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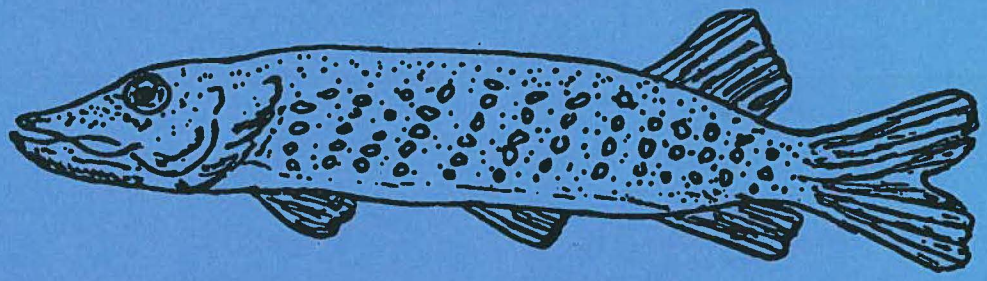
TECHNICAL REPORT

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



by

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

August 20, 1992

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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.

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ACKNOWLEDGMENTS

Fish and Wildlife Service biologist Rod Simmons initiated this study, provided guidance to refuge personnel assisting in the project, and contributed critical, constructive review comments on the draft report. Nowitna National Wildlife Refuge Manager David Stearns and Service contaminant biologists Everett Robinson-Wilson and Keith Mueller also provided able technical review of the report. We also thank Dr. Phyllis Weber-Scannell, Alaska Department of Fish and Game, and Dr. Joyce Beelman and Mr. Randy Rogers, Alaska Department of Environmental Conservation, for their technical reviews. Fish and Wildlife Field Supervisor Patrick Sousa devoted considerable time and skills editing drafts of the report. We also thank Fish and Wildlife Service biologist Larry Bright, who provided editorial review; Heather Johnson, who assisted in preparing maps and researched mining history; and Debbie Garibay, who provided typing assistance and drew the northern pike on the front cover.

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 eastern 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

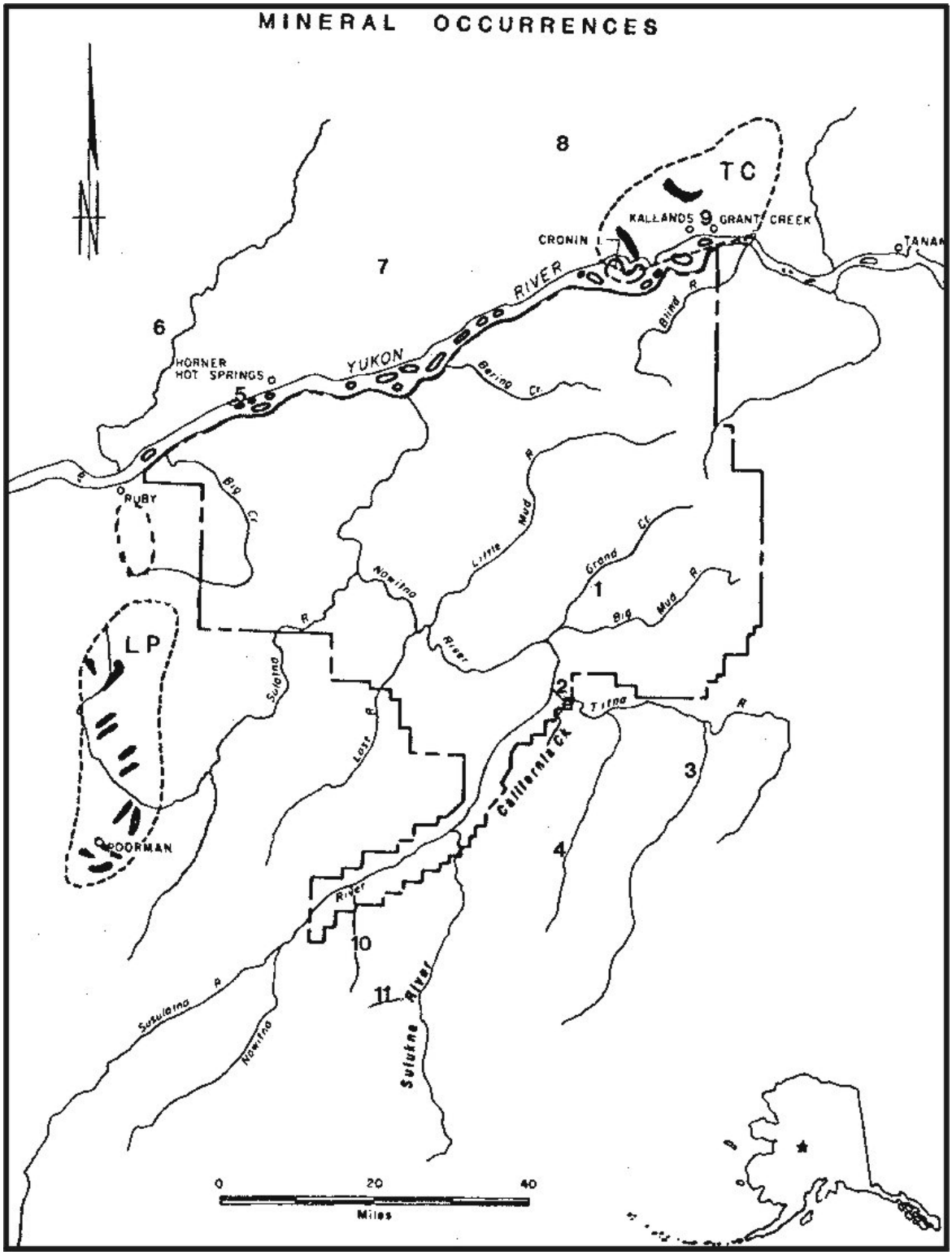


Figure 1. Regional mineral occurrences near the Nowitna National Wildlife Refuge. See text for sources.

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.

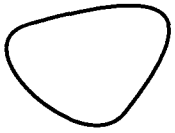
Single mineral deposits

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.

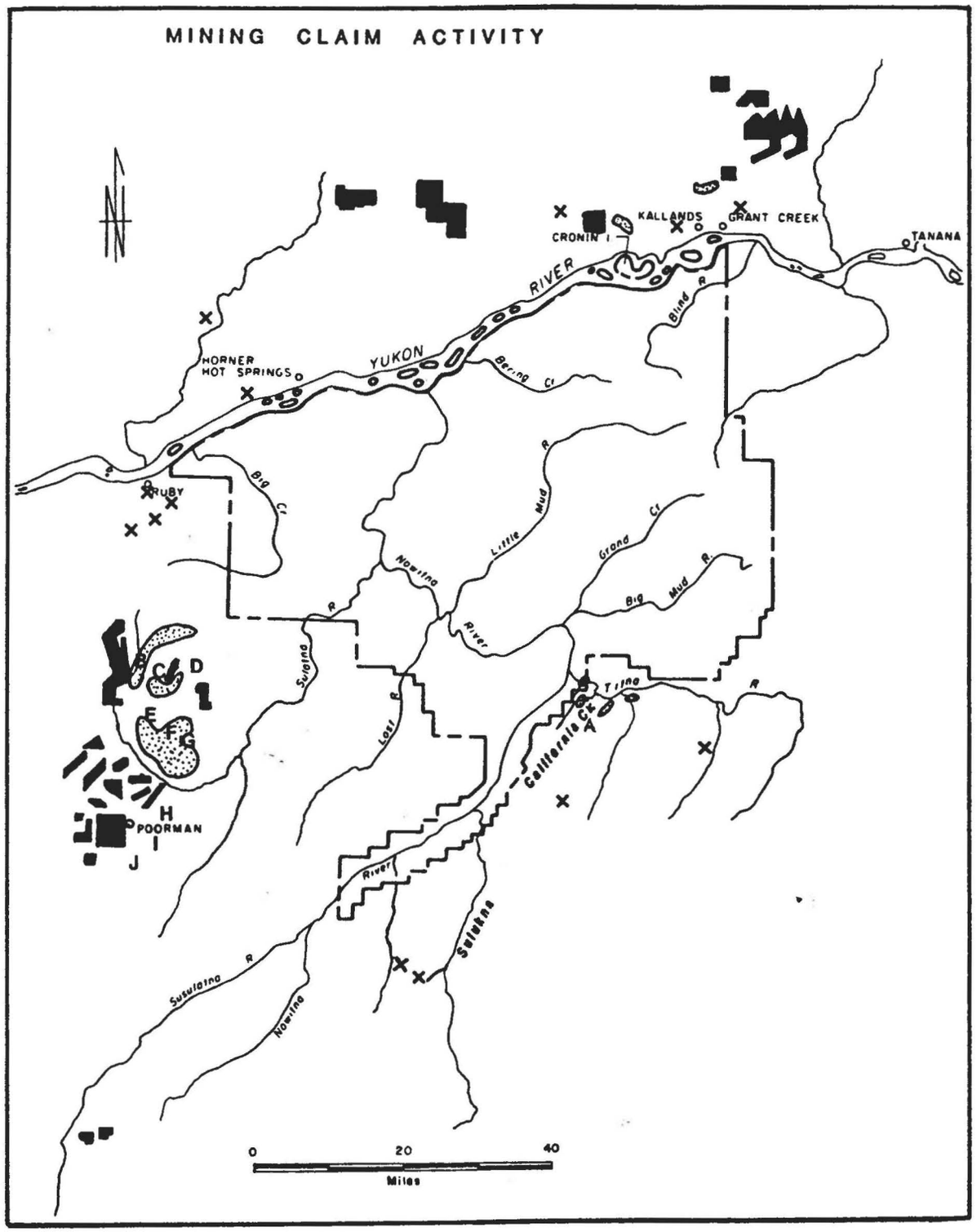


Figure 2. Mining history of the Nowitna National Wildlife Refuge and surrounding areas. See text for sources.

Legend - Mining Activity

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

15 or more claims, active between 1975 - 1982 and some 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^2 (7244 mi^2) 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^2 (1393 $miles^2$) 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.

