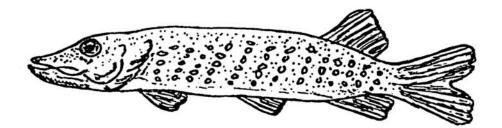
NAES-TR-92-02 August 1992

## **TECHNICAL REPORT**

# CONTAMINANT BASELINE DATA FOR WATER, SEDIMENTS, AND FISH OF THE NOWITNA NATIONAL WILDLIFE REFUGE, 1985 - 1988



by

Elaine Snyder-Conn Tim Patton Mark Bertram Patrick Scannell Candi Anthony

Fish and Wildlife Service U.S. Department of Interior Fairbanks, AK

August 20, 1992

### PREFACE

Nowitna National Wildlife Refuge was established under the Alaska National Interest Lands Conservation Act of 1980 to protect water quality, fish and wildlife populations, and subsistence use of refuge lands. This study was initiated both to examine possible impacts of placer mining on Nowitna National Wildlife Refuge resources, including water, sediments, and fish, and to determine baseline trace element concentrations in these matrices in different refuge rivers. Placer mining has been a significant element in the development of Alaska's mineral resources and economy. Many early practices, including mining within active stream beds without stream diversions, settling ponds, or water recycling; haphazard use and disposal of mercury used to amalgamate gold; and mine development without restoration, have had profound impacts on its lands, waters, fish and wildlife. Some of these practices have undoubtedly left a contaminants legacy.

In recent years, placer mining has come under increasing regulatory scrutiny and requirements designed to minimize environmental damage, including curtailment of some of these earlier practices. It is hoped that data from this preliminary baseline contaminants study, together with data from 1991 and future Service contaminant studies on Nowitna Refuge, will provide an adequate, reliable data base for water quality and contaminants residues. Only detailed, multiyear monitoring will enable identification and description of natural variation in contaminant concentrations in living and nonliving resources on the refuge. Not all contamination present on the refuge may be attributable to local mining or other developments. It is also possible to observe elevated concentrations of contaminants due to natural erosion of highly mineralized areas, events such as flooding, fires (and fire suppression), and from such non-point sources as long-range or global atmospheric deposition. For migratory species, such as northern pike, off-site contamination is also possible.

This report marks the beginning of a monitoring effort, and relies on only a relatively limited data base. Future, more detailed sampling and more precise water quality and chemical residue analyses will be needed to fully document baseline conditions and assess mining impacts to the refuge's waters, sediments, and fish; to distinguish between historic and ongoing contamination; and to detect contaminant trends in the future. Reports on additional monitoring conducted by the Service on Nowitna National Wildlife Refuge, as well as other refuges in 1991, and future years should also be consulted by the interested reader when they become available.

## **EXECUTIVE SUMMARY**

Studies were conducted by the Fish and Wildlife Service between 1985 and 1988 to obtain baseline trace element and water quality data on water, sediments, and fish in rivers of the Nowitna National Wildlife Refuge and to assess the impacts of upstream placer mining activities. One river examined, the Sulatna River, had active placer mining on its tributaries. In addition, California Creek, a tributary to the Titna River, experienced upstream placer mining from 1979 - 1986. In the early 1900's, Our Creek, and the Susulatna River, tributaries to the upper Nowitna River, were mined, as was an unnamed tributary to the Sulukna River. The Sulatna River experienced significantly higher turbidity, iron, and manganese concentrations than sites on the upper, middle, or lower Nowitna River, the Sulukna River, or California Creek. The Titna River, only sampled in 1985, also had extremely high iron concentrations in the water.

In other respects, the water quality of all sites was similar. Copper appears to be slightly elevated in water from all sites as a result of natural conditions, but meets water quality standards. However, concentrations were in the range of potential effects on young arctic grayling and other sensitive species.

No significant differences were found between sites in sediment trace element concentrations, except for mercury. Mercury concentrations were higher in Sulatna River sediments than at other sites, but occurred at elevated concentrations at all sample sites except California Creek. Fish tissue concentrations of mercury were highest in northern pike from the unmined Sulukna River. Concentrations in all five northern pike collected in 1987 exceeded the Food and Drug Administration (FDA) action level of 1 mg/kg wet weight. Northern pike from the mouth of the Nowitna River also contained elevated mercury concentrations, but concentrations did not exceed the FDA limit. Sheefish and arctic grayling were generally low in mercury concentration in comparison to the northern pike. The source of mercury in the Nowitna Refuge fish is uncertain, but is most likely derived from natural sources, rather than placer mining activity. Mercury, used historically to amalgamate gold and discharged to waters, is another potential, but less likely, source.

Mercury concentrations in northern pike were not correlated with fish length, weight, or condition index, suggesting that mercury concentrations did not affect fish health. The only negative statistical correlations found between northern pike measurements and metal concentrations were between liver copper, weight, and total length. Due to small sample sizes involved in this study, few conclusions should be drawn regarding the relationship of metal concentrations in fish and fish health at this time. The paucity of northern pike from the mined Sulatna River also precludes conclusions regarding the effect of mining on fish tissue concentrations. Other species were collected in too few numbers to conduct between-site comparisons. Additional studies are recommended to identify source areas of mercury, and to better define tissue concentrations in potentially affected biota.

## **INTRODUCTION**

Created by the Alaska National Interest Lands Conservation Act of 1980 (ANILCA), the Nowitna National Wildlife Refuge (NWR) in central Alaska is bordered on the north by the Yukon River and on the south by the Kuskokwim Mountains. The Nowitna River is a major feature of the 2,051,000-acre refuge, bisecting the entire refuge into eastem and western sections. The 359-km (223-mile) portion of the river within the refuge boundaries has been designated a National Wild River under the Wild and Scenic Rivers Act of 1968. Under this act, the head of the Fish and Wildlife Service is directed to cooperate with the Secretary of the Interior and appropriate State water pollution control agencies "for the purpose of eliminating or diminishing the pollution of waters of the river" and mining rights for such waters designated by ANILCA within the river bed or within one-half mile of its banks on Federal lands are withdrawn.

The floodplain of the Nowitna River forms an extensive oxbow, slough, and lake system highly productive for waterfowl. The most common species are tundra and trumpeter swans (*Cygnus columbianus* and *C. buccinator*), lesser Canada geese (*Branta canadensis parvipes*), greater white-fronted geese (*Anser albifrons*), green-winged teal (*Anas crecca*), American wigeon (*A. americana*), mallards (*A. platyrhynchos*), northern shovelers (*A. clypeata*), northern pintail (*A. acuta*), common and Barrow's goldeneye (*Bucephala clangula* and *B. islandica*), bufflehead (*B. albeola*), white-winged scoters (*Melanitta fusca*), greater and lesser scaup (*Aythya marila* and *A. affinis*), and red-breasted mergansers (*Mergus serrator*). The Nowitna River, its tributaries, and surrounding wetlands also support significant populations of fish, furbearers, moose (*Alces alces*), black bears (*Ursus americanus*), and gray wolves (*Canis lupus*).

Among the abundant fish within Nowitna refuge rivers are broad and humpback whitefish (Coregonus nasus and C. pidschian), sheefish (Stenodus leucichthys), and northern pike (Esox lucius). Also present in significant numbers in certain areas are Arctic grayling (Thymallus arcticus), burbot (Lota lota), longnose sucker (Catostomus catostomus), and least cisco and Bering cisco (Coregonus sardinella and C. laurettae). Low numbers of coho and chum salmon (Oncorhynchus kisutch and O. keta) are also reported in the refuge, with spawning for the summer chum reported in the Nowitna River near or upstream of the mouth of the Big Mud River and spawning of fall chum in the upper Nowitna and Sulukna Rivers (Alt 1985). Both the pike and sheefish populations of the refuge appear to remain in refuge waters, with very few migrating into the Yukon River (Alt 1985). Sheefish on the refuge are recognized as one of six discrete subpopulations in Alaska (Alt 1985), with their the Sulukna River 5 to 7 air miles upstream of the confluence serving as their primary spawning area. Northern pike are believed to overwinter in the Nowitna River and concentrate in lakes and sloughs of the mid- and lower reaches as well as in river confluences (Alt 1985, Glesne 1986). Most of the sheefish, as well as most, if not all, humpback whitefish, spawn in the Sulukna River (Alt 1985, USFWS 1991). Salmon, whitefish, northern pike, and burbot are the primary species used in the subsistence fishery on the refuge. Nowitna River pike reach trophy sizes and also are an important sport fish, particularly during the fall hunting season.

Purposes of the Nowitna NWR, prescribed in Section 3202 (6)(B) of ANILCA, include:

(1) conservation of fish and wildlife populations and habitats in their natural diversity, including ... trumpeter swans, white-fronted geese, canvasbacks and other waterfowl and migratory birds, moose, caribou, martens, wolverines and other furbearers, salmon, sheefish, and northern pike

(2) fulfillment of international treaty obligations concerning fish, wildlife, and their habitats

(3) provision of the opportunity for continued subsistence uses by local residents consistent with other purposes of the refuge, and

(4) ensuring water quality and quantity, to the maximum extent practicable, within the refuge.

To meet the above goals, Section 304(g)(2G) mandates identification and description of problems which may adversely affect fishery resources and wildlife populations. The Fish and Wildlife Service identified placer mining, within and near refuge boundaries, as potentially affecting water quality, fish and wildlife populations, and their habitats (USFWS 1987). Placer and lode mining for gold have grown dramatically in Alaska in recent decades (Alaska Department of Natural Resources 1982, U.S. Dept. Interior 1990), stimulated by deregulated gold prices and removal of ownership restraints in the early 1970's, increased instability in the world economy, and new technologies for enhanced gold recovery (Anonymous 1980, U.S. Dept. Interior 1990). These factors suggest the potential for increased mining activities near the interior Alaskan refuges.

To extract the gold in ancient alluvia, large amounts of overburden are typically removed. Mined sediment-rich effluent, transported in suspension and as bedload, may cause elevated turbidities in the water column and blanket the stream bottom, making it unsuitable for benthic aquatic life (Bjerklie and LaPerriere 1985; LaPerriere et al. 1985; Wagener and LaPerriere 1985; Weber and Post 1985; Van Nieuwenhuyse and LaPerriere 1986; Lloyd 1987; Lloyd et al. 1987). Since 1985, Environmental Protection Agency (EPA) requirements for 100 percent recycling of process water during medium- and large-scale placer mining have significantly lessened, but not eliminated, these problems in Alaska (Alaska Department of Environmental Conservation 1991).

Gold deposits are often associated with other trace elements. In interior Alaska, arsenic, copper, zinc, and lead are affiliated with placer gold, resulting in elevated concentrations of these metals in some mined streams (Madison 1981; LaPerriere et al. 1985). Other heavy

metals sometimes found with placers are antimony, aluminum, cadmium, chromium, iron, and mercury. Potential mercury sources include mercury used historically to amalgamate gold, natural lodes of cinnabar (HgS), trace amounts in silty sediments of oceanic origin and volcanic or other thermally active zones, and global atmospheric deposition.

Plant, invertebrate, and fish abundance and productivity can decline in streams with placer mines (Cordone and Kelly 1961; Van Nieuwenhuyse and LaPerriere 1986; Lloyd et al. 1987). Arctic grayling from mined streams may exhibit higher metal concentrations and liver and cellular abnormalities than fish in control streams (West 1982; West and Deschu 1984). Young grayling may also experience higher plasma glucose, depressed leucocrit levels, impaired feeding activity, reduced growth rates, and decreased survival in sediment-rich mined streams (McLeay et al. 1983, 1987; Reynolds et al. 1989). Mined streams may also contain copper at acutely toxic concentrations to early life stages, especially to sensitive Arctic grayling (Buhl and Hamilton 1990).

Mercury, readily biomagnified in the foodweb, is also among the most toxic metals to fish. It occurs in some placer mining effluent at concentrations that could potentially result in a toxic hazard to young salmonids (Buhl and Hamilton 1991). At acute toxicity levels (resulting in whole body residues of 5 to 7 mg/kg and liver residues of 26 to 68 mg/kg wet weight), gill flaring, increased frequency of respiratory movements, loss of equilibrium, and sluggishness are the first signs of mercury poisoning (Armstrong 1979 in Eisler 1987). Lower concentrations cause chronic toxicity, emaciation (from appetite loss), brain lesions, cataracts, inability to capture food or respond to light changes, and abnormal motor coordination. More than 95% of the mercury concentrated in freshwater fish is toxic methylmercury, sequestered in muscle tissue for long-term storage, as well as in liver, kidney, and other organs (EPA 1980; Eisler 1987).

## MINERAL OCCURRENCES IN THE NOWITNA NWR AREA

The geology of the Nowitna Refuge region is extremely complex, with more than a dozen distinct tectonostratigraphic terranes reported within one hundred miles of refuge boundaries (USFWS 1987). These terranes indicate the collision of multiple continental plates and microplates in this area including those of Eurasian origin with Canadian cordillera. Severe faulting and bending, thrusting, shearing, volcanism, and igneous intrusions followed collisions. In most locations, surficial deposits of silt, gravel, and driftable volcanics overlie bedrock, forming a thick alluvium, obscuring bedrock mineralogy, faulting, and minable deposits. Thus, mineral occurrences are mainly observed in upland areas most prevalent to the west and south of the refuge.

Sites of known or indicated mineralization near the Nowitna Refuge (Eberlein et al. 1977; Cobb 1970a,b, 1974a, 1975a, 1984a,b,c,d, 1985; Cobb and Chapman 1981; Cruz and Cobb 1984, 1986; U.S. Bureau of Mines 1987) are identified in Figure 1. The Nowitna Refuge is located at the intersection of three regional belts of tin-tantalum-niobium mineralization

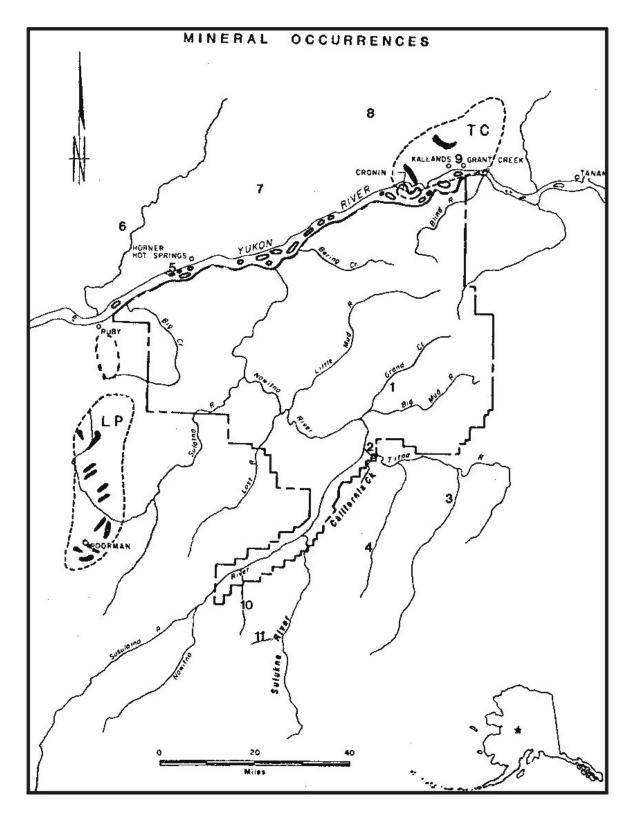


Figure 1. Regional mineral occurrences near the Nowitna National Wildlife Refuge. See text for sources.

Legend - Mineral Occurrences

Places of produced placers, prospects, visible ore minerals, favorable geology, geochemical anomalies, and other indications of mineralization. Elements in parentheses indicate presence in anomalous amounts in stream sediments and rock chips.

# Single mineral deposits

- 1. Sun Creek placer (Gold)
- 2. California Creek placer (Gold)
- 3. Baker Creek placer (Gold)
- 4. American Creek placer (Gold)
- 5. Shovel Creek placer (Gold)
- 6. Fox Creek placer (Gold)
- 7. Unnamed (Uranium, Thallium disseminations)
- 8. Melozimoran Creek placer (Gold, Tin)
- 9. Gold Hill (Gold, Silver)
- 10. Our Creek (Gold)
- 11. Unnamed tributary of Sulukna River (Gold)

Significant areas with mineral deposits

LP - Long-Poorman area - Gold, Platinum, Tungsten, and Tin

TC - Tozimoran Creek area - Gold and Tin

- Produced gold placers

often associated with gold placer concentrates (Warner 1985). The most heavily mineralized zone lies west of the refuge between Ruby and Poorman and is designated the Ruby mining district. In addition to extensive placer gold deposits, two lode deposits of gold (Cobb 1984b) occur in this region. Other minerals present include tin on numerous streams (Cruz and Cobb 1984a); lead off Beaver Creek (Thomas 1968) and off Trail Creek near Poorman (Cobb 1984a); bismuth at Glacier and Birch creeks (Cobb 1970a); copper at Beaver and Birch creeks (Cobb 1984d); uranium and rare earth metals at Solomon, Flint, and Birch creeks (Cobb 1970b); tungsten in Deep Creek and its tributaries (Cruz and Cobb 1984b); and platinum at Grant Creek (Cobb 1975a). The latest known major exploration in the Ruby mining region was by Anaconda for hard rock deposits in the mid-1980's.

Placer gold has also been found along Sun Creek, a tributary to Grand Creek, which flows into the Nowitna River in the central section of the Nowitna NWR, and California Creek, American, and Baker creeks, tributaries to the Titna River near the southern border of the refuge (Cobb 1984c). Placer deposits have also been found along Our Creek (a tributary to the upper Nowitna River) and in an unnamed tributary to the Sulukna River near Our Creek (Eakin 1918). South of the refuge, mercury and antimony are found at Wyoming Creek, a tributary to the Susulatna River, which drains into the upper Nowitna River (Cruz and Cobb 1984b, 1986). Copper was noted in upper Sulukna River drainages (Cobb 1984d). Some stream placer deposits of mercury are present in naturally occurring cinnabar (HgS). Concentrations of greater than 0.30 mg/kg dry weight mercury have been found in stream silt in drainages to the upper Sulukna River and occasionally in the Nowitna River (King et al. 1983).

Even more notable mineral resources lie further to the south of the refuge in the highly mineralized Kuskokwim Mountains. Among the important minerals present here are gold, silver, lead, antimony, mercury, tin, bismuth, and tungsten (Malone 1962; Schwab et al. 1981; Patton et al. 1982; King et al. 1980, 1983). Ninety-nine percent of all mercury produced in Alaska has come from the Kuskokwim Mountains (Malone 1962). The primary drainage for the mountains is the Kuskokwim River, which flows west and currently bypasses the refuge and is not hydrologically connected to any Nowitna refuge watershed. Prehistorically, however, the Kuskokwim River probably flowed through the refuge along some of the course now occupied by the Yukon River, and the Nowitna River drained to the west, through the Lost River (USFWS 1987).

Some drainages flowing into the upper Sulukna, Susulatna, and Nowitna rivers contain elevated metal levels in sediments due to heavy mineralizations and high erosion potential in the highlands of the Kuskokwim area. The Sulukna River originates in the highest uplands of the region, in a limestone mountain range, and flows along the foot of the volcanic Sischu Mountains. In contrast, other rivers in the refuge flow through sections of low gradient and thick overburden. Patton and Moll (1983) noted a skarn deposit (a contact metamorphic rock deposit rich in minerals) in the region south of Lone Mountain and southwest of Browns Fork, a tributary to the Sulukna River just south of the refuge boundary. Due to the anomalously high concentrations silver, arsenic, gold, copper, mercury, antimony, zinc, bismuth, and molybdenum in rock and high lead and gold in stream sediment, this area was designated as an area favorable for the occurrence of undiscovered mineral deposits. Since 1975, the Doyon

Corporation has investigated a number of heavily mineralized areas in this vicinity (Harry Noyes, Doyon Corporation, pers. comm.).

