0.30	0.11	<0.50	16.00
1991	5	0.22	<0.05	1.17	0.48	0.09	1.05	12.50
Little Missouri								
1989	1	0.11	<0.05	0.82	<0.30	0.09	0.85	21.00
1991	5	0.25	<0.05	0.91	0.38	0.04	0.75	11.70
Missouri								
1989	1	<0.10	<0.05	0.88	<0.30	0.19	0.60	41.40
Square Butte								
1989	6	<0.10	<0.05	1.12	<0.30	0.09	<0.50	44.20
NCBP								
1984--mean	-	0.14	0.03	0.65	0.11	0.10	0.42	21.70
1984--85%	-	0.27	0.05	1.00	0.22	0.17	0.73	34.20

Table 7. Mean (with minima and maxima) element concentrations ($\mu\text{g/g}$, dry-wt) in fish from the Missouri River and its major tributaries in North Dakota, 1989-91.

Stream/Year	n	Element Concentration ($\mu\text{g/g}$, dry-wt)					
		Al	As	B	Ba	Cd	Cr
Cannonball							
1989	4	23 9-34	<0.50 ND-ND	<2.20 ND-2.76	2.7 ND-5.2	<0.25 ND-ND	1.61 1.22-2.19
1991	5	--	0.63 ND-0.91	1.59 0.98-2.28	14.5 6.3-26.4	0.12 ND-0.215	9.06 2.98-20.00
Heart							
1989	6	123 8-242	<0.50 ND-ND	<2.20 ND-ND	10.1 4.2-22.5	<0.25 ND-ND	1.94 1.52-2.71
1991	5	--	0.39 ND-0.65	0.51 ND-0.78	6.2 ND-8.0	<0.10 ND-ND	2.26 ND-3.42
Knife							
1989	6	179 16-439	<0.50 ND-ND	<2.20 ND-ND	9.1 4.4-15.0	<0.25 ND-ND	2.88 1.33-6.17
1991	5	--	0.68 0.42-0.94	0.95 0.75-1.11	9.8 5.9-13.8	<0.10 ND-0.13	4.91 2.76-10.40
Little Missouri							
1991	5	--	0.68 ND-1.10	0.74 ND-1.14	7.9 ND-1.1	<0.10 ND-0.10	2.93 1.56-4.11
Missouri							
1989	1	16	<0.50	2.67	6.9	<0.25	2.67
Square Butte							
1989	6	385 101-996	<0.50 ND-ND	1.93 ND-4.59	16.6 8.0-27.7	<0.25 ND-ND	2.75 1.24-4.39

Table 7 (continued)

Stream/Year	n	Element Concentration ($\mu\text{g/g}$, dry-wt)					
		Cu	Fe	Hg	Mg	Mn	Ni
Cannonball							
1989	4	2.08 1.58-2.45	195 155-307	0.588 0.303-0.742	1190 990-1430	7.1 2.8-12.6	<1.9 ND-ND
1991	5	3.13 1.58-6.72	298 92-626	0.082 ND-0.104	1190 690-1570	15.6 6.5-30.5	1.8 ND-4.3
Heart							
1989	6	3.01 1.92-5.53	406 178-646	0.444 0.034-0.646	1430 1220-1810	13.8 5.5-20.8	1.3 <1.5-2.1
1991	5	2.70 1.97-3.12	153 82-212	0.456 0.117-0.861	1100 630-1410	10.5 8.2-13.6	<0.5 ND-1.0
Knife							
1989	6	3.56 2.57-4.41	708 220-1420	0.345 0.182-0.438	1390 1140-1680	14.4 6.0-24.5	8.9 <1.5-31.1
1991	5	3.39 1.42-7.55	437 81-891	0.264 0.157-0.384	1200 900-1360	15.0 5.6-21.9	1.0 0.6-1.4
Little Missouri							
1991	5	2.56 1.16-4.05	342 50-690	0.128 0.120-0.139	1110 870-1390	13.3 7.2-19.8	1.4 0.6-2.4
Missouri							
1989	1	3.56	221	0.781	1530	19.4	<1.9
Square Butte							
1989	6	3.95 2.53-4.74	756 284-1820	0.319 0.139-0.471	1490 930-1990	21.0 12.5-30.8	3.8 ND-10.4

Table 7 (continued)