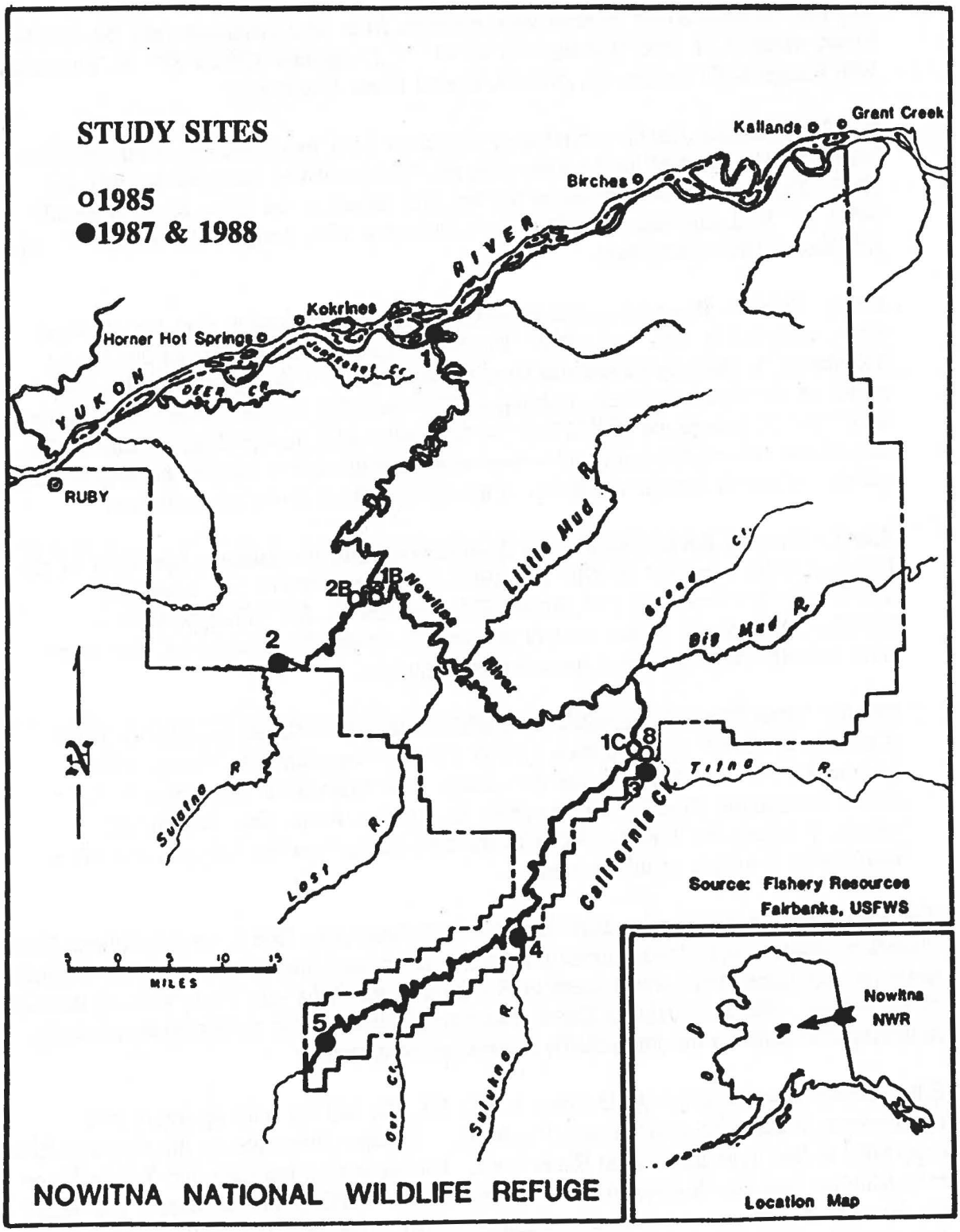


Figure 3. Study sites on Nowitna National Wildlife Refuge streams and rivers, 1985 - 1988.

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^2 (684.3-$mile^2$) 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.

TABLE 1. SAMPLES COLLECTED FROM NOWITNA NATIONAL WILDLIFE REFUGE FROM 1985 - 1988. Numbers under each analysis category are site locations where collections were made.

Year	Water Quality	Dissolved Metals	Total Rec. Metals	Sediment Metals	Fish
1985	6-9[a]	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

[a] 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

Water quality samples. Water quality samples were collected in 1985, 1987, and 1988. The 1985 samples consisted of single surface grab samples collected in 1-L Nalgene® 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® 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.

Trace element samples. 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 in the same manner as the water quality samples. The 1985 dissolved metals samples were collected using a Micropore® 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® cellulose acetate LuerLock filters, a 0.80 µm prefilter and a 0.45 µm 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.

Fish

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® 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® 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.

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

[a] ICPP = ICP with preconcentration; AA = atomic absorption
[b] TRM = = total recoverable metals analysis; DM = dissolved metals analysis
[c] Only the TRM analysis is quantitative in the data set.
[d] AA was performed in 1985 only.
[e] 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.

SEDIMENT		YEAR	
Analyte	Method[a]	1987	1988
Arsenic	ICP		1.0[b]
Beryllium	ICP	0.8	0.1
Cadmium	ICP	0.8	0.5
Chromium	ICP	2.0	1.0
Copper	ICP	2.0[b]	
Manganese	ICP		0.5
Mercury	AA	0.02[b]	
Molybdenum	ICP	6.7	
Nickel	ICP	5.0	
Selenium	AA		1.0
Strontium	ICP		1.0
Thallium	ICP		10.0
Vanadium	ICP	43.0	10.0
Zinc	ICP	4.0	1.0

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

[a] AA = atomic absorption spectrometry; ICP = inductively coupled plasma spectrometry; ICPP = ICP with preconcentration

[b] Precision for this analysis less than expected

[c] ICPP performed in 1987; ICP performed in 1988

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, 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®, 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:

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

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+® 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 µS/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

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.

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

[a] Analysis date presumed to be same as collection date, but date not recorded.
[b] Analyzed on 8/22/87
[c] Analyzed on 8/20/88
[d] Only two samples collected

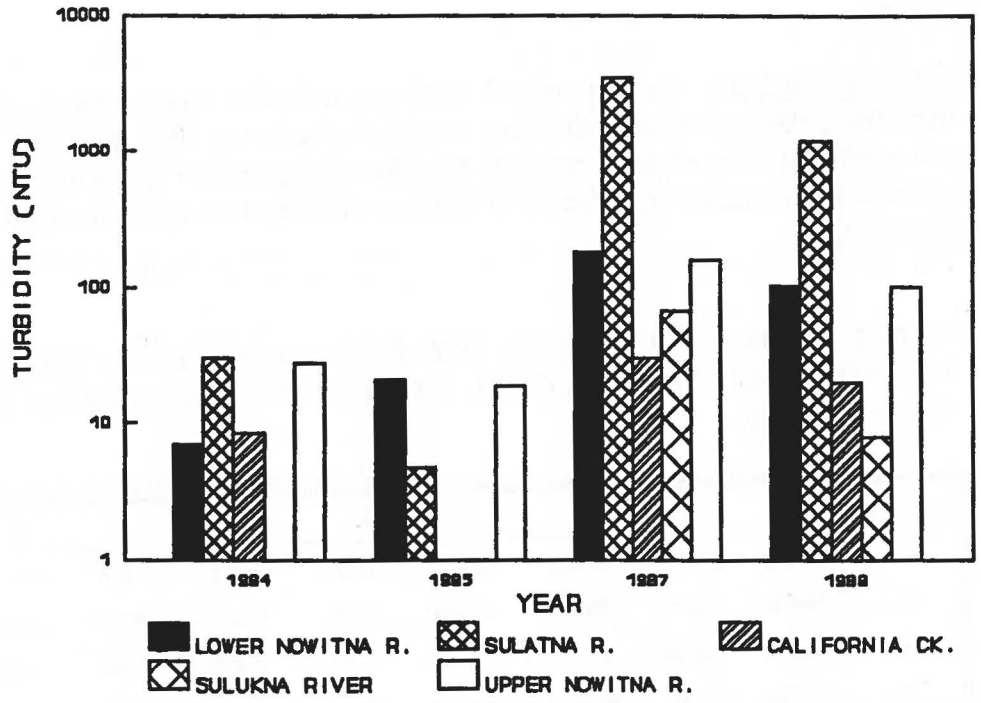


Figure 4. Turbidity in Nowitna National Wildlife Refuge drainages, 1984 - 1988. Turbidity data are shown on a logarithmic scale. The 1984 data are from Deschermeier and Hawkinson (1985). Site locations on the drainages differ slightly for 1984 and 1985 sites versus 1987 and 1988.

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

Trace elements 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 $CaCO_3$). 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 $CaCO_3$) for the protection of freshwater aquatic life from chronic toxicity. Low hardness (45 - 85 mg/L as $CaCO_3$) 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.

Trace elements in 1987. 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.

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

SITE	DATE	As	Be	Cd	Co	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
	x̄	-	-	-	-	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
	x̄	-	-	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
	x̄	-	-	-	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
	x̄	-	-	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
	x̄	-	-	-	0.002	0.011

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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.[ab]

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
	$\bar{x}$	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
	$\bar{x}$	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
	$\bar{x}$	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
	$\bar{x}$	-	-	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
	$\bar{x}$	0.057	-	0.002	0.003	0.006	0.889

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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 Nowitna 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.

Trace elements in 1988. 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

TABLE 9. DISSOLVED METAL CONCENTRATIONS IN WATER FROM NOWITNA NATIONAL WILDLIFE REFUGE, 1988. Concentrations are reported in mg/L.[ab]

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
		x̄	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
		x̄	3.4233	0.1693	0.0026
3	8/16/88		0.1600	0.0108	<0.0018
			0.2290	0.0146	<0.0018
		x̄	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
		x̄	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
		x̄	0.6783	0.0328	-

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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.[a]

SITE	DATE	As	Cd	Ni	Tl	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
	x̄	-	-	<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
	x̄	-	<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
	x̄	-	<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
	x̄	-	<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
	x̄	-	<0.0002	<0.0018	<0.0115	-

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

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 ($F_{4,14}$ = 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 mg/kg) at Site 2 (the Sulatna River) and Site 1 ($\bar{x}$ = 1.11 mg/kg) and lowest ($\bar{x}$ = 0.23 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.[ab]

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
			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
			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

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.
[b] 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

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

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
	x̄	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
	x̄	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
	x̄	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
	x̄	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
	x̄	12.9	0.45	<0.74	24.9	571.0	<0.74	23.8	<16.1	42.2	81.1

[a] Mean concentrations were computed using ½ 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.