# MINING HISTORY OF THE NOWITNA NWR AREA

Mining activity in the area of the refuge is summarized in Figure 2 based on data from Miller and Ferrians (1968), Eberlein et al. (1977), U.S. Bureau of Mines Mineral Industry Locator System records, U.S. Bureau of Mines (1987), and USFWS (1987). The first rich gold placer mined near the refuge was discovered in 1910 on Bear Pup, a tributary to Long Creek, which is a major artery of the Sulatna River. Subsequent stampedes to the area resulted in the discovery of other bonanzas. Nearly all the tributaries of the Sulatna River, which drain into the Nowitna lowlands, had placer mines (Mertie and Harrington 1924). Many of the mines have been mined intermittently for about 75 years. Gold was produced together with some tin. Placer prospects for gold were also located south of the refuge off Our Creek (a tributary to the Nowitna River) and in the unnamed tributary to the Sulukna River near Our Creek (Eakin 1918). Production from these mines was unrecorded.

Another placer gold mining area occurred on three tributaries to the Titna River. In 1979, four claims were staked on California Creek. U.S. Bureau of Mines records credit these claims as property with past production, although the amount is unspecified. The mining claims on the refuge were abandoned in 1986, and voided by BLM in 1987 (USFWS 1987). Except for one underground effort at Gold Hill, all mined deposits in and near the Nowitna Refuge area have been placers. Records show that there are ten active placer mining claims currently near the refuge (A - J, Figure 2), but none are currently on the refuge. There is one claim on California Creek just outside refuge boundaries.

# STUDY OBJECTIVES

1. To monitor water quality and contaminant concentrations of trace elements in water, stream sediments, and fish from California Creek and the Sulatna, Nowitna, and Sulukna rivers of the Nowitna Refuge.

2. To evaluate existing and potential impacts of heavy metal contamination and water quality degradation on refuge fish and wildlife populations.

3. To develop recommendations for future monitoring to protect water quality, conserve fish and wildlife populations, and to protect subsistence use, consistent with refuge goals.

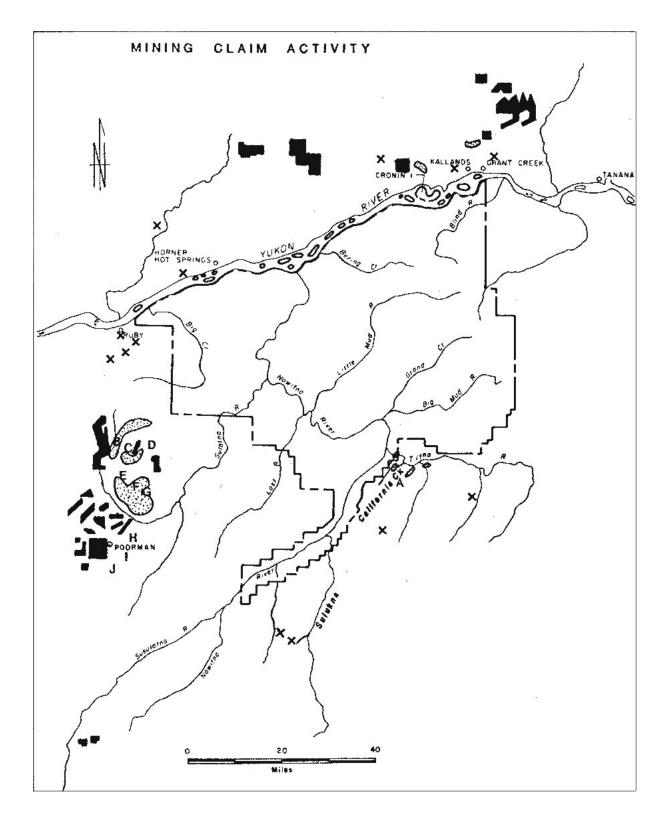
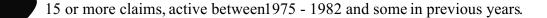


Figure 2. Mining history of the Nowitna National Wildlife Refuge and surrounding areas. See text for sources.

## Legend - Mining Activity

Less than 15 placer claims active between 1979-1982, and also in previous years.



Centers of placer mining activity, active between 1910 - 1960.

## Mining Claims Near the Refuge

## Titna River area

A. California Creek placer, H & M Tilleson, Claim #F909192

#### Sulatna River headwaters area

- B. Swift Creek placer, State mining claim, Conrad House, Claim #F905823
- C. Fourth of July Creek placer, Green Mining, Al Kangas, Claim #F907094
- D. Upper Trail Creek placer, State mining claim, Mike Sweetsir, Claim #907173
- E. Midnight Creek placer, State mining claim, Sphinx Mining, Claim #906907
- F. Monument Creek placer, State mining claim, Sphinx Mining, Claim #908984
- G. Ophir Creek placer, State mining claim, Short Gulch Mining, Jill & Toni Taylor, Claim #907480
- H. Poorman Creek placer, State Mining Claim, Howard Miscovitch, Claim #F907285
- I. Flat Creek placer, Flat Creek Mining, J. Hagglund, Claim #F905824
- J. Poorman Creek placer, State Mining Claim, M.G. Hartman, Claim #F905819

A survey of water quality and contaminant residue levels in water was initiated in 1984 by Fishery Resource personnel at six refuge sites (Deschermeier and Hawkinson 1985). Studies were continued by refuge personnel in coordination with a contaminant specialist at five sites in 1985, when replicate sampling for total recoverable metals and dissolved metals in water was performed. In 1987 and 1988, this study was expanded to include collection and analysis of sediment and fish metal concentrations in addition to water analysis. The 1985 - 1988 studies are described in detail in this report, and compared with 1984 data from the earlier study.

## DESCRIPTION OF THE STUDY SITES

Figure 3 shows the sites of the 1985 - 1988 studies. These sites are described as follows:

Site 1. Nowitna River immediately above its confluence with the East Channel of the Yukon River, 61 km (38 miles) northeast of Ruby, Alaska (Latitude 64°55'42" N, Longitude 154°17'17" W; Township 6S, Range 23E, Section 31, SE 1/4, Kateel River Meridian). This 1987 - 1988 sample location, at the mouth of the Nowitna River, has a sand/mud bottom in this reach. The Nowitna River flows northeast for 402 km (250 miles), draining 18,762 km<sup>2</sup> (7244 mi<sup>2</sup>) of watershed, beginning near the foothills of the Kuskokwim, Sunshine, Frank, and Mystery mountains, and extending through the Nowitna Lowlands. Forming a braided river and floodplain 1.6 - 9.6 km wide in this northern region, the area is surrounded by numerous lakes and wetlands.

Site 1B. Nowitna River immediately upstream of the Sulatna River, sampled in 1985 (Latitude 64°35'49" N, Longitude 154°28"01 W; Township 10S, Range 22E, Section 28, NE 1/4, Kateel River Meridian). This site also has a sand/mud bottom.

Site 1C. Nowitna River immediately upstream from the Titna River, sampled in 1985 (Latitude 64°22'38" N, Longitude 153°37'39" W; Township 13S, Range 26E, Section 12. NE 1/4, Kateel River Meridian). This stream segment flows through the the relatively straight Nowitna Canyon. Sediments are composed of approximately 30% sand and silt, 40% gravel less than 5 cm in diameter, and 30% larger gravel (Alt 1985).

Site 2. Sulatna River at the Nowitna NWR boundary, sampled in 1987 and 1988. The Sulatna River flows northeast 161 km (100 miles) to the Nowitna River 51 km (32 miles) southeast of Ruby in the Nowitna lowlands. The river drains 3608 km<sup>2</sup> (1393 miles<sup>2</sup>) of watershed, including numerous placer-mined tributaries in the area between Ruby and Poorman to the west of the refuge (Latitude 64°29'11" N, Longitude 154°48'00" W; Township 11S, Range 21E, Section 35, SE 1/4, Kateel River Meridian). A mud bottom and mud banks are present throughout this river.

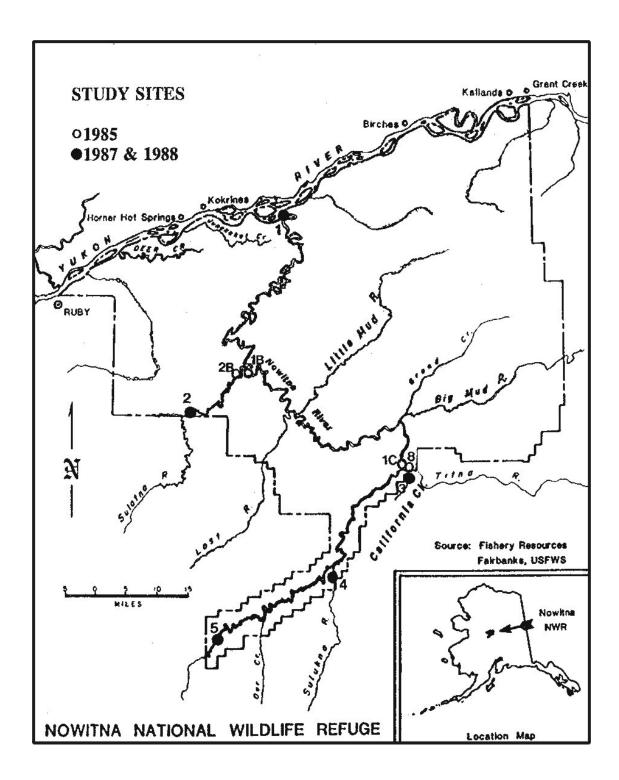


Figure 3. Study sites on Nowitna National Wildlife Refuge streams and rivers, 1985 - 1988.

Site 2B. Sulatna River immediately upstream from its confluence with the Nowitna River, sampled in 1985 (Latitude 64°35'41" N, Longitude 154°28'39" W; Township 10S, Range 22E, Section 28, NE 1/4, Kateel River Meridian).

Site 3. California Creek immediately upstream from its confluence with the Titna River, 3 miles west of its junction with the Telsitna River, sampled in 1987 and 1988. This creek flows northeast 6.9 km (4.3 miles) to the Titna River (Latitude 64°21'21" N, Longitude 153°35'31" W; Township 13S, Range 27E, Section 17, SE 1/4, Kateel River Meridian).

Site 4. Sulukna River immediately upstream of the confluence with the Nowitna River, sampled in 1987 and 1988. The Sulukna River, originating in the Sischu Mountains, is the only clearwater river in the refuge. It flows north 50 km (31 miles) to the Nowitna River, draining a 1772-km<sup>2</sup> (684.3-mile<sup>2</sup>) watershed (Latitude 64°07'50" N, Longitude 154°02'46" W; Township 16S, Range 25E, Section 1, SW 1/4, Kateel River Meridian). The river meanders through a narrow, heavily wooded valley. A gravel bottom is present at its mouth, where flows are moderate.

Site 5. Nowitna River immediately downstream from the southern boundary of the Nowitna NWR sampled in 1987 and 1988 (Latitude 64°00'02" N, Longitude 154°35'32" W; Township 17S, Range 22E, Section 21, SW 1/4, Kateel River Meridian). A gravel bottom covers this section of the Nowitna River, with some sand and silt cover in slower meandering segments.

Site 8. Titna River at the confluence with the Nowitna River, sampled in 1985 (Latitude 64°22'30" N, Longitude 153°37'21" W; Township 13S, Range 26E, Section 12, NE 1/4, Kateel River Meridian). The Titna River originates in the Sischu Mountains, flowing west to enter the Nowina River after 128 km (80 miles). It enters the Nowitna River at the constricted Nowitna Canyon and has a sand/gravel substrate at this location.

The above sites include both mined and unmined drainages. Site 2, on the Sulatna River is closest to large, active placer mines in its upper drainages, and tributaries to the Sulatna drain heavily mineralized areas south of Ruby, between Ruby and Placerville, to the west of the refuge. Site 3, California Creek, has also sustained some recent mining activity, including one active mine just outside the refuge boundaries.

Sites on the Nowitna River itself (Sites 1, 1A, 1B, 1C, and 5), both upstream and downstream, contain no past history of mining. A major influence on the Nowitna River, especially at Site 1, is the Yukon River itself. During spring breakup, the Yukon River may back up into the Nowitna River. Historic placer mining on Our Creek, a tributary to the Nowitna River near the refuge's southern border; American and Baker creeks, other tributaries to the Titna River; and Sun Creek, a tributary to Grand Creek, which drains into the Nowitna River, could also influence contaminant levels on the Nowitna River.

The Sulukna River, Site 4, was selected as a reference (control) site for 1987 and 1988 studies. No mining has occurred on drainages of this river since 1918, and only one area is reported to have been produced gold prior to this date. However, recent information on the highly mineralized nature of its upper drainages, and the presence of highly erodable deposits of different metals in these upper reaches, make the river less ideal as a reference site for the other low-gradient river sites.

## MATERIALS AND METHODS

Table 1 summarizes the types of samples collected at each sample site from 1985 through 1988.

 site locations where collections were made.

 Year
 Water

 Dissolved
 Total Rec.

 Sediment
 Fish

TABLE 1. SAMPLES COLLECTED FROM NOWITNA NATIONAL WILDLIFE

REFUGE FROM 1985 - 1988. Numbers under each analysis category are

Year	Water Quality	Dissolved Metals	Total Rec. Metals	Sediment Metals	Fish
1985	6-9ª	6-9	6-9	-	-
1987	1-5	1-5	1-5	1-5	1-4
1988	1-5	1-5	1-5	1-5	1,2,5

<sup>a</sup> Suspended solids were not measured at any site in 1985, and pH was not measured at two of four sites.

Methods for collecting and analyzing samples are described below by matrix (water, sediments, and fish tissues). A description of sample handling procedures and quality control/quality assurance (QA/QC) measures for field and analytical work follows.

## COLLECTION METHODS

#### Water

<u>Water quality samples.</u> Water quality samples were collected in 1985, 1987, and 1988. The 1985 samples consisted of single surface grab samples collected in 1-L Nalgene<sup>®</sup> polyethylene bottles from 4 sites. Five different sites were sampled in 1987 and 1988. The 1987 and 1988 surface grab samples of river water were obtained at three different locations per site, again using 1-L Nalgene<sup>®</sup> polyethylene bottles. Grab samples were taken just below the surface, with each sample bottle extended into the current upstream of the collector to avoid contamination from resuspension of sediment or from the collector. Samples were filled to the top of the bottle to minimize gaseous exchange. Each sample was double-labelled and chilled in a cooler following collection.

Samples were analyzed within five days of collection for the following water quality parameters: total alkalinity, total hardness, turbidity, conductivity, and settleable solids. Total hardness and alkalinity determinations were made using Hach hardness and alkalinity test kits employing drop count titration and color endpoints using Hach (1985) methods. No phenopthalein alkalinity was noted in any sample. Conductivity was measured with a Hach DREL/5 Conductivity Meter with automatic temperature compensation. Conductivity standards were used to check performance

of this meter prior to each measurement series. In 1987 and 1988, pH measurements were also made using a Hach Digital pH Meter Model 19000 equipped with a combination electrode and automatic temperature compensation. Prior to each measurement series, two-buffer calibrations were performed using pH buffers accurate to  $\pm$  0.02 pH units which bracketed the pH of the samples.

Three different measures of solids in the water samples were also made during 1985 - 1988 studies concurrently with other water quality measurements. Turbidity was measured using a Hach Portable Turbidity Meter Model 16800, calibrated with Gelex secondary standards for 1, 10, and 100 nephelometric turbidity units (NTU's). Total settleable solids were measured using the Imhoff Cone Method for 1-L samples (APHA et al. 1981). If settleable solids occurred, but did not exceed 0.1 mL/L, "trace" was recorded. Suspended solids (nonfilterable residue) were also measured on separate water samples submitted to Northern Testing Laboratories, Fairbanks, AK. EPA Method 160.2 (EPA 1983) was used for this determination.

<u>Trace element samples.</u> At each site where water quality samples were collected, water samples were also collected for analysis of arsenic, mercury, and other trace elements. The 1985 water samples consisted of single grab samples collected in acid-rinsed 500-mL polyethylene bottles prepared by the collector. The 1987 and 1988 samples were collected in triplicate at each site using precleaned (acid-rinsed) IChem Series 200 high-density 250- or 500-mL polyethylene bottles with teflon lids. For all years, two types of water samples were collected: samples for analysis of total metals and samples for analysis of dissolved metals. The total metals samples were collected using a Micropore<sup>®</sup> filter apparatus and hand pump. The 1987 and 1988 dissolved metal samples were collected using a disposable 50-mL syringe to sample the river water directly. After the syringe was filled, two Nalgene<sup>®</sup> cellulose acetate LuerLock filters, a 0.80  $\mu$ m prefilter and a 0.45  $\mu$ m filter, were piggybacked on the syringe tip and the sample was filtered directly into a 250- or 500-mL IChem bottle. About 120 mL were collected per dissolved metal sample.

## Sediments

Three sediment samples per site were obtained from each 1987 and 1988 study site where water samples were collected. Each sample was a composite grab sample from three adjacent locations taken underwater along the shore in water less than 0.5 meters depth. Sediments were collected in a stainless steel scoop, placed in a river-washed plastic container, homogenized with a clean glass or plastic rod, and transferred to a precleaned IChem Series 200, 250- or 500-mL polyethylene bottle with a teflon lid using a stainless steel spoon. Efforts were made at each site to select samples of silt, rather than sand or gravel at each site, to minimize bias due to grain size and to sample a fraction containing sorbed metals more likely to become solubilized and thus become bioavailable.

## <u>Fish</u>

Fish were collected from refuge study sites in both 1987 and 1988. Target fish species included adult Arctic grayling and northern pike. When these species were not available, other species were obtained, including longnose sucker, broad whitefish, and sheefish. Young fish were also collected when insufficient adult fish were found. Fish collections were made using experimental gill nets and spinning rods. Fish were weighed with a Pesola<sup>®</sup> scale to the nearest gram, and total length and fork length were measured to the nearest millimeter.

## SAMPLE HANDLING AND LABELLING

Details of sample handling and labelling are presented in Appendices A and B. Briefly, sampling was conducted following a written study plan containing designated sample locations and types of samples to be collected at each site. Samples taken were recorded in a field notebook. A sample catalog was then prepared for each year of collection prior to submittal of samples to the analytical laboratory. The catalog contained a regional identifier for the sample batch; study objectives; background information summarizing types of samples, sample and preservation methods, and additional rationale for the study; instructions to the laboratory on analyses requested; identification of the detection limits sought; addresses of data recipients; and a tabulated summary of all samples including species, tissue matrix, location, collection date, weight and other parameters.

Field identifications, although unique for a given year, were not necessarily consistent with the study plans or between years. Prior to data interpretation, field identifications were therefore converted into a 10-digit identification number using designated alphanumeric fields, as described in Appendix B. The trace element data for these samples were then entered into a contaminants data management system for northern and interior Alaskan samples, together with the 10-digit identification number using DBase IV<sup>®</sup> software.