Stream/Year	n	Element Concentration ($\mu\text{g/g}$, dry-wt)				
		Pb	Se	Sr	V	Zn
Cannonball						
1989	4	<1.50 ND-ND	<2.20 ND-1.2	66 46-82	<2.40 ND-ND	70 51-81
1991	5	2.09 ND-4.04	2.57 2.02-3.02	123 69-159	0.73 ND-1.45	42 25-64
Heart						
1989	6	<1.50 ND-ND	<2.20 ND-1.2	94 53-146	<2.40 ND-ND	59 47-83
1991	5	1.15 ND-2.05	3.61 2.16-6.14	82 5-142	<0.50 ND-0.65	43 35-58
Knife						
1989	6	<1.50 ND-ND	<2.20 ND-1.4	70 39-96	<2.40 ND-2.60	52 40-69
1991	5	1.49 0.54-2.08	3.24 2.63-4.90	109 73-141	0.79 ND-1.1	38 35-40
Little Missouri						
1991	5	1.12 0.66-2.11	2.15 1.73-2.87	86 64-121	0.71 ND-1.3	34 22-42
Missouri						
1989	1	<1.50	2.40	114	<2.40	168
Square Butte						
1989	6	<1.50 ND-ND	<2.20 ND-2.0	96 85-112	<2.40 ND-3.81	156 43-486

¹ Concentrations ($\mu\text{g/g}$, dry-wt) of the following elements were below detection limits in all samples from 1989: Ag (<2.38), Be (<0.24), Mo (<2.38), Sb (<4.76), Sn (<2.38), Th (<9.52). Concentrations ($\mu\text{g/g}$, dry-wt) of the following elements were below detection limits in all samples from 1991: Be (<0.1), Mo (<0.5). Analyses for Ag, Sb, Sn, and Th were not performed in 1991.

Table 8. Concentrations ($\mu\text{g/g}$, dry-wt) of elements in sediment samples from the Missouri River and its major tributaries in North Dakota, 1989.

Element ¹	Cannonball River	Heart River	Knife River	Little Missouri River	Missouri River	Square Butte Creek
Aluminum	6820.0	494.0	13300.0	8224.0	3210.0	10400.0
Arsenic	4.2	10.1	39.3	7.0	12.6	20.7
Barium	121.0	121.0	212.0	193.0	138.0	205.0
Beryllium	0.46	0.48	0.91	<0.48	<0.32	0.51
Boron	16.3	4.7	11.7	9.6	4.5	13.1
Cadmium	4.0	3.5	5.8	<0.5	3.2	4.6
Chromium	13.9	10.0	23.0	17.2	8.2	18.9
Copper	16.3	7.2	25.0	18.8	4.8	18.0
Iron	14688.0	13600.0	23400.0	18398.0	12300.0	19400.0
Lead	9.0	<3.0	<3.0	8.7	<3.0	<3.0
Magnesium	5037.0	4620.0	2100.0	8552.0	5450.0	8940.0
Manganese	349.0	554.0	583.0	382.0	230.0	360.0
Mercury	0.05	<0.05	<0.05	0.06	<0.05	<0.05
Nickel	22.2	12.1	25.0	28.4	12.9	20.7
Selenium	0.24	<0.20	<0.20	0.48	<0.20	<0.20
Strontium	70.8	52.2	113.0	69.9	32.4	95.3
Vanadium	21.3	18.3	37.9	26.6	17.4	34.3
Zinc	59.0	32.7	76.4	62.0	31.7	72.7

¹ Concentrations of the following elements were below detection limits at all sites: antimony (<10 $\mu\text{g/g}$), molybdenum (<5 $\mu\text{g/g}$), silver (<5 $\mu\text{g/g}$), thallium (<20 $\mu\text{g/g}$), tin (<5 $\mu\text{g/g}$).

Table 9. Geochemical baselines for soils from the western United States (Shacklette and Boerngen 1984).