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

Site	Species	Date	Weight (gm)	Total Length (mm)	Fork Length (mm)	Moisture (Percent)		
						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	0.58[a]	-	-
	Grayling	8/24/87	150	240	225	0.58[a]	-	-
	Grayling	8/24/87	200	242	225	0.63[a]	-	-
	Grayling	8/24/87	200	252	235	0.64[a]	-	-

[a] 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)	Moisture (Percent)	
						Muscle	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	0.77[a]	-
	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

[a] Whole fish samples.

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 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

Trace elements in 1987. 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.[ab]

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
	$\bar{x}$		-	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
	$\bar{x}$		-	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

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.
[b] 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.[ab]

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
	x̄		-	-	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
	x̄		-	-	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
	x̄		-	-	4.19	1178	0.09	2.25

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.
[b] Cobalt was not detected in any muscle or whole body sample.

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

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
	$\bar{x}$		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
	$\bar{x}$		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

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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 mg/kg) than pike muscle from Sites 1 and 4 ($\bar{x}$ = 4.78 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).

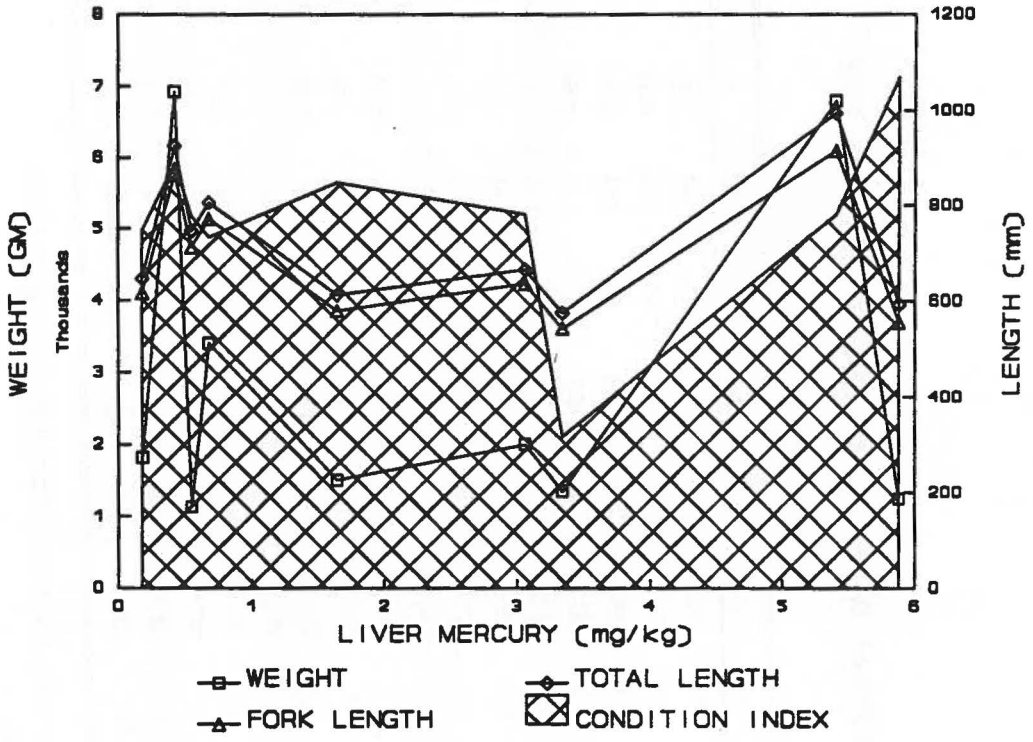


Figure 5. Mercury concentration in northern pike livers in relation to weight, length, and fish condition in 1987.

Trace elements in 1988. 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).

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

SITE	SPECIES		Ba	Be	B	Cd	Cr	Cu	Mg	Mo	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
		x̄	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
		x̄	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
		x̄	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
		x̄	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

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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.[ab]

SITE	SPECIES	Ba	Be	B	Cd	Cr	Cu	Mg	Mo	Se	Sr	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
	x̄	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
	x̄	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
	x̄	4.18	-	-	-	-	7.0	6614	-	10.9	137.40	-	117
5	Broad Whitefish	6.19	<0.49	<2.21	<2.2	<1.3	4.4	5000	<1.3	8.8	74.40	<1.33	68
2	Longnose Sucker	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
	x̄	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

[a] Mean concentrations were computed using ½ the detection limit for a nondetect if remaining replicate concentrations of an analyte were above the detection limit.

[b] 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.

[c] 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 ($r^2 = .72$, $df = 8$, $P = .002$), and zinc ($r^2 = .78$, $df = 8$, $P = .001$).

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 ($\chi^2 = 6.00$, $df = 8$, $P = .05$).

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.

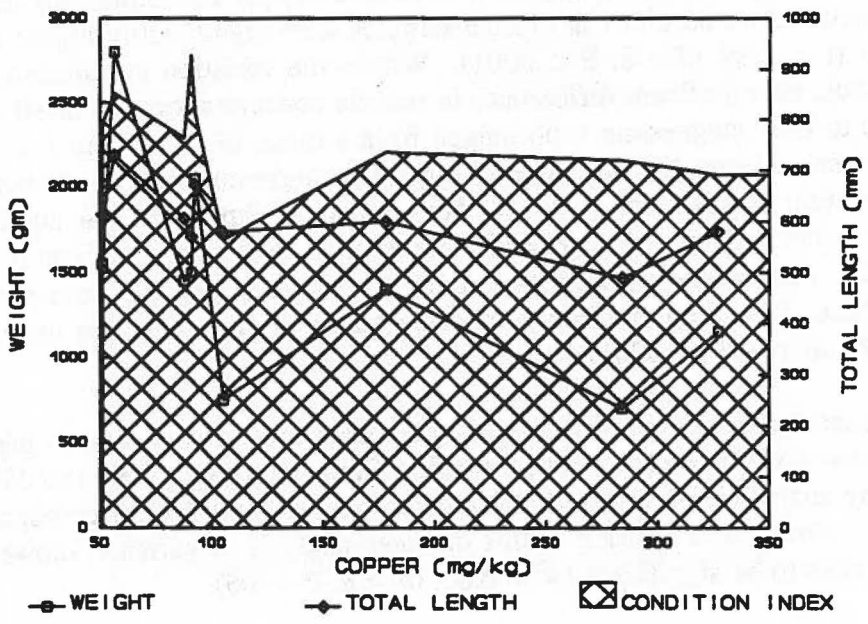


Figure 6. Copper concentration in northern pike livers in relation to weight, length, and fish condition in 1988.

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 ($r^2 = .36$, df = 8, P = .04). Both these metals were themselves highly correlated ($r^2 = .99$, df = 8, $P < .0001$), 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, 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.

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APPENDIX A

DOCUMENTATION AND SAMPLE HANDLING

STUDY PROPOSALS

A study proposal was submitted prior to each year of sampling. The 1985 study plan was prepared by Rod Simmons, Fairbanks Environmental Contaminants Specialist, and was a generic plan for sampling Nowitna, Koyukuk, Kanuti, and Innoko NWR's. Beginning in 1987, study plans were prepared by Nowitna NWR personnel, and subsequently reviewed and approved by the Fairbanks Environmental Contaminants Specialist and the Services' Region 7 (Alaska) Environmental Contaminants Coordinator following any needed revisions. The 1987 and 1988 study plans included objectives of the study, a discussion of the justification for the study including a review of related research, a methods section including discussion of collection and analysis procedures, topographic maps indicating anticipated sample locations, and a cost proposal based on number and types of samples to be collected. In addition to selection of mined sites for sampling, one or more reference sites, believed to be unaffected by mining, were identified as controls for this study after review of the mining history of the area, including past and active placer and other mine sites on both State and Federal lands within and surrounding the refuge boundaries.

FIELD DOCUMENTATION

During field studies, sample documentation was recorded in a weatherproof field notebook in permanent ink. The date and time of collections at each site were specified as were the water temperature at the sample site and results of all water quality analyses. Sample identifications were also listed by sample type for each sample collected. Data on fish species, including the whole weight, and tissue weights (if applicable), the fork length, and the total length were also listed in the field notebook.

SAMPLE CATALOG

A sample catalog was prepared for each year's samples. The catalog contained study objectives; background information (including number of water, sediment, and tissue samples); previous findings and concerns; possible interfering elements in the analyses; methods of preservation and storage; instructions to the laboratory, including a description of the analyses requested together with the suggested analytical method; a list of data recipients; a cost estimate for the requested analyses; and a tabulated summary of information on each sample. This information included the sample identification, the date

of collection, the type of sample or tissue, the species (for fish), the sample location, sample weight or volume, and analyses requested for each particular sample. For the Nowitna studies, 1985 - 1987 catalogs were submitted to the following analytical laboratories:

Catalog	Regional I.D.	Laboratory	Address	Analysis
176	R785A17	Environmental Trace Substances Research Center	Route 3 Columbia, MO 65201	6/04/86
5442	R78727F	Research Triangle Institute	Cornwallis Rd. P.O. Box 12194 Research Triangle Park, NC 27709	9/19/88
5753	R788121	Versar, Inc.	6850 Versar Center Springfield, VA 22151	3/29/90

Catalogs were inspected by a Quality Assurance Officer at the Patuxent Analytical Control Facility. Upon approval, they were forwarded to the laboratory together with the listed samples. Laboratory data were received by the authors following review and approval by the Quality Assurance Officer. Catalogs for this project were received on 11/26/86 (176), 10/10/89 (5442), and 7/18/90 (5753). Unsatisfactory results prompted reanalysis of antimony in Catalog 176, results of which were received on 7/30/87.

CHAIN OF CUSTODY

No chain of custody forms accompanied these catalogs, since sampling was performed for baseline information, and was not anticipated to be used in legal proceedings.

SAMPLE PRESERVATION/STORAGE

Following collection, water samples were immediately preserved with 1.5 ml Ultrix nitric acid to a pH < 2. Water, sediment, and fish samples were placed in coolers with ice, blue ice, or snow, and transported by boat or float plane to Galena, Alaska for temporary storage. Water samples were refrigerated from the date of collection until shipment; sediment and fish tissues were kept frozen.