All contaminants data entered into the data management system were proofed and corrected, if necessary, by comparing the original data set with the hard-copy output. This proofing was performed by an independent party following initial data entry. In addition, the 1987 and 1988 data were screened for outliers by comparing replicate values for the same matrix and site. For each year's data, mean values and standard deviations were computed for each analyte by matrix. Outliers and suspect data identified in this manner were noted in the results section, and were not utilized in drawing conclusions concerning the data. Data for trace elements in water were also screened by comparing dissolved metal composition with total metal composition. Where dissolved metal composition equalled or exceeded total metal composition, contamination, either due to field or laboratory analytical procedures, is suspected and noted in the results section.

## LABORATORY ANALYSES

Nitric acid-perchloric acid digestions were used on all matrices. Arsenic and antimony were analyzed by flameless atomic absorption spectrophotometry using hydride generation. Standard addition methods were employed for determining concentration. Mercury samples were digested

with nitric acid using reflux condensers to prevent mercury loss, and were analyzed by cold vapor atomic absorption spectrophotometry. Other metals were analyzed with inductively coupled argon plasma spectroscopy (ICP) using preconcentration, with samples adjusted to pH 6 and standard Environmental Protection Agency (EPA) methods for the year of analysis.

Prior to analysis, sediment samples were freeze-dried, sieved to remove large particles, and homogenized by grinding in a mill until it passed through a 200 mesh sieve. Tissues were also freeze-dried and homogenized. Fish tissues were digested using the method of Monk (1961) and analyzed for mercury by cold vapor atomic absorption using the method of Hatch and Ott (1986).

## QUALITY ASSURANCE/QUALITY CONTROL

#### Field Collections

Prior to sampling in 1987, refuge personnel involved in water quality and field contaminants sampling were trained by Service contaminant specialists in collection methods and water quality analysis. Samples were collected in precleaned containers (IChem Series 200) with protocols designated to reduce the potential of contaminating the samples. These included precautions to avoid direct contact between the sample container or sample and the collector or other sources of contamination (suspended sediment from the river bottom, airborne dust, metal such as aluminum boat or float plane surfaces, mosquito repellant, hand lotion, cigarette smoke, or airborne dust). Water quality sample containers were triple-rinsed in the river water prior to sampling. During 1987 and 1988, three replicates of water and sediment were collected at each site. The target for fish collections was five pike and five grayling. This goal was not always met. However, the multi-year sampling has increased confidence in the data that are presented.

Water quality measurements were supposed to have been performed the same day as collection with the exception of the suspended solids measurement, performed by an analytical laboratory. However, the quality of the data was undoubtedly compromised by performance of pH measurements on many samples up to five days after sample collection. In other respects, field quality control procedures were followed. These included instrument calibrations or calibration checks prior to measurement of pH, conductivity, and turbidity; use of fresh reagents in titrations for hardness and alkalinity; and repeat analysis if a replicate sample deviated significantly from other measurements. Suspended solid measurements were also subject to performance checks using EPA check samples.

Sample preservation and handling was another area of emphasis in the sampling program. Sample locations and replicate numbers were preassigned for each drainage in the study plan. All samples were labelled both on the lids and on the bottles to reduce problems with label loss, illegibility, condensation-related ink smudges, and mixups once samples were opened by the laboratory. Water samples were collected by direct surface grabs into the current using precleaned polyethylene containers. Water samples collected for trace element analysis were fixed with concentrated ultrapure nitric acid to pH < 2 and kept refrigerated until submitted to the analytical laboratory. Sediment sampling followed water sampling and was performed using stainless steel, plastic, and glass equipment. All sample gear was triple-rinsed in river water at the sample site prior to sampling. Composite samples consisting of three to four grabs each constituted a replicate sample. Each sample was homogenized with a glass rod prior to transferring the sample to the acid-cleaned IChem polyethylene container. During all phases of collection, care was taken to avoid any contact between the sample and hands or footwear. Samples were frozen following collection and shipped to the laboratory in coolers with dry ice by overnight air courier.

Following morphometric measurements, fish were rinsed with river water from the site of collection or distilled water to minimize external contamination. In 1987, large fish were wrapped in Saran Wrap, followed by freezer wrap; small fish (usually < 300 gm) were placed in double Ziplock bags. Fish were then frozen and shipped to the laboratory in the same manner as sediment samples. The laboratory dissected the larger fish using carbon steel dissecting equipment and ultraclean conditions. Tissues collected from larger fish for analysis of trace elements included: dorsal muscle from the midsection (above the lateral line and minus the skin), whole liver, and whole kidney. Smaller fish were similarly analyzed as whole fish, including the gut and gut contents. In 1988, dissection services were not offered by the laboratory, and were instead performed by the collector in the field. Dissections were performed with stainless steel and teflon dissection equipment on a clean metal-free surface, with new blades used on each tissue sample. Tissues were immediately placed in precleaned IChem Series 200 containers to reduce contamination and weighed in the tared container to reduce contaminant exposure. Samples were shipped to the laboratory in coolers with ice or dry ice by overnight air courier.

#### Laboratory Analyses

Laboratory QA/QC procedures, screening criteria to accept/reject analytical data, screening results, and the basis for rejection of certain analytical data, are described in Appendices C and D. In summary, duplicate (split) samples, spiked samples, and standard reference materials (SRM's) were used to evaluate data quality. In 1987 and 1988, blank data were also provided by the laboratory, and criteria were applied to eliminate samples with significant blank contamination. Tables 2 and 3 identify acceptable analytical data sets for water, sediments, and fish tissue analyses based on spike, SRM, and blank criteria and method limits of detection (LOD's) for accepted analytes.

Mercury analysis of water samples generally met all QC criteria, but were flunked due to excessive holding time. APHA et al. (1981) stipulate analysis of water samples within 28 days of sample collection; none of the samples collected in this study were analyzed until at least 6 months following collection. Therefore, mercury data for water samples are not presented in the report.

Several assumptions were required when accepting or rejecting data. For 1985, only dissolved metals samples were subjected to QA/QC screening; we therefore assumed that total recoverable metals analysis data would mirror dissolved metals data. For other years, we also assumed that,

TABLE 2. ACCEPTABLE DATA FOR METALS ANALYSIS OF WATER SHOWING LABORATORY METHOD DETECTION LIMITS IN MG/L. Shaded cells indicate duplicate analysis was conducted for an analyte with values less than twice the limit of detection. Concentrations in this region are qualitative only. Blank cells indicate unacceptable data for that year.

	WATER	YEAR			
Analyte	Method <sup>a</sup>	Matrix <sup>b</sup>	1985	1987	1988
Aluminum	ICPP	TRM/DM		0.015 <sup>c</sup>	
Arsenic	AA	TRM/DM	0.0005	0.004	0.003
Beryllium	ICPP	DM		0.001	
Cadmium	AA/ICPP <sup>d</sup>	TRM/DM	0.0001	0.001°	0.001
Cobalt	ICPP	TRM/DM		0.002	
Copper	AA/ICPP <sup>d</sup>	TRM/DM	0.0005	0.004	
Iron	AA/ICPP <sup>d</sup>	TRM/DM	0.02 <sup>e</sup>	0.01 <sup>e</sup>	0.15 <sup>c</sup>
Lead	AA	TRM/DM	0.001 <sup>e</sup>		
Manganese	ICPP	TRM/DM			0.01 <sup>ce</sup>
Nickel	ICPP	TRM/DM			0.01
Thallium	ICPP	TRM/DM			0.05
Tin	ICPP	DM		0.26	0.03
Zinc	AA/ICPP <sup>d</sup>	TRM/DM	0.01		0.03

<sup>a</sup> ICPP = ICP with preconcentration; AA = atomic absorption

<sup>b</sup> TRM = = total recoverable metals analysis; DM = dissolved metals analysis

<sup>c</sup> Only the TRM analysis is quantitative in the data set.

<sup>d</sup> AA was performed in 1985 only.

<sup>e</sup> Precision, measured by relative difference for analysis < .33, but > .17.

TABLE 3. ACCEPTABLE DATA FOR METALS ANALYSIS OF SEDIMENTS AND FISH TISSUES SHOWING LABORATORY METHOD DETECTION LIMITS IN MG/KG DRY WEIGHT. Shaded cells indicate duplicate analysis was conducted for an analyte with values less than twice the limit of detection. Concentrations in this region are qualitative. Blank cells indicate unacceptable data for that year.

SEDIMEN	YEAR		
Analyte N	Method <sup>a</sup>	1987	1988
Arsenic	ICP		1.0 <sup>b</sup>
Beryllium	ICP	0.8	0.1
Cadmium	ICP	0.8	0.5
Chromium	ICP	2.0	1.0
Copper	ICP	2.0 <sup>b</sup>	
Manganese	ICP		0.5
Mercury	AA	0.02 <sup>b</sup>	
Molybdenum	ICP	6.7	
Nickel	ICP	5.0	
Selenium	AA		1.0

FISH TI	YEAR		
Analyte	Method <sup>a</sup>	1987	1988
Arsenic	AA	4.7	
Barium	ICP		0.5
Beryllium	ICPP/ICP <sup>c</sup>	0.2	0.2
Boron	ICP		2.0
Cadmium	ICPP/ICP <sup>c</sup>	0.2	0.5
Cobalt	ICPP	0.9	
Copper	ICPP/ICP <sup>c</sup>	1.5	1.0 <sup>b</sup>
Chromium	ICP		2.0
Iron	ICPP	5.0 <sup>b</sup>	
Lead	ICPP/ICP <sup>c</sup>	2.3	4.0
Magnesium	ICP		2.0
Mercury	AA	0.02 <sup>b</sup>	
Molybdenum	ICP		1.0
Nickel	ICPP/ICP <sup>c</sup>	0.8	2.0
Selenium	ICP		0.5
Strontium	ICP		2.0
Thallium	ICP		10.0
Vanadium	ICP		1.0
Zinc	ICP		1.0

<sup>a</sup> AA = atomic absorption spectrometry; ICP = inductively coupled plasma spectrometry;

ICPP = ICP with preconcentration

<sup>b</sup> Precision for this analysis less than expected

<sup>c</sup> ICPP performed in 1987; ICP performed in 1988

if total metals data for an analyte were designated as qualitative, then dissolved metals data would also necessarily be qualitative.

Values reported for an analyte that are less than twice the detection limit should be considered qualitative only. Values between 2 and 10 times the detection limit should be

considered semi-quantitative, i.e., liable to more variability than in the zone of quantitation, where measured values are greater than 10 times the detection limit.

#### STATISTICAL ANALYSES

Data sets subjected to statistical analysis were transformed from the DBase IV data management system to Lotus 3.1<sup>®</sup>, where files were reformatted, means and sample standard deviations computed, missing values replaced with -99, and values below the detection limit replaced by one-half the detection limit. The Lotus compute function was used for computing pH logarithms and antilogs for statistical analysis of this parameter, for computing wet weight concentrations from dry weight concentrations of mercury in tissue samples, and for computations of fish condition index, using the formula:

$$K = \frac{Weight \ x \ 10^5}{Length^3}$$

where K is the condition factor (Ricker 1975).

Scatterplots were also produced in Lotus to examine variable distributions, and associations between variables. Particular attention was devoted to inspection of the relationships between metal concentrations in fish tissue and fish length, weight, and condition index, since impacts on fish condition from heavy metals might be indicated by linear or nonlinear decreases in condition with increasing metal concentration, or by bell-shaped distributions, depending on whether the metal is also a required trace element, with occurrence in limiting concentrations. Data sets with a majority of nondetected values were not submitted to these studies or to any subsequent statistical analysis. Remaining data were then imported into SPSS/PC+<sup>®</sup> statistical software for additional statistical analysis.

In virtually all cases, samples sizes between groups were similar, based on the sample approach of collecting three replicate samples of water and sediment at each site and the target of five fish of the same species per site. (Only northern pike were collected in sufficient sample sizes to permit statistical comparisons; no statistical tests were performed on the nontarget species collected.) However, on occasion, examination of these data using Cochran's C test for homogeneity of variance (Dixon and Massey 1957) indicated that the variances were not homogeneous. Data sets also contained some parameters which did not meet normality requirements for use of parametric statistics. To assure that mean differences between sites, years, and matrices were not identified as significantly different due to violations of normality or homogeneity of variance, tests for differences between means were performed concurrently using parametric tests, including one-way (single classification) analysis of variance for three or more samples with unequal sample sizes and Student t-tests for two samples, and analogous nonparametric tests, including the Kruskal-Wallis test for three or more samples and Mann-Whitney U tests, or Wilcoxin signed rank test for two-sample comparisons (Sokol and Rohlf 1981). For t-tests, a pooled variance estimate was used to calculate the t value when variances were not significantly different,

and separate variance estimate was used when variances between groups differed significantly. Results of parametric and complementary nonparametric tests were then compared. Significant differences (P < .05) or highly significant differences (P < .01) were only reported when the results agreed. On rare occasions, the probability level for the parametric test was just greater than 0.05, while the nonparametric test was just less than 0.05. These results were reported and qualified. In every comparison, results from parametric and nonparametric comparisons yielded virtually the same or very similar results. Therefore, a Scheffe multiple range test, a highly conservative parametric test for pairwise comparison of means (Sokol and Rohlf 1981), was then performed to identify differences between specific groups.

Correlations were examined using Pearson product-moment correlations for pairs of variables (Sokol and Rohlf 1981). The coefficient of determination,  $r^2$ , rather than the correlation coefficient, r, is presented for correlations in this report, together with the exact probability level in most cases. To further examine the relationship between multiple variables correlated with a dependent variable, forward stepwise regressions (Sokol and Rohlf 1980) were employed using the named variables and SPSS/PC+ default criteria.

## RESULTS

## WATER

#### Water Quality

Table 4 presents water quality data for the 1985 - 1988 studies. The methods used to measure water quality only allow for a general characterization of water quality, except in the case of conductivity and turbidity where methods were quantitative and holding times were within recommended limits. The conductivity of the study sites, an indication of the total ions in the water, ranged widely, from 100 - 380  $\mu$ S/cm, depending on location and year. Conductivity was highest at California Creek (Site 3), and lowest in the upper Nowitna River (Site 5).

The pH concentrations also differed between sites. Sites 1 and 2 (the Nowitna River at its mouth and the Sulatna River, respectively) appear circumneutral in pH, while other sites appear to have higher pH concentrations. The measured total alkalinities correlate poorly with the measured pH values at the sites, indicating a possible discrepancy in one or both measurements. Since the pH of the samples was measured several days after collection, instead of immediately, it is likely that the pH concentrations changed during the holding period. Total alkalinity (the sum of carbonates, bicarbonates, and hydroxides) at the sites ranged from moderate to high, except for the 1987 record for the upper Nowitna River. Therefore, the alkalinity data suggest that sites are relatively well buffered. Except for Site 5 in 1987 and Site 9 (the Titna River) in 1985, the sites can be described as moderately hard to hard (Sawyer 1960 in EPA 1986). Hardness values, measuring the concentration of polyvalent ions dissolved in the water, were in general agreement with alkalinity values in 1985 and 1988, suggesting that major ions in these systems are calcium and magnesium bicarbonate systems. Discrepancies between hardnesses and alkalinities in 1987 appear systematic, indicating a probable error in protocol or technique. The 1985 and 1988 data agree with 1984 data from Deschermeier and Hawkinson (1985). The techniques employed for measuring alkalinity and hardness were not precise, and values reported should be regarded as semi-quantitative.

Turbidity, a function of suspended clay, silt, organics, inorganics, and microorganisms in the water column, varied considerably among sites and sample years. However, water samples from the Sulatna River (Site 2) were an order of magnitude more turbid than other sites in both 1987 and 1988 (Figure 4). In contrast, turbidities observed in the Sulatna River in 1985 (Figure 4) and 1984 (Deschermeier and Hawkinson 1985) were comparable to other study sites, indicating that the high turbidities observed in 1987 and 1988 were probably not representative of natural baseline conditions. The turbidity of the Nowitna River, into which the Sulatna River flows, increased slightly from upstream (Site 5) to downstream (Site 1) in 1987, but negligibly in 1988. Replicate variability in turbidity was fairly high for both the Sulukna and Nowitna river samples, indicating that

Site No.	Collection Date	Conductivity µS/cm	рН	Total Alkalinity (mg/L)	Total Hardness (mg/L)	Turbidity (NTU)	Settleable Solids (mL/L)	Suspended Solids (mg/L)
1C	9/09/85ª	93	7.5	51	85	21	0.1	-
8	9/09/85ª	130	-	85	119	19	0.2	-
1B	9/27/85ª	130	7.0	85	102	4.7	0.0	-
2B	9/27/85ª	73	-	51	51	6.9	trace	-
1A	8/17/87 <sup>b</sup>	140	7.4	198	102	183	0.0	2.9
2A	8/19/87 <sup>b</sup>	140	7.3	198	85	3467	0.0	104
3	8/20/87 <sup>b</sup>	380	8.2	521	266	30	0.0	8.7
4	8/19/87 <sup>b</sup>	260	8.0	374	176	67	0.0	5.3
5	8/20/87 <sup>b</sup>	100	8.0	125	51	160	0.0	4.6
1A	8/17/88°	260	7.6	147	153	105	0.0	89
2A	8/18/88°	203	7.5	130	130	1183	0.0	15 <sup>d</sup>
3	8/16/88°	313	7.8	187	130	20	0.0	16 <sup>d</sup>
4	8/10/88°	315	8.0	193	181	8	0.0	50 <sup>d</sup>
5	8/23/88	78	8.0	68	45	101	0.0	13 <sup>d</sup>

TABLE 4. WATER QUALITY DATA FOR THE NOWITNA NATIONAL WILDLIFE REFUGE, 1985 - 1988. Each value represents the mean of three replicate values, except in 1985 when single samples were collected.

<sup>a</sup> Analysis date presumed to be same as collection date, but date not recorded. <sup>b</sup> Analyzed on 8/22/87

<sup>c</sup> Analyzed on 8/20/88

<sup>d</sup> Only two samples collected

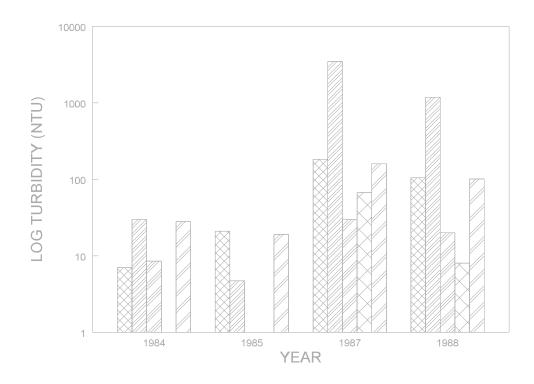


Figure 4. Turbidity in Nowitna National Wildlife Refuge drainages, 1984 - 1988. Turbidity data are shown on a logarithmic scale. The 1984 data are from Deschermeier and Hawkinson (1985). Site locations on the drainages differ slightly for 1984 and 1985 sites versus 1987 and 1988.

increased sample intensity, as well as collection of samples in sequence, based on flow rate, will be necessary to adequately examine turbidity impacts from the Sulatna River and other tributaries on Nowitna River turbidities. Little or no settleable solids were recorded at the study sites, but varying amounts of suspended solids were found. The highest suspended solids concentration, 104 mg/L, was the Sulatna River (Site 2) and corresponded to the highest turbidity recorded in this study. However, no apparent correlation was observed between suspended solids and turbidities of samples. Since suspended solids were measured after the currently recommended holding time of seven days (APHA et al. 1989), this may have resulted in compromised data quality.