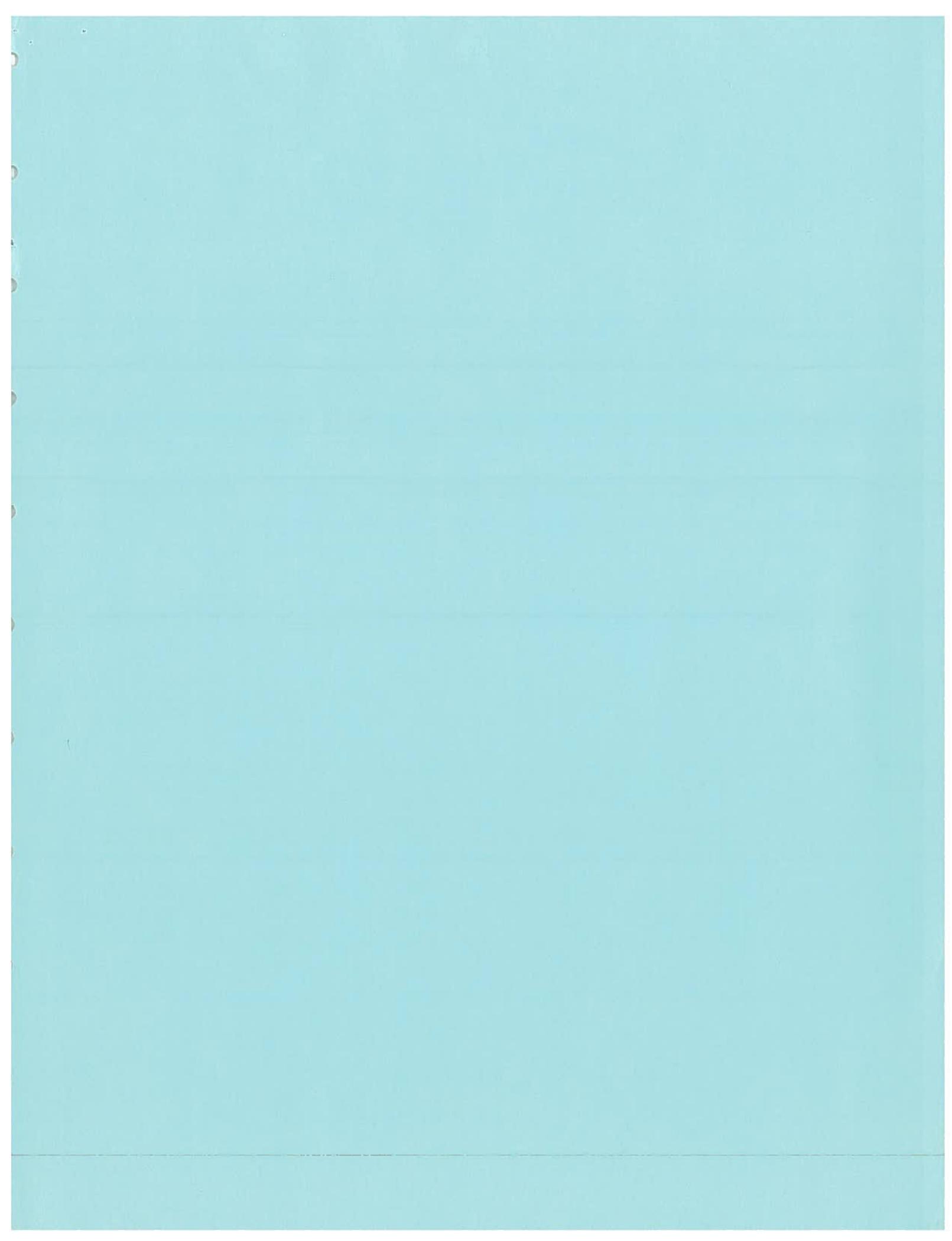
Element	Geometric Mean ($\mu\text{g/g}$, dry-wt)	Baseline Range ¹ ($\mu\text{g/g}$, dry-wt)
Arsenic	5.5	1.2-22
Barium	580	200-1700
Boron	23	5.8-91
Chromium	41	8.5-200
Copper	21	4.9-90
Lead	17	5.2-55
Manganese	380	97-1500
Mercury	0.046	0.0085-0.25
Molybdenum	0.85	0.18-4.0
Nickel	15	3.4-66
Selenium	0.23	0.039-1.4
Vanadium	70	18-270
Zinc	55	17-180