SAMPLE SHIPMENT

Samples were shipped to the laboratory by air courier. Water samples were shipped with ice; frozen samples were shipped with dry ice. All three laboratories reported that samples were received in good condition (cold if water, frozen if tissue or sediments).

SAMPLE HOLDING TIMES

Holding times for Catalogs 176, 5442, and 5753 were 9 months, 13 months, and 6 months, respectively. The prescribed holding time for mercury in water is 28 days; the maximum recommended holding time for other metals in water is 6 months (APHA et al. 1989). No holding times have been established for metals in sediments or tissues; however, it is widely assumed that loss from these media by volatilization or plating onto the container wall would be minimal. Based on the prolonged holding times, mercury is likely to have been lost from the water samples and those results should be considered invalid. For other metals, particularly cadmium, significant losses may have also occurred. However, refrigeration, in addition to acidification, may have mitigated loss of these metals. It is uncertain whether losses due to excessive holding times are significant.

APPENDIX B

SAMPLE IDENTIFICATION AND DATA BASE MANAGEMENT

Field sample numbers were transformed into identification numbers consistent with the Fairbanks Ecological Services' DBase IV Contaminants Data Base Management System for data entry. Separate files were maintained for water, sediments, and fish. Sample data pertinent to samples analysis was also entered into this system, as follows:

CONTAMINANTS DATABASE ENTRY FIELDS

Sample Identification Fields:

FIELD NAME	FIELD DESCRIPTION	EXAMPLE	ENTRY DESCRIPTION	COMMENT
CATNO	Catalog # and sequential #	5445-01	Assigned by Patuxent	Unique # for batch of samples
ID	ID	88AA501ARK	Year, location or refuge, site location #, sample session/ overflow, replicate, species code, tissue	Unique composite field
YR	Year	88	Last 2 digits of yr.	
LO	Refuge or general location	TE	Tetlin NWR	See codes
SI	Sample site number	01	Sites are assigned permanent numbers by refuge or location	Sequential
N	Sample session[1]/ overflow[2]	Numeric or alphabetic	Sample period for multiple samples/yr or overflow use	Sequential letters or numbers
R	Replicate designator	A	Alphabetic indicating Replicate A at site	Sequential letters
S	Species code or type of sample	F	Fish	See codes
T	Type/tissue	L	Liver	See codes

Auxiliary Fields:

SEX		M, F, U	Male, female or unknown	Samples of biota only
DATE	Sample date	12/13/90		
SPECIES	Genus and species	*Esox lucius*	Northern pike	Samples of biota only
NO_IN_COMP	Number of Organisms in composite sample	18	If 18 sculpin were in a sample	Samples of biota only
SAMPLE WT	Weight of submitted sample in grams	43	43 gm = weight of liver	Weight of discrete organs or subsamples
TOTAL_WT	Total weight of organism or sample if subsampled	100	100 gm = weight of whole fish	Weight of whole, original sample or organism
TLGTH	Organism's total length (mm)	25	25 mm = total length of fish	Samples of biota only
FLGTH	Fork length (mm)	23	23 mm = fork length of fish	Fish only
UNIT	Unit of analysis	ppm	milligrams per kilogram	Other units possible
MOIST	% moisture	45	45% moisture	All matrices except water
BASIS	Basis for data reported	wet or dry	Wet or dry weight	All matrices except water[3]
Detection Limit (shown as X and the metal symbol)	Less than for each metal	<	Used when value measured is less than detection limit	
As (Example)	Metal concentration	5.5	5.5 mg/kg	See basis and unit

[1] Number (#) is that of sample period at a site that year (e.g., for first sample date at a site, N = 1, the next sample date at the site within the year N = 2, etc.).

[2] Overflow is to be used when necessary to form a unique ID when S & T fields are the same for the sample site and sample period or when there are more than 99 sample locations. When not used for this purpose, it can be used to designate whether metals (M) or hydrocarbons (H) are to be analyzed.

[3] Concentrations in water are always reported on a wet weight basis. However, labs vary in how other matrices are reported.

General Location Codes

AA - Arctic NWR
BA - Barrow
KA - Kanuti NWR
MR - Minto Flats
HR - Haul Road
SR - Sagavanirktok R.
NS - Norton Sound
DP - Denali Park
YF - Yukon Flats NWR
CR - Chena River
KY - Koyukuk NWR
FA - Fairbanks
MI - Lake Minchumina
YR - Yukon River
NA - North Slope (other)
TE - Tetlin NWR
SE - Selawik NWR
NO - Nowitna NWR
PB - Prudhoe Bay
DL - Delta
CO - Colville R.
PR - Porcupine R.

Species Codes

If the study involves water, sediment, unknown species, or species without a code, use these codes:

W - water
S - sediment, soil
V - vegetation
M - mammal
I - invertebrate
B - bird
F - fish

If the study involves known species, use these codes:

Fish

A - Arctic cisco
B - burbot
C - least cisco
D - Dolly Varden/charr
E - lake chub
F - sheefish
G - Arctic grayling
H - chinook salmon
I - chum salmon
K - Alaska blackfish
L - longnose sucker
M - humpback whitefish
N - ninespine stickleback
O - coho salmon
P - northern pike
R - broad whitefish
T - lake trout
U - slimy sculpin
W - round whitefish
Y - sockeye salmon

Birds

A - osprey
B - bald eagle
C - northern harrier
D - rough-legged hawk
E - golden eagle
F - phalarope
G - American kestrel
H - merlin
I - peregrine falcon
J - gyrfalcon
K - boreal owl
L - glaucous gull
M - spectacled eider
O - oldsquaw
P - pectoral sandpiper
R - rock ptarmigan
S - Steller's eider

Type/Tissue Codes

A - sand (2.0 to .0625mm)
B - bile
C - carcass
D - dissolved metals (H_2O)
E - egg
F - feather
G - gill
H - hairU - shoots
I - silt (.0625 to .0039mm)
K - kidney
L - liver
M - muscle
N - brain
O - blood
P - bone
Q - clay (<.0039mm)
R - tot. recoverable metals (H_2O)
S - stomach
T - total metals (H_2O)
V - leaves
W - whole (tissue or sediment)
Z - stem

APPENDIX C

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) OF CHEMICAL ANALYSES

The U.S. Fish and Wildlife Service (Service) currently maintains contracts with several analytical laboratories, and also performs some internal analytical work at the Patuxent Analytical Control Facility, Patuxent National Wildlife Research Center (PACF), Laurel, Maryland, to determine the inorganic and organic composition of samples.

The contract laboratory was selected as a result of correctly analyzing a series of check samples, the chemical composition of which was unknown to the laboratory at the time of testing, and after a careful review of the laboratory, its procedures, its facilities, its experience, and its personnel by a PACF technical committee. A final step in selecting a laboratory was an inspection by representatives of the evaluation committee to confirm the presence of facilities, equipment and personnel and to observe the functioning of the laboratory. Continued round-robin testing and cross-checking of the laboratory by PACF has been used to continuously monitor laboratory performance and alert the Service's Quality Assurance Project Officer of systematic analytical problems with particular analytes. Approximately 5% of all sample catalogs submitted for analysis at a contract laboratory are also reanalyzed by the Patuxent Analytical Control Facility. In addition to these QA/QC measures, precision, accuracy, and potential laboratory contamination of samples are evaluated through the analysis of specific quality control samples. The report submitted by the contract laboratory is required to contain the following:

1. A brief description of the methods used in the analysis.

2. The analytical results.

3. Results of any QA/QC samples analyzed in conjunction with the reported catalog, including:

    a. Limits of detection for each sample

    b. Duplicate analysis

    c. Spiked sample analysis

    d. Standard reference material (SRM) analysis

    e. Procedural blank analysis

4. A description of any problems encountered in the analysis.

The laboratory may also be required to submit copies of all raw data collected during the analysis upon request. In addition to a brief description of the methods, we have typically requested that the laboratory provide a description of detailed methods, together with the equipment (including model numbers) of instrumentation.

QA/QC samples were subjected to a rigorous software program, dubbed Saint Patrick written in Dbase IV® screening program, and designed by Patrick Scannell, Ecological Services, Fairbanks. Parameters and screening criteria utilized in this software are presented below.

LIMITS OF DETECTION

The limit of detection (LOD) has been variously defined and its determination is the subject of controversy (APHA et al. 1989). Depending on the laboratory performing the analyses, the LOD referenced could refer to the instrumental detection limit for a given sample, the typical "method" detection limit, the lower limit of detection for all samples, or the limit of quantitation, above which results can be viewed as semiquantitative or quantitative. A general definition for LOD is that it is the lowest concentration level that can be distinguished statistically from a blank sample. That is, it is a reliable limit for an analyte, above which values are "real" and distinguishable from instrument noise. Samples reported as being below the detection limit in the data set are generally reported as <X where X is the detection limit. Occasionally, they may also be reported as ND (not detected), with the method LOD usually listed elsewhere in the catalog.

For analyses performed before 1989, the method of determining the LOD varied. In practice, contract laboratories usually adjusted the stated method limit of detection for typical percent moisture, sample size, and, if needed, chemical interferences. Individual sample LOD's may also be reported by the laboratory. These are generally shown adjacent to the measured concentration of an analyte in the sample.

In determining the LOD, the moisture adjustment is more significant if the sample is analyzed as a wet sample than if the sample is freeze-dried first, or is naturally dry (e.g., hair samples). The smaller the sample size, after moisture adjustment, the higher the detection limit for that sample will be. Because the method LOD actually varies depending on the nature of the individual sample, the upper LOD reported for each matrix in a sample catalog was adopted as the limit of detection for the QA/QC screening of the data. For general reference, however, the general method limits for the catalogs are reported in the methods section of the report.

ANALYTICAL PRECISION

Precision refers to the degree of agreement among repeated measurements of a given sample at the same time, and is not a measure of accuracy. Precision varies with such factors as the homogeneity of the sample, sample volume, sample matrix, instrumental method, instrumental drift, chemical interferences, and the analyte concentration in the sample. Estimates of precision for this study were made using duplicate analysis, where two separate subsamples of a homogenized sample are collected and analyzed by the contract laboratory. While this method of creating duplicates lacks the measurement errors associated with improper or incomplete mixing of samples split in the field, it may entail bias by the laboratory, since the expected result is known. Precision is monitored by the contract laboratory by using range ratio control charts for each analyte (metal or hydrocarbon) for each matrix (water, sediment, tissue). For our screening of data from sample catalogs, the measure selected for estimating precision is the relative percent difference (RPD):

$$RPD = ([D_1 - D_2]/([D_1 + D_2)/2]) \times 100$$

where RPD is the relative percent difference, D_1 is the concentration as measured in the first analysis, and D_2 is the concentration in the second analysis.