#### Trace Elements

<u>Trace elements</u> in 1985. Quality control screening indicates that arsenic, cadmium, copper, iron, lead, manganese, and zinc data were acceptable for 1985 data sets. Tables 5 and 6 show results of trace element analysis for filtered (dissolved) water and unfiltered (total) respectively, for samples collected in October 1985 and analyzed for total recoverable metals.

TABLE 5. DISSOLVED METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1985. Concentrations are reported in mg/L.

SITE	DATE	As	Cd	Cu	Fe	Pb	Mn	Zn
1B	9/27/85	0.0010	0.0001	0.0060	0.89	0.0020	0.025	< 0.010
1C	9/09/85	0.0006	< 0.0001	0.0068	0.70	0.0033	0.028	< 0.010
2B	9/25/85	0.0008	0.0002	0.0073	1.40	0.0010	0.057	0.010
8	9/09/85	0.0006	< 0.0001	0.0073	0.70	0.0010	0.032	< 0.010

TABLE 6. TOTAL METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1985. Concentrations are reported in mg/L.

SITE	DATE	As	Cd	Cu	Fe	Pb	Mn	Zn
1B	9/27/85	0.0028	< 0.0001	0.0022	1.6	0.0020	0.032	< 0.010
1C	9/09/85	0.0028	< 0.0001	0.0058	5.1	0.0032	0.180	0.010
2B	9/27/85	0.0016	< 0.0001	0.0054	2.4	< 0.0010	0.065	< 0.010
8	9/09/85	0.0010	< 0.0001	0.0072	4.3	0.0032	0.130	0.010

Relatively high concentrations of iron and manganese occurred at all four sites. Total recoverable manganese in unfiltered water exceeded the EPA(1986)/State maximum contaminant level for drinking water criterion (0.05 mg/L) at 3 of 4 sites. At all four sites, the total recoverable iron in unfiltered water samples exceeded the drinking water criterion (0.3 mg/L), as well as the criterion for protection of freshwater life from chronic toxicity (1.00 mg/L), assuming that this concentration occurs on four or more consecutive days per year. Dissolved manganese constituted from 25 - 78 percent of the manganese present, while dissolved iron accounted for 14 - 58 percent of the iron present. The Nowitna River upstream of its confluence with the Titna River had the highest iron concentration, 5.1 mg/L, in unfiltered water. Only 14 percent of the iron was in the dissolved form, indicating an iron-rich particulate load in the water column. The Titna River also showed an extremely high concentration of iron, 4.3 mg/L total iron. Turbidity was strongly correlated with both total iron ( $r^2 = .98$ , df = 2, P < .05) and total manganese ( $r^2 = .94$ ,

df = 2, P < .05) in the four samples.

Arsenic, cadmium, and zinc were undetected or present at extremely low concentrations, in both total and dissolved forms, at all four sites. More dissolved copper was present than total copper, indicating an external source of contamination of this metal in the dissolved water samples, and possibly, the total metals samples. Total copper concentrations in the samples are typical of urban waters and below current EPA (1986)/State criteria for protection of aquatic life from chronic toxicity (0.012 mg/L for water at a total hardness of 100 mg/L as CaCO<sub>3</sub>). However, copper concentrations are within published ranges for affecting sensitive species of algae, invertebrates and fish. The highest concentration of copper (0.0072 mg/L) was observed on the Titna River.

Lead concentrations in water samples were similar for total and dissolved metals samples indicating that virtually all lead was in the dissolved form. Concentrations at all sites are substantially lower than the current EPA (1986) maximum contaminant level for drinking water (0.015 mg/L). However, concentrations at two of the sites, the Titna River (Site 8), and the Nowitna River just upstream of the Titna River (Site 1C) are at the EPA/State criterion of 0.0032 mg/L (at a total hardness of 100 mg/L as CaCO<sub>3</sub>) for the protection of freshwater aquatic life from chronic toxicity. Low hardness (45 - 85 mg/L as CaCO<sub>3</sub>) was reported for the upper Nowitna River in 1985 - 1988 (Table 4), suggesting that lead levels in this area could affect sensitive species over a prolonged period.

<u>Trace elements in 1987.</u> In 1987 two sites were sampled on the Nowitna River, and one site was sampled on the Sulatna River, but these sites were at different locations than 1985 locations. Also, two new locations were sampled, California Creek, which empties into the Titna River, and the Sulukna River, which drains into the Nowitna River (see Figure 3).

Quality control screening indicates that arsenic, beryllium, cadmium, cobalt, copper, and tin data sets are satisfactory for the dissolved metals analysis. Similarly, aluminum, arsenic, beryllium, cadmium, cobalt, copper, and iron metals data sets are acceptable for total metals analysis in 1987. Tables 7 and 8 show the trace element analytical results for dissolved and total recoverable metals, respectively. Iron concentrations again exceeded the EPA (1986) maximum

contaminant level for drinking water on the lower Nowitna River (Site 1) and the Sulatna River (Site 2), as well as on the Sulukna River (Site 4). No other trace element exceeded drinking water quality standards. The mean iron concentration in the Sulatna River also exceeded the EPA/State criterion for protection of aquatic life from chronic toxicity. The mean concentrations of other trace elements did not exceed water quality criteria.

SITE	DATE	As	Be	Cd	Со	Cu
1	8/17/87	< 0.004	< 0.001	< 0.001	0.004	0.015
		< 0.004	< 0.001	< 0.001	< 0.002	0.005
		< 0.004	< 0.001	< 0.001	< 0.002	0.014
	Ā	-	-	-	-	0.011
2	8/19/87	< 0.004	< 0.001	0.002	0.002	0.009
		< 0.004	< 0.001	0.001	< 0.002	0.011
		< 0.004	< 0.001	< 0.001	0.004	0.008
11	x	-	-	0.001	0.002	0.009
3	8/19/87	< 0.004	< 0.001	< 0.001	< 0.002	0.009
		< 0.004	< 0.001	0.002	0.002	< 0.004
		< 0.004	< 0.001	< 0.001	0.006	0.010
1	x	-	-	-	0.003	0.007
4	8/19/87	< 0.004	< 0.001	< 0.001	0.003	0.007
		< 0.004	< 0.001	0.001	0.002	0.007
		< 0.004	< 0.001	0.002	< 0.002	0.009
	x	-	-	0.001	0.002	0.008
5	8/18/87	< 0.004	< 0.001	< 0.001	0.002	0.010
		< 0.004	< 0.001	< 0.001	0.002	0.009
		< 0.004	< 0.001	< 0.001	0.002	0.015
	Ā	-	-	-	0.002	0.011

TABLE 7. DISSOLVED METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1987. Concentrations are reported in mg/L.<sup>ab</sup>

<sup>a</sup> Mean concentrations were computed using  $\dot{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> No tin was detected in any sample.

TABLE 8. TOTAL METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1987. Concentrations are reported in mg/L.<sup>ab</sup>

SITE	DATE	Al	As	Cd	Co	Cu	Fe
1	8/17/87	0.046	0.004	< 0.001	0.003	0.005	0.806
		0.092	< 0.004	< 0.001	< 0.002	0.011	0.883
		0.023	< 0.004	< 0.001	0.002	0.008	0.854
	Ā	0.054	-	-	0.002	0.008	0.848
2	8/19/87	0.106	< 0.004	< 0.001	0.004	0.010	2.010
		0.047	< 0.004	0.001	0.007	0.013	2.500
		0.150	< 0.004	0.001	0.004	0.011	3.250
	Ā	0.101	-	0.001	0.005	0.011	2.587
3	8/19/87	0.015	< 0.004	< 0.001	< 0.002	0.009	0.016
		< 0.015	< 0.004	0.001	0.002	0.008	0.023
		0.027	< 0.004	< 0.001	< 0.001	0.006	0.034
	ĪX	0.016	-	-	-	0.008	0.024
4	8/19/87	< 0.015	< 0.004	0.001	< 0.002	< 0.004	0.169
		< 0.015	< 0.004	< 0.001	< 0.002	0.006	0.184
		< 0.015	< 0.004	0.002	0.002	0.006	0.189
	ĪX	-	-	0.001	-	0.005	0.181
5	8/18/87	0.069	< 0.004	0.002	0.003	0.006	0.866
		0.053	< 0.004	0.001	0.003	< 0.004	0.710
		0.048	< 0.004	0.003	0.002	0.009	1.090
	ĪX	0.057	-	0.002	0.003	0.006	0.889

<sup>a</sup> Mean concentrations were computed using  $\hat{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Beryllium was not detected in any sample.

Results of one-way analysis of variance and the Kruskal-Wallis test of n-independent samples paralleled one another. The former statistical results showed that total iron concentrations were significantly different among sites ( $F_{4,10} = 36.1827$ , P < .0001); Site 2 iron concentrations were significantly different (P < .05) than all other sites, which formed a homogeneous subset. Total aluminum concentrations were also significantly different among sites ( $F_{4,10} = 4.9756$ , P = .018), but the only demonstrated significant difference among specific sites shown in the Scheffe

multiple range test was between Sites 2 and 4. No significant differences in total copper concentrations occurred among sites ( $F_{4,10} = 3.16$ , P = .064). Total iron was significantly correlated with total aluminum ( $r^2 = 0.93$ , df = 3,

P < .01) and with turbidity ( $r^2 = 0.88$ , df = 3, P < .05), but aluminum was not significantly correlated with turbidity.

As predicted by the trace concentrations reported in 1985 data sets, arsenic was not detected in water at any of the sites sampled in 1987. Tin and beryllium were also not detected in any sample. Total aluminum ranged from below detection (<0.015 mg/L) in the Sulukna River to 0.101 mg/L in the Sulatna River, below any concentration of biological concern at the pH concentrations reported for these rivers (Hunn et al. 1985, Jagoe and Haines 1987, Cleveland et al. 1989). Mean total cadmium concentrations exceeded the detection limit of 0.001 mg/L at three sites: the Nowitna River near its mouth (Site 1), the Sulatna River at the refuge border (Site 2), and the Sulukna River near its mouth (Site 4). The data suggest that much of this cadmium could be in the dissolved form. Since the detection limit of cadmium in 1987 was approximately equal to the chronic toxicity criterion of 0.0011 mg/L, there is a possibility of adverse effects on aquatic life; however, additional study with lower detection limits is needed to quantify concentrations present. Mean total cobalt concentrations were also detectable at Sites 1, 2, and 5. Cobalt is an essential nutrient; concentrations are in sufficiently trace amounts that levels are not of biological concern. Total and dissolved copper concentrations were similar to those reported in 1985 for the Nowitna and Sulatna rivers. Dissolved copper concentrations slightly exceeded total copper concentrations in three of five samples, suggesting analytical imprecision or sporadic laboratory contamination of dissolved, and possibly total, metals samples. Lower detection limits and additional study is needed to confirm and quantify the copper present in Nowith water samples. If concentrations for copper are accurate, they are in the range to result in adverse effects to sensitive aquatic life, particularly young Arctic grayling stages.

<u>Trace elements in 1988.</u> Quality control screening indicates that dissolved arsenic, cadmium, iron, manganese, nickel, tin, thallium, and zinc data are acceptable for the 1988 data set. Similarly, total arsenic, cadmium, nickel, thallium, and zinc data sets are satisfactory. Tables 9 and 10 show results of dissolved and total metals analysis of water, respectively, for samples collected in August 1988 and analyzed for total recoverable metals.

Arsenic was not detected in any dissolved metals sample and in most total metals samples, confirming earlier results. Also, dissolved cadmium was not detected in any sample. Total cadmium concentrations were also extremely low at all sites, in agreement with 1985 results and with 1987 results at two of five sites. Nickel was only detected in samples from the Sulatna River, and only in trace amounts. Thallium was detected in only one of three replicates at Site 1; no dissolved thallium was found. Similarly, zinc concentrations were low or undetected. No total iron or manganese data are available. However, the 1988 dissolved metals data set again reveals very high iron and manganese concentrations in refuge waters with the highest concentrations occurring in the Sulatna River, Site 2. Dissolved iron differed significantly among sites ( $F_{4,14} = 86.8687$ , P < .0001), with Site 2 concentrations significantly higher (P < .05) than all other sites. Dissolved manganese concentrations also differed among sites ( $F_{4,14} = 86.8687$ , P < .0001), with Site 2 concentrations significantly higher (P < .05)

# TABLE 9. DISSOLVED METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1988. Concentrations are reported in mg/L.<sup>ab</sup>

SITE	DATE		Fe	Mn	Ni
1	8/09/88		0.0440	0.0067	< 0.0036
			0.1170	0.0190	< 0.0018
			0.1030	0.0157	< 0.0018
		Ā	0.0880	0.0138	-
2	8/10/88		3.4900	0.1850	0.0046
			2.8100	0.1350	< 0.0018
			3.9700	0.1880	0.0023
		X	3.4233	0.1693	0.0026
3	8/16/88		0.1600	0.0108	< 0.0018
			0.2290	0.0146	< 0.0018
		Ā	0.1945	0.0127	-
4	8/10/88		0.0733	0.0161	< 0.0018
			0.1040	0.0195	< 0.0018
			0.1380	0.0230	< 0.0018
		Ā	0.0887	0.0195	-
5	8/15/88		0.8020	0.0331	< 0.0018
			0.6500	0.0372	< 0.0018
			0.5830	0.0280	< 0.0018
		Ā	0.6783	0.0328	-

<sup>a</sup> Mean concentrations were computed using  $\mathring{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Arsenic, cadmium, tin, thallium, and zinc were not detected in any sample.

TABLE 10. TOTAL METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1988. Concentrations are reported in mg/L.<sup>a</sup>

SITE	DATE	As	Cd	Ni	T1	Zn
1	8/09/88	< 0.003	0.0005	< 0.0018	< 0.0118	0.0127
		< 0.003	< 0.0004	< 0.0036	< 0.0236	0.0036
		< 0.003	< 0.0002	< 0.0018	0.0179	<0.0001
	X	-	-	<0.0024	-	0.0055
2	8/10/88	0.004	< 0.0002	0.0002	<0.0118	< 0.0001
		< 0.003	< 0.0002	< 0.0018	< 0.0118	<0.0001
		< 0.003	< 0.0002	< 0.0018	< 0.0118	<0.0001
	X	-	< 0.0002	-	< 0.0118	< 0.0001
3	8/16/88	< 0.003	< 0.0002	< 0.0018	< 0.0118	< 0.0001
		0.003	< 0.0002	< 0.0018	<0.0118	< 0.0001
	X	-	< 0.0002	< 0.0018	<0.0118	< 0.0001
4	8/10/88	< 0.003	< 0.0002	< 0.0018	<0.0118	< 0.0001
		< 0.003	< 0.0002	< 0.0018	<0.0118	0.0011
		< 0.003	< 0.0002	< 0.0018	<0.0118	<0.0001
	X	-	< 0.0002	< 0.0018	<0.0118	-
5	8/15/88	< 0.003	< 0.0002	< 0.0018	<0.0118	0.0007
		< 0.003	< 0.0002	< 0.0018	< 0.0118	<0.0001
		< 0.003	< 0.0002	< 0.0109	< 0.0109	<0.0001
	X	-	< 0.0002	< 0.0018	< 0.0115	-

<sup>a</sup> Mean concentrations were computed using  $\hat{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

70.6494, P < .0001), with Site 2 concentrations significantly higher than at all other sites (P < .05), which formed a homogeneous subset. Both dissolved iron and dissolved manganese concentrations were significantly correlated with turbidity ( $r^2 = .98$ , df = 3, P < .01).

#### **SEDIMENTS**

#### Trace Elements in 1987

Metals identified as acceptable from quality control screening of 1987 sediment analyses included beryllium, cadmium, chromium, copper, mercury, molybdenum, nickel, vanadium, and zinc (Table 11). Cadmium and molybdenum were not detected in any sample. Mean metal concentrations at the sites in mg/kg dry weight were beryllium, 0.89 - 1.42; chromium, 52.0 - 74.4; copper, 17.4 - 31.4; mercury, 0.23 - 1.58; nickel, 25.0 - 38.3; vanadium, 120.8 - 172.7; and zinc 52.8 - 95.4.

Although there were several cases where significant differences among sites were identified using one-way analysis of variance, significant differences among specific sites demonstrable by the Scheffe range test were only identified for mercury. Mercury sediment concentrations were highest ( $\bar{x} = 1.58 \text{ mg/kg}$ ) at Site 2 (the Sulatna River) and Site 1 ( $\bar{x} = 1.11 \text{ mg/kg}$ ) and lowest ( $\bar{x} = 0.23 \text{ mg/kg}$ ) at Site 3. Site 2 concentrations were significantly higher than those of Sites 3 (California Creek) and 4 (the Sulukna River); Site 1 (the lower Nowitna River) concentrations were also significantly higher than those of Site 3. Mean mercury concentrations in sediments at each site were negatively correlated with mean surface water pH at the sites ( $r^2 = .875$ , df = 3, P < .01), but not with any other water quality variable.

Table 12 shows correlations among sediment metals for the 1987 data set. No significant correlations are observed between mercury and any other metal, but numerous other positive, significant relationships among metals are present. Nickel, chromium, and vanadium are highly correlated with each other.

#### Trace Elements in 1988

Metals meeting quality control standards in 1988 sediments included arsenic, beryllium, cadmium, chromium, manganese, selenium, strontium, thallium, vanadium, and zinc (Table 13). Most cadmium, selenium, and thallium concentrations were below detection, with the notable exception of thallium in sediment at Site 4, the Sulukna River, indicating a potential source of this rare earth in the drainage. Mean trace element concentrations at

TABLE 11. TOTAL RECOVERABLE METAL CONCENTRATIONS IN SEDIMENT FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1987. Concentrations are reported in mg/kg dry weight.<sup>ab</sup>

SITE	DATE	Be	Cr	Cu	Hg	Ni	V	Zn
1	8/17/87	1.06	63.5	21.30	1.12	30.1	146.0	58.0
		1.21	69.4	22.10	1.10	34.0	156.0	69.1
		< 0.80	27.7	8.71	1.12	10.9	60.4	31.3
		x 0.89	53.5	17.37	1.11	25.0	120.8	52.8
2	8/18/87	1.40	72.5	23.70	1.61	36.3	169.0	75.3
		1.45	73.1	25.80	1.38	36.2	167.0	78.6
l		1.30	81.4	23.30	1.74	39.1	182.0	94.2
		x 1.38	75.7	24.27	1.58	37.2	172.7	82.7
3	8/19/87	1.07	73.2	31.20	0.27	37.6	161.0	82.1
		1.24	70.5	28.00	0.05	35.7	154.0	74.2
l		1.07	79.6	35.10	0.38	41.6	171.0	83.8
		x 1.13	74.4	31.43	0.23	38.3	162.0	80.0
4	8/19/87	0.97	58.2	24.10	0.85	31.1	130.0	61.2
		< 0.80	39.3	9.93	0.26	23.2	93.1	46.8
		0.92	58.4	24.40	0.77	32.5	126.0	77.8
		x 0.76	52.0	19.48	0.62	28.9	116.4	61.9
5	8/18/87	1.48	72.6	22.10	1.23	36.3	168.0	81.8
		1.40	74.1	22.80	0.79	36.3	173.0	96.4
		1.38	76.7	25.30	0.35	37.4	174.0	108.0
		x 1.42	74.5	23.40	0.79	36.7	171.7	95.4

<sup>a</sup> Mean concentrations were computed using η the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.
 <sup>b</sup> No cadmium or molybdenum were detected in any sample.

TABLE 12. CORRELATION MATRIX FOR 1987 SEDIMENT METALS FROM FIVE NOWITNA RIVER SITES, WITH THREE REPLICATES PER SITE. Significant correlation coefficients (r) are presented for one-tailed tests.