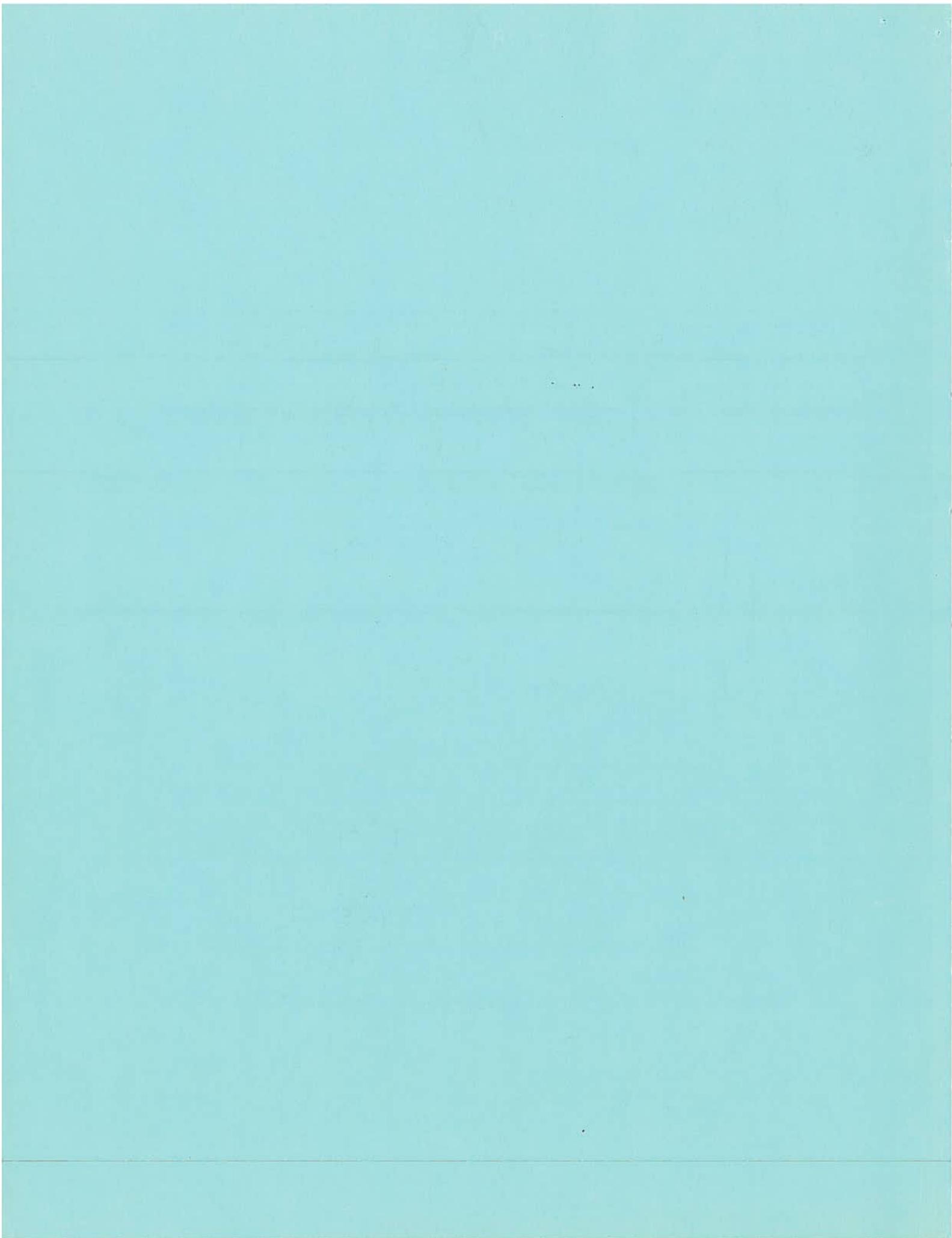
¹ The baseline range includes all values within the 95 percent confidence interval of the mean.

Table 1. Chemical and physical characteristics of the water in the western United States.

Parameter	Mean (SD)	Range
Alkalinity	120	100-140
Calcium	100	80-120
Chloride	20	10-30
Copper	0.1	0.05-0.2
Lead	0.1	0.05-0.2
Magnesium	80	60-100
Hardness	200	180-220
Iron	0.05	0.02-0.1
Total Dissolved Solids	250	200-300
Fluoride	0.1	0.05-0.2
Nitrate	10	5-15
Sulfate	50	40-60
Zinc	0.1	0.05-0.2

The range of values is given in parentheses. The mean values are given in boldface.





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