Acceptable precision is based not only on the absolute value of the RPD, but also on the relationship of the sample concentration of the analyte to the LOD for that analyte in the particular sample. For duplicate samples with analyte concentrations where both values are < LOD, no estimate of average precision is made in the screening software, since this comparison is normally inappropriate (APHA et al. 1989). Less commonly, one duplicate value is less than the LOD and the other is greater than the LOD. In these cases, an RPD is calculated by assuming that the number < LOD equals the LOD. In the QA/QC report, an asterisk is used to identify cases where the RPD cannot be calculated. For sample concentrations less than twice the limit of detection, precision is expected to be low, since instrument performance typically declines as the LOD is approached. The 95% confidence interval for these cases is assumed to be $\pm$ 2 LOD (or up to 200% of the actual reported value of a single sample). Samples with concentrations <2 LOD are not rejected, based on poor precision; however, these data are flagged as being "qualitative only" in the screening program.

Since the LOD may vary according to sample, the LOD entered in the QA/QC screening is the highest LOD identified for the sample matrix in the actual sample data set. Average RPD's for each analyte and each matrix are calculated separately. For concentrations of an analyte > 2 LOD and <10 LOD, results are only expected to be semiquantitative, and dependent on closeness to the LOD. In other words, both precision and accuracy may be reduced. For measurements > 10 LOD, the analysis can be expected to be highly quantitative, and rigorous criteria are applicable to determine whether average precision is sufficient to guarantee repeatability.

Numerical criteria used to screen both semi-quantitative (2-10 LOD) and quantitative (>10 LOD) duplicate data for this sample catalog are presented in Table C-1. The software program first computes the RPD's for all duplicate analyses performed for a given analyte, then averages the RPD's for that analyte, and then compares the average RPD for that analyte and matrix to the appropriate criterion. If only one pair of duplicates was compared for a given matrix by the analytical laboratory, the average RPD is actually the single RPD value.

TABLE C-1. ACCEPTABLE AVERAGE PRECISION (RPD) FOR EACH ANALYTE BASED ON RELATIONSHIP TO THE LIMIT OF DETECTION (LOD)

METHOD	ACCEPTABLE MEAN RPD[a]	
	<10x LOD	>10x LOD
ICP SCAN[b]	200%	33.3%
ATOMIC ABSORPTION	200%	33.3%

[a] The relative percent difference is the average of all the relative percent differences for an analyte in a given matrix.

[b] Inductively coupled plasma emission spectroscopy, including direct and preconcentrated scans.

The criteria selected for precision (above) are not particularly rigorous. However, since water and soil samples from the sites were collected in triplicate, and since multiple fish were collected per site, these criteria probably ensure adequate average precision for the prescribed use of the data.

ANALYTICAL ACCURACY

Spiked Samples

In addition to precision, measurements of correctness of the analytical analysis are needed to guarantee the quality of the data that are semiquantitative (>2 LOD) or quantitative (>10 LOD) and to estimate chemical interferences that may occur with particular types of samples. One method used by Fish and Wildlife Service contract laboratories to estimate accuracy and gauge interference is that of spiked samples. After a sample in the sample catalog is homogenized, two separate subsamples are taken. One is analyzed as a sample. The other subsample is "spiked" with a known quantity of one or more analytes, and then analyzed. The difference between the two subsamples, after accounting for any differences

in sample weight, is the spike recovery. This value is usually reported as a percentage of the amount added. Recovery rates greater than 100% may indicate that the instrument was incorrectly calibrated, subject to upward drift since the original calibration, or that contamination of the sample may have occurred. If the spike recovery is less than 100%, then the analyte was not fully recovered. This could occur due to loss of the analyte during the sample procedure (e.g., loss of mercury due to volatility), instrument drift following initial calibration, errors in the calibration procedure, or chemical interferences inherent in the particular matrix being analyzed. Another important source of incomplete metal recoveries is incomplete digestion of the sample material. Unless specified in the catalog instructions, metal digestions performed by contract laboratories are incomplete, resulting in the release of some, but not all, of the analyte. Such digestions give what are referred to as "total recoverable metals" or "acid-soluble metals." The metals released are those that would be readily available for release in an acidic environment. Theoretically, these are the metal concentrations of biological significance, in terms of availability for rapid biogeochemical cycling. Metals that remain bound in the matrix are more tightly bound, either by chemical complexing or by physical processes, and may not become biologically available under any natural circumstance. Occasionally, total digestion (using hydrofluoric acid rather than the previous nitric/perchloric acid) is performed when spike recoveries are not satisfactory during the partial digestion.

Usually, the amount of spiking solution added to a sample is sufficient to result in a concentration of that analyte of more than twice the original concentration in the sample and >2 LOD. Some laboratories use an asterisk or "spike too low" to indicate that, for a given analyte, the spike added little analyte to the sample compared to the amount of analyte already present in the sample. The St. Patrick program examines spike recovery for all spiked samples, even if the spike was low.

In general, Service contract laboratories perform incomplete digestions with nitric and perchloric acids, rather than complete digestions, since our interests center on the metals that are biologically available. The result is often nearly complete recovery of trace metals, such as cadmium, and poorer recovery of common metals, such as aluminum, iron, and manganese, which tend to form numerous tightly bound metallic complexes. If poor metal recoveries show this pattern in general, this may be the correct explanation. Depending on the use of the data, this may still be a significant finding, since contaminants could remain bound to materials in media, and thus be unavailable for biogeochemical cycling.

The spike recovery criteria adopted in the QA/QC screening program are summarized in Table C-2.

TABLE C-2. ACCEPTABLE ACCURACY FOR RECOVERY OF SPIKED SAMPLES BY METHOD BASED ON FISH AND WILDLIFE SERVICE CRITERIA PRESENTED BY MOORE (1990) AND APHA ET AL. (1989)

Analyte/Method	Average Recovery (%)
Metals Scan - ICP[a]	80-120
Metals - Atomic Absorption[b]	85-115

[a] ICP = Inductively Coupled Plasma Emission Spectroscopy, including direct and preconcentrated scans.

[b] Including cold vapor, hydride generation, and graphite furnace techniques.

The St. Patrick software program identifies all analytes for which the average spike recovery (average of all spikes for that analyte and matrix) exceeds the above criteria. These criteria are as stringent or more stringent than APHA et al. (1989) criteria for performance evaluation samples of water and wastewater.

Standard Reference Materials

Standard reference materials (SRM's) or interim reference materials (IRM's) provided by an outside agency or commercial source represent an additional means of gauging the accuracy of the analytical results. Usually the SRM analyzed concurrently with the samples is of the same matrix type. SRM's typically contain natural or slightly elevated levels of each analyte in the diversity of valence states, compounds, and complexes that may naturally be present in water, sediments, and tissues. Therefore, high accuracy in performing SRM analysis is frequently more difficult than accuracy in performing spike analysis.

Sources of SRM's for the Nowitna studies included the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards), the Environmental Protection Agency (EPA), and the National Research Council of Canada (NRCC). Particular SRM's associated with each catalog are summarized in the QA/QC reports (Appendix D).

Certified values provided by the source are usually determined by repeated analysis of the analyte using several different methods (e.g., atomic absorption spectrometry, X-ray fluorescence, and inductively coupled plasma spectrometry). The certified value for each analyte, or "true value," is typically the weighted mean of the different methods. A standard deviation is also calculated and used to provide a certified range. The method for creating

this range varies somewhat depending on source of the analyte, but is supposed to provide a 95% confidence interval about which values different from the certified value might actually occur due to variability in the SRM as well as the methodology. In some cases, a considerable amount of professional judgement is used to define this range.

Some analyte values may hover in the vicinity of the LOD, making quantitative comparisons unreliable; hence, both spikes and SRM's are valuable QC components . There are also certain elements for which no certified values or ranges have been developed. In the case of NIST SRM's, consensus values, together with standard deviations (SD's), have been presented for many of these analytes (Gladney et al. 1987). These are values collated from published research by a variety of investigators.

No comparison is made between the SRM "true" value and the measured value by the laboratory if the concentration reported by the laboratory was < 2 LOD, since this comparison would be qualitative only. The QA/QC Summary Sheet lists "Ref. Val. < LOD" for these cases. The following screening criteria were used to evaluate accuracy of SRM analyses for which measured values were > 2 LOD.

If the mean value of an analyte as measured by the laboratory is within the range of the certified value $\pm$ 3 SD, the SRM data are considered acceptable or "good." For certified values $\geq$ 2 LOD, a printout is also given of analytes for which the measured values fall outside $\pm$ 3 SD; these data are listed as questionable. On the QA/QC Summary Sheet for each catalog (Appendix D), "Low SRM" and "High SRM" show this confidence interval. Where the SD is not known, it is defined as 10% of the certified value, and the same range is allowed as above. Use of 10% as the estimated standard deviation is based on examination of the average relationship between the mean and standard deviation for several NIST SRM's for a suite of metals. Typically, the standard deviation is 5 - 10% of the true value. In this test, if no certified value for the analyte is available, the consensus value $\pm$ 3 standard deviations is used to screen performance.

This screening method results in acceptance/rejection of SRM performance comparable to that of the National Status and Trends Program which relies on acceptance of all values within $\pm$ 15% of the certified value (Freitas et al. 1989). However, it evaluates the laboratory performance in terms of accuracy achieved by the agency providing the SRM. Thus, greater accuracy is required for analytes for which measurement accuracy is typically higher than for difficult-to-quantify analytes.

The more SRM's used on a given matrix, the higher the probability that the laboratory will fail to meet acceptance criteria defined above in all tests. The final screening criterion developed for SRM evaluation avoids penalizing laboratories for performing additional testing. When more than one comparison with a given SRM is performed, we compared the mean measured value to the true value (or consensus value) $\pm$ 3 SD. Occasionally this average measured SRM value is less than twice the LOD. In this case, "AvgSRM < 2 * LOD" appears on the QA/QC Summary Sheet. If two different SRM's are used for the same

matrix and analytes, then each measured value is compared to the acceptable range for that SRM, and the Z-Score is averaged. In the QA/QC Summary Sheet, the Z-score (also known as a standard score) is given for each analyte by SRM. This score indicates how many SD's above or below the mean the measured value of the SRM falls. All Z-scores outside the range of the certified value $\pm$ 3 SD are also sorted to the "Questionable Quality Data" report.