Element	Be	Cr	Cu	Hg	Ni	V
Cr	.8950**					
Cu	.6315*	.8309**				
Hg	.3008	.1018	2164			
Ni	.8225**	.9701**	.8699**	0203		
V	.9235**	.9915**	.7678**	.1543	.9539**	
Zn	.8020**	.8814**	.6850*	0346	.8656**	.8788**

\* 0.01 probability level \*\* 0.001 probability level

SITE	DATE	As	Be	Cd	Cr	Mn	Se	Sr	Tl	V	Zn
1	8/09/88	9.3	0.34	<0.78	24.2	346.3	< 0.78	24.1	<16.9	42.5	68.8
		13.8	0.53	1.07	30.7	412.6	< 0.80	28.8	<17.6	49.5	86.2
		14.2	0.54	<0.90	34.4	454.1	< 0.90	31.2	20.7	56.8	98.9
	Ā	12.4	0.47	-	29.8	404.0	< 0.83	28.0	-	49.6	84.7
2	8/10/88	23.8	0.50	<0.90	31.5	632.6	< 0.89	34.1	<19.5	53.9	97.3
		18.2	0.41	< 0.83	27.7	645.1	< 0.83	31.2	<18.1	48.6	88.2
		15.7	0.36	0.83	26.3	356.9	<0.77	21.8	20.0	43.5	81.5
	Ā	19.2	0.43	-	28.5	545.0	< 0.83	29.0	-	48.7	89.0
3	8/16/88	27.9	0.68	1.13	37.7	1023.4	<1.06	56.6	<23.2	66.2	111.7
		15.4	0.36	<0.75	21.5	702.5	< 0.75	38.4	<16.3	37.1	68.9
		12.5	0.61	<0.96	29.5	873.5	< 0.96	59.0	<20.9	50.2	98.5
	Ā	18.6	0.55	-	29.6	867.0	< 0.92	51.3	<20.1	51.1	93.0
4	8/10/88	9.5	0.25	<0.62	13.1	405.2	< 0.62	26.6	17.5	20.3	39.2
		34.8	0.76	<1.19	40.1	1090.6	2.17	102.9	28.4	63.0	119.6
		17.7	0.34	<0.74	18.0	657.7	<0.74	38.2	19.6	26.6	53.7
	Ā	20.7	0.45	<0.85	23.7	718.0	-	55.9	21.8	36.7	70.8
5	8/15/88	14.2	0.44	<0.82	25.4	567.9	< 0.81	21.1	<17.8	44.5	87.6
		15.1	0.60	<0.84	35.3	848.7	<0.84	40.7	<18.3	55.8	108.9
		9.3	0.30	<0.56	14.0	296.8	< 0.56	9.7	<12.2	26.2	46.8
	Ā	12.9	0.45	<0.74	24.9	571.0	< 0.74	23.8	<16.1	42.2	81.1

TABLE 13. TOTAL RECOVERABLE METAL CONCENTRATIONS IN SEDIMENT FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1988. Concentrations are in mg/kg dry weight.<sup>a</sup>

<sup>a</sup> Mean concentrations were computed using  $\hat{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

the sites in mg/kg dry weight were arsenic, 12.4 - 20.7; beryllium, 0.43 - 0.55; chromium, 23.7 - 29.8; manganese, 404 - 867; strontium, 23.8 - 55.9; vanadium, 36.7 - 51.1; and zinc, 70.8 - 93.0.

Significant between-year differences occurred in mean concentrations of beryllium (t = 4.74, df = 4, P < .01); chromium (t = 7.30, df = 4, P < .01); and vanadium (t = 8.78, df = 4, P < .01), with 1987 concentrations of these metals being more than double the 1988 concentrations. Mean site concentrations in 1987 and 1988 were not significantly correlated, suggesting differences in sample method or sample site, or the existence of a systematic laboratory error. Between-year differences in beryllium are comparatively small and within potential deviations when concentrations are below 10 times the detection limit. However, between-year differences for chromium and vanadium were in the zone of quantitation where errors of this type are not expected. The 1987 concentrations are unusually high for Alaskan

river sediments, raising questions as to analytical validity. Additional data are needed to clarify this issue.

There were no significant differences among sites for arsenic, beryllium, chromium, manganese, strontium, vanadium, or zinc. Large differences in site means sometimes occurred, but high within-site variation in replicate concentrations accounted for lack of statistical differentiation among sites.

Significant positive correlations were again demonstrated among metal concentrations in sediment samples, the strongest association again being among chromium, vanadium, and zinc. Arsenic was most strongly correlated with manganese and strontium, two other divalent cations, but the associations were not sufficiently strong ( $r^2 = .58$  and .63) to predict arsenic concentrations. No significant correlations were found between sediment metals and water quality parameters.

#### FISH

Fish collected at 1987 study sites (Table 14) included four northern pike from Site 1, five northern pike from Site 4, one longnose sucker from Site 2, one sheefish each from Sites 1 and 2, and four Arctic grayling from Site 3. Arctic grayling were analyzed as whole fish. Liver, muscle, and kidney were analyzed from northern pike and sheefish; only muscle was analyzed from the one longnose sucker collected. Fish collected in 1988 (Table 15) included five northern pike from Site 1, four northern pike from Site 2, and 3 northern pike from Site 5; also, one broad whitefish was collected from Site 5 and two longnose suckers were collected from Site 2. One small northern pike was analyzed as a whole fish. Dorsal muscle and liver tissues were analyzed from the other samples.

#### Fish Length, Weight, and Condition

Northern pike was the only species represented in sufficient numbers to allow statistical comparisons of fish metrics, including fish condition between years at Site 1 and among sites within years. The condition factor (K) for northern pike ranged from 0.32 to 2.44 at refuge sites. Mean condition in 1987 (0.73) and 1988 (1.13) for pike from Site 1 did not differ significantly between years, when (1) all data were included for these sites (t = -1.02, df = 7, P = .341) or (2) when the data were censored to eliminate extreme sizes (weights  $\leq$  200 gm and  $\geq$  3500 gm) (t = -1.27, df = 5, P= .328). Similarly, no significant differences were demonstrated in fork lengths or weights of northern pike at Site 1 between years.

Student's paired t tests comparing fork lengths, weights, and condition indices between Sites 1 and 4 showed no significant difference in 1987 using either censored or uncensored data sets. Also, analysis of variance revealed no significant differences among Sites 1, 2, and 5 in fork length or weight in 1988. Condition differed significantly among sites in 1988 ( $F_{2,6} = 6.06$ , P = .036) in the censored data set, but not in the uncensored data set. Site 1 fish were generally

## TABLE 14. FISH SAMPLES COLLECTED FROM THE NOWITNA NATIONAL WILDLIFE REFUGE FOR TRACE ELEMENT ANALYSIS, 1987.

Site	Species	Date	Weight (gm)	Total Length	Fork Length	Mo	oisture (Perc	<u>eent)</u>
			(gm)	(mm)	(mm)	Muscle	Liver	Kidney
1	Northern Pike	8/19/87	1135	745	710	0.79	0.71	0.74
	Northern Pike	8/19/87	3405	805	770	0.79	0.62	0.79
	Northern Pike	8/19/87	1816	645	615	0.80	0.70	0.91
	Northern Pike	8/19/87	6923	925	865	0.74	0.60	0.84
4	Northern Pike	8/20/87	1350	574	542	0.81	0.74	0.62
	Northern Pike	8/20/87	1250	593	555	0.78	0.76	0.74
	Northern Pike	8/20/87	1500	611	578	0.82	0.74	0.79
	Northern Pike	8/20/87	2000	664	635	0.76	0.69	0.70
	Northern Pike	8/20/87	6800	995	915	0.76	0.71	0.75
2	Longnose Sucker	8/21/87	1000	450	420	0.77	-	-
1	Sheefish	8/19/87	2497	680	630	0.74	0.78	0.77
2	Sheefish	8/16/87	2000	575	525	0.75	0.79	0.83
3	Grayling	8/24/87	200	255	245	0.58ª	-	-
	Grayling	8/24/87	150	240	225	0.58ª	-	-
	Grayling	8/24/87	200	242	225	0.63ª	-	-
	Grayling	8/24/87	200	252	235	0.64ª	-	-

<sup>a</sup> Whole fish samples

# TABLE 15. FISH SAMPLES COLLECTED FROM THE NOWITNA NATIONAL WILDLIFE REFUGE FOR TRACE ELEMENT ANALYSIS, 1988.

Site	Species	Date	Weight (gm)	Total Length (mm)	Fork Length (mm)	<u>Moisture (</u> Muscle	Percent) Liver
1	Northern Pike	8/17/88	2050	670	632	0.79	0.72
	Northern Pike	8/17/88	1550	612	580	0.79	0.65
	Northern Pike	8/17/88	131	190	175	0.77ª	-
	Northern Pike	8/17/88	2800	730	690	0.79	0.69
	Northern Pike	8/20/88	1450	605	575	0.78	0.68
2	Northern Pike	8/18/88	200	330	310	0.80	0.65
	Northern Pike	8/22/88	1500	570	545	0.79	0.76
	Northern Pike	8/24/88	1400	600	575	0.80	0.70
5	Northern Pike	8/23/88	1150	580	550	0.82	0.80
	Northern Pike	8/23/88	750	580	510	0.81	0.74
	Northern Pike	8/23/88	700	490	460	0.74	0.78
2	Longnose Sucker	8/18/88	700	415	395	0.81	0.76
	Longnose Sucker	8/18/88	1200	500	465	0.80	0.71
5	Broad Whitefish	8/24/88	200	242	225	0.77	0.70

<sup>a</sup> Whole fish samples.

lower in condition than Site 5 fish, with Site 2 fish being intermediate in condition factor. However, Mann-Whitney U tests of differences between Sites 1 and 4 in 1987 and Kruskal-Wallis comparisons of Sites 1, 2, and 5 in 1988 did not disclose significant differences (P > .05) in weight, fork length, or condition in either year on censored or uncensored data. Some differences were in the range of P < .10, indicating the need for additional sampling to confirm or reject this finding.

#### Trace Elements

<u>Trace elements in 1987.</u> Analytes passing quality control screening include arsenic, beryllium, cadmium, cobalt, copper, iron, lead, mercury, and nickel. Tables 16, 17, and 18 show results of these analyses by tissue and species.

### TABLE 16. TRACE ELEMENTS IN NOWITNA NATIONAL WILDLIFE REFUGE FISH LIVERS, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

SITE	DATE	SPECIES	Cd	Cu	Fe	Hg	Ni
1	8/19/87	Northern Pike	< 0.200	23.20	245	0.55	2.29
		Northern Pike	0.374	27.00	654	0.68	1.38
		Northern Pike	< 0.200	25.50	177	0.18	0.91
		Northern Pike	< 0.200	8.44	219	0.42	1.81
	x		-	21.04	324	0.46	1.60
4	8/20/87	Northern Pike	< 0.200	25.80	1560	3.34	<0.80
		Northern Pike	< 0.200	22.90	1760	5.88	1.74
		Northern Pike	0.307	18.90	339	1.61	<0.80
		Northern Pike	< 0.200	23.90	1120	3.06	0.88
		Northern Pike	0.314	25.10	234	5.40	<0.80
	x		-	23.32	1003	3.86	-
1	8/19/87	Sheefish	< 0.200	68.60	725	0.87	<0.80
2	8/16/87	Sheefish	0.897	126.00	1420	0.56	2.16

<sup>a</sup> Mean concentrations were computed using  $\dot{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Arsenic and cobalt were not detected in any liver tissue.

*Liver tissue.* Arsenic was not detected in fish livers, and cadmium was below detection except in four liver samples, two northern pike from Site 4 (0.307 and 0.314 mg/kg), a pike from Site 1 (0.374 mg/kg) and a sheefish from Site 2 (0.897 mg/kg). Nickel was detected in all Site 1 northern pike, but from only two of five pike at Site 4. The sheefish from Site 2 also had detectable nickel. Copper, iron, and mercury were detected in all liver samples. Copper concentrations in pike livers were consistent among samples (18.9 - 27.0 mg/kg) except in one liver (8.44 mg/kg), while iron concentrations were more variable in the northern pike (219 - 1760 mg/kg). Mercury concentrations varied less, ranging from 0.18 - 5.88 mg/kg dry weight. The two sheefish sampled had lower mercury concentrations than most of the northern pike.

#### TABLE 17. TRACE ELEMENTS IN NOWITNA NATIONAL WILDLIFE REFUGE FISH MUSCLE AND WHOLE ARCTIC GRAYLING, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

SITE	DATE	SPECIES	As	Cd	Cu	Fe	Hg	Ni
1	8/19/87	Northern Pike	<0.4	< 0.200	4.67	9.74	2.49	<0.80
		Northern Pike	<0.4	0.202	2.71	15.70	2.72	1.09
		Northern Pike	<0.4	< 0.200	2.33	11.70	0.61	<0.80
		Northern Pike	0.7	<0.200	1.65	9.32	2.45	<0.80
	x		-	-	2.78	13.21	1.80	-
4	8/20/87	Northern Pike	<0.4	< 0.200	1.64	19.20	5.38	<0.80
		Northern Pike	<0.4	0.324	22.20	1770	13.2	<0.80
		Northern Pike	<0.4	0.212	2.08	16.30	4.02	<0.80
		Northern Pike	<0.4	< 0.200	2.51	15.50	5.47	<0.80
		Northern Pike	<0.4	<0.200	<1.50	11.90	6.72	<0.80
1	x		-	-	5.84	366.6	6.96	-
2	8/21/87	Longnose Sucker	<0.4	< 0.200	1.63	20.80	0.75	<0.80
		Sheefish	<0.4	< 0.200	2.52	19.60	0.73	1.86
	8/16/87	Sheefish	<0.4	< 0.200	3.09	30.80	0.44	0.88
3	8/24/87	Arctic Grayling	<0.4	< 0.200	4.60	1260	0.08	1.80
		Arctic Grayling	0.7	< 0.200	4.84	1650	0.09	2.48
		Arctic Grayling	0.8	0.205	5.07	1250	0.09	2.72
		Arctic Grayling	<0.4	<0.200	2.25	552	0.08	2.01
	x		-	-	4.19	1178	0.09	2.25

 $^a$  Mean concentrations were computed using  $\dot{\eta}\,$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit. <sup>b</sup> Cobalt was not detected in any muscle or whole body sample.

SITE	DATE	SPECIES	Cd	Co	Cu	Ni	Fe	Hg
1	8/19/87	Northern Pike	0.264	<0.9	4.93	1.08	496	0.90
		Northern Pike	0.491	<0.9	5.70	2.36	648	0.61
		Northern Pike	0.318	<0.9	6.16	1.46	598	0.28
		Northern Pike	< 0.200	<0.9	5.18	<0.80	516	1.68
	x		0.293	-	5.49	1.33	564	0.87
4	8/20/87	Northern Pike	-	-	-	-	-	4.21
		Northern Pike	0.382	<0.9	6.17	1.81	473	9.17
		Northern Pike	0.845	<0.9	8.45	<0.80	582	4.82
		Northern Pike	<0.200	<0.9	6.37	1.82	632	5.93
		Northern Pike	2.060	<0.9	5.88	1.40	447	11.80
	x		0.846	-	6.72	1.36	533	7.93
1	8/19/87	Sheefish	0.638	<0.9	6.70	1.57	580	0.64
2	8/16/87	Sheefish	1.350	1.4	4.98	2.67	1280	0.69

TABLE 18. TRACE ELEMENTS IN NOWITNA NATIONAL WILDLIFE REFUGE FISH KIDNEYS, 1987. Residues are reported in mg/kg dry weight.<sup>ab</sup>

<sup>a</sup> Mean concentrations were computed using  $\mathring{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Arsenic and cobalt were not detected in any kidney sample.

Iron concentrations varied considerably among fish, and differences in liver iron between Sites 1 and 4, the only sites with sufficient pike for statistical comparisons, were not significant. Copper liver concentrations were also not significantly different between sites. Highly significant differences between Sites 1 and 4 occurred in liver mercury content (t = -4.31, df = 4.15, P = .012). Site 1 mercury concentrations in pike livers averaged 0.46 mg/kg, while Site 4 liver concentrations averaged 3.86 mg/kg, more than eight times higher. Liver mercury and liver iron concentrations were themselves positively correlated ( $r^2 = .37$ , df= 8, P = .039).

*Muscle tissue and whole fish samples.* Cobalt was not detected in any muscle or whole fish, and arsenic and cadmium were detected in only a few fish. However, two of the whole Arctic grayling contained detectable arsenic (0.7 and 0.8 mg/kg), while only one northern pike contained detectable arsenic in muscle tissue. Nickel was also found in all four Arctic grayling and both sheefish, but only in one Site 1 northern pike muscle sample. Iron and copper concentrations in muscle samples were generally low in comparison to those in livers and whole

fish (Arctic grayling). Liver mercury concentrations were highly correlated with muscle mercury concentrations ( $r^2 = .82$ , df = 8, P < .0001), and also correlated with muscle copper ( $r^2 = .64$ , df = 8, P = .004) and iron ( $r^2 = .74$ , df = 8, P = .002). However, the absolute concentrations of mercury were significantly higher in muscle than in liver tissue of northern pike (paired t = 3.78, df = 8, P = .005).

Whole Arctic grayling from Site 3 were significantly lower in mercury ( $\bar{x} = 0.09 \text{ mg/kg}$ ) than pike muscle from Sites 1 and 4 ( $\bar{x} = 4.78 \text{ mg/kg}$ ) (t = 3.82, df = 8, P = .005). Muscle mercury concentrations of the longnose sucker from Site 1 and the sheefish from Sites 1 and 2 were higher than those of Arctic grayling, but lower than all but one pike.

Mercury concentrations in northern pike muscle were also significantly different between sites (t = -2.60, df = 7, P = 0.036), with Site 4 mercury concentrations averaging 6.96 mg/kg and Site 1 mercury concentrations averaging 2.06 mg/kg, a threefold difference. A pronounced difference also occurred in mercury concentrations in northern pike kidney at Sites 1 and 4 (t = -4.31, df = 4.34, P = .01), with Site 4 mercury concentrations averaging 7.18 mg/kg and Site 1 concentrations averaging 0.86 mg/kg.

*Kidney tissue.* Neither cobalt nor arsenic were detected in Nowitna fish kidney samples. However, measurable cadmium was detected in most fish kidneys, with 2.06 mg/kg in a northern pike from Site 4 being the highest concentration. Nickel and copper were also present in all kidneys, with copper concentrations in the kidney at concentrations lower than those in liver, but higher than muscle copper concentrations. Concentrations of copper and cadmium in kidneys were highly correlated with one another ( $r^2 = .99$ , df = 8, P < .0001), as were kidney copper and nickel ( $r^2 = .99$ , df = 8, P < .0001). Kidney iron concentrations were also highly correlated with those of cadmium, copper, and nickel.

Mercury concentrations ranged from 0.28 to 11.8 mg/kg dry weight in northern pike from Sites 1 and 4. For the northern pike, kidney mercury concentrations were highly correlated with both liver mercury ( $r^2 = .89$ , df = 8, P < .0001) and muscle mercury concentrations ( $r^2 = .63$ , df = 8, P = .005), but not with other metals in kidneys. Kidney mercury concentrations were not significantly different from muscle mercury concentrations in the same fish, but were significantly higher than mercury concentrations in the fish livers (paired t = -2.88, df = 8, P = .01).

*Trace element concentrations in relation to fish metrics and site.* The relationship of fish metrics for northern pike, including weight, fork length, total length, and condition factor (K) was explored for each trace element in liver, muscle and kidney through the use of scatterplots and through correlation and regression analysis. Weight, length, and condition factor were often negatively correlated with tissue metal levels, but none of the relationships examined was statistically significant. No other interpretable patterns were observed in metal concentrations versus fish metrics and condition. In particular, no relationship was discernable between mercury concentrations of pike livers (or other tissues) and weight, length, or condition index (Figure 5).

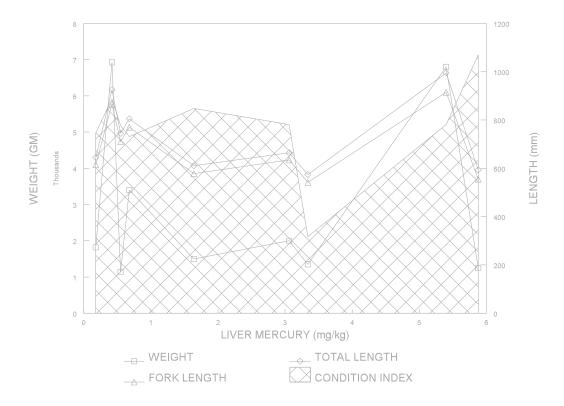


Figure 5. Mercury concentration in northern pike livers in relation to weight, length, and fish condition in 1987.

<u>Trace elements in 1988.</u> Tissues analyzed in 1988 included liver (Table 19) and muscle tissue (Table 20). One whole pike was also analyzed (Table 20). Neither mercury nor arsenic analysis met quality control criteria for these tissues. For the same reasons, aluminum, antimony, iron, manganese, silver, thallium, and tin data are questionable and were omitted from presentation. Trace element analysis revealed that lead and nickel were below detection limits for all samples. Thallium was present in reportable concentration in only one fish sample, a muscle tissue from a longnose sucker at Site 5 (not shown in Table 20). Beryllium was only reported in one pike muscle sample from Site 1 (0.76 mg/kg), and one whole northern pike sample from Site 1 (0.56 mg/kg). Boron concentrations were below the detection limit in fish muscle tissue, but boron was present above detection limit in two liver samples each from Sites 1 and 5. Reportable cadmium was limited to one northern pike sample from Site 1 (3.6 mg/kg) and two longnose suckers from Site 2 (2.3-8.3 mg/kg). Molybdenum concentrations were sporadically above detection at all three sample sites in both tissues. Vanadium was not detected in any muscle sample, but was detected in five fish liver samples (1.80 - 3.34 mg/kg).

SITE	SPECIES		Ba	Be	В	Cd	Cr	Cu	Mg	Мо	Se	Sr	V	Zn
1	Northern Pike		1.90	1.68	2.94	3.6	19.4	92.5	1573	3.9	28.3	6.68	2.01	659
			0.91	0.74	2.50	<1.4	4.8	51.1	1020	1.0	16.8	2.50	< 0.85	287
			0.35	< 0.32	<1.60	<1.6	3.5	56.5	1240	<1.0	9.3	2.04	< 0.96	219
			< 0.31	< 0.31	<1.57	<1.6	3.1	87.7	1264	<0.9	21.1	1.98	<0.94	327
		X	0.83	-	-	-	7.7	72.0	1274	-	18.9	3.30	-	373
2	Northern Pike		0.41	< 0.34	<1.69	<1.7	3.2	178.0	2431	1.5	22.0	<1.15	1.80	407
			0.61	< 0.41	<2.05	<2.0	4.5	91.0	2570	<1.2	27.0	3.36	<1.23	553
		х	0.51	-	-	-	3.8	134.5	2500	-	24.5	-	-	480
5	Northern Pike		1.21	< 0.51	5.08	<2.6	2.5	105.1	2535	<1.6	26.6	9.00	<1.56	668
			2.84	< 0.51	7.61	<2.5	4.3	326.9	5381	1.8	58.4	33.50	4.26	1264
			1.01	< 0.46	<2.30	<2.3	3.3	283.9	3207	<1.4	19.8	4.67	<1.38	756
		х	1.69	-	4.61	-	3.4	238.6	3708	-	34.9	15.72	-	896
2	Longnose Sucker		23.75	< 0.42	<2.08	2.3	6.7	31.3	1488	<1.3	17.9	17.36	2.75	152
			1.45	< 0.38	<1.83	8.3	4.5	145.9	2883	2.7	26.9	4.76	3.34	326
1		х	12.6	-	-	5.3	5.6	88.6	2185	-	22.4	11.06	3.05	239
5	Broad Whitefish		<1.11	<1.11	10.40	<5.7	16.1	620.8	2473	<3.4	16.4	9.46	<3.36	544

TABLE 19. TRACE ELEMENTS IN NOWITNA NATIONAL WILDLIFE REFUGE FISH LIVERS, 1988. Residues are reported in mg/kg dry weight.<sup>ab</sup>

<sup>a</sup> Mean concentrations were computed using  $\hat{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Lead, nickel, and thallium were not detected in any sample.

TABLE 20. TRACE ELEMENTS IN NOWITNA NATIONAL WILDLIFE REFUGE FISH MUSCLE TISSUE AND WHOLE FISH, 1988. Residues are reported in mg/kg dry weight.<sup>ab</sup>

SITE	SPECIES	Ba	Be	В	Cd	Cr	Cu	Mg	Мо	Se Se	Sr	V V	Zn
1	Northern Pike	1.27	<0.49	<2.44	<2.4	<1.5	4.9	7024	1.8	<24.4	30.93	<1.46	75
		0.52	0.76	<2.37	<2.4	<1.4	5.7	6872	1.5	<23.7	12.35	<1.42	71
		1.63	<0.48	<2.40	<2.4	<1.4	4.4	7019	<1.4	7.7	46.23	<1.44	74
		0.65	<0.46	<2.30	<2.3	<1.4	3.6	6590	<1.4	5.5	15.08	<1.38	77
11	X	1.02	-	-	-	-	4.6	6876	-	-	26.15	-	74
2	Northern Pike	2.76	<0.48	<2.38	<2.4	1.6	5.2	6286	<1.4	11.4	90.70	<1.43	197
		0.59	< 0.50	<2.48	<2.5	2.3	6.4	7228	<1.5	<2.5	5.45	<1.49	89
		3.08	< 0.51	3.03	<2.5	<1.5	5.1	7121	<1.5	6.1	45.91	<1.52	106
11	X	2.15	-	-	-	1.6	5.6	6878	-	6.3	47.35	-	131
5	Northern Pike	2.73	< 0.39	<1.95	<2.0	2.0	4.7	5117	<1.2	11.7	83.92	<1.17	117
		1.92	< 0.57	<2.82	<2.8	<1.7	9.6	7514	<1.7	13.0	73.41	<1.69	96
		7.89	< 0.53	<2.63	<2.6	<1.6	6.8	7211	<1.6	7.9	254.85	<1.58	137
11	X	4.18	-	-	-	-	7.0	6614	-	10.9	137.40	-	117
5	Broad	6.19	<0.49	<2.21	<2.2	<1.3	4.4	5000	<1.3	8.8	74.40	<1.33	68
2	Longnose	1.72	<0.52	<2.60	<2.6	<1.6	10.4	7552	<1.6	8.3	46.12	<1.56	78
	"	0.98	<0.49	<2.45	<2.5	<1.5	6.4	7206	1.9	12.7	2.35	<1.47	67
11	Х	1.35	-	-	-	-	8.4	7379	-	10.5	24.23	-	73
1	Northern	21.98	0.56	<2.16	<2.2	8.6	8.6	6509	<1.3	<2.2	155.60	<1.29	621

<sup>a</sup> Mean concentrations were computed using  $\dot{\eta}$  the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

<sup>b</sup> Lead and nickel were not detected in muscle or whole body samples. One longnose sucker from Site 5 contained 53 mg/kg thallium; thallium was not detected in other samples.

<sup>c</sup> Whole fish analyzed

*Liver tissue.* One liver sample from Site 1 proved too small for analysis of metals. Beryllium was above the detection limit in two pike liver samples from Site 1 (1.68 and 0.74 mg/kg). Similarly, boron and molybdenum were above detection limits in too few livers to allow statistical analysis or site comparisons. Reportable cadmium was limited to the liver of one northern pike from Site 1 (3.6 mg/kg) and two longnose suckers from Site 2 (2.3 and 8.3 mg/kg). Molybdenum concentrations were sporadically above detection at all three sample sites in liver tissues. Vanadium was detected in five fish liver samples (1.80 - 3.34 mg/kg), but no among-site trends were apparent.

Barium, chromium, copper, magnesium, selenium, strontium, and zinc were present in most fish livers from most sites. Barium occurred in concentrations above the detection limit in all but two northern pike liver samples, but there were no significant differences in barium concentrations among sites. Similarly, there were no significant differences among sites in liver chromium, selenium, or strontium concentrations. Copper differences among sites were almost significant ( $F_{2,6} = 4.37$ , P = .07). However, this finding is suspect since copper concentrations reported in 1988 livers were more than three times higher than 1987 concentrations.

Significant among-site differences were revealed for magnesium ( $F_{2,6} = 6.67$ , P = .03), with Site 5 concentrations being significantly higher (P < .05) than Site 1 magnesium concentrations, and Site 2 concentrations being intermediate in value. Zinc concentrations varied somewhat in fish livers from different sites, but differences were not quite significant ( $F_{2,6} = 4.42$ , P = .06). Many of the metals in the pike livers were themselves strongly correlated. Thus, barium was positively correlated with magnesium ( $r^2 = .49$ , df = 8, P = .02), strontium ( $r^2 = .78$ , df = 8, P = .001), selenium ( $r^2 = .72$ , df = 8, P = .001).

*Muscle tissue and whole fish samples.* No lead, nickel, cadmium, or vanadium were detected in fish muscle, and boron was only observed in one northern pike muscle sample from Site 2. Beryllium was also only detected in two northern pike samples, a muscle sample and a whole fish sample from Site 1. Chromium, molybdenum, and selenium were also only present sporadically in muscle and whole body samples. The highest chromium concentration (8.6 mg/kg) was found in the small whole pike from this site. Other concentrations were close to the limit of detection. Selenium detection limits varied considerably from sample to sample making interpretation of these data difficult.

Barium, copper, magnesium, strontium, and zinc were present in all muscle and whole fish samples. Barium concentrations in muscle samples were not significantly different than those in liver samples from northern pike. Concentrations averaged between 1.02 mg/kg (Site 1) and 4.18 mg/kg (Site 5). Also, the barium content of pike muscle and liver tissue from the same pike were not statistically correlated with each other and barium muscle concentrations in muscle did not differ significantly among sites. Copper muscle concentrations were low, ranging from a mean of 4.6 mg/kg (Site 1) to 7.0 mg/kg (Site 5). Differences in copper concentrations at Sites 1, 2, and 5 were not significant. Copper concentrations in muscle samples were much lower than those reported for liver samples (which are suspect) and consistent with muscle copper concentrations reported in 1987. Magnesium concentrations in muscle samples were

significantly higher than concentrations in liver (t = -8.89, df = 8, P < .0001). Within-site variation in muscle magnesium was high; thus, no significant differences in muscle concentrations occurred among sites. The muscle to liver magnesium ratio ranged from a mean of 5.5 at Site 1 to 2.1 at Site 5, with Site 2 being intermediate in value (4.1 mg/kg), suggesting some differences in sequestration of this metal in tissues between sites. Strontium was another metal for which muscle concentrations were generally higher than liver concentrations (t = 3.041, df = 8,

P = .02). Among-site differences in muscle strontium concentrations were not statistically significant. Strontium and barium concentrations in muscle tissues were highly correlated ( $r^2 = .99$ , df = 8, P < .0001).

Zinc concentrations in pike muscle samples were much lower than in pike liver samples (paired t = 4.47, df = 8, P = .001), ranging from 74 mg/kg (Site 1) to 131 mg/kg (Site 2). One-way analysis of variance did not disclose significant site differences in muscle zinc content. However, a Kruskal-Wallis one-way analysis of variance showed differences among sites to be significant ( $X^2 = 6.00$ , df = 8, P = .05).

*Trace element concentrations in relation to fish metrics and site.* The relationship of fish metrics and tissue metal concentrations for northern pike, including weight, fork length, total length, and condition factor (K) was examined through the use of scatterplots and through linear correlation and multiple regression analysis. Scatterplots did not reveal any clear cases where metal deficiency is clearly implicated by poor growth or condition at lower concentrations of metals. No clear-cut bell-shaped distributions were observed. However, possible inverse relationships between weight, total length, and liver copper were observed. In linear correlation analysis, liver barium, copper, magnesium, selenium, strontium, and zinc were all negatively correlated with northern pike weight, fork lengths, total lengths, and condition factors, while liver chromium showed a weak, positive association with these measures. However, the only statistically significant correlations were the negative relationships between liver copper and total length ( $r^2 = .38$ , df = 8, P = .04), and liver copper and weight ( $r^2 = .32$ , df = 8, P = .05) (Figure 6).

Muscle metal levels of barium, chromium, copper, strontium, and zinc were negatively correlated with weight and total length, and muscle magnesium was positively correlated with total length. However, the only statistically significant relationship demonstrated was between muscle magnesium concentration and total length ( $r^2 = .43$ , df = 9, P = .03). Interestingly, fork lengths were positively correlated with muscle barium, chromium, copper, magnesium, strontium, and zinc. Relationships between fork length and muscle barium ( $r^2 = .40$ , df = 9, P = .04), copper ( $r^2 = .40$ , df = 9, P = .03), and strontium ( $r^2 = .40$ , df = 9, P = .03) were all significant.

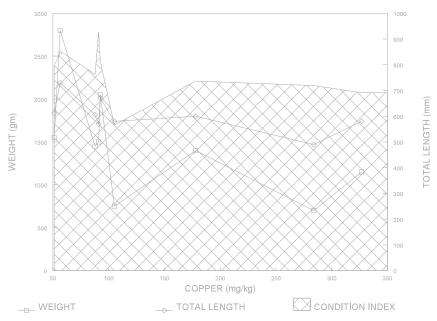


Figure 6. Copper concentration in northern pike livers in relation to weight, length, and fish condition in 1988.

The condition factor (K) of northern pike was not related to any muscle metal concentration. In forward stepwise multiple regressions, no group of metals in muscle tissue was identified as enhancing predictions of length, weight, or condition. For muscle samples, negative correlations were observed with barium, copper, strontium, zinc, and selenium when these factors were regressed on weight, total length and fork length. Negative correlations between condition index and barium, copper, magnesium, and strontium were also obtained. Statistically significant relationships were observed between muscle barium and condition index ( $r^2 = .36$ , df = 8, P = .04), and between strontium and condition index ( $r^2 = .99$ , df = 8, P = .001), indicating that one of the former relationships may be the result of covariance.

The condition factor was also positively correlated with weight ( $r^2 = .45$ , df = 8, P = .02), indicating possible bias resulting from larger fish being in somewhat better condition. Significant or nearly significant differences also occurred among sites in fish weight ( $F_{2,6} = 4.87$ , P = .055), fork length ( $F_{2,6} = 4.99$ , P = .053), and condition ( $F_{2,6} = 4.14$ , P = .07). However, specific differences between site pairs were not demonstrated by the Scheffe multiple range test. It should be noted that sample sizes for the above analyses were small.

Since most of these metals were themselves strongly correlated, multiple stepwise regressions were used to identify metals as a group that contributed to predictions of weight, total length,

fork length, and condition factor. No combination of metals was identified as being more predictive of fish condition, fish weight, or length than the single metals identified above. Therefore, some of the relationships between fish metrics and metals, at the levels observed in this study, may be spurious or related to covariance of metals with each other.

It would also be desirable to examine fish condition and tissue metal concentrations in relation to water quality, water metal concentrations, and sediment metal concentrations. However, as in 1987 analyses, too few sample sites were sampled for fish to enable these comparisons.

#### **DISCUSSION AND CONCLUSIONS**

This study was performed to evaluate potential impacts from off-refuge placer mining on refuge fish and riverine habitat and to obtain baseline data on unmined drainages. One river examined, the Sulatna River, had active placer mining on its tributaries. In addition, California Creek, a tributary to the Titna River, experienced upstream placer mining from 1979 - 1986. In the early 1900's, Our Creek, and the Susulatna River, tributaries to the upper Nowitna River, were mined, as was an unnamed tributary to the Sulukna River.

In most respects, water quality measurements, including pH, conductivity, alkalinity, hardness, and settleable solids, in the mined Sulatna River resembled other sites -- slightly basic in pH, with moderate hardness and alkalinity, indicative of a well-buffered calcium/magnesium bicarbonate watershed. However, the Sulatna River experienced anomalously high turbidity levels in surface waters in both 1987 and 1988 in comparison to a much lower turbidity, comparable to other sites, at the mouth of the Sulatna River in 1985. Alt (1985) noted that the waters of the Sulatna River were extremely turbid due to placer mining activity, indicating that our 1985 turbidity measurement may have been made at a time when no mining effluent was being released. Concentrations at the refuge boundary, 3467 and 1183 NTU's, for 1987 and 1988, respectively, were more than an order of magnitude larger than turbidities at all other sites. This sample site was approximately 100 km from actual mining, suggesting long-distance transport of fine particulates and/or organics. Such high turbidities, typically correlated with high suspended solids, have been associated with interference with visual feeders (Scannell 1988) and reproductive impairment, particularly in salmonids (see review by Peterson et al. 1985) and fish-eating birds (Barr 1986). High turbidity is also known to lower primary productivity and limit invertebrate and fish diversity and abundance (Cordone and Kelley 1961; Van Nieuwenhuyse and LaPerriere 1986; Lloyd et al. 1987).

Most trace element concentrations in water and sediment were within the range expected for uncontaminated watersheds. However, total recoverable iron in Sulatna River water was more than double that of the other four sites in 1987. In 1988, dissolved iron and manganese were also highly elevated in the Sulatna River in comparison with remaining sites. Turbidity, dissolved iron, and manganese concentrations were highly correlated, suggesting the occurrence of iron- and manganese-rich fine particulates in suspension. Other metals elevated in Sulatna River samples included total recoverable aluminum and cobalt, but concentrations of these metals were not particularly high, and biological impacts from these metals, at the observed concentrations, are unlikely.

Iron and manganese were also enriched in the upper and lower Nowitna River and the Titna River, approaching and sometimes violating State drinking water quality standards (1 mg/L for iron and 0.05 mg/L for manganese). The Titna River, sampled only in 1985, was especially high in iron and should be subject to continuing study. Elevated iron and manganese in the water can contribute to increased turbidity, reduced primary productivity, and avoidance by visual feeders such as Arctic grayling. Concentrations greater than 2.0 mg/L iron may also

cause significant invertebrate and fish egg losses, due to suffocation from precipitated  $Fe(OH)_3$  (Goettl and Davies 1977), suggesting that these potential impacts should be further investigated.

Both total and dissolved copper concentrations in water were slightly elevated at all sites in comparison to most unpolluted waters, which range from 0.001 - 0.005 mg/L (Moore and Ramamoorthy 1984). The concentrations found are unlikely to impact most fish species, but could result in acute toxicity to sensitive juvenile Arctic grayling at concentrations found at the study sites (Buhl and Hamilton 1990), as well as subchronic effects such as avoidance by salmonids (Giattina et al. 1982). Hyperactivity, reduced exploratory activity, and reduced migration are other behavioral changes induced in salmonids in the range of 0.005 - 0.060 mg/L copper (see review by Sorensen 1991). Also, toxicity of mercury could be enhanced by the synergistic action of copper and mercury on aquatic organisms (Corner and Sparrow 1956 in Wershaw 1970).