BLANKS

Blanks are samples expected to have negligible or undetected concentrations of the analytes of interest. Blanks may be used to evaluate the presence of contaminants as a result of either field or lab procedures. Blanks generally consist of distilled and/or deionized water, although some laboratories may utilize other matrices. Field (or transport) blanks may be used to estimate incidental contamination in the field and during storage and shipment. Capped and clean containers are taken into the field, uncapped for the required sample period, filled with distilled water and preservative (if applicable), and treated like other field samples in regards to chilling or freezing, handling, and labelling. They are stored, shipped, and analyzed with the other samples. Alternatively, reference study site samples (control samples) may be used to evaluate natural or incidental contamination.

In the case of the Nowitna samples, no field blanks were collected. However, field blanks were collected using the same sample containers and same acid preservation at the Arctic National Wildlife Refuge in 1988. No contaminants were detected during subsequent metals analysis, indicating that the sample containers and acid were probably contaminant-free. However, incidental contamination of water samples from dust or filtration equipment (dissolved metals samples) cannot be ruled out. Control samples were taken in the Nowitna Refuge in both 1987 and 1988 (see text).

In addition to field blanks, several types of blanks may be employed by the analytical laboratory to estimate external contamination. These include a sample preparation blank, matrix blank, and reagent blank. The sample preparation blank is used to detect contamination when stirring, blending or subsampling occurs. This type blank can therefore be used to evaluate whether the equipment cleaning procedures are adequate. For this blank, double-distilled and/or deionized water is processed in the apparatus after it has been cleaned according to standard operating procedures and then analyzed along with the samples being processed. Matrix blanks are sometimes also used when the samples are not water and when a reagent blank analysis indicates contamination. A reagent blank is distilled and deionized water that is passed through the analytical procedure as a normal sample with the other samples. It includes all the acid treatment to digest the samples and any other reagents used (e.g., to control interferences).

The laboratory may run a single blank through the entire analytical process, including sample preparation and reagent treatment. If contaminants detected during the entire process are negligible, then separate sample preparation and reagent blanks are not necessary. Also, if

blank contaminant levels are recurring (i.e., nonrandom), the data set may be developed by blank subtraction. If contaminants are detected at levels that may compromise the results of the analysis and are not systematic, the above breakdown is needed to identify sources of contamination. Blank samples used in quality control for the Nowitna sample catalogs are summarized in Appendix D.

The St. Patrick program examines blank contamination in relation to concentrations of each analyte detected in the duplicate analyses (selected randomly from the sample set). The maximum blank concentration of an analyte is compared to the mean analyte for the duplicates. If the maximum blank concentration exceeds 15 percent of the mean value for all the duplicates and if this concentration is above the maximum LOD, the percent of this mean result represented by the maximum blank concentration of the analyte is reported, resulting in rejection of the data.

APPENDIX D

QUALITY ASSURANCE/QUALITY CONTROL SCREENING RESULTS (RAW DATA)

Page No. 1 QAQC SUMMARY FOR : 5182 NOMITNA WATER/MTLS
09/20/91 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	25.00	1	99.0	0.0	1	-9.0000	0.0005
Cadmium	1	0.00	1	98.0	0.0	1	-9.0000	0.0001
Copper	1	0.00	1	98.0	0.0	1	-9.0000	0.0005
Iron	1	7.41	1	114.0	0.0	1	-9.0000	0.0200
Lead	1	0.00	1	105.0	0.0	1	-9.0000	0.0010
Manganese	1	7.02	1	99.0	0.0	1	-9.0000	0.0010
Mercury	1	0.00	1	108.0	0.0	1	-9.0000	0.0002
Nickel	1	43.14	1	109.0	0.0	1	-9.0000	0.0010
Zinc	1	0.00	1	95.0	0.0	1	-9.0000	0.0100

Page No. 1 QAQC SUMMARY FOR : KANUTI 5182(NOWITNA WATER/MTLS)
09/20/91 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	0.0370	0.0344	0.0516	ERA 9902	0.0005	-1.4000
Cadmium	0.0570	0.0504	0.0756	ERA 9902	0.0001	-0.9500
Copper	0.0770	0.0656	0.0984	ERA 9902	0.0005	-0.6100
Iron	0.1000	0.0864	0.1296	ERA 9902	0.0200	-0.7400
Lead	0.1800	0.1488	0.2232	ERA 9902	0.0010	-0.3200
Manganese	0.1100	0.0992	0.1488	ERA 9902	0.0010	-1.1300
Mercury	0.0031	0.0024	0.0036	ERA 9902	0.0002	0.3300
Nickel	0.1200	0.0888	0.1332	ERA 9902	0.0010	0.8100
Zinc	0.1600	0.1328	0.1992	ERA 9902	0.0100	-0.3600

Page No. 2 QAQC SUMMARY FOR : 5182 NOWITNA WATER/MTLS
09/20/91 FOR MATRIX: WaterR and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Antimony	1	0.00	1	94.0	0.0	1	-9.0000	0.0005

QAQC SUMMARY FOR : 5182 NOWITNA WATER/MTLS

09/20/91 FOR MATRIX: WaterR and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Antimony	0.0250	0.0448	0.0672	ERA 9902	0.0005	-5.5400

QAQC SUMMARY FOR : NOWIINA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterD and METHOD: ICPP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	2	53.66	1	97.0	0.0	2	-9.0000	0.0150
Beryllium	2	0.00	1	85.0	0.0	2	-9.0000	0.0010
Cadmium	2	0.00	1	94.0	0.0	2	-9.0000	0.0010
Chromium	2	73.34	1	93.0	0.0	2	0.0020	0.0020
Cobalt	2	53.34	1	95.0	0.0	2	-9.0000	0.0020
Copper	2	13.85	1	98.0	0.0	2	-9.0000	0.0040
Iron	2	37.62	1	58.0	0.0	2	0.0150	0.0100
Lead	2	0.00	1	88.0	0.0	2	-9.0000	0.0120
Manganese	2	32.91	1	34.0	0.0	2	-9.0000	0.0020
Nickel	2	22.22	1	113.0	0.0	2	-9.0000	0.0040
Tin	2	0.00	1	93.0	0.0	2	-9.0000	0.2600
Zinc	2	44.05	1	88.0	0.0	2	0.0120	0.0100

QAQC SUMMARY FOR : NOWITNA 5442/NAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	2	0.00	1	97.0	0.0	2	-9.0000	0.0040
Mercury	2	0.00	1	110.0	0.0	3	0.0002	0.0002

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterD and METHOD: ICPP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	
		Low SRM	Hi SRM				
Aluminum	0.5737	0.4226	0.6226	WP 386	0.0150	1.0200	
Beryllium	0.1067	0.0861	0.1117	WP 386	0.0010	1.2200	
Cadmium	0.0247	0.0200	0.0276	WP 386	0.0010	0.4700	
Chromium	0.1000	0.0777	0.1185	WP 386	0.0020	0.1900	
Cobalt	0.0997	0.0856	0.1124	WP 386	0.0020	0.1000	
Copper	0.0960	0.0878	0.1126	WP 386	0.0040	-0.6800	
Iron	0.0933	0.0833	0.1185	WP 386	0.0100	-0.8600	
Lead	0.0707	0.0828	0.1164	WP 386	0.0120	-3.4400	
Manganese	0.1053	0.0876	0.1108	WP 386	0.0020	1.0500	
Nickel	0.0633	0.0841	0.1157	WP 386	0.0040	-4.6300	
Thallium	0.1735			WP 386	0.0000	0.0000	No R
Tin	0.2600			WP 386	0.2600	0.0000	No R
Zinc	0.0920	0.0859	0.1155	WP 386	0.0100	-1.1800	

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	0.0968	0.0772	0.1212	WP 386	0.0040	-0.2200
Mercury	0.1808	0.0900	0.2500	WP 1085	0.0002	0.2700

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterT and METHOD: ICPP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	1	2.86	1	89.0	0.0	2	-9.0000	0.0150
Beryllium	1	0.00	1	74.0	0.0	2	-9.0000	0.0010
Cadmium	1	0.00	1	98.0	0.0	2	-9.0000	0.0010
Chromium	1	57.14	1	95.0	0.0	2	0.0020	0.0020
Cobalt	1	40.00	1	99.0	0.0	2	-9.0000	0.0020
Copper	1	28.57	1	104.0	0.0	2	-9.0000	0.0040
Iron	1	16.82	1	92.0	0.0	2	0.0150	0.0100
Lead	1	0.00	1	98.0	0.0	2	-9.0000	0.0120
Manganese	1	0.00	1	41.0	0.0	2	-9.0000	0.0020
Nickel	1	0.00	1	106.0	0.0	2	-9.0000	0.0040
Tin	1	0.00	1	69.0	0.0	1	-9.0000	0.2600
Zinc	1	41.38	1	90.0	0.0	2	0.0120	0.0100

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterT and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	0.00	2	98.0	2.0	2	0.0040	0.0040
Mercury	1	0.00	2	100.0	8.0	2	0.0002	0.0002

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterT and METHOD: ICPP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	
		Low SRM	Hi SRM				
Aluminum	0.5737	0.4226	0.6226	WP 386	0.0150	1.0200	
Beryllium	0.1067	0.0861	0.1117	WP 386	0.0010	1.2200	
Cadmium	0.0247	0.0200	0.0276	WP 386	0.0010	0.4700	
Chromium	0.1000	0.0777	0.1185	WP 386	0.0020	0.1900	
Cobalt	0.0997	0.0856	0.1124	WP 386	0.0020	0.1000	
Copper	0.0960	0.0878	0.1126	WP 386	0.0040	-0.6800	
Iron	0.0933	0.0833	0.1185	WP 386	0.0100	-0.8600	
Lead	0.0707	0.0828	0.1164	WP 386	0.0120	-3.4400	
Manganese	0.1053	0.0876	0.1108	WP 386	0.0020	1.0500	
Nickel	0.0633	0.0841	0.1157	WP 386	0.0040	-4.6300	
Tin	0.2023			WP 386	0.2600	0.0000	No Ref.
Zinc	0.0920	0.0859	0.1155	WP 386	0.0100	-1.1800	