Significant differences in sediment concentrations of trace elements among sites were not demonstrated for any element except mercury in 1987 sampling. A significant negative correlation is seen between sediment mercury and pH in this data set. Sediment mercury concentrations were not correlated with concentrations of other trace elements in sediments, although most other metal concentrations, especially transition elements (Cr, Fe, Mn, Ni, V, Zn), were highly correlated with each other within sediment samples.

Sufficient northern pike were obtained for trace element analysis and statistical treatment only from Sites 1 and 4 in 1987 and from Sites 1, 2, and 5 in 1988. In 1987, mercury concentrations in northern pike muscle, liver, and kidney samples were significantly higher in Sulukna River (Site 4) pike than in lower Nowitna River pike (Site 1). Mercury concentrations in Sulukna River pike ranged from 1.61 - 5.88 mg/kg dry weight (0.41 - 1.42 mg/kg wet weight) in liver; 4.02 - 13.20 mg/kg dry weight (0.72 - 2.93 mg/kg wet weight) in muscle; and 4.21 - 11.80 mg/kg dry weight (1.60 - 3.00 mg/kg wet weight) in kidney. The level of mercury in fish from the Sulukna River is indicative of heavy mercury contamination. The predominance of mercury in muscle versus liver tissue in Sulukna River pike ( $\bar{x}$  liver:muscle ratio = 0.60) suggests steady state conditions in fish of this drainage, whereas much lower ratios in lower Nowitna fish ( $\bar{x}$  liver:muscle ratio = 0.23) probably indicates ongoing depuration at this site (Jernelov and Lann 1971).

The mean muscle mercury concentration from the five Sulukna River fish (7.93 mg/kg dry weight, or 1.51 mg/kg wet weight) exceeded the National Contaminant Biomonitoring Program's maximum reported concentration for mercury (0.37 mg/kg wet weight) reported for whole fish from 50 rivers nationwide between 1976 and 1984 (Schmitt and Brumbaugh 1990). One or more tissues from each of these fish also exceeded the Food and Drug Administration (FDA) action level for mercury of 1 part per million (mg/kg) wet weight. Mercury was also present at high concentrations in kidneys and livers of these fish, but was often highest in muscle tissue that would constitute edible flesh. In contrast, northern pike from the mouth of the Nowitna River did not exceed the FDA criterion in any tissue sample, and were significantly lower in tissue mercury. Arctic grayling from Site 3 were very low in mercury concentration, as is typical

of grayling in other rivers of interior Alaska (Snyder-Conn, unpublished). Longnose sucker and sheefish were intermediate in mercury content.

Sites with the highest sediment mercury had a much lower incidence of mercury in fish tissue. A lack of correlation between sediment mercury and mercury in aquatic organisms has also been reported by others (Lindestrom and Grahn 1982, in Regnell 1990; Paasivirta et al. 1983, in Rada et al. 1986; Wiener et al. 1984; Rada et al. 1986; Sorensen et al. 1990). Most frequently, water quality characteristics are correlated with mercury uptake in fish. Conditions facilitating bioaccumulation in lakes include low pH (< 6), low alkalinity, low waterborne calcium (generally reflected by hardness), high humic acid content, high volatile organics content, low conductivity, oligotrophy, high drainage area to waterbody volume, and low retention time (Wren and MacCrimmon 1983; Allard and Stokes 1989; Cope et al. 1990; Lee and Hultberg 1990; Sorensen et al. 1990; Wiener et al. 1990). Low pH (<7), low hardness (34 mg/L), and low alkalinity (34 mg/L) were conditions noted in several Nowitna refuge lakes (Glesne 1986). Therefore, sources of mercury in lakes cannot be ruled out until northern pike in Nowitna lake systems are sampled. Also, low pH, although not observed in any river drainage during this study, might be observed following spring breakup, since snowmelt is typically acidic (Haines 1981). Thus, an early summer study of pH concentrations could reveal critical pH differences among sites not observed in late summer collections.

A possible explanation for the inverse relationship between sediment and fish mercury content is that manganese and iron, known to bind mercury making it biologically unavailable (Hammond et al. 1971), occurred at much lower concentrations in the Sulukna River in comparison to the lower Nowitna River site.

Potential sources of mercury are limited. Typical industrial sources (Wershaw 1970; Van Den Berg 1971; Eisler 1987) are not present near the refuge. The most likely source of mercury in Nowitna River fish is mercury in stream placers as a result of mercury in local mineralizations (Wershaw 1970). High levels of naturally occurring mercury have been correlated with mineral deposits such as greenstone velts in northwestern Ontario (Barr 1986); with isolated deposits in the Canadian Precambrian Shield (Wren and McCrimmon 1983); and with glacial drift derived from mercury source regions in Alaska and Siberia (Nelson et al. 1975). A major source of mercury in Alaska (and the United States as a whole) is cinnabar (HgS) from the nearby Kuskokwim Mountains (Malone 1962). Dispersal from lode sources through natural erosion and disturbance from mining has resulted in high mercury content in water, suspended sediments, and stream sediments throughout the 840-km Kuskokwim River system. High concentrations of mercury

(> 1 mg/kg) were observed in panned sediment from 10 to 25 km downstream in rivers and from 32 to 72 km downstream from source tributaries with mineralizations (Nelson et al. 1977). While most drainages from the Kuskokwim Mountains, just to the south and southwest of the refuge, do not enter the Nowitna Refuge, some potential drainage from the north side of the Kuskokwim Mountains or similar, isolated highly mineralized areas in the Lone Indian Mountain or Browns Fork areas could introduce mercury into the Sulukna River. Also, glacial drift and previous drainage patterns connecting the Kuskokwim River and the Yukon River could have introduced sediment rich in mercury into the Sulukna River and other drainages. In

support of this hypothesis, we found high mercury concentrations (>0.30 mg/kg dry weight) at all sites except California Creek. Also, geological studies in the vicinity of the upper Sulukna River also showed high mercury at numerous sites in this drainage in stream sediments (King et al. 1983).

Another local source of mercury may be mercury to amalgamate gold, a procedure common during periods of historic mining in interior Alaska and elsewhere (Malone 1962; Cooper 1983). Ongoing studies in the Amazon River, where mercury is currently employed to amalgamate placer gold and then discharged to the river, indicate that this mercury, introduced into freshwater as elemental mercury, is methylated, forming toxic methylmercury and results in fish contamination at levels similar to those observed in the Sulukna River (Malm et al. 1990). Contamination can become extensive; in the Amazon, mercury contamination of carnivorous fish extends as much as 182 km downstream.

Other contributing sources of mercury can also not be ruled out. Studies indicate an increasing mercury burden from atmospheric deposition of mercury itself in regions remote from industry in the northern United States, Canada, and Scandinavia (Rada et al. 1989, Schroder et al. 1989, Sorenson et al. 1990, Haines 1991). In addition, acid deposition (especially in areas receiving acid rain) followed by localized leaching of mercury (Akielaszek and Haines 1981; Haines 1981; Wiener 1988; Rada et al. 1989; Sorensen et al. 1990; Wiener et al. 1990) has been demonstrated in numerous watersheds. Acid leaching induced by snowmelt and humic acid runoff from forested and terrestrial systems is also a natural source (Lee and Hultberg 1990; Sorensen et al. 1990). Increased mercury body burdens in fish have also been demonstrated in newly flooded or impounded sites such as reservoirs (Bodaly et al. 1984). These increases are attributed to increased bacterial methylation of naturally occurring mercury in flooded terrestrial areas. Mercury is then concentrated in fine-grained sediments (indicated by high aluminum) and sediments high in organic content (Rada et al. 1986; Sorensen et al. 1990). Since high water events and flooding are commonplace in Nowitna refuge (USFWS 1991) and since mercury enrichment occurs locally, as evidenced by cinnabar in stream placers, the release of mercury due to these sources may be normal in the refuge.

Further study will be needed to define watersheds within the refuge with high mercury in fish and to establish which fish species are enriched in mercury. Fish with high mercury may have bioaccumulated the mercury in waters other than the sample sites themselves, since the half-life of mercury retention in northern pike is 100 days (Eisler 1987). Although populations of both northern pike and sheefish are believed to remain on the refuge, with little migration off refuge by way of the Yukon River, based on tagging and gill net studies (Alt 1985), considerable fish movement is likely within the Refuge. Based on the above study, northern pike and sheefish collected from the Sulukna River during late August and September are likely to have been migrants from the lower and mid-Nowitna River system. Most northern pike may feed and spawn in the latter system. However, the predominance of mercury in muscle versus liver tissue in Sulukna River pike in contrast to Nowitna River pike suggests that fish from the Sulukna River were probably closer to a mercury source area than fish collected at the mouth of the Nowitna River. Identifying actual source areas may depend on analysis of mercury from water samples. Unfortunately, no mercury data for water were available in this study due to excessive holding times of water samples prior to analysis. Detectable mercury (0.0002 mg/L) was observed in September 1984 water samples from the mouth of the Sulatna River, California Creek, and Bering Creek, and similar concentrations (0.0003 to 0.0005 mg/L) were found at sites on the Nowitna River from the mouth of the Sulukna River to downstream of the Sulatna River (Deschermeier and Hawkinson 1985). These levels exceed State/Federal criteria for the protection of aquatic life from chronic toxicity and, if confirmed, indicate elevated mercury in the Nowitna River system and some of its tributaries.

Effects of high mercury in the environment may extend to many species of predatory fish and wildlife. High dietary mercury has been linked to emaciation, paralysis and death in fish and birds (see reviews by Stickel et al. 1971; Fimreite 1979; Eisler 1987; Sorensen 1991) and to disorientation, blindness, and loss of olfaction in canines (Wren 1986). Cellular destruction of the central nervous system, often followed by death, is associated with these symptoms. At extremely high concentrations, sensitive birds and carnivorous mammals have entirely disappeared from mercury-rich areas (Fimreite and Reynolds 1973; Wren 1986).

At concentrations reported in this study, more subtle, chronic impacts are likely in species that remain affiliated with source areas of mercury for extended time periods. These include increased respiratory movements, sluggishness, abnormal coordination and appetite loss, cataracts and brain lesions in fish (Eisler 1987). In waterfowl and fish-eating birds, impaired reproduction (Fimreite 1974), decreased hatchability in bird eggs (Borg et al. 1969 in Fimreite 1974; Heinz 1979), and behavioral abnormalities, such as reduced territorial and nest fidelity (Barr 1986), difficulty in controlling wing movements (Fimreite and Karstad 1971; Fimreite 1974), and decreased duckling response to maternal calls (Heinz 1979), occur under long-term chronic concentrations. Mercury enrichment in birds has also been linked to slight eggshell thinning in certain species (Fimreite 1979).

In addition, enhanced concentration of methylmercury in birds from mercury-enriched sites may add to body burdens in predatory species and human users. Vulnerable wildlife species in the Nowitna Refuge include mink, river otter, foxes, and wolves. Herbivorous species are unlikely to be affected. Response to mercury is highly species-specific. In fish, it also depends on such factors as sex, age, metabolism, temperature, diet, and mucus coat, as well as environmental concentrations of antagonistic and synergistic contaminants such as selenium and DDT. Generally, increased concentration with increased size and age is reported in fish (Busch 1983; Cooper 1983; Rada et al. 1986; Barak and Mason 1990; Sorensen 1991). Also, in fish, the percentage of toxic methylmercury typically increases with size and age (Busch 1983). However, this study did not show any positive relationship between mercury concentration in fish tissues and fish size. Nor was any systematic relationship observed between fish mercury concentration and fish condition. Since mercury is concentrated to some extent in lipid tissues (Barack and Mason 1990), the lack of a negative correlation with condition index is predictable. However, the lack of correlation with both length and weight is unexpected. Small sample size may have precluded observation of expected correlations in the other parameters. Alternately, high mercury in the recent environment of some of the fish could have obscured fish size versus

mercury relationships observed in lake studies, where the mercury exposure of fish is constant. In the latter case, one would predict mercury residue/size relationships on a separate basis for each watershed.

In 1988, mercury data in water, fish, and sediments did not meet quality control criteria. The only statistical differences in northern pike tissue trace element concentrations between sites was for magnesium in liver samples and zinc in pike muscle samples. Significant between-site differences in pike muscle zinc concentrations were also revealed, with Sulatna River pike showing almost twice the zinc concentration as northern pike from the lower Nowitna River. Magnesium differences were not apparently related to mining. While upper Nowitna River fish had significantly higher magnesium concentrations than northern pike from the lower Nowitna River form River, concentrations in northern pike livers from the mined Sulatna River were intermediate in concentration.

Although few site differences were identified in fish trace element concentrations or condition, several significant correlations were observed between northern pike condition and certain metal concentrations. A significant negative relationship was demonstrated between liver copper and both weight and total length, while a significant positive relationship was found between muscle magnesium and condition index in the 1988 data set. Given the small size of these data sets, additional data should be obtained before confidence in these relationships is high. However, a negative relationship between copper and fish health was observed by Buhl and Hamilton (1990), who found that copper was more toxic to young Arctic grayling and salmonids than zinc, lead, or arsenic at concentrations associated with placer mining in central Alaska.

#### RECOMMENDATIONS

- 1. Intensified study of water, sediment, fish, and forage should be conducted to to determine the geographic extent of mercury contamination and potential source areas in the vicinity of Nowitna NWR. Sampling should be concentrated in former mined and actively mined tributaries connected to the Nowitna, Titna, Sulukna, and Sulatna Rivers and in adjoining oxbow lakes.
- 2. At least 10 adult northern pike should be obtained from each waterbody. Salmon at locations of local subsistence fisheries should also be sampled. Mink or otter, waterfowl, and raptors should be sampled from selected waterbodies to obtain baseline data.
- 3. Skin, muscle, and liver tissues of fish should be analyzed, since partitioning between these tissues can provide information on sources of the mercury. Primary growth feathers from birds and hair from mammals will also provide information on local mercury distribution.
- 4. Water quality measurements should be made on site following breakup to identify acidic streams and tributaries to Nowitna Refuge rivers. Sample collections should then focus on low pH, poorly buffered systems.
- 5. Precision should be improved in water quality measurement through use of calibration buffers, standards, or standard additions. Blanks and spiked samples should be submitted to the analytical laboratory together with actual samples to further evaluate laboratory performance.
- 6. Water samples collected at each site should be submitted separately for quick turnaround analysis of mercury. Teflon containers are recommended.
- 7. Study plans should be developed in cooperation with the Alaska Departments of Fish and Game and Environmental Conservation.
- 8. Reanalysis should be required if quality assurance/quality control objectives for analytes of concern are not met by the analytical laboratory.
- 9. Acid-volatile sulfides and total organic carbon should be measured in water and sediments; aluminum, copper, iron, manganese, and selenium should be measured in all matrices collected; and mercury should be measured in pore water.
- 10. Other measures of fish health and ecosystem health should be incorporated into study plans.

#### LITERATURE CITED

Akielaszek, J.J., and T.A. Haines. 1981. Mercury in the muscle tissue of fish from three northern Maine lakes. Bull. Environ. Contam. Toxicol. 27:201-208.

Alaska Department of Environmental Conservation. 1991. 1990 Annual Mining Report. 39 pp.

Alaska Department of Natural Resources. 1982. New claims soar to all-time high. Alaska Mines and Geology 31(1):5.

Allard, M., and P.M. Stokes. 1989. Mercury in crayfish species from thirteen Ontario Lakes in relation to water chemistry and smallmouth bass (*Micropterus dolomieui*) mercury. Can J. Fish. Aquat. Sci. 46:1040-1046.

Alt, K.T. 1985. Annual performance report for inventory and cataloging of sport fish and sport fish waters of western Alaska -- Nowitna and Fish-Niukluk Rivers, sheefish enhancement assessment. pp. 135-171 <u>in</u> Inventorying and Cataloging. Federal Aid in Fish Restoration and Anadromous Fish Studies. Vol. 26. Alaska Dept. Fish and Game, Juneau, AK.

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation. 1981. Standard Methods for the Examination of Water and Wastewater. 15th Edition, 1980. Washington D.C., 1134 pp.

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation. 1989. Standard Methods for the Examination of Water and Wastewater. 17th Edition. Washington D.C., v.p.

Anonymous. 1980. Alaska gold mining industry under goes [sic] a revitalization. Alaska Industry Magazine, June 1980. 4 pp.

Armstrong, F.A.J. 1979. Effects of mercury compounds on fish. pp. 657-670 <u>in</u> J.O. Nriagu (ed.). The biogeochemistry of mercury in the environment. Elsevier/North-Holland Biomedical Press, New York.

Barak, N.A-E., and C.F. Mason. 1990. Mercury, cadmium, and lead in eels and roach: the effects of size, season, and locality on metal concentrations in flesh and liver. Science of the Total Environment 92:249-256.

Barr, J.F. 1986. Population dynamics of the Common Loon (*Gavia immer*) associated with mercury-contaminated waters in northwestern Ontario. Can. Wildl. Serv. Occasional Paper 56. 23 pp.

Bjerklie, D.M., and J.D. LaPerriere. 1985. Gold-mining effects on stream hydrology and water quality, Circle Quadrangle, Alaska. Water Resources Bull. 21:235-243.

Bodaly, R.A., R.E. Hecky, and R.J.P. Fudge. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River Diversion, northern Manitoba. Can. J. Fish. Aquat. Sci. 41:682-691.

Buhl, K.J., and S.J. Hamilton. 1990. Comparative toxicity of inorganic contaminants released by placer mining to early life stages of salmonids. Ecotoxicol. Environ. Safety 20:325-342.

Buhl, K.J. and S.J. Hamilton. 1991. Relative sensitivity of early life stages of Arctic grayling, coho salmon, and rainbow trout to nine inorganics. Ecotoxicol. Environ. Safety 22:184-197.

Busch, W-D. N. 1983. Decline of mercury in young fishes from western Lake Erie between 1970-71 and 1974. Prog. Fish-Cult. 45:202-206.

Cleveland, L., E.E. Little, R.H. Wiedmeyer, and D.R. Buckler. 1989. Chronic no-observedeffect concentrations of aluminum for brook trout exposed in low-calcium, dilute acidic water. pp. 229 - 245 *in* T.E. Lewis, ed. Environmental chemistry and toxicology of aluminum. Lewis Publishers, Inc., Chelsea, MI. 344 pp.

Cobb, E.H. 1964. Iron occurrences in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-40 and Reference List [on map].

Cobb, E.H. 1970a. Bismuth occurrences in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-53 and Reference List. 2 pp.

Cobb, E.H. 1970b. Uranium, thorium, and rare-earth elements in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-56 and Reference List. 3 pp.

Cobb, E.H. 1974a. Map showing occurrences of lode gold and silver in Alaska. Mineral Investigations Resource Map. U.S. Geological Survey, Map MR-84 and Reference List, 16 pp.

Cobb, E.H. 1974b. Cobalt occurrences in Alaska. Mineral Investigations Resource Map. U.S. Geological Survey, Map MR-61 and Reference List. 2 pp.

Cobb, E.H. 1974c. Nickel occurrences in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-63 and Reference List. 2 pp.

Cobb, E.H. 1975a. Occurrences of platinum group metals in Alaska. U.S. Geological Survey, Mineral Investigation Resource Map MR-64 and Reference List. 2 pp.

Cobb, E.H. 1975b. Zinc occurrences in Alaska. U.S. Geological Survey, Mineral Investigation Resource Map MR-67, and Reference List. 9 pp.

Cobb, E.H. 1975c. Chromite occurrences in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-68 and Reference List. 2 pp.

Cobb, E.H. 1984a. Map showing occurrences of lead minerals in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-91 and Reference List. 11 pp.

Cobb, E.H. 1984b. Map showing occurrences of lode gold and silver in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-84 and Reference List. 16 pp.

Cobb, E.H. 1984c. Map showing occurrences of placer gold in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-83 and Reference List. 18 pp.

Cobb, E.H. 1984d. Map showing occurrences of copper minerals in Alaska. U.S. Geological Survey, Mineral Resource Map MR-90 and Reference List. 19 pp.

Cobb, E.H. 1984e. Map showing occurrences of molybdenum minerals in Alaska. U.S. Geological Survey, Mineral Resource Map MR-86 and Reference List. 5 pp.

Cobb, E.H. 1985. Map showing occurrences of tungsten mineral in Alaska. U.S. Geological Survey, Mineral Investigation Resource Map MR-85 and Reference List. 6 pp.

Cooper, J.J. 1983. Total mercury in fishes and selected biota in Lahontan Reservoir, Nevada: 1981. Bull. Environ. Contam. Toxicol. 31:9-17.

Cope, W.G., J.G. Wiener, and R.G. Rada. 1990. Mercury accumulation in yellow perch in Wisconsin seepage lakes: relation to lake characteristics. Environ. Toxicol. Chem. 9: 931-940.

Cordone, A.J., and D.W. Kelley. 1961. The influences of inorganic sediment on the aquatic life of streams. Calif. Fish Game 47:189-228.

Corner, E.D.S., and B.W. Sparrow. 1956. The modes of action of toxic agents; 1, Poisoning of certain crustaceans by copper and mercury. Marine Biol. Assoc. U.K. Jour. 35:531-548.

Cruz, E.L., and E.H. Cobb. 1984a. Map showing occurrences of tin minerals in Alaska. U.S. Geological Survey, Mineral Investigation Resource Map MR-89 and Reference List. 4 pp.

Cruz, E.L., and E.H. Cobb. 1984b. Map showing occurrences of mercury minerals in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-87 and Reference List. 4 pp.

Cruz, E.L., and E.H. Cobb. 1986. Map showing occurrences of antimony mineral in Alaska. U.S. Geological Survey, Mineral Investigations Resource Map MR-93 and Reference List. 5 pp.

Deschermeier, S., and J. Hawkinson. 1985. Stream investigations report: Nowitna and Koyukuk National Wildlife Refuges 1984. U.S. Fish and Wildlife Service, Fairbanks Fishery Resources Report No. FY 85/4. Fairbanks, AK. 37 pp.

Dixon, W.J., and F.J. Massey, Jr. 1957. Introduction to Statistical Analysis. McGraw-Hill Co., NY. 488 pp.

Eakin, H.M. 1918. The Cosna-Nowitna Region, Alaska. U.S. Geological Survey Bull. 642. Washington D.C. 54 pp.

Eberline, G.D., and O.J. Ferrians, Jr. 1968. Suggested areas for prospecting in the central Koyukuk River region. U.S. Geological Survey Circular 570. 12 pp.

Eberlein, G.D., R.M. Chapman, H.L. Foster, and J.S. Gassaway. 1977. Table describing known metalliferous and selected nonmetalliferous mineral deposits in central Alaska. U.S. Geological Survey Open-File Report 77-168D.

Eisler, R. 1987. Mercury hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish Wildl. Serv. Biol. Rep. 85(1.10). 90 pp.

EPA. 1980. Ambient water quality criteria for mercury. Office of Water Regulations and Standards, U.S. Environmental Protection Agency. EPA 440/5-80-058.

EPA. 1983. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory Office of Research and Development, U.S. Environmental Protection Agency. EPA-600/4-79-0202.

Fimreite, N. 1974. Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38:120-131.

Fimreite, N. 1979. Accumulation and effects of mercury on birds. pp. 601-627 *in* J.O. Nriagu, ed. The Biogeochemistry of Mercury in the Environment. Elsevier/North-Holland Biomedical Press, NY.

Fimreite, N., and L. Karstad. 1971. Effects of dietary methyl mercury on red-tailed hawks. J. Wildl. Manage. 35:293-300.

Fimreite, N., and L.M. Reynolds. 1973. Mercury contamination of fish in northwestern Ontario. J. Wildl. Manage. 37:62-68.

Fitzgerald, C.J. Watras, and R.G. Rada. 1990. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. Environ. Toxicol. Chem. 9:909-918.

Freitas, S.T., C. Peven, L. Altshul, W. Steinhauer, R. Hillman, E. Crecelius, A. Uhler, N. Young, and H. Trulli. 1989. National Status and Trends Program mussel watch phase 4: work/quality assurance project plan. Prepared for U.S. Dept. Commerce, National Oceanic and Atmospheric Administration by Battelle Ocean Sciences, Duxbury, MA.

Giattina, J.D., R.R. Garton, and D.G. Stevens. 1982. Avoidance of copper and nickel by rainbow trout as monitored by a computer-based data acquisition system. Trans. Am. Fish. Soc. 111:491-504.

Gladney, E.S., B.T. O'Malley, I. Roelasdtz, and T.E. Gills. 1987. Standard Reference Materials: Compilation of Elemental Concentration Data for National Bureau of Standards Clinical, Biological, Geological, and Environmental Standard Reference Materials. National Bureau of Standards. 532 pp.

Glesne, R.S. 1986. Progress report: lake fishery habitat survey and classification on interior Alaska national wildlife refuges, 1984 and 1985. Fairbanks Fishery Resources Progress Report FY-86/7. U.S. Fish and Wildlife Service. 116 pp.

Goettl, J.P., Jr. and P.H. Davies. 1977. Water pollution studies: study of the effects of mining and milling operations on high mountain streams. Job Progress Report, Federal Aid Project F-33-R-12. Colorado Division of Wildlife, Department of Natural Resources. 68 pp.

Hach Company. 1985. Water Analysis Handbook. Loveland, CO.

Haines, T.A. 1981. Acidic precipitation and its consequences for aquatic ecosystems: a review. Trans. Am. Fish. Soc. 110:669-707.

Haines, T.A. 1991. Atmospheric deposition is a major source of mercury to aquatic and terrestrial systems. U.S. Fish Wildl. Serv. Research Information Bull. 91-116. 2 pp.

Hatch, W.R. and W.L. Ott. 1986. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem. 40:2085-2087.

Heinz, G.H. 1979. Methylmercury: reproductive and behavioral effects on three generations of mallard ducks. J. Wildl. Manage. 43:394-401.

Hunn, J.B., L. Cleveland, and D.R. Buckler. 1985. Addition of calcium reduces effects of low pH and aluminum on developing brook trout eggs and fry. U.S. Fish Wildl. Serv. Research Information Bull. 85-11. 2 pp.

Jackson, R. 1990. Report of findings: Innoko National Wildlife Refuge placer mining study. Prepared by Ecological Services - Anchorage for Innoko National Wildlife Refuge, McGrath, Alaska.

Jagoe, C.H. and T.A. Haines. 1987. Aluminum exposure causes abnormal gill development in Atlantic salmon fry. U.S. Fish Wildl. Serv. Research Information Bull. 87-118. 2 pp.

Jernelov, A. and H. Lann. 1971. Mercury accumulation in food chains. Oikos 22: 403-406.

King, H.D., R.M. O'Leary, D.A. Risoli, and D.W. Galland. 1983. Distribution and abundance of antimony and mercury in minus-80-mesh-stream sediment and antimony in nonmagnetic and moderately magnetic heavy-mineral-concentrate samples, Medfra quadrangle, Alaska. U.S. Geological Survey Open-File Rep. 80-811L. 3 plates.

King, H.D., D.A. Risoli, E.F. Cooley, R.M. O'Leary, W.A. Speckman, D.L. Spiesman Jr., and D.W. Galland. 1980. Final results and statistical summary of analysis of geochemical samples from the Medfra quadrangle, Alaska. U.S. Geological Survey Open-File Report 80-811F. 134 pp., 1 plate.

Krynitsky, A. 1987. Preparation of biological tissue for determination of As and Se by graphite furnace AA spectrometry. Anal. Chem. 59(14):1884-1886.

LaPerriere, J.D., S.M. Wagener, and D.M. Bjerklie. 1985. Gold-mining effects on heavy metals in streams, Circle Quadrangle, Alaska. Water Resources Bull. 21:245-252.

Lee, Y-H., and H. Hultberg. 1990. Methylmercury in some Swedish surface waters. Environ. Toxicol. Chem. 9:833-841.

Lindestrom, L., and O. Grahn. 1982. Antagonistic effects to mercury in some mine drainage areas. Ambio 11:359-361.

Lloyd, D.S. 1987. Turbidity as a water quality standard for salmonid habitats in Alaska. N. Am. J. Fish. Manage. 7:34-45.

Lloyd, D.S., J.P. Koenings, and J.D. LaPerriere. 1987. Effects of turbidity in fresh waters of Alaska. N. Am. J. Fish. Manage. 7:18-33.

McLeay, D.J., I.K. Birtwell, G.F. Hartman, and G.L. Ennis. 1987. Responses of Arctic grayling (*Thymallus arcticus*) to acute and prolonged exposure to Yukon placer mining sediment. Can. J. Fish. Aquat. Sci. 44:658-673.

McLeay, D.J., A.J. Knox, J.G. Malick, I.K. Birtwell, G. Hartman, and G.L. Ennis. 1983. Effects on Arctic grayling (*Thymallus arcticus*) of short-term exposure to Yukon placer mining sediments: laboratory and field studies. Can. Tech. Rep. Fish. Aquat. Sci. No. 1171. 134 pp.

MacCrimmon, H.R., C.D. Wren, and B.L. Gots. 1983. Mercury uptake by lake trout, *Salvelinus namaycush*, relative to age, growth, and diet in Tadenac Lake with comparative data from other PreCambrian Shield lakes. Can. J. Fish. Aquat. Sci. 40:114-120.

Madison, R.J. 1981. Effects of placer mining on hydrologic systems in Alaska - status of knowledge. U.S. Geological Survey Open-File Report 81-217.

Malm, O., W.C. Pfeiffer, C.M.M. Souza, and R. Reuther. 1990. Mercury pollution due to gold mining in the Madeira River Basin, Brazil. Ambio 19:11-15.

Malone, K. 1962. Mercury occurrences in Alaska. U.S. Bureau of Mines. Information Circular 8131. 57 pp.

Mavrodineanu, R. (ed.). 1977. Procedures used at the National Bureau of Standards to Determine Selected Trace Elements in Biological and Botanical Materials. NBS Special Publication. 492 pp.

Mertie, J.B., Jr., and G.L. Harrington. 1924. The Ruby-Kuskokwim region, Alaska: U.S. Geological Survey, Geological Survey Bulletin 754. 192 pp.

Miller, T.P., and O.J. Ferrians, Jr. 1968. Suggested areas for prospecting in the central Koyukuk River region. U.S. Geological Survey Circular 570. 12 pp.

Monk, H.E. 1961. Recommended methods of analysis for pesticide residues in foodstuffs. Report by the Joint Mercury Residues Panel. Analyst 86:608-614.

Moore, J. (ed.). 1990. Patuxent Analytical Control Facility Reference Manual. June 1990. Patuxent Analytical Control Facility, U.S. Fish and Wildlife Service, Laurel, MD.

Moore, J.W., and S. Ramamoorthy. 1984. Heavy metals in natural waters: applied monitoring and impact assessment. Springer-Verlag, NY. 268 pp.

Nelson, C.H., D.E. Pierce, K.W. Leong, and F.F.H. Wang. 1975. Mercury distribution in ancient and modern sediment of northeastern Bering Sea. Mar. Geol. 18:91-104.

Nelson, H., B.R. Larsen, E.A. Jenne, and D.H. Sorg. 1977. Mercury dispersal from lode sources in the Kuskokwim River drainage, Alaska. Science 198:820-824.

Paasivirta, J., J. Sarkka, K. Surma-Aho, T. Humppi, T. Kuokkanen, and M. Marttinen. 1983. Chemosphere 12:239. [no title available]

Patton, W.W., Jr., J.W. Cady, and E.J. Moll. 1982. Aeromagnetic interpretation of the Medfra quadrangle, Alaska. U.S. Geological Survey Open-File Rep. 80-811E. 14 pp.

Patton, W.W., Jr., and E.J. Moll. 1983. Mineral resources assessment map of the Medfra quadrangle, Alaska. U.S. Geological Survey Open-File Rep. 80-911G.

Peterson, L.A., G.E. Nichols, N.B. Hemming, J.A. Glaspell. 1985. Alaska Particulates Criteria Review. L.A. Peterson and Associates, Inc., Fairbanks, AK. 245 pp.

Rada, R.G., J.E. Findley, and J.G. Wiener. 1986. Environmental fate of mercury discharged into the upper Wisconsin River. Water, Air, and Soil Pollution 29:57-76.

Rada, R.G., J.G. Wiener, M.R. Winfrey, and D.E. Powell. 1989. Recent increases in atmospheric deposition of mercury to north-central Wisconsin lakes inferred from sediment analyses. Arch. Environ. Contam. Toxicol. 18:175-181.

Regnell, O. 1990. Conversion and partitioning of radio-labelled mercury chloride in aquatic model systems. Can. J. Fish Aquat. Sci. 47:548-553.

Reynolds, J.B., R.C. Simmons, and A.R. Burkholder. 1989. Effects of placer mining discharge on health and food of Arctic grayling. Water Resources Bull. 25:625-635.

Ricker, W.E. 1975. Computation and interpretation of biological statistics of fish populations. Bull. Fish. Res. Bd. Can. 191. 382 pp.

Scannell, P.O. 1988. Effects of elevated sediment levels from placer mining on survival and behavior of immature Arctic grayling. M.S. Thesis, Alaska Cooperative Fishery Research Unit, University of Alaska, Fairbanks, AK. 84 pp.

Schmitt, C.J., and W.G. Brumbaugh. 1990. National Contaminant Biomonitoring Program: concentrations of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in U.S. freshwater fish, 1976-1984. Arch. Environ. Contam. Toxicol. 19:731-747.

Schwab, C.E., E.J. Moll, and W.W. Patton, Jr. 1981. Mineral occurrences map of the Medfra quadrangle, Alaska. U.S. Geological Survey Open-File Rep. 80-811B. 2 sheets, scale 1:250:000.

Selikoff, I.J. (ed.) 1971. Hazards of Mercury. Study Group on Mercury Hazards. Environmental Research 4. 69 pp.

Schroeder, W.H., J. Munthe, and O. Lindqvist. 1989. Cycling of mercury between water, air, and soil compartments of the environment. Water Air Soil Pollut. 48:337-347.

Sokol, R.R., and F.J. Rohlf. 1981. Biometry. W.H. Freeman and Co., San Francisco, CA. 859 pp.

Sorensen, E.M. 1991. Metal Poisoning in Fish. CRC Press, Inc., Boca Raton, FL. 374 pp.

Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rapp, Jr. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. Environ. Sci. Technol. 24: 1716-1727.

Stickel, W. 1971. Ecological effects of methylmercury contamination. pp. 31-41 *in* I.J. Selikoff, ed. Hazards of Mercury. Environ. Res. 4(1).

Thomas, B.I. 1964. Galena-bearing gossans, Beaver Creek, Ruby District, Yukon River, west central Alaska. U.S. Bureau of Mines Open-File Report 39. 28 pp.

U.S. Bureau of Mines. 1987. Alaska 1:250,000 scale quadrangle map overlays showing mineral deposit locations, principal minerals, and number and type of claims. Updated 1986, 1987. 95 overlays. Fairbanks, AK.

U.S. Department of Interior. 1990. Mining and minerals policy--1990. Annual Report of the Secretary of the Interior under the Mining and Minerals Policy Act of 1970 (Public Law 91-631). 70 pp.

U.S. Fish and Wildlife Service (USFWS). 1987. Nowitna National Wildlife Refuge Comprehensive Conservation Plan. Environmental Impact Statement. Wilderness Review.Wild River Plan. U.S. Fish and Wildlife Service, U.S. Department of Interior, Anchorage, AK. 372 pp.

USFWS. 1991. Fisheries Management Plan: Nowitna National Wildlife Refuge. Nowitna National Wildlife Refuge, Galena, AK and Fish and Wildlife Enhancement Fishery Assistance Office, Fairbanks, AK. 44 pp.

Van Den Berg, L.A. 1971. Sources, distribution, and control. pp. 26-31 *in* I.J. Selikoff, ed. Hazards of Mercury. Environ. Res. 4(1).

Van Nieuwenhuyse, E.E., and J.D. LaPerriere. 1986. Effects of placer gold mining on primary production in subarctic streams of Alaska. Water Resources Bull. 22:91-99.

Wagener, S.M., and J.D. LaPerriere. 1985. Effects of placer mining on the invertebrate communities of interior Alaska streams. Freshwat. Invertebr. Biol. 4:208-214.

Warner, J.D. 1985. Critical and strategic minerals in Alaska - tin, tantalum, and columbium. U.S. Bureau of Mines, Information Circular 9037. 19 pp.

Weber, P. and R. Post. 1985. Aquatic habitat assessment in mined and unmined portions of the Birch Creek watershed. Alaska Dept. Fish Game, Habitat Division Report 85-2, Juneau, AK.

Wershaw, R.L. 1970. Sources and behavior of mercury in surface waters. pp. 29-34 *in* R.L. Wershaw, ed. Mercury in the Environment. U.S. Geol. Surv. Prof. Paper 713.

West, R.L. 1982. Kantishna Hills heavy metals investigations: Denali National Park, 1982. U.S. Fish and Wildlife Service Report to the National Park Service under Interagency Agreement 14-16-0007-82-5524, Fairbanks, AK.

West, R.L., and N. Deschu. 1984. Kantishna Hills heavy metals investigations: Denali National Park, 1983. U.S. Fish and Wildlife Service/U.S. Park Service Report under Interagency Agreement No. 14-16-007-82-5524, Fairbanks, AK. 42 pp.

Wiener, J.G., G.A. Jackson, T.W. May, and B.P. Cole. 1984. Longitudinal distribution of trace elements (As, Cd, Cr, Hg, Pb, and Se) in fishes and sediments in the upper Mississippi River. pp. 139-170 *in* J.G. Wiener, R.V. Anderson, and D.R. McConville, eds. Contaminants in the Upper Mississippi River. Proceedings of the 15th Annual Meeting of the Mississippi River Research Consortium. Butterworth Publishers, Boston, MA.

Wren, C.D. 1986. A review of metal accumulation and toxicity in wild mammals. Environ. Res. 40:210-244.

Wren, C.D., and H.R. MacCrimmon. 1983. Mercury levels in the sunfish, *Lepomis gibbosus*, relative to pH and other environmental variables of Precambrian Shield lakes. Can. J. Fish. Aquat. Sci. 40:1737-1744.

Wren, C.D., W.A. Scheider, D.L. Wales, B.W. Muncaster, and I.M. Gray. 1991. Relation between mercury concentrations in walleye (*Stizostedion vitreum vitreum*) and northern pike (*Esox lucius*) in Ontario Lakes and influence of environmental factors. Can. J. Fish. Aquat. Sci. 48:132-139.