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: WaterT and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	0.0968	0.0772	0.1212	NP 386	0.0040	-0.2200
Mercury	0.1808	0.0900	0.2500	NP 1085	0.0002	0.2700

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: Sediment and METHOD: ICP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	1	26.82	0	****.*	***.*	1	-9.0000	30.0000
Antimony	1	0.00	1	20.0	0.0	1	-9.0000	25.0000
Barium	1	49.35	1	76.0	0.0	1	22.0000	1.5000
Beryllium	1	8.15	1	101.0	0.0	1	-9.0000	0.8000
Boron	1	17.73	1	96.0	0.0	1	-9.0000	3.3000
Cadmium	1	0.00	1	102.0	0.0	1	-9.0000	0.8000
Chromium	1	5.81	1	101.0	0.0	1	2.8000	2.0000
Copper	1	19.02	1	100.0	0.0	1	-9.0000	2.0000
Iron	1	7.41	0	****.*	***.*	1	-9.0000	40.0000
Lead	1	0.00	1	75.5	0.0	1	-9.0000	16.0000
Magnesium	1	32.59	0	****.*	***.*	1	-9.0000	2.0000
Manganese	1	13.49	1	226.0	0.0	1	-9.0000	2.0000
Molybdenum	1	0.00	1	92.5	0.0	1	-9.0000	6.7000
Nickel	1	8.59	1	101.0	0.0	1	-9.0000	5.0000
Silver	1	0.00	1	162.0	0.0	1	-9.0000	4.2000
Strontium	1	26.66	1	132.0	0.0	1	-9.0000	1.0000
Tin	1	0.00	1	29.5	0.0	1	-9.0000	43.0000
Vanadium	1	4.68	1	98.5	0.0	1	-9.0000	5.0000
Zinc	1	0.17	1	109.0	0.0	1	5.0000	4.0000

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: Sediment and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	10.90	1	78.0	0.0	1	-9.0000	0.4000
Mercury	2	6.98	1	105.0	0.0	1	-9.0000	0.0200

QAQC SUMMARY FOR : NOWITNA 5442/MAT/SED/FISH/METL

01/06/92 FOR MATRIX: Sediment and METHOD: ICP

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	Comments
		Low SRM	Hi SRM				
Aluminum	22100.0000	21800.0000	23400.0000	NBS 1645	30.0000	-1.2500	
Antimony	25.0000			NBS 1645	25.0000	0.0000	No Ref. Val.
Barium	334.0000	322.0000	426.0000	NBS 1645	1.5000	-1.5400	
Beryllium	0.8950	0.8000	1.2000	NBS 1645	0.8000	0.0000	AvgSRM < 2 * LOI
Boron	162.0000	26.4000	39.6000	NBS 1645	3.3000	39.0900	
Cadmium	7.9700	7.2000	13.2000	NBS 1645	0.8000	-1.4900	
Chromium	25900.0000	24000.0000	35200.0000	NBS 1645	2.0000	-1.3200	
Copper	109.0000	71.0000	147.0000	NBS 1645	2.0000	0.0000	
Iron	99800.0000	89000.0000	137000.0000	NBS 1645	40.0000	-1.1000	
Lead	656.0000	658.0000	770.0000	NBS 1645	16.0000	-2.0700	
Magnesium	6920.0000	7000.0000	7800.0000	NBS 1645	2.0000	-2.4000	
Manganese	690.0000	591.0000	979.0000	NBS 1645	2.0000	-0.9800	
Molybdenum	0.1790	18.0000	50.0000	NBS 1645	6.7000	0.0000	AvgSRM < 2 * LOI
Nickel	42.4000	40.0000	51.6000	NBS 1645	5.0000	-1.1700	
Silver	4.2000	1.4000	2.1000	NBS 1645	4.2000	0.0000	Ref. Val. < LOD
Strontium	849.0000	700.0000	1060.0000	NBS 1645	1.0000	-0.3400	
Tin	43.0000	260.0000	460.0000	NBS 1645	43.0000	0.0000	AvgSRM < 2 * LOI
Vanadium	26.1000	9.7000	37.3000	NBS 1645	5.0000	0.3800	
Zinc	1590.0000	1380.0000	2060.0000	NBS 1645	4.0000	-0.7600	

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: Sediment and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	47.2000	61.0000	73.0000	NBS 1645	0.4000	-6.6000
Mercury	1.1950	0.1000	2.1000	NBS 1645	0.0200	0.1900

QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL

01/06/92 FOR MATRIX: Animal and METHOD: ICPP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	4	34.16	3	118.0	19.9	2	-9.0000	4.7000
Beryllium	4	0.00	3	81.7	0.9	2	-9.0000	0.2000
Cadmium	4	22.27	3	101.3	9.7	2	-9.0000	0.2000
Chromium	4	0.00	3	87.8	4.0	2	2.0000	0.6200
Cobalt	4	0.00	3	94.5	9.1	2	-9.0000	0.9000
Copper	4	10.45	3	107.3	10.5	2	-9.0000	1.5000
Iron	4	24.27	3	100.2	2.6	2	-9.0000	5.0000
Lead	4	0.00	3	99.2	7.7	2	-9.0000	2.3000
Manganese	4	49.37	3	32.5	12.5	2	-9.0000	0.8000
Nickel	4	15.36	3	108.7	6.8	2	-9.0000	0.8000
Tin	4	0.00	3	45.2	4.9	2	-9.0000	6.0000
Zinc	4	20.99	3	116.0	16.6	2	5.2000	3.0000

Page No. 1 QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL:
01/06/92 FOR MATRIX: Animal and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	4	29.08	4	101.0	3.1	2	-9.0000	0.4000
Mercury	3	17.11	2	101.5	8.5	2	-9.0000	0.0200

QAQC SUMMARY FOR : NOWITNA 5442/MAT/SED/FISH/METL

01/06/92 FOR MATRIX: Animal and METHOD: ICPP

ANALYTE	Average SRM	Reference Values Low SRM	Hi SRM	SRM Number	LOD	Z-Score	Comments
Aluminum	4.7000			NRCC DOLT1	4.7000	0.0000	No Ref. Val.
Aluminum	4.7000			TORT-1	4.7000	0.0000	No Ref. Val.
Beryllium	0.2000			NRCC DOLT1	0.2000	0.0000	No Ref. Val.
Beryllium	0.2000			TORT-1	0.2000	0.0000	No Ref. Val.
Cadmium	3.7300	3.6200	4.7400	NRCC DOLT1	0.2000	-1.6100	
Cadmium	25.8000	22.1000	30.5000	TORT-1	0.2000	-0.2400	
Chromium	0.9710	0.2600	0.5400	NRCC DOLT1	0.6200	0.0000	Ref. Val. < LOI
Chromium	0.6200	1.2000	3.6000	TORT-1	0.6200	0.0000	AvgSRM < 2 * LO
Cobalt	0.9000	0.0830	0.2310	NRCC DOLT1	0.9000	0.0000	Ref. Val. < LOI
Cobalt	0.9000	-0.4800	1.3200	TORT-1	0.9000	0.0000	AvgSRM < 2 * LO
Copper	20.5000	18.4000	23.2000	NRCC DOLT1	1.5000	-0.2500	
Copper	403.0000	395.0000	483.0000	TORT-1	1.5000	-1.6400	
Iron	618.0000	616.0000	808.0000	NRCC DOLT1	5.0000	-1.9600	
Iron	181.0000	164.0000	208.0000	TORT-1	5.0000	-0.4500	
Lead	2.3000	0.7800	1.9400	NRCC DOLT1	2.3000	0.0000	Ref. Val. < LOD
Lead	10.7000	6.4000	14.4000	TORT-1	2.3000	0.1500	
Manganese	1.0800	7.6600	9.7800	NRCC DOLT1	0.8000	0.0000	AvgSRM < 2 * LOI
Manganese	17.4000	21.4000	25.4000	TORT-1	0.8000	-6.0000	
Nickel	0.8000	0.1400	0.3800	NRCC DOLT1	0.8000	0.0000	Ref. Val. < LOD
Nickel	2.3900	1.7000	2.9000	TORT-1	0.8000	0.3000	
Tin	6.0000			NRCC DOLT1	6.0000	0.0000	No Ref. Val.
Tin	6.0000	0.1170	0.1610	TORT-1	6.0000	0.0000	Ref. Val. < LOD
Zinc	58.4000	87.9000	97.1000	NRCC DOLT1	3.0000	-14.8300	
Zinc	169.0000	157.0000	197.0000	TORT-1	3.0000	-0.8000	

Page No. 1 QAQC SUMMARY FOR : NOWITNA 5442/WAT/SED/FISH/METL
01/06/92 FOR MATRIX: Animal and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score	
		Low SRM	Hi SRM				
Arsenic	10.1000	7.3000	12.9000	NRCC DOLT1	0.4000	0.0000	
Arsenic	17.9000			NRCC DORM-1	0.4000	0.0000	No Ref.
Arsenic	25.0000	20.2000	29.0000	TORT-1	0.4000	0.1800	
Mercury	0.2200	0.1510	0.2990	NRCC DOLT1	0.0200	-0.1400	
Mercury	0.8700			NRCC DORM-1	0.0200	0.0000	No Ref.
Mercury	0.3100	0.2100	0.4500	TORT-1	0.0200	-0.3300	

QAQC SUMMARY FOR : NOWITNA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: WaterD and METHOD: ICPP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	1	0.00	1	56.8	0.0	1	-9.0000	0.0500
Beryllium	1	107.69	1	45.8	0.0	1	0.0005	0.0005
Cadmium	1	0.00	1	100.8	0.0	1	0.0010	0.0010
Chromium	1	0.00	1	74.4	0.0	1	0.0039	0.0150
Copper	1	0.00	1	65.4	0.0	1	0.0087	0.0150
Iron	1	21.86	1	99.3	0.0	1	0.0127	0.1500
Lead	1	0.00	1	72.8	0.0	1	0.0112	0.0150
Manganese	1	7.75	1	95.9	0.0	1	0.0034	0.0100
Nickel	1	0.00	1	94.0	0.0	1	-9.0000	0.0100
Thallium	1	0.00	1	91.9	0.0	1	0.0123	0.0500
Tin	1	0.00	1	91.2	0.0	1	0.0135	0.0300
Zinc	1	0.00	1	98.0	0.0	1	0.0133	0.0300

QAQC SUMMARY FOR : NOWIINA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	0.00	1	89.1	0.0	1	-9.0000	0.0030
Mercury	1	0.00	1	109.2	0.0	1	-9.0000	0.0002
Selenium	1	0.00	1	120.3	0.0	1	-9.0000	0.0025

ANALYTE	Average SRM	Reference Values Low SRM	Hi SRM	SRM Number	LOD	Z-Score	Comments
Aluminum	1.8557	1.6000	2.4000	EPA LV	0.0500	-0.7200	
Aluminum	0.2776	0.4000	0.6000	NBS 5753	0.0500	-4.4500	
Beryllium	0.4493	0.4008	0.6012	EPA LV	0.0005	-1.0300	
Beryllium	0.0153	0.0200	0.0300	NBS 5753	0.0005	-3.8800	
Cadmium	0.4694	0.3936	0.5904	EPA LV	0.0010	-0.4600	
Cadmium	0.0223	0.0200	0.0300	NBS 5753	0.0010	-1.0800	
Chromium	0.4511	0.4024	0.6036	EPA LV	0.0150	-1.0300	
Chromium	0.0172	0.0200	0.0300	NBS 5753	0.0150	0.0000	AvgSRM < 2 * L
Copper	0.4577	0.4160	0.6240	EPA LV	0.0150	-1.2000	
Copper	0.0317	0.0400	0.0600	NBS 5753	0.0150	-3.6600	
Iron	1.7617	1.6648	2.4972	EPA LV	0.1500	-1.5300	
Iron	0.4476	0.4000	0.6000	NBS 5753	0.1500	-1.0500	
Lead	3.9525	3.9680	5.9520	EPA LV	0.0150	-2.0300	
Lead	0.0387	0.0400	0.0600	NBS 5753	0.0150	-2.2600	
Manganese	0.4194	0.4032	0.6048	EPA LV	0.0100	-1.6800	
Manganese	0.1139	0.1000	0.1500	NBS 5753	0.0100	-0.8900	
Nickel	0.4453	0.3880	0.5820	EPA LV	0.0100	-0.8200	
Nickel	0.0476	0.0400	0.0600	NBS 5753	0.0100	-0.4800	
Thallium	4.4231	4.0000	6.0000	NBS 5753	0.0500	-1.1500	
Tin	0.0911	0.0800	0.1200	NBS 5753	0.0300	-0.8900	
Zinc	2.7545	2.3360	3.5040	EPA LV	0.0300	-0.5700	
Zinc	0.0800	0.0800	0.1200	NBS 5753	0.0300	-2.0000	

QAQC SUMMARY FOR : NOWITNA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: WaterD and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Mercury	0.0051	-0.9751	0.9849	EPA LV	0.0002	0.0004

QAQC SUMMARY FOR : NOWINA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: WaterT and METHOD: ICPP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	1	97.32	1	9.2	0.0	1	0.0120	0.0500
Beryllium	1	0.00	1	71.3	0.0	1	0.0003	0.0005
Cadmium	1	0.00	1	95.6	0.0	1	0.0010	0.0010
Chromium	1	0.00	1	64.6	0.0	1	0.0076	0.0150
Copper	1	0.00	1	74.8	0.0	1	0.0087	0.0150
Iron	1	41.55	1	73.7	0.0	1	0.0289	0.1500
Lead	1	0.00	1	76.6	0.0	1	0.0089	0.0150
Manganese	1	29.15	1	100.3	0.0	1	0.0033	0.0100
Nickel	1	0.00	1	119.5	0.0	1	-9.0000	0.0100
Thallium	1	0.00	1	101.8	0.0	1	-9.0000	0.0500
Tin	1	0.00	1	75.4	0.0	1	0.0163	0.0300
Zinc	1	178.95	1	94.2	0.0	1	0.0102	0.0300

QAQC SUMMARY FOR : NOWITNA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: Water? and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	0.00	1	96.1	0.0	1	-9.0000	0.0030
Mercury	0	0.00	0	****.*	***.*	1	-9.0000	0.0002
Selenium	1	0.00	1	117.9	0.0	1	-9.0000	0.0025

ANALYTE	Average SRM	Reference Values Low SRM	Reference Values Hi SRM	SRM Number	LOD	Z-Score	Comments
Aluminum	2.0830	1.6000	2.4000	EPA LV	0.0500	0.4200	
Aluminum	0.2850	0.4000	0.6000	NBS 5753	0.0500	-4.3000	
Beryllium	0.5531	0.4008	0.6012	EPA LV	0.0005	1.0400	
Beryllium	0.0180	0.0200	0.0300	NBS 5753	0.0005	-2.8000	
Cadmium	0.5221	0.3936	0.5904	EPA LV	0.0010	0.6100	
Cadmium	0.0235	0.0200	0.0300	NBS 5753	0.0010	-0.6000	
Chromium	0.5159	0.4024	0.6036	EPA LV	0.0150	0.2600	
Chromium	0.0146	0.0200	0.0300	NBS 5753	0.0150	0.0000	AvgSRM < 2 * LOD
Copper	0.5670	0.4160	0.6240	EPA LV	0.0150	0.9000	
Copper	0.0340	0.0400	0.0600	NBS 5753	0.0150	-3.2000	
Iron	2.0706	1.6648	2.4972	EPA LV	0.1500	-0.0500	
Iron	0.4399	0.4000	0.6000	NBS 5753	0.1500	-1.2000	
Lead	4.5268	3.9680	5.9520	EPA LV	0.0150	-0.8700	
Lead	0.0377	0.0400	0.0600	NBS 5753	0.0150	-2.4600	
Manganese	0.5134	0.4032	0.6048	EPA LV	0.0100	0.1900	
Manganese	0.1231	0.1000	0.1500	NBS 5753	0.0100	-0.1500	
Nickel	0.5265	0.3880	0.5820	EPA LV	0.0100	0.8600	
Nickel	0.0532	0.0400	0.0600	NBS 5753	0.0100	0.6400	
Thallium	4.8523	4.0000	6.0000	NBS 5753	0.0500	-0.3000	
Tin	0.0860	0.0800	0.1200	NBS 5753	0.0300	-1.4000	
Zinc	3.1193	2.3360	3.5040	EPA LV	0.0300	0.6800	
Zinc	0.0842	0.0800	0.1200	NBS 5753	0.0300	-1.5800	

QAQC SUMMARY FOR : NOWITNA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: WaterT and METHOD: AA

ANALYTE	Average SRM	Reference Values		SRM Number	LOD	Z-Score
		Low SRM	Hi SRM			
Arsenic	0.0481	0.0376	0.0564	EPA LV	0.0030	0.2300
Arsenic	0.0408	0.0400	0.0600	NBS 5753	0.0030	-1.8400
Selenium	0.1049	0.0832	0.1248	EPA LV	0.0025	0.0900
Selenium	0.0573	0.0400	0.0600	NBS 5753	0.0025	1.4600

QAQC SUMMARY FOR : NOWIINA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: Sediment and METHOD: ICP

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Aluminum	1	7.93	1	264.7	0.0	1	4.4160	50.0000
Antimony	1	19.84	1	44.9	0.0	1	-9.0000	5.0000
Barium	1	4.26	1	121.2	0.0	1	-9.0000	0.5000
Beryllium	1	9.52	1	84.5	0.0	1	-9.0000	0.1000
Boron	1	0.65	1	78.1	0.0	1	-9.0000	1.0000
Cadmium	1	0.00	1	80.7	0.0	1	-9.0000	0.5000
Chromium	1	6.64	1	85.1	0.0	1	-9.0000	1.0000
Copper	1	23.13	1	78.4	0.0	1	-9.0000	0.5000
Iron	1	7.02	1	180.3	0.0	1	1.5490	10.0000
Lead	1	31.55	1	71.8	0.0	1	-9.0000	5.0000
Magnesium	1	7.99	1	192.3	0.0	1	0.8000	20.0000
Manganese	1	6.12	1	100.1	0.0	1	-9.0000	0.5000
Molybdenum	1	0.00	1	79.3	0.0	1	-9.0000	1.0000
Nickel	1	10.11	1	79.5	0.0	1	-9.0000	2.0000
Silver	1	0.00	1	72.7	0.0	1	-9.0000	1.0000
Strontium	1	6.47	1	91.6	0.0	1	-9.0000	1.0000
Thallium	1	0.00	1	83.9	0.0	1	-9.0000	10.0000
Tin	1	3.00	1	1.3	0.0	1	10.0810	10.0000
Vanadium	1	8.10	1	91.0	0.0	1	-9.0000	1.0000
Zinc	1	4.93	1	81.2	0.0	1	-9.0000	1.0000

QAQC SUMMARY FOR : NOWITNA 5753/WAT/FISH/SED/METL

01/06/92 FOR MATRIX: Sediment and METHOD: AA

ANALYTE	N	MEAN RPD	N	MEAN SPIKE	STD SPIKE	N	MAX. BLANK	LOD
Arsenic	1	27.59	1	112.6	0.0	1	-9.0000	1.0000
Mercury	1	0.00	1	1.0	0.0	1	-9.0000	0.1000
Selenium	1	0.00	1	91.6	0.0	1	-9.0000	1.0000

ANALYTE	Average SRM	Reference Values Low SRM	Hi SRM	SRM Number	LOD	Z-Score	Comments
Cadmium	0.5000	0.0688	0.1032	EPA-CN	0.5000	0.0000	Ref. Val. < LOD
Chromium	2.9000	2.8800	4.3200	EPA-CN	2.0000	0.0000	AvgSRM < 2 * LOD
Copper	5.1000	4.1760	6.2640	EPA-CN	1.0000	-0.2300	
Iron	58.6000	50.8800	76.3200	EPA-CN	2.0000	-0.7900	
Lead	2.8000	0.3200	0.4800	EPA-CN	4.0000	0.0000	Ref. Val. < LOD
Manganese	1.2000	1.0560	1.5840	EPA-CN	1.0000	0.0000	AvgSRM < 2 * LOD
Nickel	1.0000	0.9600	1.4400	EPA-CN	2.0000	0.0000	Ref. Val. < LOD
Selenium	3.0000	0.2960	0.4440	EPA-CN	0.5000	0.0000	Ref. Val. < LOD
Zinc	18.5000	17.0400	25.5600	EPA-CN	1.0000	-1.3100	